

Experimental

Tri-*n*-butylborane, prepared by the method of Johnson, *et al.*,⁸ was refluxed at 125 to 130° at 10 mm. pressure for 10 days. The low boiling decomposition product was trapped in a -196° cold trap. At intervals small samples of the higher boiling product were tapped off.

The low boiling product from the cold trap was identified as *trans*-butene-2 from its infrared spectrum. Molecular weight calculated for C₄H₈, 56.10; found, 56.78.

When milder conditions were used (refluxing at 90 to 100° at 5 mm. pressure for 2 days) the low boiling decomposition product was identified as butene-1 by its infrared spectrum.

The high boiling decomposition product in the first case was identified as dibutylborane. This compound reduced silver nitrate solution and reacted vigorously with ethanol to give hydrogen. The infrared spectra showed absorption bands in the regions characteristically associated with CH, BH and BH (bridge) stretching frequencies (see Table I).

Anal. Calcd. for C₈H₂₂B₂: C, 68.68; H, 15.85; B, 15.47. Found: C, 68.79; H, 16.27; B, 15.27.

TABLE I

INFRARED ABSORPTION BANDS USED TO IDENTIFY DIBUTYL-DIBORANE

Frequency, cm. ⁻¹	Relative intensity	Motion
2930	VS	CH stretch
2840	VS	CH stretch
2530	S	BH stretch
2460	S	BH stretch
2020	W	BH (bridge) stretch
1915	VW	BH (bridge) stretch

A form of the Antoine equation may be used to give the vapor pressure-temperature relationship for this compound.

$$\log p = 5.374 - \frac{1233}{t + 230} \quad p = \text{pressure in mm.} \\ t = \text{temp. in } ^\circ\text{C.}$$

Since this compound begins to decompose at temperatures where any readable vapor pressures are exhibited, there was much difficulty in obtaining good vapor pressure data. This being the case, not too much reliance can be placed on the constants in the above equation.

(8) J. R. Johnson, H. R. Snyder and M. G. Van Campen, *THIS JOURNAL*, **60**, 115 (1938).

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Melt Viscosities of Dimethylpolysiloxanes

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Melt viscosities have been measured for four fractions obtained from a solution fraction of a high molecular weight dimethylpolysiloxane. Together with viscosity data for pure compounds, the linear dimethylpolysiloxanes,¹ the viscosity-molecular weight data for the fractions define two straight lines on a plot of $\log \eta_0$ (zero shear viscosity) *vs.* $\log M_v$. The high molecular weight branch has a slope of 3.64, quite close to the slope values found by Fox and Flory² for polyisobutylene and polystyrene. The low molecular weight branch has a slope of 1.43 which is only slightly greater than that suggested by Bueche.³ The point of intersection lies at a molecular weight of 40,000. Bueche sug-

(1) M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *THIS JOURNAL*, **68**, 2284 (1946).

(2) T. G. Fox, P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221 (1951).

(3) F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).

gests this is the point of pseudo network formation due to polymer entanglements and in our case would represent a distance between entanglements of 1100 chain atoms.

The polymer used in the fractionation was prepared from pure octamethylcyclotetrasiloxane by an alkaline polymerization of the type described by Hyde.⁴ The polymer was washed free of alkaline catalyst, dried and devolatilized at 1 mm. for 24 hours. During this period roughly 12% of volatile cyclic polymers were removed. The intrinsic viscosity of the polymer in toluene was 1.36. Barry's relationship⁵ yielded a viscosity average molecular weight of 641,000. Fractionation of the polymer was carried out at 25° from a solution in ethyl acetate which was 2% by volume. Acetone was the precipitant. Fractions were obtained which were roughly one-fourth of the total sample in size. The procedure was repeated eight times taking a new sample of polymer each time with cuts removed at about the same precipitant volumes. All corresponding cuts were combined, redissolved, reprecipitated and dried. Solvent was removed at 1 mm. pressure at 50-70° for four to eight hours' pumping. This gave four fractions of roughly 200 g. each. These rather large samples were necessary for rheological studies. It is recognized that effectively this was a single fractionation and did not yield the narrow range of molecular weights which a multiple fractionation would produce. However, the size of sample required by the extrusion type rheometer made such an extensive multiple fractionation prohibitive. The distribution of materials in the cuts is included in column 4 of Table I.

Viscosities at very low rates of shear (η_0 or zero shear viscosity) were obtained by measuring the rate of fall of 1/16" diameter steel balls in polymer held in one inch test-tubes. All polymer samples were centrifuged in the tubes to remove air bubbles. Viscosities of cuts 2, 3 and 4 were such that reasonable rates of fall for the balls were obtained. Faxen's equation⁶ was used to calculate the viscosities from these rates of fall. Cut 1, however, was too viscous and it was necessary to increase the sedimenting force by centrifuging to roughly 2000 times gravity. To provide a basis for calculation cuts 1 and 2 were centrifuged simultaneously. The rate of fall of a 1/16" ball in cut 2, whose viscosity had been previously determined at unit gravity, gave a calibration of the sedimentation force. From this and the rate of fall of a 1/16"-ball in cut one in the same centrifuge period, the viscosity of cut no. 1 was calculated. Molecular weights were obtained from intrinsic viscosities in toluene using Barry's value.⁵ The data are summarized in Table I.

TABLE I

Cut	M_v	η_0 , poise, 40°	% in fraction ^a
1	1,260,000	1.61×10^7	23.6
2	851,000	2.23×10^6	30.0
3	477,000	8.58×10^4	25.1
4	214,000	6.45×10^3	21.3

^a Based on recovered polymer.

(4) J. F. Hyde, U. S. Patent 2,490,357.

(5) A. J. Barry, *J. App. Phys.*, **17**, 1020 (1946).

(6) C. J. Malm, L. B. Genug and C. B. Lapham, *Anal. Chem.*, **22**, 656 (1950).

These four points together with the viscosity-molecular weight data for pure linear dimethylpolysiloxanes with trimethylsiloxy ends¹ define two straight lines on the plot of $\log \eta_0$ vs. $\log M_v$ as in Fig. 1. Points calculated from the melt viscosity

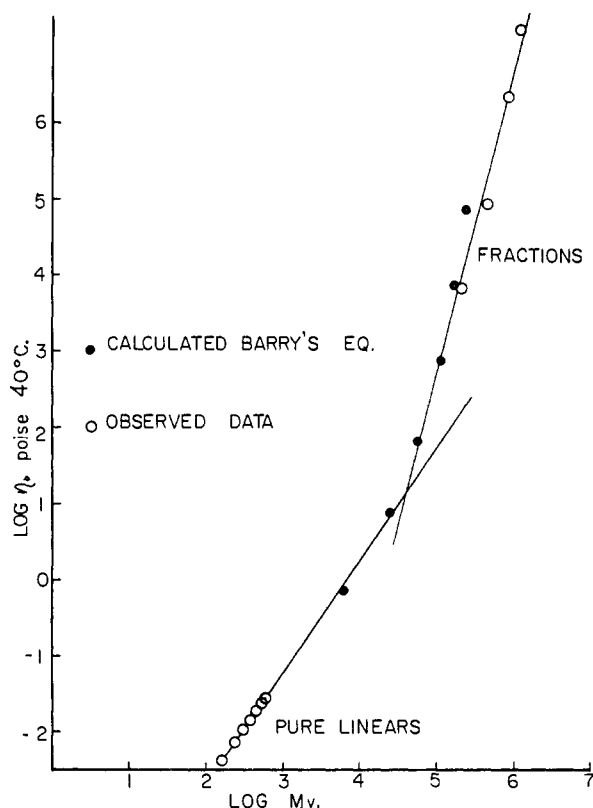


Fig. 1.—Dimethylpolysiloxane viscosity-molecular weight relationship.

relationship in Barry's paper⁵

$$\log \eta_{c.s.} = 1 + 0.0123M^{1/2}$$

are also plotted in Fig. 1. Clearly such a relationship holds in the region of the break but deviates at higher molecular weights. There is the faint suggestion of curvature in the points for the fractions.

The analytical expression for the higher molecular weight branch (above 40,000 M_v) is

$$\log \eta_{40^\circ} = 3.64 \log M_v - 15.44$$

Fox and Flory found quite similar relationships for

$$\text{Polyisobutylene } >17,000 \quad \log \eta_{217^\circ} = 3.4 \log M - 13.52$$

$$\text{Polystyrene } >50,000 \quad \log \eta_{217^\circ} = 3.4 \log M - 13.4$$

Below 40,000 molecular weight our data fit the expression

$$\log \eta_{40^\circ} = 1.43 \log M_v - 5.54$$

Bueche³ predicted a slope of unity below the break and 2.5 above. The significance of the break seems to be the molecular weight at which one has just enough effective entanglements to form a network. In our case this would represent a distance between effective chain entanglements of 1100 chain atoms.

Rheological studies of these materials at higher shear rates have been made and seem to define reduced viscosity rate of shear plots⁷ which are independent of molecular weight.

ADDED IN PROOF.—Since this note was submitted a similar curve of $\log \eta$ versus $\log M_w$ for whole polymers was published by Charlesby.⁸

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(7) E. L. Warrick, paper given before the Division of Paint, Plastics and Printing Ink Chemistry, Kansas City, March, 1954.

(8) A. Charlesby, *Proc. Roy. Soc. (London)*, **A230**, 120 (1955).