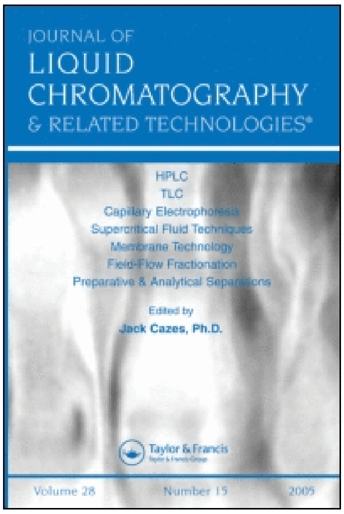

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MOLECULAR WEIGHT DISTRIBUTIONS AND MONODISPERSE INTRINSIC VISCOSITY-MOLECULAR WEIGHT EQUATION OF SILICONE ELASTOMER*

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ABSTRACT

The experimental curves of Gel Permeation Chromatography of methyl vinylsilicone elastomer polymerized by a basic catalyst and containing a small amount vinyl groups are given.

They are in consistent with the theoretical curves calculted from logarithmic-normal distribution function. Thereby, the molecular weight distribution of the samples determined belong to the logarithmic-normal distribution. With GPC, $[\eta]$ and $\langle M\rangle_n$ of the polydispersed sample the monodispersed $[\eta]$ - M relationship of the methyl vinyl silicone elastomer was established.

This relation agrees with the monodispersed $[\eta]$ - M relation established by Qian Ren-yuan, et al.(1)

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INTRODUCTION

The Mark-Houwink equation of the intrinsic viscosity-molecular weight relationship of high polymer solution shows,

$$[\eta] = K M^{\alpha} \qquad (1)$$

The molecular weight obtained only from the parameter K and α in the monodispersed equation for the $[\eta]$ value of a polydispersed sample is in accordance with the viscosity average molecular weight of which the definition is well-known.

$$\langle M \rangle_{\eta} = (\sum_{i=1}^{n} W_i M_i^{\alpha})^{1/\alpha} \qquad (2)$$

In determining the parameter in the equation, monodispersed samples are necessary. But they are difficult to obtain, even with careful fractionation of a polydispersed sample. Therefore, a correction of dispersed effect must be made on the equation obtained experimentally.(2,3,4)

The relation between intrinsic viscosity $[\eta]$ and average molecular weight, $\langle M \rangle_w$ or $\langle M \rangle_n$, for a polydispersed sample is:

$$\langle [\eta] \rangle = K_w \langle M \rangle_w^{\alpha} = q_w K \langle M \rangle_w^{\alpha} \qquad (3)$$

or

$$\langle [\eta] \rangle = K_n \langle M \rangle_n^{\alpha} = q_n K \langle M \rangle_n^{\alpha} \qquad (4)$$

Where q_n and q_w are the correction factors polydispersed. They are related with types of distribution of the sample and the distribution breadth.(2,3,4) Therefore, to obtain monodispersed Mark-Houwink equation, a definite knowledge of the molecular weight distribution of the sample must be known.

Qian Ren-yuan et al.(1) established monodispersed $[\eta]$ - M relationship of polydimethylsiloxane after determining the distribution of sedimentation coefficients, $\langle M \rangle_w$, $[\eta]_\theta$ and $[\eta]_{toluene}$.

However, the molecules of the commercial silicone elastomer contain a small amount of vinyl groups. In order to study their influence on the $[\eta]$ - M relationship, we determined the molecular weight distribution of some polydispersed samples of polymethyl vinyl siloxane by Gel Permeation Chromatograph, as well as the number-average molecular weights and intrinsic viscosities in toluene solution for each sample. The monodispersed equation of polymethyl vinyl siloxane is so obtained. It agrees with the monodispersed equation of polydimethylsiloxane proposed by Qian Ren-yuen et al. Thus, the existence of a small amount of vinyl groups has no obvious influence on the solution properties of polysiloxane.

EXPERIMENTAL

SAMPLES

The silicone elastomer samples used are non-fractionated polydispersed samples from our laboratory. They were obtained by polymerizing the dimethylcyclosiloxane containing a small amount of cyclic vinyl siloxane at the presence basic catalyst.

VISCOMETRY

The intrinsic viscosity of the polydimethyl vinyl siloxane was determined in toluene at 25 °C by ubbelonde dilution viscometer.

OSMOTIC PRESSURE

The number-average molecular weight of the polymethyl vinyl siloxane was determined in toluene at 27 °C with KNAUER menbrane osmometer.

GEL PERMEATION CHROMATOGRAPH

The determination of Gel Permeation Chromatograph was accomplished in an equipment with the column length 2.5m, interal diameter 9 mm, syphon volume 3.0 ml and porous silica beads of 120 - 140 mesh as the packing (treated with hexamethyldilazane). Whole elution volume of the column was 130 ml. Eluted solvent was toluene. Operated at room temperature with a flow rate of 0.7 ml / min. The concentration of the injected samples of polystyrene and polymethyl vinyl siloxane were 1 mg / ml and 4 mg / ml respectively. Injected volume was 1 ml. The concentrations of the eluted solution were determined by the turbidity mothed.

The column was caliorated with a series of narrowly distributed polystyrene samples. The viscosity equation of the polystyrene is

$$[\eta] = 1.1 \times 10^{-4} M^{0.73} \qquad (5)$$

The universal calibration relation of the column is obtained:

$$\log J = \log [\eta] M$$

$$\log J = 13.08 - 0.079 V \qquad (6)$$

The universal calibration curves is shown in Figure 1.

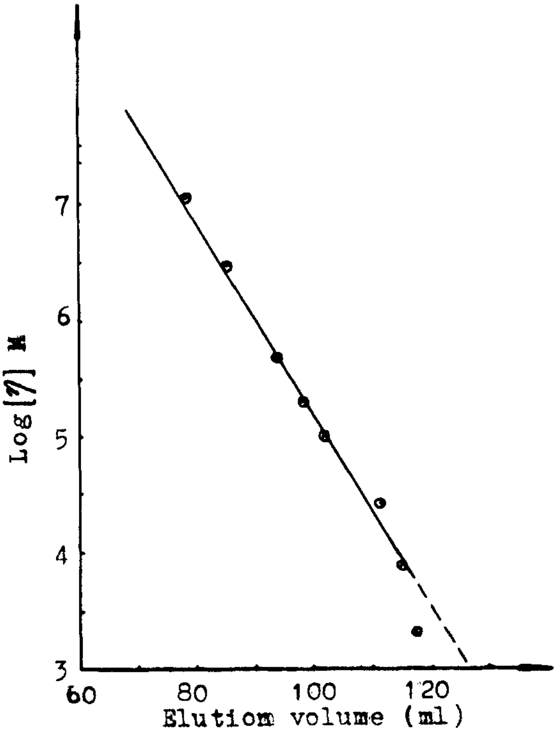

Figure 1. Universal calibration curve

RESULTS AND DISCUSSION

The GPC curves of all the samples are shown in Figure 2. According to the following equation,

$$\bar{V} = \sum_{i=1}^{n} W_i \; V_i$$

$$\sigma^2 = \sum_{i=1}^{n} W_i \; (V - \bar{V})^2$$

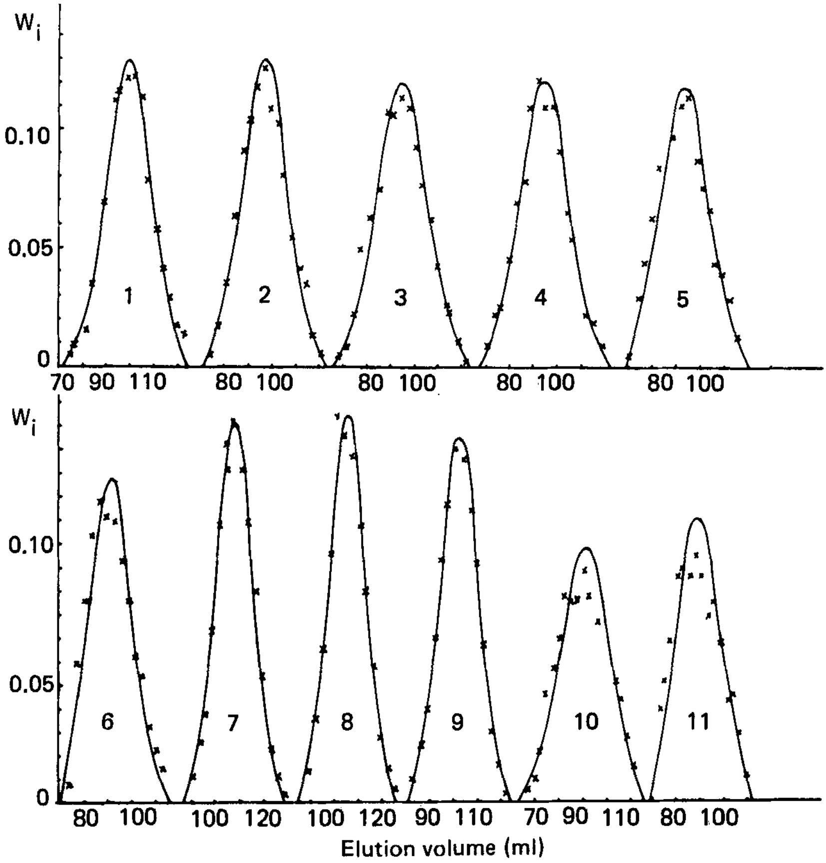

Figure 2.

Table 1.

$\bar{V}$, σ^2, $[\eta]$, $\langle M\rangle_n$, $\langle M\rangle_w / \langle M\rangle_n$ of the samples

sample	$\bar{V}$ (ml)	σ^2	$[\eta]$ (dl/g)	$\langle M\rangle_n \times 10^{-4}$ (OP)	$\langle M\rangle_w/\langle M\rangle_n$
1	99.51	91.53	0.84	14.7	2.80
2	97.17	90.83	1.03	20.0	2.72
3	94.85	112.26	1.17	22.5	3.43
4	94.95	102.65	1.24	25.4	3.10
5	93.60	107.32	1.39	30.0	3.18
6	91.83	82.70	1.60	39.2	2.48
				average	2.95
7	107.86	56.74	0.42	8.7	1.89
8	105.77	54.13	0.45	9.2	1.84
9	102.60	59.56	0.58	13.2	1.95
10**	90.93	99.43	1.11	34.8	1.81
11**	89.52	82.04	1.24	42.2	1.63
				average	1.82

: The data for 10 and 11** were determined by another column with the universal calibration equation as

$$\log J = 11.06 - 0.058\ V$$

and from our experimental curves, calculted the mean elution volume $\bar{V}$ and standard deviation σ^2 as shown in Table 1. In the equation, W_i and V_i are the weight fraction and elution volume of each individual fraction. $[\eta]$ and $\langle M\rangle_n$ of each sample obtained from the viscosity and osmotic pressure measurements are also listed in Table 1.

Log$[\eta]$ values were plotted against log $\langle M\rangle_n$ for each sample in Figure 3.

Line a in Figure 3 is for the samples 1 to 6, and line b for the samples 7 to 11. $a = 0.70$ and $K_m = 2.0 \times 10^{-4}$ are taken from the slope and the intercept of the line a, $a = 0.70$ and $K_m = 1.51 \times 10^{-4}$ from the slope and intercept of the line b.

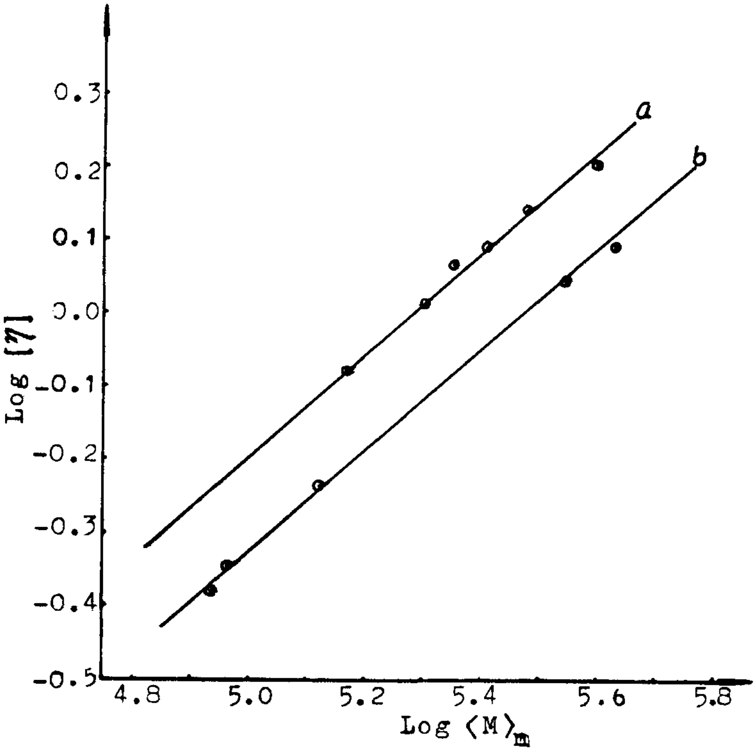

Figure 3. Log $[\eta]$ vs. log $\langle M\rangle_m$

In determining the average molecular weight of polymers by GPC, the principle of the universal calibration may be used, i.e.

$$\langle M\rangle_w = K^{-\frac{1}{1+\alpha}} \cdot \sum_{i=1}^{n} W_i \, J_i^{\frac{1}{1+\alpha}} \qquad (7)$$

$$\langle M\rangle_m = K^{-\frac{1}{1+\alpha}} \Big/ \sum_{i=1}^{n} W_i \, J_i^{-\frac{1}{1+\alpha}} \qquad (8)$$

$$\frac{\langle M\rangle_w}{\langle M\rangle_n} = \sum_{i=1}^{n} W_i \, J_i^{\frac{1}{1+\alpha}} \cdot \sum_{i=1}^{n} W_i \, J_i^{-\frac{1}{1+\alpha}} \qquad (9)$$

Therefore, distribution breadth index, $\langle M\rangle_w / \langle M\rangle_n$, obtained are independent of the parameter K. From the experimental curve of each sample take $\alpha = 0.70$ (the slope of a, b lines in Figure 3). The distribution breadth index $\langle M\rangle_w / \langle M\rangle_n$ of the eleven samples are obtained by the equation (9). See the results in Table 1. Take the samples 1 to 6 as one group and the average value of the distribution breadth index is 2.95, while another group, the samples 7 to 11, gives the average value of the distribution breadth index as 1.82 also shown in Table 1.

The experimental curve of each sample shows good symmetry, so Gauss normal distribution function

$$F(V) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left[- \frac{1}{2\sigma^2} (V - \bar{V})^2 \right] \qquad (10)$$

can be used.

The normalized distribution curves calculated from the average value and the standard deviation of each sample (in Table 1) and with equation (10) agrees well with the experimental results, as shown in Figure 2. As the calibration curve of our GPC column is linear, the molecular weight distribution of the samples studied may be described by log-normal distribution function. For the polydispersed sample with log normal distribution,(2,3,4)

$$q_w = \left(\frac{\langle M\rangle_w}{\langle M\rangle_n} \right)^{\frac{1}{2}\alpha(\alpha - 1)} \qquad (11)$$

$$q_m = \left(\frac{\langle M\rangle_w}{\langle M\rangle_n} \right)^{\frac{1}{2}\alpha(\alpha + 1)} \qquad (12)$$

Substitute into the equation (12) the average values of the distribution index of two groups and α values. The q_n values of two groups so obtained are 1.903 and 1.428 respectively. From the K_n and q_n of two groups, we obtain:

$K = 1.05 \times 10^{-4}$ and $K = 1.06 \times 10^{-4}$

Therefore, $[\eta]$ - M relation in the momodispered solution may be expressed as

$$[\eta] = 1.06 \times 10^{-4}\ M^{0.70} \qquad (13)$$

Since

$$[\eta] = K \langle M\rangle_\eta^\alpha = K \left(\frac{\langle M\rangle_w}{\langle M\rangle_n}\right)^{\frac{1}{2}\alpha(\alpha+1)} \cdot \langle M\rangle_n^\alpha$$

$$= K \left[\left(\frac{\langle M\rangle_w}{\langle M\rangle_n}\right)^{\frac{1}{2}(\alpha+1)} \cdot \langle M\rangle_n \right]^\alpha$$

then

$$\langle M\rangle_\eta = \left(\frac{\langle M\rangle_w}{\langle M\rangle_n}\right)^{\frac{1}{2}(\alpha+1)} \cdot \langle M\rangle_m \qquad (14)$$

The viscosity average molecular weight $\langle M\rangle_\eta$ of each sample may be obtained by substituting $\langle M\rangle_n$, α and $\frac{\langle M\rangle_w}{\langle M\rangle_n}$ of eleven samples into the equation (14)

Plot $\log[\eta]$ against $\log \langle M\rangle_\eta$ as shown in Figure 4. It can be seen that the experimental points of two sample groups fall on the line for the monodispersed $[\eta]$ - M relation (13). It is independent of the size of the distribution breadth.

Qian Ren-yuan, Ying Qi-zong et al, obtained the monodispersed $[\eta]$ - M relationship for polydimethylsiloxane as

$$[\eta] = 9.53 \times 10^{-5}\ M^{0.71} \qquad (15)$$

shown by dotted line in Figure 4. The solid line and dotted line overlap each other.

It can be seen that the presence of a small amount of the vinyl groups in the molecular chain of polydimethylsiloxane has shown no evident change in the property of solution and the flexibility of the molecular chain.

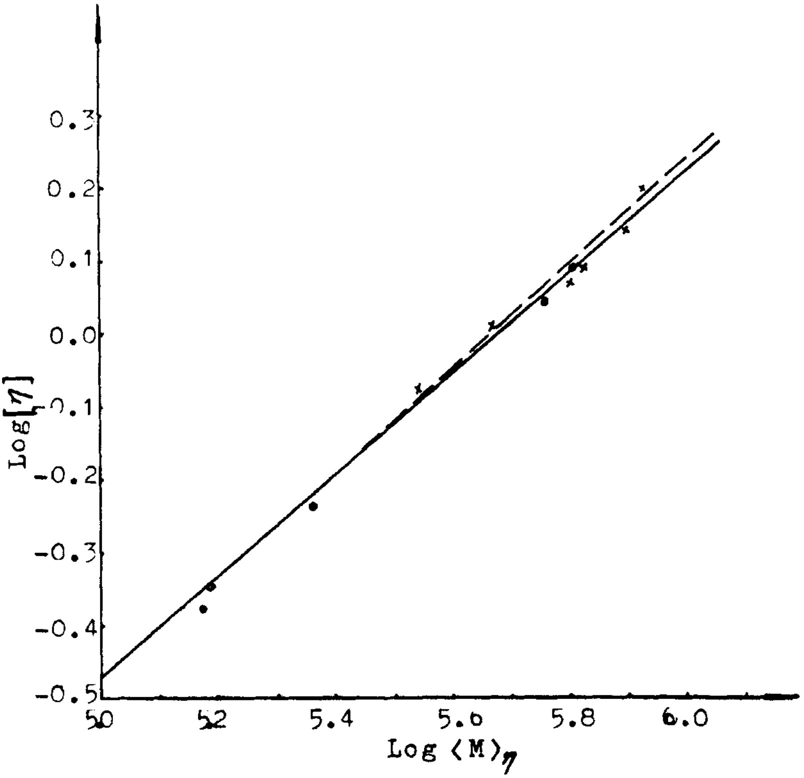

Figure 4. log[η] vs. log$\langle M \rangle_\eta$

o and x : equation (14)
solid line : equation (13)
dotted line : equation (15)

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REFERENCES

1. Qian Ren-yuan, Ying Qi-zong, Polymer Communications 6, 459 (1964).

2. M. Kurata, Y. Tsunashima, M.Iwama, K. Kamada, J. Brandrup, E. H. Immergut, (Editors), Polymer Handbook (Second Edition) IV-2, 1975.
3.H.P.Framk, J.Polymer Sci. ,7, 567 (1951).
4. R.Koningsveld, C,A.F. Tuijuman, Makromol. Chem. , 38, 39 (1960).