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

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Abstract : The applicability of “single-point” methods as represented by Solomon’s equation for determining intrinsic viscosity using viscosity data at one low concentration has been tested to the PVC-THF system at 25°C, 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°C 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 $K=1.16 \times 10^3$ 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.
Characterization of PVC by GPC

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,

\[ w_i = h_i / \sum h_i \]

(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

\[ \log M = f(V_e) = \sum_{i=0}^{a} D_i V_e^i \]

(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).

\[ [\eta] = \phi_0 \langle r^2 \rangle^{1/2} / M \]

(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 \( \phi_0 \) is the universal constant.

\[ [\eta] = K M^n \]

(4)

where \( K \) and \( n \) are constants for a given system, a normally lying between 0.5~0.9 for flexible polymers, and \( M_n \) is the viscosity-average MW defined by\(^6\)

\[ M_n = \left( \sum w_i M_i^3 \right)^{1/3} \]

(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 \( n \), as shown later. However, the evaluation of \( K \) and \( n \) 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 \( n \) values for poly(vinyl chloride) (PVC)-tetrahydrofuran (THF) system at 25°C, 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

Determinant 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 (eq. (6)) and Kraemer (eq. (7)).

\[
\eta_p / c = (1/2) \eta \ln(1 + \eta_p/c)
\]

(6)

\[
\ln \eta_p / c = (1/2) \eta + (3/2) \eta_p
\]

(7)

where \( \eta \) and \( \eta_p \) 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 \( k' = 0.5 \) derived by Taylor’s series expansion of \( \ln \eta_p = \ln(1 + \eta_p) \) near \( c = 0 \).

\[
\eta = (\sqrt{2}/c) \sqrt{\eta_p} - \ln \eta_p
\]

(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. (eq. (9)) and that due to Rao et al. (eq. (10)).

\[
\eta = (1/2c) (\eta_p + \ln \eta_p)
\]

(9)

\[
\eta = (1/c) (3 \ln \eta_p + (3/2) \eta_p - 3 \eta_p)^{1/3}
\]

(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

\[
\log J = \sum_{i=0}^{n} D_i V_i
\]

(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 monodisperse standards. In a polydisperse sample composed of a mixture of a molecular species, each with molecular weight \( M_k \), weight fraction \( w \), and intrinsic viscosity \( [\eta] \), in GPC solvent, the following holds for both each species and mixture, resp.

\[
[\eta] = KM_k^2; \quad J_i = [\eta], M_i = KM_i^{1+a}
\]

(12)

\[
[\eta] = \Sigma w_i [\eta_i] = KM_i^2
\]

(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.

\[
M_i = 1 / \Sigma (w_i / M_i) = K^{1/(1+a)} / \Sigma (w_i / J_i)^{1/(1+a)}
\]

(14)

\[
M_w = \Sigma w_i M_i = K^{1/(1+a)} (\Sigma w_i J_i)^{1/(1+a)}
\]

(15)

\[
M_v = K^{1/(1+a)} (\Sigma w_i J_i^{1/(1+a)})^{1/(1+a)}
\]

(16)

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

(17)

By inspection of the above eqs., we can realize that a knowledge of the \( M_i \) 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 \( a \), a using only GPC and IV data, Mahabadi has defined the "hydrodynamic volume-average molecular weight" \( M_v \) as

\[
M_v = \Sigma w_i [\eta_i], M_i / \Sigma w_i [\eta_i] = \Sigma w_i J_i / [\eta]
\]

(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, \( M_v \) of a polydisperse sample can be obtained from IV and GPC chromatographic data. Then, \( M_v \) relation (eq. (4)) can be redefined using \( M_v \) according to Mahabadi as

\[
[\eta] = K^{1/2} M_v^2 = K_v, M_v^a = \delta K M_v^a
\]

(19)

\[
\delta = (\Sigma w_i J_i^{1/(1+a)})^{1+a} / (\Sigma w_i J_i)^a
\]

(20)

If the parameter \( \delta \) remains constant through the

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132

**Polymer(Korea) Vol. 14, No. 2, April 1990**
Characterization of PVC by GPC

change of $[\eta]$ and $M_w$ then a log-log plot of $[\eta]$ vs. $M_w$ gives the linear relationship. In fact, this is often the case because $\delta$ is nearly constant for polymer samples having the same polydispersity or having very broad MWD, as shown later. The constants $a$ and $K_e$ (hence $K_e = K / \delta$) can be obtained from the slope and intercept of such lines, resp. Then, several kinds of average MW and MWD can be calculated from eqs. (14) to (15) with these constants.\textsuperscript{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°C with a Cannon-Fenske (#75) viscometer.

**GPC Measurements**
GPC experiments were performed at 25°C 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 $\mu$-Styrage packed columns, with nominal exclusion sizes of $10^5$, $10^4$, and $10^3$ Å (Waters designation) and refractive index(RI) detector were used. Other experimental conditions employed were: concentration of injected solution, 0.2% (w/v); injected volum, 100 $\mu$l; 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.

$$[\eta]^{25}_{\text{MPF}} = 1.14 \times 10^4 M_w^{0.72} \quad (21)$$

**RESULTS AND DISCUSSION**

**Intrinsic Viscosity**

<table>
<thead>
<tr>
<th>MW*</th>
<th>$[\eta]$ (dl/g)</th>
<th>$M_v**$</th>
</tr>
</thead>
<tbody>
<tr>
<td>240000</td>
<td>0.83</td>
<td>233000</td>
</tr>
<tr>
<td>100000</td>
<td>0.45</td>
<td>98700</td>
</tr>
<tr>
<td>50000</td>
<td>0.27</td>
<td>47400</td>
</tr>
<tr>
<td>8500</td>
<td>0.08</td>
<td>9100</td>
</tr>
<tr>
<td>4000</td>
<td>0.04</td>
<td>3600</td>
</tr>
<tr>
<td>1800</td>
<td>0.03</td>
<td>2100</td>
</tr>
</tbody>
</table>

*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°C : (□) PVC-A : (△) PVC-B : (○) PVC-C.

Fig. 1 shows the determination of IV's for three PVC samples in THF at 25°C via the simultaneous
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 \( \eta_{\rho} \ll 1 \)) 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-

![](image)

**Fig. 2.** GPC chromatograms for three PVC samples run on \( \mu \)-Styrage columns with THF as eluent.

![](image)

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

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**Table 2.** Calculated Values of \( k, k' \) and \( k-k' \)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( k )</th>
<th>( k' )</th>
<th>( k-k' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC-A</td>
<td>0.57</td>
<td>-0.09</td>
<td>0.66</td>
</tr>
<tr>
<td>PVC-B</td>
<td>0.22</td>
<td>-0.19</td>
<td>0.41</td>
</tr>
<tr>
<td>PVC-C</td>
<td>0.48</td>
<td>-0.08</td>
<td>0.56</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>C (g/dl)</th>
<th>PVC-A</th>
<th>PVC-B</th>
<th>PVC-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([\eta]^a)</td>
<td>([\eta]^b)</td>
<td>([\eta]^c)</td>
</tr>
<tr>
<td>0.70</td>
<td>1.47</td>
<td>1.59</td>
<td>1.63</td>
</tr>
<tr>
<td>0.56</td>
<td>1.40</td>
<td>1.49</td>
<td>1.52</td>
</tr>
<tr>
<td>0.14</td>
<td>1.37</td>
<td>1.49</td>
<td>1.39</td>
</tr>
<tr>
<td>EXT*</td>
<td>1.34</td>
<td></td>
<td>1.16</td>
</tr>
</tbody>
</table>

*Extrapolation, unit = dl/g.

*a*Calculated by using eq. (8), *b*Calculated by using eq. (9), *c*Calculated by using eq. (10)
Characterization of PVC by GPC

In eq. (11) were then obtained by fitting to a third degree polynomial through a least-squares analysis, giving $D_0 = 0.5390 \times 10^5$, $D_1 = -0.5672 \times 10^3$, $D_2 = 0.2310$, 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, $M_n$’s of PVC samples were calculated according to eq. (18) with the $[\eta]$ and GPC data ($J$, $w$) obtained through use of the universal calibration curve established, the results being $2.91 \times 10^3$, $1.39 \times 10^3$, and $1.03 \times 10^3$ for PVC-A, -B, and -C, resp. The log-log plot of the calculated $M_n$ and measured $[\eta]$ values seems to give the expected linear relationship as shown in Fig. 4.

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

The results are reported in Table 4. The mean value of $\delta$ 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 $\delta$ as given by eq. (20) should be dependent only on MWD, as exemplified by the exponential distribution function defined as\textsuperscript{16}

$$w(M) = \frac{(y^{n-1} / \Gamma(n+1)) M^n \exp(-yM)}{(1 + a + h) / \Gamma(1 + h)}$$

$$\gamma = h/M_n = (h+1) / M_n$$

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

$$\delta = \langle M^n \rangle^{1/n} / \langle M^{1+n} \rangle^{1/n} = \left( \frac{\Gamma(1+a+h)}{\Gamma(1+h)} \right) / (1 + a + h)^a$$

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 $\delta$ is a function of only $h$ characterizing the MWD (i.e., $h = (M_n / M_w) - 1$ from eq. (23) for given $a$ and further that $\delta$ is constant for very broad distributions (where $h \rightarrow 0$), implying that $\delta$ 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 $K = 1.5 - 5.0 \times 10^3$ 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-

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**Table 4. Mark-Houwink Constants for PVC-THF System at 25°C Obtained by Using Eq. (19)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$K_{(dl/g)} \times 10^4$</th>
<th>$\delta$</th>
<th>$a$</th>
<th>$K_{(dl/g)} \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC-A</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC-B</td>
<td>7.61</td>
<td>0.68</td>
<td>0.60</td>
<td>11.6</td>
</tr>
<tr>
<td>PVC-C</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Fig. 4.** $\log[\eta]$ vs. $\log M_n$ 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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M^* \times 10^4$</th>
<th>$M_w \times 10^4$</th>
<th>MWD</th>
<th>$M^* \times 10^4$</th>
<th>$M_w \times 10^4$</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC-A</td>
<td>3.41</td>
<td>29.1</td>
<td>8.51</td>
<td>6.89</td>
<td>15.3</td>
<td>2.23</td>
</tr>
<tr>
<td>PVC-B</td>
<td>2.06</td>
<td>13.9</td>
<td>6.73</td>
<td>4.83</td>
<td>9.56</td>
<td>1.98</td>
</tr>
<tr>
<td>PVC-C</td>
<td>1.14</td>
<td>10.3</td>
<td>8.97</td>
<td>2.58</td>
<td>5.48</td>
<td>2.12</td>
</tr>
</tbody>
</table>

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, $M_n$ and $M_w$ 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 polydisperser 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)

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

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

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 “ficticious” 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°C 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°C, 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.

**REFERENCES**

Characterization of PVC by GPC

Cornell Univ. Press, 1953.


