A Viscosity–Molecular Weight Relationship for Polydimethylsiloxanes

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INTRODUCTION

The relationship of limiting viscosity to molecular weight of polydimethylsiloxanes has been reported by Barry[1] and by Flory et al.[2] Flory and his co-workers studied the molecular dimensions of these polymers in methyl ethyl ketone under ideal conditions in which the system was free of polymer–solvent interaction. The relationship of intrinsic viscosity to number-average molecular weight was expressed by Flory in the form of the modified Staudinger equation. Earlier, Barry had reported the viscosities in toluene at 25°C. of polydimethylsiloxanes over a wide range of molecular weights. The molecular weights were determined by endgroup analysis for $2500 < M < 25,000$, by light scattering for $25,000 < M < 70,000$, and by osmotic pressure for $70,000 < M < 150,000$. The modified Staudinger expression

$$[\eta] = 2 \times 10^{-4} M^{0.66}$$

given by Barry is for number-average molecular weight and holds well for $2500 < M < 200,000$.

In the present study the relationship of molecular weight to intrinsic viscosity was determined. This work parallels that of Barry, differing in that weight-average molecular weights were used.

PROCEDURE

Seven Dow-Corning 200 fluids (polydimethylsiloxanes) with bulk viscosities of 200 to 100,000 cstokes were used. No attempt was made to fractionate the polymer. The DC-200 fluid described as having a bulk viscosity of 3425 cstokes was prepared from 48.74 wt.-% of DC-200 fluid of 12,500 cstokes and 51.26 wt.-% of DC-200 fluid of 1000 cstokes viscosity. The purpose was to obtain a fluid of mean molecular weight in the range of 55,000 to 60,000.

The light-scattering measurements were carried out with a Brice-Phoenix Photometer, 1000 Series,[3] and a Brice-Phoenix Differential Refractometer.[4]

The solutions were filtered through a fine-pore glass frit having a maximum porosity of 5 μ. Refractive index gradients dn/dc for the seven polymer solutions of varying molecular weights were 0.103 ± 0.005 for $\lambda = 435$ mμ and 0.094 $\pm$ 0.003 for $\lambda = 546$ mμ. The concentrations of the solutions used for these measurements ranged from 1.05 to 4.00 g. of solute per 100 ml. of solution. All measurements were made in a temperature-controlled room provided with filtered air.

Kinematic viscosities of the toluene solutions of seven DC-200 fluids were measured in a constant temperature bath at 25 $\pm$ 0.02°C. Ostwald-Fenske-type viscosity pipets (Series 50, 0.8 to 3 cstokes, and Series 100, 3.0 to 10 cstokes) were used; these had been calibrated with National Bureau of Standards oils. Readings were taken with a precision of one tenth of a second, and the mean of three measurements was used in subsequent calculations. Kinetic corrections were applied to all viscosity measurements.

RESULTS AND DISCUSSION

Figures 1 and 2 show the reciprocal turbidity data for polydimethylsiloxane in toluene at 436 mμ and 546 mμ, respectively. The weight-average molecular weights were calculated by the extrapolation of Hc/τ values to zero concentration by the least squares method.

The second virial coefficient A of the familiar light-scattering expression[3]
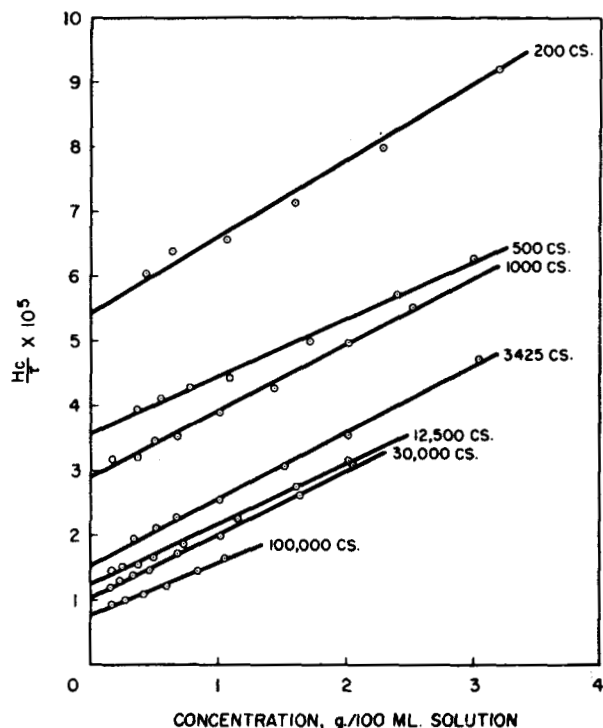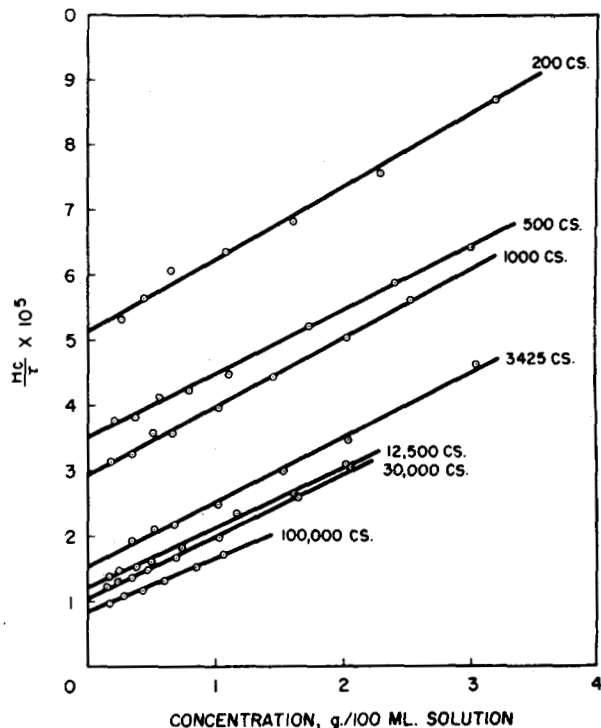
$$Hc/\tau = (1/M) + 2Ac \qquad (1)$$

generally showed a gradual decrease with increase in molecular weight as predicted by theory.

The viscosity data were described more accurately by Martin's equation[5,6]

$$\log (\eta_{sp}/c) = \log [\eta] + k[\eta]c \qquad (2)$$

than by Huggin's[7] equation

$$n_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (3)$$

Fig. 1. Hc/τ vs. c for DC-200 fluids in toluene at 436 mμ.

Fig. 2. Hc/τ vs. c for DC-200 fluids in toluene at 546 mμ.

and the former was used throughout. The plot of log (η_{sp}/c) versus c is shown in Figure 3. The intrinsic viscosity $[\eta]$ was determined by the extrapolation of log (η_{sp}/c) to zero concentration by the method of averages.

Although Martin[5] reported the value of k in eq. (2) to be a constant for a given polymer–solvent system, the experiments reported here confirmed Barry's observation that k decreases with increasing molecular weight. However, there is no indication
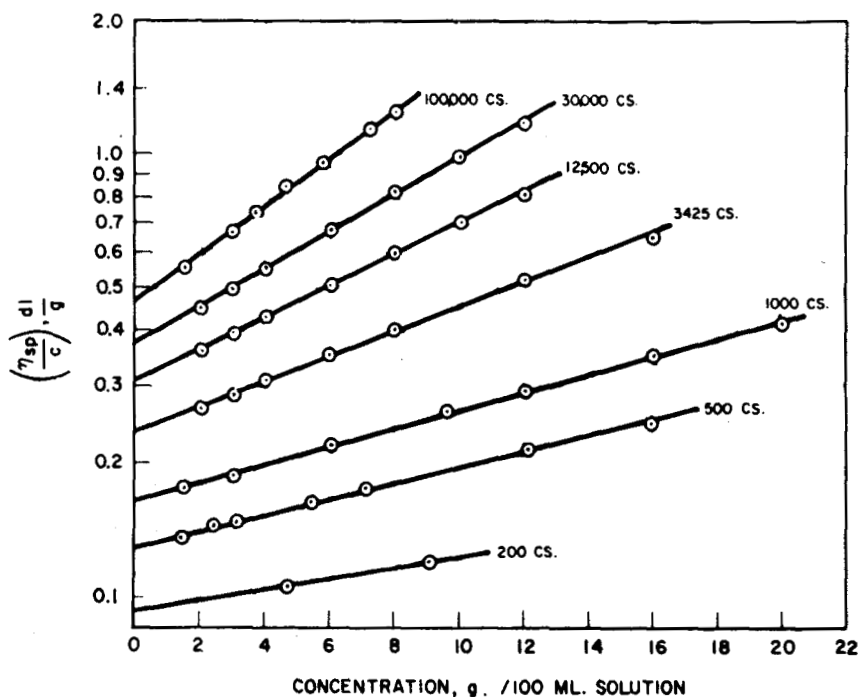
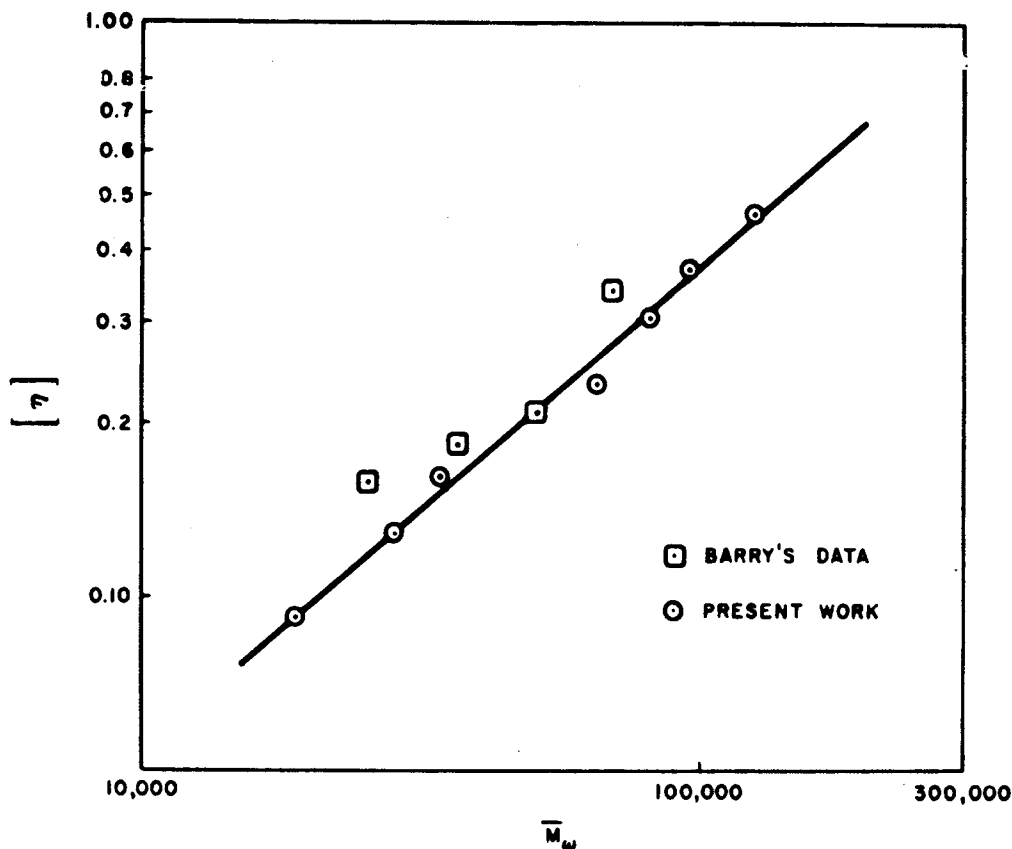Fig. 3. η_{sp}/c vs. c for DC-200 fluids in toluene.

Fig. 4. $[\eta]$ vs. $\bar{M}_w$ for DC-200 fluids in toluene.

that k approaches a limiting value with increasing molecular weight as Barry[1] suggested, although the present data are not inconsistent with this suggestion. It was found for the range of weight-average molecular weight $\bar{M}_w$ that the values of k range from 0.132 to 0.113 and are about 0.9 of those found by Barry.

The results of the viscosity and light-scattering measurements of dilute toluene solutions of seven polydimethylsiloxanes described by their bulk viscosities are given in Table I. The molecular weights are average values for measurements made at $\lambda = 546$ mμ and 436 mμ.

The plot of the log $[\eta]$ versus log $\bar{M}_w$ is shown in Figure 4. The curve is well described by the modified Staudinger equation as obtained by the least-squares method:

$$\log [\eta] = 0.838 \log \bar{M}_w - 4.61466 \quad (4)$$

or

$$[\eta] = 2.43 \times 10^{-5} \; \bar{M}_w^{0.84} \quad (5)$$

The value obtained here for the exponent a is higher, and that for the coefficient K is considerably lower, than the respective values reported for polydimethylsiloxane in toluene by Barry,[1] who obtained the following relationship:

$$[\eta] = 2 \times 10^{-4} \; M^{0.66} \quad (6)$$

The discrepancy between eqs. (5) and (6) may perhaps be explained by the fact that eq. (6) is based

TABLE I
Properties of Polydimethylsiloxanes in Toluene

Bulk viscosity, cstokes	$[\eta]$, dl./g.	$\bar{M}_w \times 10^{-3a}$	$\bar{M}_w \times 10^{-3b}$
200	0.0926	18.9	18.8
500	0.1293	28.1	28.0
1,000	0.1638	34.2	37.1
3,425	0.2366	64.7	57.5
12,500	0.3085	81.0	78.9
30,000	0.3752	95.7	99.7
100,000	0.4665	124.5	129.3

[a] Obtained from light-scattering measurements by use of the equation $Hc/\tau = (1/M) + 2 Ac$.

[b] Calculated from $[\eta] = 2.43 \times 10^{-5} \; \bar{M}_w^{0.84}$.

upon number-average molecular weights (from end-group analysis) for molecular weights in the lower and intermediate parts of the range (up to $M \simeq$ 14,000). In the upper range (to $M \simeq$ 70,000) Barry used weight-average molecular weights from light-scattering measurements as well as one osmometric number-average molecular weight $M = 148,000$. The weight-average molecular weights of polydisperse polymers are in general larger than the number-average molecular weights for the same polymers. Thus, the use of $\bar{M}_w$ for the high molecular weight polymers and $\bar{M}_n$ for the low polymers would tend to give a low a and a high K in the equation, $[\eta] = K\bar{M}^a$. In this study the results are different because they show the relationship of intrinsic viscosity only to weight-average molecular weight.

This explanation of the discrepancy is supported by Figure 4 in which Barry's weight-average molecular weight data are plotted together with the results of the present work. The range of molecular weights $\bar{M}_w$ determined in the present investigation by the light-scattering method is considerably greater than the range covered by Barry. While the average of the weight-average molecular weights in this work is somewhat higher than Barry's for given values of $[\eta]$, the slope of log $[\eta]$ versus log $\bar{M}_w$ given by his data is scarcely distinguishable from the value for the a in $[\eta] = K\bar{M}_w^a$ of the present study.

The commercial samples of polydimethylsiloxanes utilized in this work were high viscosity fluids from which the low polymers were removed by distillation. Thus, the molecular weight distribution is not that found from a normal probability function, nor is it the same as would be found in a fractionated polymer. It is interesting to note that the polydimethylsiloxane having bulk viscosity of 3425 cstokes falls relatively well in line with other points in the plot of log $[\eta]$ versus log $\bar{M}_w$ (Fig. 4). This polymer was prepared by mixing two polydimethylsiloxanes of widely differing molecular weights, and thus it represented a polydisperse system. Because of the excellent correlation between the viscosity and light-scattering data, it is believed that the modified Staudinger relationship of $[\eta] = 2.43 \times 10^{-5}\bar{M}_w^{0.84}$ is a reliable one for these fluids.

References

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Synopsis

The relationship of intrinsic viscosity $[\eta]$ to the weight-average molecular weight $\bar{M}_w$ of polydimethylsiloxane in toluene at 25°C. has been determined. The modified Staudinger equation, $[\eta] = K\bar{M}_w^a$, with $K = 2.43 \times 10^{-5}$ and $a = 0.84$, describes the relationship for the above polymers in the range of weight-average molecular weight from 18,900 to 124,500 (as determined by light-scattering measurements). These constants differ from the values reported by Barry, where $K = 2 \times 10^{-4}$ and $a = 0.66$ were obtained. The difference is attributed to the fact that Barry dealt with number-average rather than weight-average molecular weight.

Résumé

On a déterminé la relation entre la viscosité intrinsèque $[\eta]$ et le poids moléculaire moyen en poids $\bar{M}_w$ du polydiméthylsyloxane dans le toluene à 25°C. La relation modifiée de Staudinger $[\eta] = K\bar{M}_w^a$, où la valeur de $K = 2.43 \times 10^{-5}$ et de $a = 0.84$ décrit la relation pour le polymère précité pour un domaine de poids moléculaire moyen en poids s'étendant entre 18900 et 124500 (déterminé par des mesures de diffusion lumineuse). Ces constantes diffèrent des valeurs rapportées par Barry où K est de 2.10^{-4} et a de 0.66. On attribue la différence au fait que Barry se base sur une moyenne en nombre plutôt qu'une moyenne en poids pour le poids moléculaire.

Zusammenfassung

Die Beziehung zwischen Viskositätszahl $[\eta]$ und Gewichtsmittelwert des Molekulargewichts $\bar{M}_w$ wurde für Polydimethylsiloxan in Toluol bei 25°C bestimmt. Die modifizierte Staudingergleichung $[\eta] = K\bar{M}_w^a$ mit $K = 2.43 \times 10^{-5}$ und $a = 0,84$ gilt für die genannten Polymeren im Bereich des Molekulargewichts-Gewichtsmittelwertes von 18900 bis 124500 (durch Lichtstreuungsmessungen bestimmt). Diese Konstanten unterscheiden sich von den von Barry mitgeteilten Werten $K = 2 \times 10^{-4}$ und $a = 0,66$. Der Unterschied wird darauf zurückgeführt, dass die Werte von Barry nicht für den Gewichtsmittelwert sondern den Zahlenmittelwert des Molekulargewichts gelten.