One-Point Method for Determination of Number-Average Molecular Weight

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Synopsis

The following well-known equation permits the ready determination of $\bar{M}_n$ from a single osmotic pressure measurement at a known concentration, if the second virial coefficient is previously given:

$$(\pi/C)^{1/2} = (RT/\bar{M}_n)^{1/2}(1 + \Gamma_2 C/2).$$

On this basis, the one-point method was investigated to determine the number-average molecular weight. It was found that this method was applicable to commercial polymers. However, in this application, the dependence of Γ_2 on molecular weight distribution has to be kept in mind.

INTRODUCTION

The one-point intrinsic viscosity method is well known as a rapid method for the determination of molecular weight.[1-3] However, the number-average molecular weight $\bar{M}_n$ obtained in such a way is remarkably affected by the molecular weight distribution,[4] because the intrinsic viscosity must be converted to the number-average molecular weight by using Mark-Houwink-Sakurada's equation, the parameter in its equation highly depending on the molecular weight distribution.

On the other hand, measurement of osmotic pressure has become rapid and easy by the recent development of high-speed membrane osmometers. Therefore, one-point determination is possible by using these instruments. The determination of the number-average molecular weight is especially straightforward, and the time required for washing of the cell is usually shorter than the time required for viscosity measurements.

Osmotic pressure is generally expressed by eq. (1) in the virial expansion:

$$\pi/C = (RT/\bar{M}_n) \times (1 + \Gamma_2 C + \Gamma_3 C^2) \tag{1}$$

where Γ_2 and Γ_3 are the second and the third virial coefficients, respectively. Accordingly, when Γ_2 and Γ_3 are known at a given temperature, $\bar{M}_n$ can be determined from π at a given concentration. And by setting $\Gamma_3 = 1/4 \, \Gamma_2{}^2$ in accordance with Stockmayer's theory,[5] eq. (1) can be reduced to eq. (2):

$$(\pi/C)^{1/2} = (RT/\bar{M}_n)^{1/2} \times (1 + \Gamma_2 C/2) \tag{2}$$

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In this case, if only Γ_2 is previously known, $\bar{M}_n$ of a sample can be determined by the measurement of one-point osmotic pressure.   On the basis of this idea, the one-point method was investigated.

EXPERIMENTAL

Commercial polypropylene homopolymers and their fractions were used. The $\bar{M}_w/\bar{M}_n$ of the fractions was within 1.3.   A Hewlett Packard Model 502 high-speed membrane osmometer was employed, and the determinations were made at 130°C for tetralin solutions containing 0.2% Ionol with a pretreated Ultracella filter (allerfeinst), which had been successively treated with water, isopropanol and finally tetralin.[6]

A plot of π/C against C, as shown in Figure 1, displayed a downward curvature owing to the third virial coefficient.   Therefore, when the curve is extrapolated to $C = 0$, the reduced osmotic pressure obtained involves ambiguity, which increases the reading error.   Extrapolation of the plot of $(\pi/C)^{1/2}$ against C, as shown in Figure 2, was linear, and the error of reading decreased.   Thus, the form of eq. (2) was adopted for the one-point osmotic pressure method.
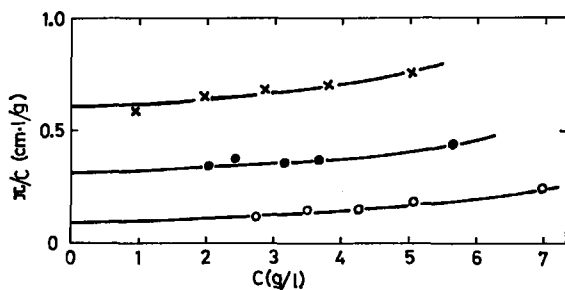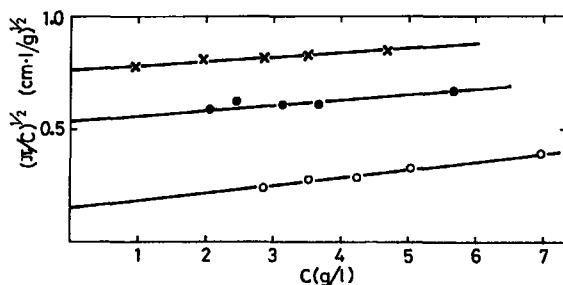

Fig. 1. Plot of π/C vs. C.

Fig. 2. Plot of $(\pi/C)^{1/2}$ vs. C.

RESULTS AND DISCUSSION

From the theoretical and experimental points of view, it is well known that Γ_2 in eq. (2) highly depends on molecular weight.[7-9]   The dependence was examined under our experimental conditions, and the result is shown in
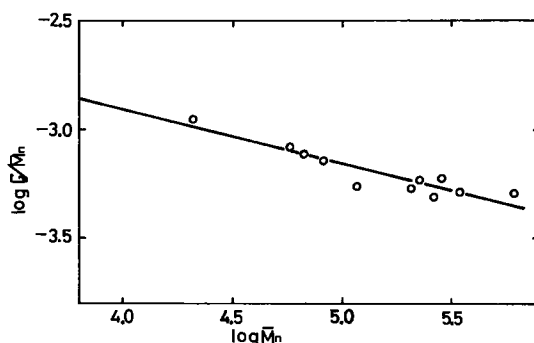
Fig. 3. Dependence of $\log \Gamma_2/\bar{M}_n$ on $\log \bar{M}_n$.

Figure 3.   Log $\Gamma_2/\bar{M}_n$ decreases linearly with log $\bar{M}_n$ in this figure, and Γ_2 is given by

$$\Gamma_2 = 1.15 \times 10^{-5} \, \bar{M}_n^{0.76} \, (\text{l./g}). \tag{3}$$

Substitution of the above equation for eq. (2) yields eq. (4):

$$\pi = (RTC/\bar{M}_n) \times (1 + 0.575 \times 10^{-5} \, C\bar{M}_n^{0.76})^2. \tag{4}$$

In eq. (4), though $\bar{M}_n$ can be determined by eq. (4) at a known concentration, the relationship of π for $\bar{M}_n$ is very tedious.   Therefore, it is favorable that $\bar{M}_n$ is graphically determined as shown in Figure 4.
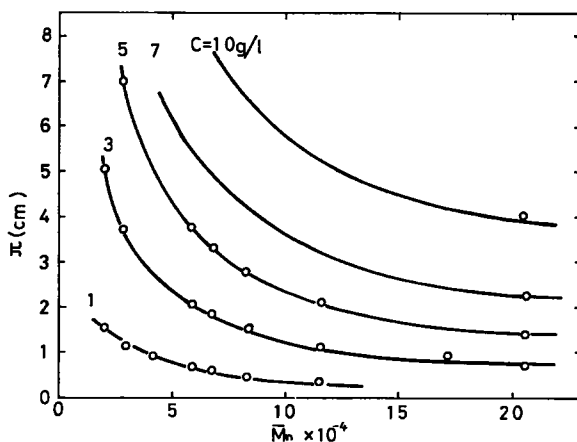

Fig. 4. Relationships of π for $\bar{M}_n$ at given concentrations: (O) experimental points.

The usefulness of this method depends greatly on how high the accuracy can be kept.   Thus, the errors in this method will hereinafter be discussed in detail.   If the cause for the errors in $\bar{M}_n$ is the variations in reading of osmotic pressure, concentration of polymer, and the second virial coeffi-
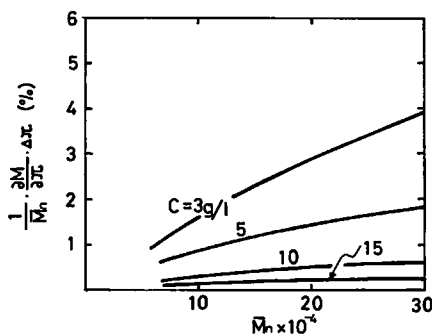
Fig. 5. Effect of the variation in reading π on $\bar{M}_n$.

cient, the maximum error of $\delta M/\bar{M}_n$ is given by eq. (5) based on the theory of errors:

$$\frac{\delta M}{\bar{M}_n} = \frac{1}{\bar{M}_n} \left\{ \left| \frac{\partial M}{\partial \pi} \cdot \delta \pi \right| + \left| \frac{\partial M}{\partial C} \cdot \delta C \right| + \left| \frac{\partial M}{\partial \Gamma_2} \cdot \delta \Gamma_2 \right| \right\} \qquad (5)$$

where $\delta \pi$, δC, and $\delta \Gamma_2$ are the variations of π, C, and Γ_2, respectively.

The error due to the variation of π is expressed as eq. (6) by partial differential of eq. (2):

$$\frac{1}{\bar{M}_n} \cdot \frac{\partial M}{\partial \pi} = -\frac{4\bar{M}_n}{RTC} (2 + \Gamma_2 C)^{-2}. \qquad (6)$$

This error is attributed to the variation in reading of the meniscus of the osmometer, and it is generally expected that $|\delta \pi| = 0.01$ cm. As shown in Figure 5, the error in this case is within 5%, and accordingly it is worth little consideration. Next, the error due to the variation of C is expressed as

$$\frac{1}{\bar{M}_n} \frac{\partial M}{\partial C} = \frac{1}{C} \left\{ 1 + 2C(2 + \Gamma_2 C)^{-1} \right\}. \qquad (7)$$

This error is shown in Figure 6, in the case that $C = 0.2$ g/l. from the error in preparing the solution. It is obvious that the error increases when the measurement is performed in dilute solution, but in general it is hardly worthy of attention. Third, the error due to the variation of the second virial coefficient is expressed as

$$\frac{1}{\bar{M}_n} \frac{\partial M}{\partial \Gamma_2} = \frac{2C}{(2 + \Gamma_2 C)}. \qquad (8)$$

Γ_2 is expected to depend on not only molecular weight but also on molecular weight distribution. The effect of the latter is very important, because the determination is usually made by samples having various extent of molecular weight distribution. Thus, the Γ_2 values of commercial polypropylene were determined and are shown in Table I. On the other hand, the dependence of Γ_2 on molecular weight distribution was determined by using samples prepared by Sato's method,[10] and the result is shown in Figure 7. From these data, to determine the number-average molecular weight of
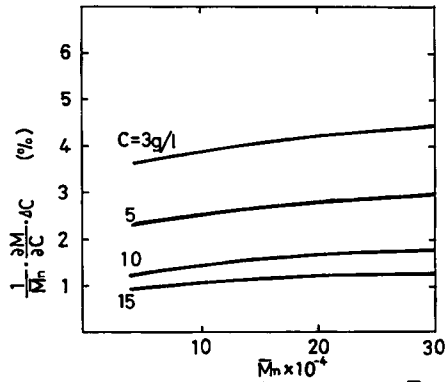
Fig. 6. Effect of the variation of C on $\bar{M}_n$.

commercial polypropylene, it was confirmed that 0.2 in log $\Gamma_2/\bar{M}_n$ must be added to eq. (3), and moreover, that the variation of 0.08 in log $\Gamma_2/\bar{M}_n$ has to be taken into account. In this case, as shown in Figure 8, the error is larger than that of other factors which were discussed above. Therefore,

TABLE I

$\Gamma_2/\bar{M}_n$ of Commercial Polypropylene

Sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	log $\Gamma_2/\bar{M}_n$	log $\Gamma_2/\bar{M}_n$[a]	Δlog $\Gamma_2/\bar{M}_n$[b]
A	6.53	4.3	−2.99	−3.12	+0.13
B	6.53	—	−3.01	−3.12	+0.11
C	7.28	—	−3.07	−3.13	+0.06
D	7.65	3.1	−2.95	−3.13	+0.18
E	8.88	2.8	−3.03	−3.15	+0.12
F	9.65	2.1	−2.91	−3.16	+0.25
G	12.6	2.5	−3.01	−3.19	+0.18
H	14.6	2.4	−2.87	−3.20	+0.33
Average					+0.17
Standard deviation					0.08

[a] Calculated by eq. (3).
[b] Δlog $\Gamma_2/\bar{M}_n$ = log $\Gamma_2/\bar{M}_n$ − log $\Gamma_2/\bar{M}_n$.
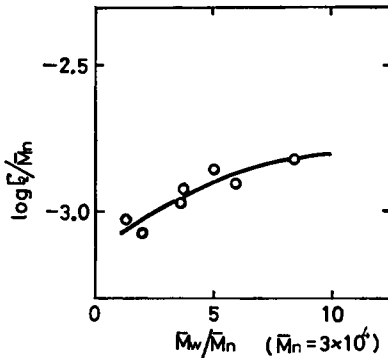

Fig. 7. Dependence of Γ_2 on molecular weight distribution.

TABLE II

Number-Average Molecular Weight of Commercial Polypropylene Determined by One-Point and Ordinary Methods

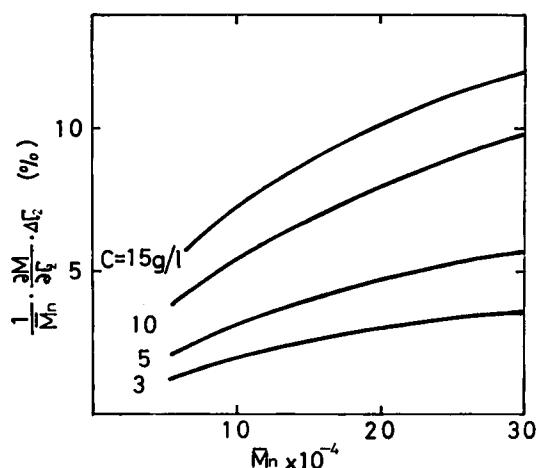| Sample	One-point method								Ordinary method, $\bar{M}_n \times 10^{-4}$
	1 g/l.		3 g/l.		5 g/l.		7 g/l.		
	$\bar{M}_n \times 10^{-4}$	Error, %	$\bar{M}_n \times 10^{-4}$	Error, %	$\bar{M}_n \times 10^{-4}$	Error, %	$\bar{M}_n \times 10^{-4}$	Error, %	
A	5.3	−18.5	6.6	+1.5	6.9	+6.2	7.0	+7.7	6.5
B	6.7	+1.5	6.9	+4.5	6.8	+3.0	7.1	+7.6	6.6
C	12.7	+74.0	7.6	+9.6	8.0	+9.6	—	—	7.3
D	6.9	−10.4	7.6	−1.3	7.5	−2.6	7.4	−3.9	7.7
E	8.4	−5.6	8.2	−7.9	9.9	+11.2	—	—	8.9
F	13.0	−3.2	12.8	+1.6	11.8	−6.3	—	—	12.6

Fig. 8. Effect of the variation of Γ_2 on $\bar{M}_n$.

in the actual operation for commercial polymers, it is important to decrease the error due to variation of Γ_2.

Examples applied to commercial polypropylene are shown in Table II, together with the values determined by the ordinary method. In this table the relative error was calculated on the basis of the values which were determined by the ordinary method. On account of the error due mainly to the π reading, the measured values at the concentration of 1 g/l. often deviate from those by the ordinary method. However, with this exception, the agreement between the values by one-point and ordinary methods is satisfactory.

In this report, we have discussed the subject which occurred after the instrument had been completely set. The measurement of osmotic pressure at high temperature is not easy, because the preparation of the appropriate membrane requires some technical skill. However, this method is much preferred for polymers, the measurement of which can be achieved at ordinary temperatures.

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