Gel Permeation Chromatography에 의한 범용 Poly(Vinyl Chloride)의 특성 결정

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Characterization of Commercial Poly(Vinyl Chloride) by Gel Permeation Chromatography

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요 약 : 한 낮은 농도의 점도 data를 이용하여 고유점도를 결정하는, Solomon 등이 제안한, "single-point"법의 적용가능성이 25℃, PVC-THF계에서 종래의 외삽법에 의한 값들과 비교 시험되었다. GPC로 3종의 다른 PVC 시료들의 정확한 분자량과 분자량 분포를 구하기 위하여 "hydrodynamic volume average molecular weight 개념"에 근거한 Mahabadi의 방법에 따라 단지 고유점도와 GPC data만으로 25℃, PVC-THF 계의 Mark-Houwink 상수를 평가 하였는데 얻어진 값은 K=1.16× 10^{-3} dl/gr이고 a=0.60이었다. 이들 K, a값을 이용하여 수평균(Mn), 중량평균(Mw) 분자량 및 이들의 비(Mw/Mn)인 분자량 분포 (MWD)를 계산하였고, 고유점도의 실험치와 Mark-Houwink 상수를 이용하여 계산한 값의 비교를 통해 Mahabadi 이론의 타당성도 함께 조사되었다. 또한 "universal calibration법"에 의해 분자량과 분자량 분포를 평가할때 범하기 쉬운 오류도 지적하였다.

Abstract : The applicability of "single-point" methods as represented by Solomon'sequation for determining intrinsic viscosity using viscosity data at one low concentration has been tested to the PVC-THF system at 25℃, in comparison with the values obtained by conventional extrapolation methods. In order to determine correct MW's and MWD's of three different PVC samples by GPC, Mark-Houwink constants of the PVC-THF system at 25℃ have been evaluated following Mahabadi's procedure, based on the "hydrodynamic volume-average molecular weight concept", using only intrinsic viscosity(IV) and GPC data, yielding K= 1.16 × 10^{-3} dl/gr and a=0.60. The number(Mn) and weight (Mw) average MW's, and hence MWD expressed in terms of Mw/Mn, have been calculated using these K and a values, together with the validity test of Mahabadi's theory through comparison of calculated and experimental values of intrinsic viscosity. In addition, a fallacy liable to occur in the evaluation of MW and MWD by "universal calibration technique" was pointed out to prevent erroneous results.

INTRODUCTION

Information on molecular weight(MW) and molecular weight distribution(MWD) of synthetic polymers is of great value to both polymer scientists and practical engineers. Hence, gel permeation chromatography (GPC) is one of the most powerful tools for determining the MW or size of polymers in dilute solution in that the weight fraction can be directly obtained from chromatograms through the following relation, thus enabling us to calculate various of average MW's and MWD's,

$$w_i = h_i / \Sigma\, h_i \tag{1}$$

where w_i and h_i are the weight fraction and chromatographic height corresponding to molecular species having molecular weight M_i, respectively (resp.). For MW and MWD determination of unknown samples by GPC, it is necessary to establish the calibration function, i.e., quantitative relationship between molecular weight M and elution volume V_e, usually made by using monodisperse polystyrene(PS) standards in case of nonaqueous systems.[1,2] The calibration can be adequately described by a polynomial for a given set of experimental conditions, as

$$\text{Log } M = f(V_e) = \sum_{i=0}^{n} D_i\, V_e^i \tag{2}$$

where D_i is the coefficient and n is the degree of the polynomial, usually taken as 1 or 3. However, GPC separation mechanism is not molecular weight but hydrodynamic size in solution in a strict sense. Therefore, the hydrodynamic volume-based universal calibration procedure proposed by Benoit et al.[3,4] should be adopted for a variety of polymers, which uses $[\eta]M$, a measure of the hydrodynamic volume of a polymer chain as implied by the following Flory-Fox eq.,[5] instead of M in eq.(2).

$$[\eta] = \phi_0\, \langle r^2 \rangle^{3/2} / M \tag{3}$$

where $[\eta]$ is the intrinsic viscosity for a given polymer-solvent system used to estimate (relative) average MW through the Mark-Houwink(M−H)

relation(eq.(4)), $\langle r^2 \rangle$ is the mean square end-to-end distance of a polymer chain, and ϕ_0 is the universal constant.

$$[\eta] = K\, M_v^a \tag{4}$$

where K and a are constants for a given system, a normally lying between 0.5~0.9 for flexible polymers, and M_v is the viscosity-average MW defined by[6]

$$M_v = (\Sigma\, w_i\, M_i^a)^{1/a} \tag{5}$$

Once the universal calibration relationship is established, molecular weights for monodisperse samples can be determined by dividing $[\eta]M$ corresponding to peak V_e by experimentally determined $[\eta]$ value. On the other hand, the MW and MWD determination of polydisperse samples from GPC universal calibration principle requires correct values of K and a, as shown later. However, the evaluation of K and a is a laborious process made by using well characterized samples ; in addition, there are few reliable data available in the literature. Here, several methods have been proposed so far to evaluate the M−H constants only from GPC and viscometric data, among them Mahabadi's procedure appears to be one of the most powerful means in view of accuracy and convenience. In the present study, the K and a values for poly(vinyl chloride) (PVC)-tetrahydrofuran (THF) system at 25℃, and hence MW's for three different PVC samples have been estimated by using GPC and viscometric data following Mahabadi's treatment, in comparison with the literature values. In addition the so-called "single-point" methods of recent interest for quick determination of $[\eta]$ have also been tested for this system.

THEORETICAL BACKGROUND

Determination of Intrinsic Viscosity(IV)

The determination of $[\eta]$ is a tedious job because it is generally determined by extrapolating

viscometric data obtained in dilute polymer solutions to infinite dilution. The typical relationships used for this purpose are those of Huggins[7](eq. (6)) and Kraemer[8](eq. (7)).

$$\eta_{sp} / c = [\eta] + k [\eta]^2 c \tag{6}$$

$$(\ln \eta_r) / c = [\eta] + k'[\eta]^2 c \tag{7}$$

where η_r and η_{sp} are relative and specific viscosities of polymer solutions, resp. These eqs. are actually truncated versions of virial expressions in concentration c, and hence valid only for dilute concentration regions, and k and k' are constants for a given polymer-solvent system, in particular k lying between 0.3 and 0.5 for flexible coils. In order to save considerable time and effort in determination of $[\eta]$, Solomon et al.[9] have obtained the following single-point method by combining the above two eqs. via the relation k-k'=0.5 derived by Taylor's series expansion of $\ln \eta_r = \ln (1+\eta_{sp})$ near c=0

$$[\eta] = (\sqrt{2} / c) \sqrt{\eta_{sp} - \ln \eta_r} \tag{8}$$

Eq. (8), which does not contain constants, allows us to determine by using viscosity data only at one fairly low concentration. Other useful single-point methods are that due to Deb et al.[10](eq. (9)) and that due to Rao et al.[11] eq. (10).

$$[\eta] = (1/2c) (\eta_{sp} + \ln \eta_r) \tag{9}$$

$$[\eta] = (1/c) (3 \ln \eta_r + (3/2) \eta_{sp}^2 - 3 \eta_{sp})^{1/3} \tag{10}$$

Evaluation of Mark-Houwink Constants

According to universal calibration principle, a wide range of homopolymers and copolymers having linear and branched structures are expected to fall on a universal curve, provided that there are no significant interactions with the packing material, represented as

$$\text{Log } J = \sum_{i=0}^{n} D_i V_e^i \tag{11}$$

where $J \equiv [\eta]M$ is the hydrodynamic parameter. The calibration coefficients D_i's can be statistically determined by measuring the peak elution volume and intrinsic viscosities of a series of monodis-

perse standards. In a polydisperse sample composed of a mixture of a molecular species, each with molecular weight M_i, weight faction w_i and intrinsic viscosity $[\eta]_i$ in GPC solvent, the followig holds for both each species and mixture, resp.

$$[\eta]_i = KM_i^a, \quad J_i = [\eta]_i M_i = KM_i^{1+a} \tag{12}$$

$$[\eta] = \sum w_i [\eta]_i = KM_v^a \tag{13}$$

Using the relation $M_i = (J_i / K)^{1/(1+a)}$ from eq. (12), we can get the following expressions for number-, weight-, viscosity-average molecular weights, and for IV, resp.

$$M_n = 1 / \sum (w_i / M_i) = K^{-1/(1+a)} / \sum (w_i / J_i^{1/(1+a)}) \tag{14}$$

$$M_w = \sum w_i M_i = K^{-1/(1+a)} (\sum w_i J_i^{1/(1+a)}) \tag{15}$$

$$M_v = K^{-1/(1+a)} (\sum w_i J_i^{a/(1+a)})^{1/a} \tag{16}$$

$$[\eta] = K^{1/(1+a)} (\sum_{i=0} w_i J_i^{a/(1+a)}) \tag{17}$$

By inspection of the above eqs., we can realize that a knowledge of the M−H constants K and a is needed for the calculation of MW and MWD for a polydisperse sample by universal calibration technique. In order to evaluate K and a using only GPC and IV data, Mahabadi has defined the "hydrodynamic volume-average molecular weight" M_x as

$$M_x = \sum w_i [\eta]_i M_i / \sum w_i [\eta]_i = \sum w_i J_i / [\eta] \tag{18}$$

where J_i can be read directly from the universal calibration curve established (eq. (11)) and w_i is equated to the ratio of the area of the GPC detector response at elution volume V_e to the total area under the GPC chromatogram. Hence, M_x of a polydisperse sample can be obtained from IV and GPC chromatographic data. Then, M−H relation(eq. (4)) can be redefined using M_x according to Mahabadi as

$$[\eta] = K M_v^a = K_x M_x^a = \delta K M_x^a \tag{19}$$

$$\delta = (\sum w_i J_i^{a/(1+a)})^{1+a} / (\sum w_i J_i)^a \tag{20}$$

If the parameter δ remains constant through the

change of $[\eta]$ and M_x, then a log-log plot of $[\eta]$ vs. M_x gives the linear relationship. In fact, this is often the case because δ is nearly constant for polymer samples having the same polydispersity or having very broad MWD, as shown later. The constants a and K_x (hence $K = K_x / \delta$) can be obtained from the slope and intercept of such lines, resp. Then, several kinds of average MW' sand MWD can be calculated from eqs. (14)~(15) with these constants.[12~15]

EXPERIMENTAL SECTION

Materials

Three different PVC samples, designated by PVC-A, -B, and -C in the decreasing order of MW, were purchased from Aldrich Co., Ltd. THF used as solvent for GPC and IV measurements was HPLC grade.

Intrinsic Viscosity Measurements

The IV's of PVC samples were measured in THF at 25℃ with a Cannon-Fenske (#75) viscometer.

GPC Measurements

GPC experiments were performed at 25℃ with THF as eluent by using a Waters Associates GPC equipped with a high pressure solvent delivery system (Model M 6000A). A series arrangement of three μ-Styragel packed columns, with nominal exclusion sizes of 10^5, 10^4, and 10^3 Å (Waters designation) and refactive index(RI) detector were used. Other experimental conditions employed were : concentration of injected solution, 0.2% (w/v) ; injected volum, 100 μl ; flow rate, 1.0 ml/min. A universal calibration curve (eq. (11)) was made using monodisperse PS standards, data on whose molecular weights and intrinsic viscosities, calculated according to eq. (21), are displayed in Table 1.

$$[\eta]_{\text{TMF}}^{25C} = 1.14 \times 10^{-4} \, M_v^{0.72} \tag{21}$$

RESULTS AND DISCUSSION

Intrinsic Viscosity

Table 1. Molecular Weights and Intrinsic Viscosities of Standard Polystyrene

MW*	$[\eta]$ (dl/g)	Mv**
240000	0.83	233000
100000	0.45	98700
50000	0.27	47400
8500	0.08	9100
4000	0.04	3600
1800	0.03	2100

*Peak molecular weight by GPC(data supplied by Waters Associates, Inc.).

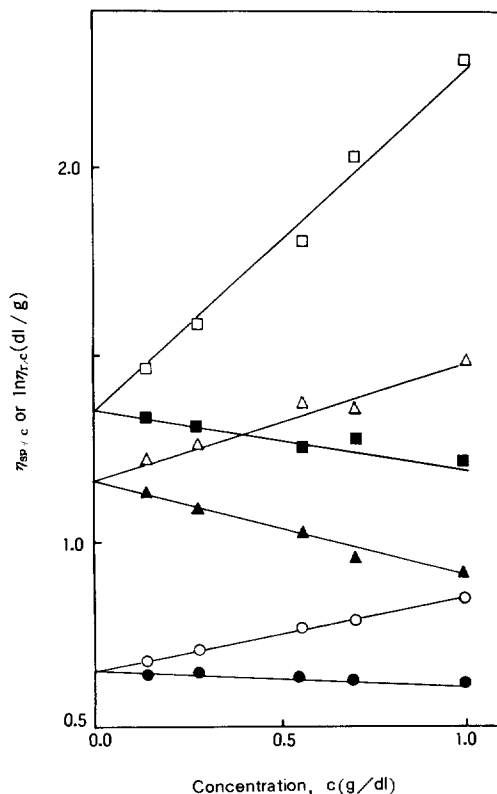**Viscosity average molecular weight(data supplied by Pressure Chemical Co.).

Fig. 1. The Huggins(open) and Kraemer(filled) plots for extrapolation of viscometric data for PVC-THF system at 25℃ : (□) PVC-A ; (△)PVC-B ; (○)PVC-C.

Fig. 1 shows the determination of IV's for three PVC samples in THF at 25℃ via the simultaneous

Woo Choi, Jang-Oo Lee, and Tae-Kyung Park

use of Huggins' and Kraemer's eqs.

The values of k,k', and k-k' obtained from the slopes of these linear plots are displayed in Table 2, revealing that the values of k-k' do not largely deviate from the expected value of 0.5.

In Table 3, comparisons of $[\eta]$ values obtained by extrapolation to infinite dilution and those calculated by single-point methods are made for three PVC samples.

From this table we can realize that $[\eta]$ values calculated from one-point methods using data at fairly low concentration (where $\eta_{sp} \ll 1$) are in close agreement with the extrapolated values. In practice, for PVC-C sample there is a good agreement between single-point (at $c = 0.14$ g/dl) and extrapolation methods, attributable to the fact that k-k' value for PVC-C is nearest to 0.5. From these results, we may expect the possible use of one-point methods for quick determination of IV for the PVC-THF system.

GPC Calibration

GPC chromatograms for three different PVC samples are illustrated in Fig. 2, showing that molecular species having high MW are first eluted. Fig. 3 represents the typical (log M vs. V_e plot) and universal (log $[\eta]$M vs. V_e plot) calib-

ration curves made by using monodisperse PS standards, revealing different functional dependences on V_e for both calibrations.

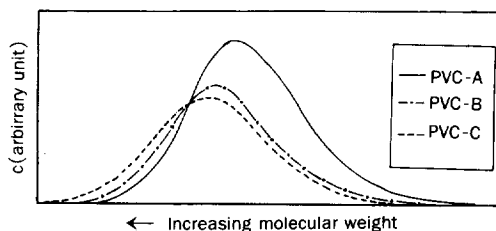Universal calibration coefficients D_i's appearing

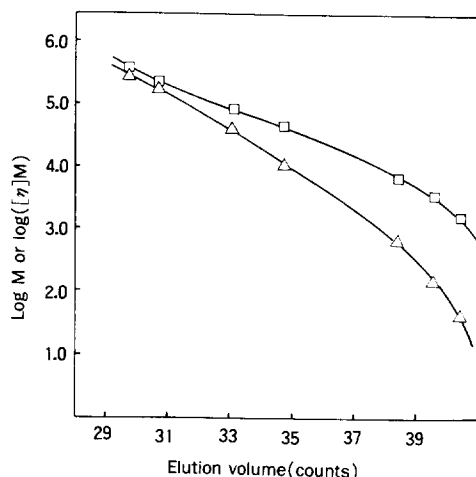**Fig. 2.** GPC chromatograms for threee PVC samples run on μ-Styragel columns with THF as eluent.

Fig. 3. Typical and universal GPC calibration curves established by means of monodisperse polystyrene standards : ($\triangle$) for log M ; ($\square$) for log($[\eta]$M).

Table 2. Calculated Values of k, k' and k-k'

Polymer	k	k'	k-k'
PVC-A	0.57	−0.09	0.66
PVC-B	0.22	−0.19	0.41
PVC-C	0.48	−0.08	0.56

Table 3. Comparison of $[\eta]$ Values Obtained by Single-Point and Extrapolation Methods

C	PVC-A			PVC-B			PVC-C		
(g/dl)	$[\eta]^a$	$[\eta]^b$	$[\eta]^c$	$[\eta]^a$	$[\eta]^b$	$[\eta]^c$	$[\eta]^a$	$[\eta]^b$	$[\eta]^c$
0.70	1.47	1.59	1.63	1.06	1.12	1.14	0.67	0.70	0.70
0.56	1.40	1.49	1.52	1.12	1.17	1.19	0.68	0.70	0.70
0.14	1.37	1.49	1.39	1.15	1.16	1.16	0.65	0.65	0.65
EXT*		1.34			1.16			0.65	

*Extrapolation, unit = dl/g.

[a] Calculated by using eq. (8), [b] Calculated by using eq. (9), [c] Calculated by using eq. (10)

in eq. (11) were then obtained by fitting to a third degree polynomial through a least-squares analysis, giving $D_o = 0.5390 \times 10^2$, $D_1 = -0.5672 \times 10$, $D_2 = 0.2310$, and $D_3 = -0.3314 \times 10^2$.

Evaluation of Mark-Houwink Constants

In order to evaluate K and a for the PVC-THF system at 25°C following Mahabadi's procedure, M_x's of PVC samples were calculated according to eq. (18) with the $[\eta]$ and GPC data (J_i, w_i) obtained through use of the universal calibration curve established, the results being $2.91\times$, $1.39\times$, and 1.03×10^5 for PVC-A, -B, and -C, resp. The log-log plot of the calculated M_x and measured $[\eta]$ values seems to give the expected linear relationship as shown in Fig. 4.

The values of K_x and a determined from this plot by the least squares method are 7.61×10^{-4} dl/g and 0.60, resp. This a value is then used with the GPC curves of samples to calculate δ and hence K, by means of eq. (20).

The results are reported in Table 4. The mean value of δ was used for the calculation of K since there was some variation in the calculated values, which may arise from the difference in MW and MWD among the PVC samples. In fact, it must be noted that δ as given by eq. (20) should be dependent only on MWD, as exemplified by the exponential distribution function defined as[16]
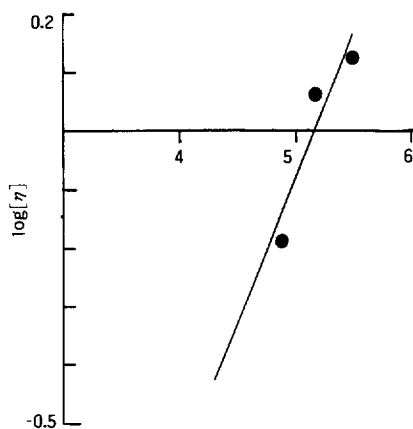
Table 4. Mark-Houwink Constants for PVC-THF System at 25°C Obtained by Using Eq. (19)

Polymer	K_x(dl/g)$\times 10^4$	δ	a	K(dl/g)$\times 10^4$
PVC-A		0.60		
PVC-B	7.61	0.68	0.60	11.6
PVC-C		0.68		
Average		0.65		

$$w(M) = (y^{h+1} / \Gamma(h+1)) \ M^h \ \exp(-yM) \quad (22)$$

$$y = h/Mn = (h+1) / M_w \quad (23)$$

By substitution of eq. (12) for J_i into eq. (20) and using the Gamma function identity,[17] $\Gamma(n+1) = n\Gamma(n)$, we can get

$$\delta = \langle M^a \rangle^{1+a} / \langle M^{1+a} \rangle^a =$$
$$(\Gamma(1+a+h) / \Gamma(1+h)) / (1+a+h)^a \quad (24)$$

where $\langle M^n \rangle$ denotes the nth moment of molecular weight M with respect to the weight fraction. Examination of eq. (24) reveals that δ is a function of only h characterizing the MWD (i.e., $h^{-1} = (M_w / M_n) - 1$ from eq. (23) for given a and further that δ is constant for very b. ad distributions (where $h \rightarrow 0$), implying that δ is constant for polymer samples having the same polydispersity or very broad MWD.

Meanwhile, the values of K and a given in Table 4 for the PVC-THF system at 25°C show considerable deviation from the literature values, where $K = 1.5 \sim 5.0 \times 10^{-4}$ dl/g, $a = 0.69 - 0.77$. This difference might be attributable to not only limitations possibly inherent in the hydrodynamic volume-based universal calibration principle but also some experimental problems encountered in this study like lack of polymer samples, difficulty in the accurate temperature control, and GPC peak broadening effect rather than to the deficiency of Mahabadi's method itself apart from the requirement for about the same MWD. Therefore, it has been found, in principle, to evaluate M−H constants only using IV and GPC data according to Mahabadi's procedure without recourse to well-characterized samples and/or other expen-

Fig. 4. log$[\eta]$ vs. log M_x plot for three PVC samples in THF at 25°C according to eq. (19).

Table 5. Comparison of Fictious(M*) and True(M) Average Molecular Weights of PVC Samples Calculated by Mahabadi's Method

Polymer	$Mn^* \times 10^{-4}$	$Mw^* \times 10^{-4}$	MWD	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	MWD
PVC-A	3.41	29.1	8.51	6.89	15.3	2.23
PVC-B	2.06	13.9	6.73	4.83	9.56	1.98
PVC-C	1.14	10.3	8.97	2.58	5.48	2.12

sive equipments, provided that experiments are carefully carried out with sufficient number of samples with similar MWD's.

Determination of MW and MWD

With the K and a values thus obtained, Mn and Mw of PVC samples were calculated from eqs. (14) and (15). On the other hand, there is one thing which needs special care when estimating average MW's of a polydisperse sample by GPC universal calibration technique. Namely, one might easily mistake the following expressions for the number-and weight-average MW's instead of eqs. (14) − (15)

$$M_n^* = (\Sigma w_i / J_i)^{-1} / [\eta] = K^{-1/(1+a)} /$$

$$(\Sigma w_i / J_i) (\Sigma w_i J_i^{a/(1+a)}) \quad (25)$$

$$M_w^* = M_x = (\Sigma w_i / J_i) / [\eta] = K^{-1/(1+a)}$$

$$(\Sigma w_i J_i) / (\Sigma w_i J_i^{a/(1+a)}) \quad (26)$$

From the above eqs., we may easily realize that $M_n \neq M_n^*$ and $M_w \neq M_w^*$ except when a=0. In fact, these "fictious" average MW's as given by eqs. (25) − (26) should not be confused with the "true" average MW's for the value generally lies between 0.5 and 0.9 for flexible coils in solution. The values of fictious and true average MW's calculated by Mahabadi's method for samples are displayed in Table 5 together with the corresponding MWD's.

Finally, the intrinsic viscosities of PVC samples in THF at 25℃ were calculated according to eq. (17) for the validity test of Mahabadi's theory : the values obtained were 1.30, 1.03, and 0.74 dl/g for PVC-A, -B, and-C, resp. These calculated values show relatively good agreement with the

extrapolated values as given in Table 3, indicating the predictive power of Mahabadi's theory.

CONCLUSION

The main conclusions to be drawn from the above results are as follows.

Calculation of intrinsic viscosities by single-point methods has given the values in close agreement with the extrapolated value to infinite dilution for the PVC-THF system at 25℃, suggesting the possible use of one-point method for quick determination of for this system. In addition, it has been found that Mahabadi's method, which consists in evaluating Mark-Houwink constants for the correct determination of MW and MWD of polydisperse samples using only intrinsic viscosity and GPC data via hydrodynamic volume-based universal calibration technique, is applicable to the PVC-THF system, provided that sufficient number of samples with similar MWD's are available.

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