

A NEW METHOD FOR ESTIMATION OF WEIGHT-AVERAGE MOLECULAR WEIGHT OF POLYMER FROM THE INTRINSIC VISCOSITY AND CHROMATOGRAM

ZHANG Zhaomu (张兆谟) and YANG Guojun (杨国钧)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

A new method is proposed for estimation of weight-average molecular weight from the intrinsic viscosity and GPC chromatogram of a polymer sample for which Mark-Houwink coefficients are not known. The method bases on an approximate relationship between GPC data and the intrinsic viscosity of the sample. Reliability of this method was tested by comparing with the universal calibration method which requires known Mark-Houwink coefficients for seven samples having different molecular weight distributions. Results obtained by the new method are in excellent agreement with those by the universal calibration method.

INTRODUCTION

Gel permeation chromatography (GPC) is a powerful tool for the estimation of molecular weight averages and molecular weight distribution of polymers, whereas GPC is only a relative approach for the determination of molecular weight averages. In order to obtain reliable values of the averages from GPC data, a GPC system has to be calibrated previously using a series of standards with very narrow molecular weight distribution, but it is very difficult to get the standards, except for a few polymers, e.g. polystyrene.

In order to avoid the difficulty, one attempted to find a universal calibration parameter even in the early period of GPC development. Harmon^[1] and Maley^[2] used an extended chain length of a polymer molecule in solution as the universal parameter and was partially successful in practice.

Using the hydrodynamic volume of polymer molecule in solution as universal parameter was proposed by Benoit and his collaborators^[3]. In good solvents the hydrodynamic volume of molecule is proportional to the product of its molecular weight and intrinsic viscosity and the product was easily obtained, so now the product was used as the universal calibration parameter. Many authors have verified this product as the parameter. In addition, Casassa^[4] has theoretically showed the mechanism of separation in GPC system is on the basis of the hydrodynamic volume of polymer molecule in solution.

Since the universal calibration theory was proposed, it looks as if the estimation of

molecular weight averages from GPC chromatogram has been solved. In fact, the problem is not so simple. The conversion from the universal calibration parameter J into the molecular weight M of polymer requires Mark-Houwink coefficients K and α in eq. (1)

$$[\eta] = KM^\alpha \quad (1)$$

and by means of eq. (2)

$$J = KM^{1+\alpha} \quad (2)$$

Unfortunately, when the universal calibration method is used, two difficulties usually appear:

1. For a new polymer it is laborious to determine the Mark-Houwink coefficients in experiment.
2. For an existing polymer the coefficients may be found in the literature, but sometimes conditions of determining the coefficients are not the same as that used in the GPC experiment, so that the coefficients can not be used. In addition, there may appear several different coefficients in the literature for the same polymer at the same conditions, so that it is difficult to decide which one is the best.

Without suitable coefficients, though GPC chromatogram has been done, even a qualitative result can not be obtained. For avoiding the difficulties, Weiss^[5] and Bobbin^[6] suggested a procedure of estimating K and α from two samples with different intrinsic viscosities of the same polymer; Mahabadi^[7] estimated K and α from the intrinsic viscosity and number-average molecular weight of the same polymer sample; Ambler^[8] described a method for estimation of K : empirically specifying α as 0.74 and substituting it into

$$[\eta] = K^{1/(1+\alpha)} \sum w_i J_i^{\alpha/(1+\alpha)} \quad (3)$$

and solving for K with $[\eta]$ measured independently in the GPC conditions. The above methods have something in common: finding the apparent K and α and then using universal calibration method to calculate molecular weight averages. Even without suitable K and α Rudin^[9] used a quasi-molecular weight M_x by

$$M_x = \sum w_i J_i / [\eta] \quad (4)$$

Recently Mahabadi^[10] proposed an approach for estimation of visco-average molecular weight from GPC chromatogram and intrinsic viscosity of a polymer sample. In this paper we give a new method for the estimation of weight-average molecular weight M_w from GPC chromatogram and intrinsic viscosity of a polymer sample. The method is simpler and more accurate.

THEORY

In a set of operational conditions GPC calibration curve is obtained by using a number of standards, e.g. PS, with known molecular weight, intrinsic viscosity and very narrow molecular weight distribution and expressed as

$$\ln J_i = D_0 + D_1 V_i + D_2 V_i^2 + D_3 V_i^3 \quad (5)$$

or

$$J_i = \exp(D_0 + D_1 V_i + D_2 V_i^2 + D_3 V_i^3) \quad (5')$$

where D_0, D_1, D_2, D_3 are constants; V_i is retention volume of a piece of polymer with molecular weight M_i and intrinsic viscosity $[\eta]_i$; J_i is the product of M_i and $[\eta]_i$. If relation between

M_i and $[\eta]_i$ can be described by Mark-Houwink equation we have

$$J_i = KM_i^{1+\alpha} \quad (6)$$

From the definitions of intrinsic viscosity $[\eta]$ and weight-average molecular weight M_w , eq. (6) yields

$$[\eta] = \sum w_i [\eta]_i = K^{1/(1+\alpha)} A(\alpha) \quad (7)$$

$$M_w = \sum w_i M_i = K^{-1/(1+\alpha)} A_1(\alpha) \quad (8)$$

where

$$A(\alpha) = \sum w_i J_i^{\alpha/(1+\alpha)} \quad (9)$$

$$A_1(\alpha) = \sum w_i J_i^{1/(1+\alpha)} \quad (10)$$

or

$$A(\alpha) = \sum w_i \exp((D_0 + D_1 V_i + D_2 V_i^2 + D_3 V_i^3)\alpha/(1+\alpha)) \quad (9')$$

$$A_1(\alpha) = \sum w_i \exp((D_0 + D_1 V_i + D_2 V_i^2 + D_3 V_i^3)/(1+\alpha)) \quad (10')$$

Multiplying eq. (7) by eq. (8) we get

$$M_w [\eta] = A(\alpha) A_1(\alpha) \quad (11)$$

or

$$M_w = A(\alpha) A_1(\alpha) / [\eta] \quad (11')$$

Comparing eq. (9) with (10), we find the difference between (9) and (10) is only in the exponents; and $A(\alpha)$ is an increasing function of α ; $A_1(\alpha)$ decreasing function of α ; the sum of the two exponents,

$$\alpha/(1+\alpha) + 1/(1+\alpha) = 1 \quad (12)$$

is always equal to 1; and $A(\alpha) = A_1(\alpha)$ at $\alpha = 1$. It is expected that the increasing rate of $A(\alpha)$ is almost the same as the decreasing rate of $A_1(\alpha)$, although they are not exactly equal. In other words, $A(\alpha)A_1(\alpha)$ is almost independent of α , as shown in Fig. 1. Since the change of $A(\alpha)$ and $A_1(\alpha)$ with α is too great, for the convenience of drawing, $\log A(\alpha)$, $\log A_1(\alpha)$ and $\log A(\alpha)A_1(\alpha)$ were used instead of $A(\alpha)$, $A_1(\alpha)$ and $A(\alpha)A_1(\alpha)$. Because the change of

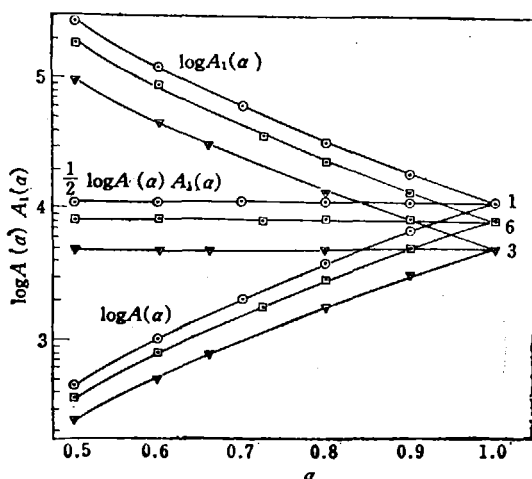


Fig. 1 Change of $A(\alpha)$, $A_1(\alpha)$ and $A(\alpha)A_1(\alpha)$ with α . 1, 6 and 3 are number of the samples

$A(\alpha)A_1(\alpha)$ is very small, the value of M_w computed by eq. (11) at any α specified is a very good approximation of true weight-average molecular weight. However there should be only one weight-average molecular weight for a polymer sample, we suggest that the geometrical mean of M_w computed by eq. (11) at $\alpha=0.5$ and $\alpha=1.0$ may be used as the weight average molecular weight $\bar{M}_w$ of the sample

$$\bar{M}_w = (A(0.5)A_1(0.5))^{1/2} A(1.0) / [\eta] \quad (13)$$

TESTING AND DISCUSSION

For testing the reliability of the new method, five polystyrene samples with different molecular weight distributions and two *cis*-1,4-polybutadiene samples with different peak shapes are chosen; samples 2 and 5 have narrow molecular weight distributions, 1,4 and 6 are middling, 3 and 7 are broad. In addition, sample 6 has double peak distributions and 7 has long-tail distribution, as shown in Figs. 2 and 3.

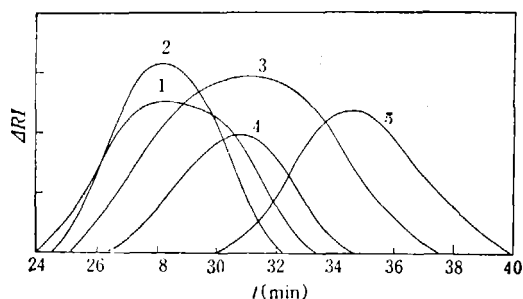


Fig. 2 GPC chromatograms of five polystyrene samples 1,2,3,4 and 5 are number of the samples

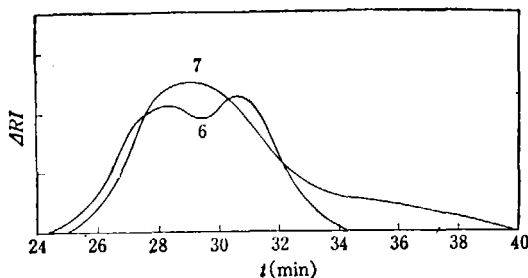


Fig. 3 GPC chromatograms of two polybutadiene samples

The universal calibration curve was determined on Waters 150C Chromatograph with a set of home made columns at 35°C and flow rate of 1ml/min. Using THF as solvent and PS standards $D_0=43.14314604$, $D_1=-0.882433889$, D_2 and D_3 are zero.

For testing the new method and eliminating error introduced experimentally, the $[\eta]$ calculated by eq. (7) replaced that measured experimentally and M_w calculated by eq. (8) was considered as real weight-average molecular weight. In this way, zone spreading of GPC system does not effect the comparison of the results computed by both the new method and

the universal calibration method. When $[\eta]$ measured experimentally and chromatogram of a polymer sample were employed to calculate M_w , in principle, the chromatogram must be corrected. In this case, the correction method of zone spreading presented by Cheng^[9] is convenient.

Table 1 gives the results calculated by both the new method and the universal calibration. Through number 1 to 5 are polystyrene which has K of 2.2×10^{-4} dl/g and α of 0.66. Number 6 and 7 refer to *cis*-1,4-polybutadiene which has K of 2.51×10^{-4} dl/g and α of 0.725.

Table 1 Results computed by both new method and universal calibration method

No.	$[\eta]$ (dl/g)	$M_w \times 10^{-3}$ @	$M_n \times 10^{-3}$ @	M_w/M_n	$\bar{M}_w \times 10^{-3}$	(%)
1	1.531	762.6	218.5	2.71	762.6	0.00
2	1.553	745.8	409.4	1.82	742.2	0.43
3	0.7656	294.8	59.80	4.92	292.6	0.74
4	0.1630	25.75	9.410	2.74	25.91	0.62
5	0.7167	236.2	119.6	1.98	237.6	0.59
6	2.114	294.0	112.2	2.62	299.4	1.8
7	1.664	215.4	25.18	8.56	217.9	1.2

Note: @ refers to the results computed by universal method.

M_w in the third column was computed by means of eq. (8) and $\bar{M}_w$ in the 6th column by eq. (13). The 7th column gives the relative error between M_w and $\bar{M}_w$. The results in the table show that M_w is in excellent agreement with $\bar{M}_w$.

Table 2 gives the change of M_w with α for seven samples.

Table 2 Change of M_w with α , mean and deviation of M_w for seven samples

α	$M_w \times 10^{-3}$						
	1	2	3	4	5	6	7
0.50	786.0	766.5	309.5	26.66	243.6	309.6	224.8
0.60	766.5	752.4	299.6	26.00	238.4	307.7	218.8
0.66	762.6	745.8	294.8	25.74	236.2	—	—
0.725	—	—	—	—	—	294.0	215.5
0.80	746.3	738.8	287.9	25.35	233.2	291.7	212.8
0.90	742.3	736.2	285.8	25.21	232.2	290.1	211.7
1.00	738.4	719.3	285.1	25.17	231.9	289.6	211.3
Mean	757.0	743.3	293.9	25.60	235.9	297.2	215.8
Devia.	± 15.6	± 14.6	± 8.7	± 0.53	± 4.1	± 8.2	± 4.7

The last two rows give the mean and deviation of M_w for seven samples. From the table it is very clear that though the difference in molecular weight distribution as well as the inherent coefficients of Mark-Houwink equation are large, the change of M_w with α is very small.

Fig. 4 shows the change of M_w with α for 4 samples as an example of the change, and for others it is similar. Fig. 4 shows that M_w is slightly decreasing as increasing of α and has a minimum at $\alpha=1.0$.

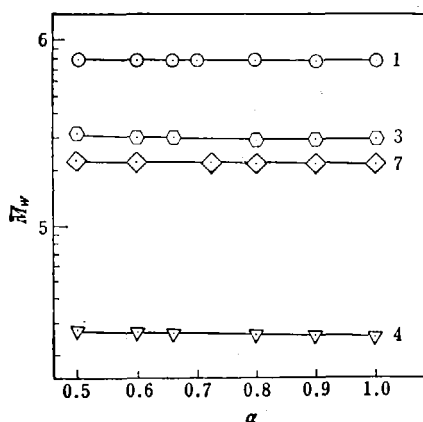


Fig. 4 Change of M_w with α for samples 1,3,4 and 7

CONCLUSION

From the definitions of $[\eta]$ and M_w of polymer, it was found that the product of $[\eta]$ and M_w is equal to the product of function $A(\alpha)$ and $A_1(\alpha)$ which are almost compensated with each other. Therefore it becomes feasible to estimate weight-average molecular weight from the intrinsic viscosity and GPC chromatogram of a polymer sample if the intrinsic viscosity is measured independently in GPC conditions. The new method bases on the universal calibration theory but does not require the values of K and α of the polymer. It is very convenient for estimation of M_w of polymers which do not have suitable K and α .

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