[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Osmotic Pressure Measurements with Polydimethylsilicone Fractions

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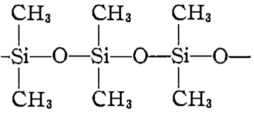
The present investigation was undertaken to study the molecular weight and molecular size distribution of high molecular weight polydimethylsilicone. Osmotic pressure data, and the molecular weight values resulting therefrom, are reported for the fractions obtained by fractionation of a sample of this polymer.

Experimental

Polydimethylsilicone—The polymer used in this investigation was prepared from starting material carefully purified to remove potential branching or cross-linking units. Consequently it consisted essentially of linear (or possibly cyclic) molecules having the structure



$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ - & Si & -O- & Si & -O- & Si & -O- \\ & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & \end{array}$$

Fractionation.—The polydimethylsilicone was fractionated by precipitation from solution. The solvent used was a mixture of ethyl acetate and acetone of such composition that the polymer was completely soluble in it above 25° but only partially soluble at lower temperatures. Precipitation was accomplished by cooling to that temperature at which the desired amount of polymer was thrown out of solution. To obtain more clean-cut separation, each original fraction was dissolved and then precipitated a second time, the lower molecular weight material removed by this reprecipitation being combined with the remaining polymer prior to precipitating the next fraction. Polymer concentrations of from two to four weight per cent. were used.

Initial exploratory studies of the solubility behavior of polydimethylsilicone showed that when a non-solvent is added to a dilute solution of this polymer, precipitation of nearly all of the polymer occurs in a range of non-solvent concentration or only a few tenths of a per cent. Also, when a solution of the polymer in a solvent–precipitant mixture is cooled, precipitation of nearly all of the polymer occurs within a temperature interval of only a few tenths of a degree. This behavior was observed with all of numerous solvent–precipitant pairs investigated. The narrowness of the temperature interval within which most of the polymer precipitates made precise temperature control essential to satisfactory fractionation of the polymer.

For fractionation, a 600-g. sample of polydimethylsilicone was taken. A solution of this material in the ethyl acetate-acetone mixture was placed in a large bottle immersed in a water thermostat, and, by a process of trial and error, was brought to the temperature at which the desired amount of precipitation was obtained. Following this, the mixture was stirred for thirty minutes to insure attainment of equilibrium, and then allowed to stand two hours to permit complete phase separation to occur. Finally the clear upper layer was carefully siphoned off. The precipitate—polymer highly swollen with solvent—was redissolved in ethyl acetate–acetone mixture and a second precipitation was carried out exactly as before. The precipitate from this second precipitation was steeped in methanol to deswell the polymer, which was then dried in vacuum at 100° to yield the first fraction.

The combined upper layers from the two precipitations were reduced to a suitable volume by first distilling off the acetone and part of the ethyl acetate, and then adding acetone sufficient to give the required concentration. By carrying out two successive precipitations exactly as before, a second fraction was obtained. Repeating this procedure twice more, a third and a fourth fraction were obtained. Finally by evaporating solvent from the combined upper layers resulting from precipitating the fourth fraction, a fifth fraction was obtained.

Osmotic Pressure Determinations.—An osmometer of the type described by Fuoss and Mead[1] was used. Temperature control was achieved by enclosing the instrument, exclusive of vertical capillaries, standpipes and valves, in a container through which oil at constant temperature was circulated. When methyl ethyl ketone was used as solvent, the osmotic pressures were determined by the dynamic method. With octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, as solvent, the slow rate at which equilibrium was established necessitated using the static method.

Dissolving polydimethylsilicone in methyl ethyl ketone results in a lowering of the surface tension. Up to concentrations of about 0.25 g. polymer/kg. of solution, the surface tension decreases with increasing concentration of polymer; for concentrations higher than this it is virtually independent of polymer concentration. The necessity of applying a troublesome and at best somewhat uncertain correction for the difference in surface tension of solvent and solution in the two capillaries of the osmometer was circumvented in the following manner.

A dilute solution (about 0.30 g. of polymer/kg. of solution) was used on the "solvent" side of the osmometer and the more concentrated solutions on the "solution" side. Since both solutions were in the concentration range in which the surface tension is virtually independent of concentration, no surface tension correction was required.

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[1] Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943).

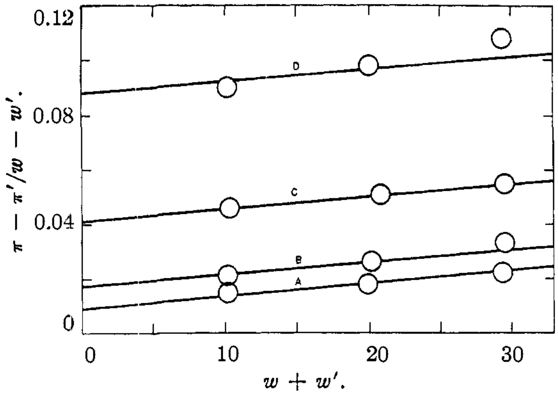

Fig. 1.—Osmotic pressure-concentration ratio *vs.* concentration for methyl ethyl ketone solutions of the polydimethylsilicone fractions at 25.0°.

The osmotic pressure, π, in cm. of solution may be expressed as a function of weight concentration, w, in g. polymer/kg. of solution, by the equation[1]

$$\pi = (1033RT/M)w + Aw^2 \qquad (1)$$

if terms in powers of the concentration higher than the square can be neglected. Here R is the gas constant in lit. atm./deg.; T, the absolute temperature; M, the molecular weight; and A, a constant. The difference in osmotic pressure of two solutions of different concentration is given by

$$\pi - \pi' = (1033RT/M)(w - w') + A(w^2 - w'^2) \qquad (2)$$

where the primed quantities refer to the dilute solution and the unprimed to the more concentrated solution. The difference, $(\pi - \pi')$, is the quantity measured when dilute solution is used on the "solvent" side of the osmometer. Dividing by $(w - w')$, one obtains

$$(\pi - \pi')/(w - w') = 1033RT/M + A(w + w') \qquad (3)$$

A plot of $(\pi - \pi')/(w - w')$ *vs.* $(w + w')$ has a slope A and an intercept inversely proportional to the molecular weight, thus being equivalent to the usual π/w *vs.* w plot employed when pure solvent is used on one side of the osmometer.

Results and Discussion

The five polydimethylsilicone fractions are listed in Table I. They account for 91% of the original polymer, the remaining 9% representing the inevitable losses entailed by the large number of operations required for such a fractionation. Fig. 1 shows the $(\pi - \pi')/(w - w')$ *vs.* $(w + w')$ plots of the osmotic pressure data at 25.0° for solutions of the four highest molecular weight fractions in methyl ethyl ketone. From the intercepts, the number average molecular weight values given in Table I were obtained.

TABLE I

POLYDIMETHYLSILICONE FRACTIONS

Fraction	Description	Polymer, %	No. av. mol. wt.
A	Elastic	17	2.8×10^6
B	Soft and plastic	14	1.5×10^6
C	Soft and plastic	18	6.1×10^5
D	Very plastic	27	2.9×10^5
E	Viscous liquid	15	[a]

[a] No value is reported for this fraction because it contained some low molecular weight material which diffused through the membrane so rapidly that osmotic pressure results were uncertain.

A comparison of the plastic properties of the various fractions with the observed molecular weights is quite striking. The molecular weights are much higher than would be expected from the plastic properties, by analogy with other polymers, as, for example, polyisobutylene. Only the first fraction, having an average molecular weight of about three million, shows any rubber-like elasticity. Fraction D, with an average molecular weight of nearly 300,000, actually flows to the extent that it forms a flat meniscus upon standing in a container at room temperature for several days.

The fact that the original unfractionated polymer consisted so preponderantly of species of unusually high molecular weight accounts for the narrowness of the range of non-solvent concentration and small temperature interval within which most of the polymer was found to precipitate from solution. Theories of polymer solubility and fractionation[2,3] predict such behavior for a polymer whose molecular size distribution lies mainly in the range of very high molecular weights.

The observed points in Fig. 1 fall reasonably well on straight lines of the same slope. According to current theories of high polymer solutions,[4,5] the osmotic pressure of dilute solutions of a polymer may be expressed by

$$\frac{\pi}{v_2} = \frac{RT}{V_2} + \frac{RT}{V_1}(1/2 - \mu)v_2 + \text{terms in higher powers of } v_2 \qquad (4)$$

where v_2 is the volume fraction of polymer in the solution, V_1 and V_2 are the molar volumes of solvent and polymer respectively, and μ is a constant characteristic of the system polymer–solvent. The slopes of the lines as drawn in Fig. 1 correspond to a value for μ of 0.498.[5a]

Osmotic pressure measurements with solutions of Fraction A in methyl ethyl ketone were made at 35.0° as well as at 25.0°. The data for the two temperatures are plotted for comparison in Fig. 2. At 35.0° a value for μ of 0.495 is obtained. The slope of the $(\pi - \pi')/(w - w')$ *vs.* $(w + w')$ plot at 35.0° is about two and a half times as great as at

(2) Schultz, *Z. physik. Chem.*, **A179**, 321 (1937).

(3) Flory, *J. Chem. Phys.*, **12**, 425 (1944).

(4) Huggins, *ibid.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); THIS JOURNAL, **64**, 1712 (1942).

(5) Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942); **12**, 425 (1944).

(5a) For converting weight concentrations to volume fractions the density of the polymer was taken to be 0.98 at 25°.

25.0°. This strong temperature dependence of the slope is to be expected when the heat of mixing of polymer and solvent is large, as has been pointed out by Alfrey and Doty.[6] At the highest concentration studied, the osmotic pressure at 35.0° was more than *twice* that at 25.0°. Although this may be an extreme case, it illustrates the necessity of good temperature control in osmotic pressure measurements.

Osmotic pressure data were also obtained for solutions of Fraction C in $[(CH_3)_2SiO]_4$. In this system both the polymer and solvent molecules are composed of the same structural units and the heat of mixing may be expected to be very small. Osmotic pressures were measured at both 25.0° and at 35.0°. The measurements were not sufficiently precise to yield a reliable value for the temperature coefficient of osmotic pressure, but they did show that it was small, the increase in osmotic pressure over the 10.0° temperature interval being approximately the three per cent. to be expected if there were no heat of mixing. The data obtained at 25.0° are listed in Table II and are plotted in Fig. 2 along with the corresponding data for methyl ethyl ketone solutions of the same fraction.

TABLE II

FRACTION C IN $[(CH_3)_2SiO]_4$ AT 25.0°[a,b]

$w - w'$ g./kg.	$w + w'$ g./kg.	$\pi - \pi'$ cm. soln.
4.86	5.72	0.45
9.60	10.46	1.29
14.08	14.94	2.8
19.02	19.88	5.2

[a] The intrinsic viscosity of Fraction C in $[(CH_3)_2SiO]_4$ at 25.0° was measured and found to be 2.04 (g./100 ml.)$^{-1}$.
[b] The density of $[(CH_3)_2SiO]_4$ at 25.0° is 0.9502—Hurd, THIS JOURNAL, **68**, 364 (1946).

Osmotic pressure data for a number of other polymer-solvent systems where the heat of mixing is small have been summarized and discussed by Flory.[7] The results obtained here for Fraction C in $[(CH_3)_2SiO]_4$ are qualitatively similar to those for the systems discussed by Flory in that the $(\pi - \pi')/(w - w')$ *vs.* $(w + w')$ plot has a definite curvature and the initial slope is less than would be calculated from equation 4 with μ, the heat of mixing term, set equal to zero.

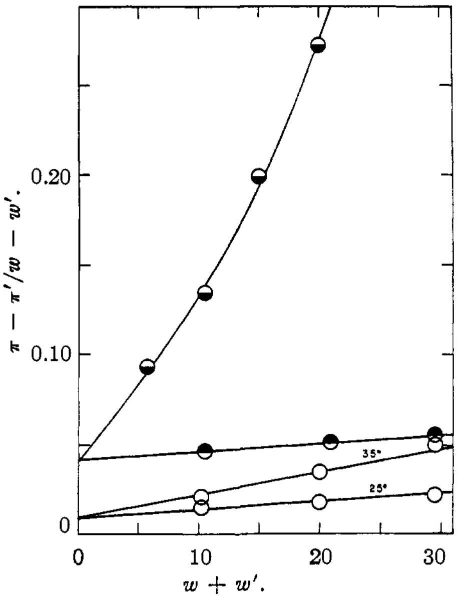

Fig. 2.—Osmotic pressure–concentration ratio *vs.* concentration for solutions of polydimethylsilicone Fractions: ○, Fraction A in methyl ethyl ketone at 25.0 and 35.0°; ◐, Fraction C in methyl ethyl ketone at 25.0°; ◓, Fraction C in $[(CH_3)_2SiO]_4$ at 25.0°.

Summary

1. High molecular weight polydimethylsilicone was fractionated and the molecular weights of the fractions were determined by osmotic pressure measurements.

2. Osmotic pressure data are reported for the approximately athermal system polydimethylsilicone–$[(CH_3)_2SiO]_4$.

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[6] Alfrey and Doty, *J. Chem. Phys.*, **13**, 77 (1945).
[7] Flory, *ibid.*, **13**, 453 (1945).