Optimized calibration curve for size exclusion chromatography applied to poly(vinyl chloride)

Muhammad Atiqullah* and Ikram Hussain
Petroleum and Gas Technology Division, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

and Aqil Jamal
Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

(Received 24 February 1993; revised 23 June 1993)

The problem of using a polystyrene-standard-based calibration curve for other polymers has been overcome by developing an algorithm based on the concept of parameter estimation and optimization. The algorithm modifies the regression coefficients of the polystyrene-standard-based calibration curve by interactively using the chromatographic output and the absolute number-average molecular weight of the experimental polymer. Analytical expressions have been derived for calculating the directional derivatives, which ensure rapid convergence of the objective function. The algorithm, applied to commercial poly(vinyl chloride), offered a number-average molecular weight of 32 037 whereas that measured by membrane osmometry is 32 000. The polymer characterization parameters calculated from the optimized calibration curve closely matched those obtained from the universal calibration curve and Q-factor values. The algorithm needs no narrow standard of the experimental polymer, and holds for homopolymers, copolymers and polymer blends. It can be easily incorporated into commercial size exclusion chromatography data-reduction software packages.

(Keywords: poly(vinyl chloride); size exclusion chromatography; universal calibration)

INTRODUCTION

The degradation mechanism[1–4], as well as the processing and end-use characteristics, of polymers can be studied by monitoring the changes in the molecular-weight distributions and their averages. Therefore, these characterization parameters need to be measured as accurately as possible. Size exclusion chromatography (s.e.c.), previously called gel permeation chromatography (g.p.c.), is routinely used for this purpose.

Automatic fractionator and multiple detectors[5,6] have improved instrumentation of size exclusion chromatography. However, the data-reduction problem, which results from the conventional use of a polystyrene-standard-based calibration curve for other polymers, is still ahead of us. Ideally, standards of the same chemical composition as that of the experimental polymer should be used. However, narrow-polydispersity standards other than those of polystyrene have limited availability commercially, and at the same time are difficult to synthesize. Apart from this, the chromatographic detector response differs from polymer to polymer owing to the variation in molecular structure and size. All these complicate the calibration problem. To overcome this situation, two approaches are practised.

One approach uses the Q-factor values to convert the polystyrene-standard-based molecular weight to the corresponding molecular weight of the experimental polymer. The Q-factor approach, a relative measure of the extended chain length for a given polymer, has the following limitations:

(i) The tacit assumption that the calibration curve resulting from modifying the molecular weights of the polystyrene standards, using the Q-factor values of the experimental polymer and polystyrene, is parallel to the polystyrene-standard-based calibration curve does not always hold.

(ii) Q-factors can be affected by changes in solvents, temperature, molecular weight and side branching.

The other approach is the universal calibration method as suggested by Grubisic *et al.*[7]. The universal calibration method assumes the following[8,9]:

(i) The hydrodynamic volume, that is, the logarithm of the product of intrinsic viscosity and molecular weight at the same elution volume, is constant for all polymers in a given solvent at a given temperature.

(ii) The polymer molecules in solution are present as simple swollen spheres.

(iii) No adsorption occurs between the polymer and the column packing material.

The universal calibration method applies the intrinsic viscosity, or the Mark–Houwink constants, which are, in

---

* To whom correspondence should be addressed

0032-3861/94/04/0765–06

turn, obtained using several narrow fractions of the experimental polymer. Here, the difficulty lies with fractionating the polymer, which is quite cumbersome. Goldwasser *et al.*[10] suggested that the hydrodynamic-average molecular weight of several wide-dispersity polymers of the same type as the experimental polymer be used. This approach holds only if the wide-dispersity polymers differ significantly in intrinsic viscosity and hydrodynamic-average molecular weight[11].

Purdon and Mate[12] introduced the concept of modifying the polystyrene-standard-based calibration curve using wide-dispersity polymer with known number-average and/or weight-average molecular weight. The limitations of this method are the linearization, and the trial-and-error adjustment of the first-order regression coefficients of the polystyrene-standard-based calibration curve. This has prevented it from being routinely incorporated into commercial size exclusion chromatographic data-reduction software. Therefore, the objectives of the present study are as follows:

(1) Use the concept of parameter estimation and optimization to modify the regression coefficients of the polystyrene-standard-based calibration curve.

(2) Develop a mathematical algorithm that can be efficiently executed using a computer.

(3) Compare the results from the optimized calibration curve with those from *Q*-factor and universal calibration methods.

Poly(vinyl chloride) will be used as a case study because of its commercial importance, and known *Q*-factor and Mark–Houwink constants[13]. To be the best of our knowledge, no work along the lines of the present study has been reported in the literature.

THEORETICAL

The objective function $\phi(\boldsymbol{p})$, consisting of the parameters to be estimated, is related to the measurement/output vector $\boldsymbol{y}_{\mathrm{m}}$ and the model-predicted vector $\boldsymbol{y}_{\mathrm{p}}$ as follows[14]:

$$\phi(\boldsymbol{p})=(\boldsymbol{y}_{\mathrm{m}}-\boldsymbol{y}_{\mathrm{p}})^{\mathrm{T}}\boldsymbol{W}(\boldsymbol{y}_{\mathrm{m}}-\boldsymbol{y}_{\mathrm{p}}) \tag{1}$$

where $\boldsymbol{p}$ is the parameter vector, and $\boldsymbol{W}$ is a positive-definite weighting matrix. A convenient choice for $\boldsymbol{W}$ is the identity matrix $\boldsymbol{I}$. Then equation (1) becomes:

$$\phi(\boldsymbol{p})=\min_{\bar{p}}\|\boldsymbol{y}_{\mathrm{m}}-\boldsymbol{y}_{\mathrm{p}}\|^2 \tag{2}$$

which is converted to an unconstrained optimization problem; here $\|\quad\|$ is the l_2 (Euclidian) norm.

Size exclusion chromatographic experiments confirm that the molecular weight of the polystyrene standards M_{PS} can be related to the elution time t in the following manner[15,16]:

$$\log M_{\mathrm{PS}}=p_0+p_1t+p_2t^2+p_3t^3 \tag{3}$$

where p_0, p_1, p_2 and p_3 are the regression coefficients of a third-order polynomial. Comparing equation (3) with equation (1), we can write:

$$\boldsymbol{p}=[p_0, p_1, p_2, p_3]^{\mathrm{T}} \tag{4}$$

where T indicates the transpose of the parameter vector $\boldsymbol{p}$.

Here the absolute, average molecular weight of the experimental polymer is the measured/output variable. The average molecular weight calculated from the polystyrene-standard-based calibration curve is the predicted variable. Therefore, we can write:

$$y_{\mathrm{m}1}=\bar{M}_{\mathrm{n}} \qquad y_{\mathrm{p}1}=\bar{M}_{\mathrm{n,PS}} \tag{5}$$

where $\bar{M}_{\mathrm{n}}$ is the number-average molecular weight measured by membrane osmometry. $\bar{M}_{\mathrm{n,PS}}$ is the number-average molecular weight calculated from the polystyrene-standard-based calibration curve, and is given by[15]:

$$\bar{M}_{\mathrm{n,PS}}=\sum A_i/(\sum A_i/M_i) \tag{6}$$

where A_i is the elemental sliced area of the size exclusion chromatogram of the experimental polymer, and M_i is the corresponding molecular weight.

Equations (2) and (5) can be combined to give the following:

$$\phi(\boldsymbol{p})/\bar{M}_{\mathrm{n}}^2=f=(\bar{M}_{\mathrm{n,PS}}/\bar{M}_{\mathrm{n}}-1)^2 \tag{7}$$

which is the desired objective function for the current optimization problem. For fast convergence near the optimum, analytic expressions for the directional derivatives $\partial f/\partial p_0$, $\partial f/\partial p_1$, $\partial f/\partial p_2$ and $\partial f/\partial p_3$ are required. They can be derived from equations (6) and (7), the final forms of which are given below:

$$\frac{\partial f}{\partial p_j}=\frac{2}{\bar{M}_{\mathrm{n}}}\left(\frac{\bar{M}_{\mathrm{n,PS}}}{\bar{M}_{\mathrm{n}}}-1\right)\frac{(\sum A_i)\ln 10}{(\sum A_i/M_i)^2}\sum\left(\frac{A_it_i^j}{M_i}\right) \tag{8}$$

where $j=0$, 1, 2 and 3.

Equation (8) explains how the directional derivatives can be obtained analytically using the chromatogram of the experiment polymer and its absolute number-average molecular weight measured by membrane osmometry.

In the present problem, the objective function has been formulated using only the absolute number-average molecular weight $\bar{M}_{\mathrm{n}}$. However, it can be developed also incorporating the absolute weight-average molecular weight $\bar{M}_{\mathrm{w}}$, or both. If $\bar{M}_{\mathrm{w}}$ of the polymer is also to be included, the right-hand side of equation (7) will have another similar squared term that will contain $\bar{M}_{\mathrm{w}}$. Directional derivatives of the resulting objective function can also be obtained analytically. The influence of these variations on the accuracy of the optimized calibration curve is subject to tests which depend on the availability of both the absolute molecular weights.

EXPERIMENTAL

The experimental poly(vinyl chloride) (PVC) was a commercial, suspension-polymerized particulate material. The resin characteristic morphological parameters have been reported elsewhere[17]. The number-average molecular weight was 32 000 ± 2%, which was measured by a Knauer membrane osmometer. The osmometry experiments were performed at 31°C using reagent-grade tetrahydrofuran (THF) as the solvent. The standard error ±2% was obtained through statistical data analysis[18], which has been detailed in the Appendix.

The chromatographic analysis was carried out using a Waters 150C s.e.c. instrument interfaced with the model 730 data module. Solutions with a concentration of 0.15% (m/v) for each polystyrene standard in THF were injected, operating the data module in the liquid chromatographic mode. The retention time obtained from the chromatogram of each polystyrene standard was fed into the data module to calibrate the s.e.c. system and for subsequent analysis of the PVC resin. *Table 1* summarizes the operating conditions for the s.e.c. analysis. The system was calibrated using several polystyrene standards having peak molecular weights of 1800 to 1 850 000 (*Table 2*).

RESULTS AND DISCUSSION

Table 2 lists the molecular weights of the polystyrene standards and their respective retention times. The logarithm of the molecular weight has been correlated with the retention time following a third-order polynomial, which is shown in *Figure 1*. The standard error of the data fit is 0.0124, which corresponds to a correlation coefficient of 0.999.

Table 3 presents the chromatographic output of the experimental poly(vinyl chloride) obtained from the polystyrene-standard-based calibration curve. These data have been used to calculate analytically the directional derivatives (equation (8)) and to minimize the objective function f (equation (7)) using a quasi-Newton method[19,20]. *Table 4* compares the optimized regression coefficients with those of the polystyrene-standard-based calibration curve. The regression coefficients, except p_0, changed on optimization. The polystyrene-standard-based regression coefficients were used as the initial values of the parameters to find the optimized coefficients. *Figure 1* shows that the optimized calibration curve for poly(vinyl chloride) runs parallel to and below the polystyrene-standard-based calibration curve.

Figures 2 and *3* show the effect of various calibration methods on the differential and integral molecular-weight distributions, respectively. The distributions calculated using the optimized calibration curve, universal calibration and the Q-factor values are close to each other. The differential distributions are significantly translated towards the left from the polystyrene-standard-based distribution (*Figure 2*), while the elongated S-shaped integral distributions are shifted upwards (*Figure 3*). The distributions have been calculated using the data presented in *Table 3* and the above calibration methods.

The following values of the Mark–Houwink constants and Q-factors have been taken from the literature[13]:

	Mark–Houwink constants		
	$K\times10^3$ (ml g^{-1})	a	Q-factors
Polystyrene	12.58	0.7155	41
Poly(vinyl chloride)	15.56	0.690	25

The molecular weight M_i in *Table 3*, calculated from the polystyrene-standard-based calibration curve, has been converted to the corresponding molecular weight of poly(vinyl chloride) using the Mark–Houwink constants as follows[9,13]:

$$\log M_{\mathrm{PVC}}=\left(\frac{1}{1+a_{\mathrm{PVC}}}\right)\log\left(\frac{K_{\mathrm{PS}}}{K_{\mathrm{PVC}}}\right)+\left(\frac{1+a_{\mathrm{PVC}}}{1+a_{\mathrm{PS}}}\right)\log M_{\mathrm{PS}} \tag{9}$$

Table 1 Operating conditions for the s.e.c. analysis

Column type	Ultrastyragel
Column configuration	500 Å, two linear columns
Solvent	Tetrahydrofuran (THF, reagent-grade)
Flow rate	1 ml min^{-1}
Solution concentration	0.15% mass/volume (m/v)
Sample injection volume	80 μl
Operating temperature	35°C
Polymeric sample solution	Fresh solution made at 35°C, filtered through stainless-steel filter (0.5 μm) prior to injection

Table 2 S.e.c. calibration table

Polystyrene standards molecular weight $\times10^{-4}$	Retention time (min)
0.18	19.60
1.02	17.60
2.80	16.30
8.70	15.03
19.40	14.56
86.00	13.73
185.00	13.30

Table 3 Chromatographic output of the experimental poly(vinyl chloride) obtained from the polystyrene-standard-based calibration curve

Retention time, t_i (min)	Chromatogram sliced area, A_i	Molecular weight, $M_i\times10^{-4}$
13.82	12 900	65.4625
14.02	49 526	44.9652
14.22	167 472	31.6871
14.42	431 079	22.9353
14.62	828 605	16.9741
14.82	1 174 300	12.8321
15.02	1 201 610	9.87145
15.22	969 144	7.76725
15.42	760 271	6.18389
15.62	634 867	5.02219
15.82	521 944	4.11626
16.02	406 581	3.42133
16.22	311 091	2.87403
16.42	237 431	2.43666
16.62	180 341	2.08584
16.82	142 311	1.78811
17.02	112 161	1.54724
17.22	90 821	1.33965
17.42	76 711	1.16435
17.62	61 981	1.00924

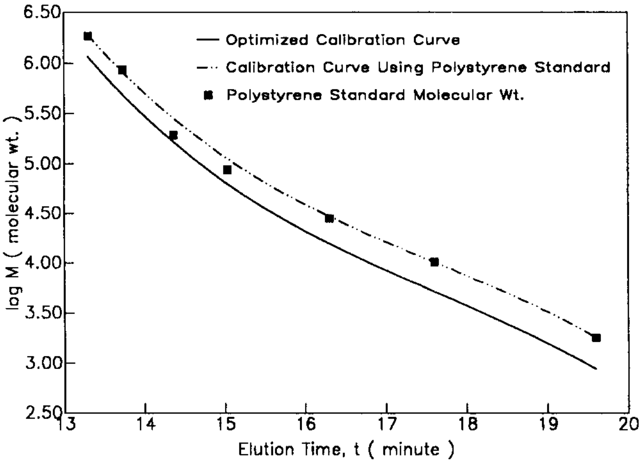

Figure 1 Comparison of the optimized calibration curve with the polystyrene-standard-based calibration curve

where K_{PS} and a_{PS}, and K_{PVC} and a_{PVC} are the Mark–Houwink constants of polystyrene and poly(vinyl chloride), respectively. M_{PS} and M_{PVC} are the molecular weights of polystyrene and poly(vinyl chloride), respectively.

While using the Q-factor values, M_{PS} or, in other words, M_i has been converted to M_{PVC} using the following relationship:

$$M_{\mathrm{PVC}}=\left(\frac{a_{\mathrm{PVS}}}{a_{\mathrm{PS}}}\right)M_{\mathrm{PS}} \tag{10}$$

Table 4 Comparison of optimized regression coefficients with those of the polystyrene-standard-based calibration curve

Calibration methods	Regression coefficients				Function value, f (equation (7))
	p_0	p_1	p_2	p_3	
Polystyrene-standard-based	65.33	−9.755	0.5337	−0.01008	0.7414
Optimized values based on $\bar{M}_n$	65.33	−9.758	0.5320	−0.01003	1.343×10^{-6}

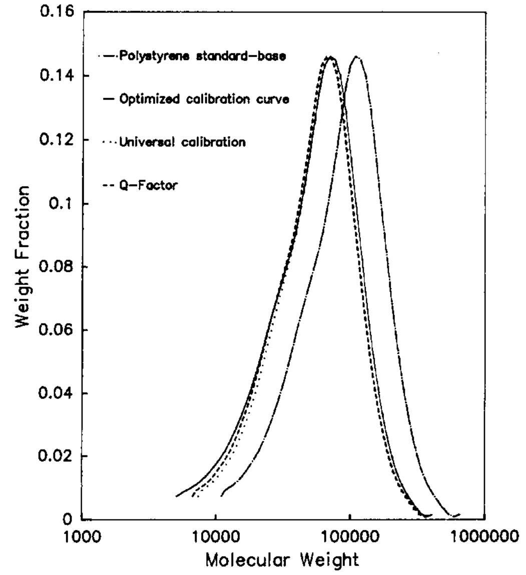

Figure 2 Effect of calibration methods on the differential molecular-weight distribution of the experimental poly(vinyl chloride)

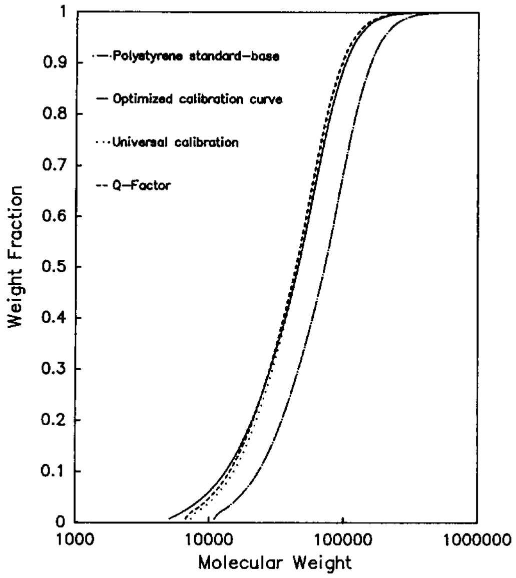

Figure 3 Effect of calibration methods on the integral molecular-weight distribution of the experimental poly(vinyl chloride)

Table 5 Characterization parameters of the experimental poly(vinyl chloride) resin

Calibration methods	Characterization parameters					
	$\bar{M}_n$[a]	$\bar{M}_w$	$\bar{M}_z$	*PDI*	DP_{min}	DP_{max}
Polystyrene-standard-based	54 308	96 489	151 350	1.78	176	10 474
Δ^b (%)	69.52	56.37	54.20	−4.81	117.3	59.71
Optimized calibration curve	32 037	61 705	98 154	1.87	81	6558
Universal calibration	34 956	60 042	91 925	1.72	118	6195
Δ^b (%)	9.11	−2.70	−6.35	−8.02	45.68	−5.53
Q-factor approach	33 128	58 858	92 324	1.78	107	6389
Δ^b (%)	3.40	−4.61	−5.93	−4.81	32.10	−2.58

[a] $\bar{M}_n$ measured by membrane osmometry is 32 000

[b] Percentage difference of the characterization parameters with respect to those obtained using the optimized calibration curve

Table 5 compares the number-average molecular weight $\bar{M}_n$, the weight-average molecular weight $\bar{M}_w$, the z-average molecular weight $\bar{M}_z$, the polydispersity index *PDI*, the minimum degree of polymerization DP_{min} and the maximum degree of polymerization DP_{max} calculated on the basis of the various calibration methods. The number-average molecular weight calculated using the optimized calibration curve is 32 037 whereas that measured by membrane osmometry is 32 000. The number-average, weight-average and z-average molecular weights estimated from the polystyrene-standard-based calibration curve differ significantly from those calculated by other methods. However, the polydispersity index values are close to each other. The universal-calibration-based $\bar{M}_n$ is 34 956, which is above that measured by membrane osmometry. This finding is opposite to what has been previously reported in the literature[21]. The absolute difference of the above characterization parameters from those calculated using the optimized calibration curve can be arranged as follows:

$\bar{M}_n$: PS-standard-based > Universal calibration > Q-factor > Optimized calibration

$\bar{M}_w$: PS-standard-based > Optimized calibration > Universal calibration > Q-factor

$\bar{M}_z$: PS-standard-based > Optimized calibration > Q-factor > Universal calibration
PDI: Optimized calibration > PS-standard-based, Q-factor ≈ Universal calibration
$DP_{\min}$: PS-standard-based > Universal calibration > Q-factor > Optimized calibration
$DP_{\max}$: PS-standard-based > Optimized calibration > Q-factor > Universal calibration

$\bar{M}_w$, $\bar{M}_n$, PDI, $DP_{\min}$ and $DP_{\max}$ have been calculated using the following experssions:

$$\bar{M}_w = \frac{\sum A_i M_i}{\sum A_i} \qquad \bar{M}_z = \frac{\sum A_i M_i^2}{\sum A_i} \qquad PDI = \frac{\bar{M}_w}{\bar{M}_n} \tag{11}$$

$$DP_{\min} = \frac{M_{i,\min}}{62.5} \qquad DP_{\max} = \frac{M_{i,\max}}{62.5} \tag{12}$$

where 62.5 is the weight of one repeat unit.

CONCLUSIONS

The conclusions of the present study can be summarized as follows:

An algorithm based on the concept of parameter estimation and optimization has been developed to modify the regression coefficients of the polystyrene-standard-based calibration curve. Mathematical expressions for analytically calculating the directional derivatives have been derived, which have resulted in fast convergence of the optimized parameters.

The above algorithm interactively uses the absolute number-average molecular weight of the polymer and the chromatographic output obtained from the polystyrene-standard-based calibration curve. Unlike the Purdon and Mate method, no linearization and no trial-and-error adjustment of the regression coefficients of the polystyrene-standard-based calibration curve are required. Therefore, the developed algorithm can be easily incorporated into commercial size exclusion chromatography data-reduction software packages.

The molecular-weight distributions, the average molecular weights, the polydispersity index and the limits of degree of polymerization of a suspension-grade, commercial poly(vinyl chloride) calculated from the optimized calibration curve have been compared with those obtained from the polystyrene-standard-based calibration curve, universal calibration and Q-factor values. The number-average molecular weight calculated using the optimized calibration curve is 32 037 whereas that measured by membrane osmometry is 32 000. The molecular-weight distributions estimated using the optimized calibration curve, universal calibration and Q-factor values practically overlap each other, and the resulting average molecular weights are close to each other. All the polystyrene-standard-based characterization parameters, except the polydispersity index, differ significantly from those calculated from the above three methods. The range of degree of polymerization varied from one calibration method to another.

The algorithm does not require any narrow standard of the experimental polymer. Therefore, it can be equally well applied to characterize homopolymers, copolymers and polymer blends, which highlights the versatility.

ACKNOWLEDGEMENTS

The authors acknowledge the Research Institute of the King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, for supporting this work. The technical assistance of Mr K. Alam is highly appreciated.

APPENDIX

In membrane osmometry experiments, the hydrostatic pressure head or osmometric height h is related to the concentration of the polymer solution c as follows:

$$\Delta h/c = (RT/\rho g)(1/\bar{M}_n + A_2 c) \tag{A1}$$

where R is the universal gas constant, T is the experimental temperature in absolute units, ρ is the density of the solvent, g is the acceleration due to gravity, $\bar{M}_n$ is the number-average molecular weight and A_2 is the second virial coefficient.

According to the linear least-squares method, the intercept of equation (A1) is given by:

$$RT/\rho g\bar{M}_n = (\sum \Delta h/c - a_1 \sum c)/n \tag{A2}$$

where

$$a_1 = [n \sum c(\Delta h/c) - (\sum c)(\sum \Delta h/c)]/D \tag{A3}$$

and

$$D = n \sum c^2 - (\sum c)^2 \tag{A4}$$

In the above equations, n stands for the number of different concentrations of the stock solutions. In the present study, n equals 4. $\sum$ means summation over n concentrations. From equations (A2), (A3) and (A4), $\bar{M}_n$ can be calculated. The procedure of calculating the standard error of $\bar{M}_n$ is explained below.

Let S ($\bar{M}_n$) denote the standard error of $\bar{M}_n$. Then this is given by:

$$S(\bar{M}_n) = \{[\partial \bar{M}_n/\partial(RT/\rho g\bar{M}_n)]^2 S^2(RT/\rho g\bar{M}_n)\}^{1/2} \tag{A5}$$

or

$$S(\bar{M}_n) = [(\bar{M}_n \rho g/RT)^2 S^2(RT/\rho g\bar{M}_n)]^{1/2} \tag{A6}$$

where

$$S(RT/\rho g\bar{M}_n) = [S_0(\sum c^2)/(n-2)D]^{1/2} \tag{A7}$$

In equation (A7), $S(RT/\rho g\bar{M}_n)$ means the standard error for $RT/\rho g\bar{M}_n$, and S_0 is given by:

$$S_0 = \sum(\Delta h/c)^2 - [(\sum \Delta h/c)^2/n] - a_1[\sum(c)(\Delta h/c) - (\sum c \sum \Delta h/c)/n] \tag{A8}$$

A computer program was developed to calculate $\bar{M}_n$ and $S(\bar{M}_n)$ using equations (A2) to (A8). From the data of *Table 6*, $\bar{M}_n$ and $S(\bar{M}_n)$ are obtained as

Table 6 Experimental osmometric data for the experimental poly(vinyl chloride)

Concentration ($\mathrm{g\,l^{-1}}$)	Osmotic height of THF, Δh (cm)	$\Delta h/c$ ($\mathrm{cm\,g^{-1}\,l^{-1}}$)
2	2.04	1.02
4	4.56	1.14
6	7.38	1.23
8	10.68	1.34

3.15×10^4 g mol^{-1} and 363 g mol^{-1}, respectively. Therefore, $\bar{M}_n$ for the experimental poly(vinyl chloride) resin may be written as:

$$\bar{M}_n = (3.15 \pm 0.03) \times 10^4 \text{ g mol}^{-1} \qquad \text{(A9)}$$

The limit of $\pm 2S(\bar{M}_n)$ was rounded up to $\pm 2\%$. Hence, it can be written that $\bar{M}_n = 3.2(\pm 2\%) \times 10^4$ g mol^{-1}. In the above calculation, the following values of R, T, ρ and g have been used:

$$R = 8.314 \times 10^7 \text{ g cm}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

$$T = 304 \text{ K} \qquad \rho = 0.89 \text{ g cm}^{-3} \qquad g = 981.0 \text{ cm s}^{-2}$$

REFERENCES

1 Abbås, K. B. and Sorvik, E. M. *J. Appl. Polym. Sci.* 1973, **17**, 3577
2 Abbås, K. B. and Sorvik, E. M. *J. Appl. Polym. Sci.* 1975, **19**, 2991
3 Daro, A., Trojan, M., Jacobs, R. and David, C. *Eur. Polym. J.* 1990, **26**, 47
4 Turzynski, Z., Witkowski, K. and Wolinski, L. *J. Polym. Sci. (B) Polym. Phys.* 1990, **28**, 467
5 Cooper, A. R. *Polym. Eng. Sci.* 1989, **29**, 2
6 Pang, S. and Rudia, A. *Polymer* 1992, **33**, 1949
7 Grubisic, Z., Rempp, P. and Benoit, H. *Polym. Lett.* 1967, **5**, 753
8 Gilding, D. K., Reed, A. M. and Askill, I. N. *Polymer* 1981, **22**, 505
9 Allcock, H. R. and Lampe, F. W. 'Contemporary Polymer Chemistry', Prentice-Hall, Englewood Cliffs, NJ, 1981
10 Goldwasser, J. M., Rudin, A. and Elsdon, W. L. *J. Liq. Chromatogr.* 1982, **1**, 2253
11 Dayal, V. *J. Appl. Polym. Sci.* 1992, **45**, 119
12 Purdon, J. R. and Mate, R. D. *J. Polym. Sci. (A-1)* 1968, **6**, 243
13 Perkins, G. and Haehn, J. *J. Vinyl Technol.* 1990, **12**, 2
14 Jang, S.-S., Joseph, B. and Mukai, H. *Ind. Eng. Chem., Process Des. Dev.* 1986, **25**, 809
15 Waters Associates Data Module 730, Operator's Manual
16 Atiqullah, M., Ph.D. thesis, Rensselaer Polytechnic Institute, Troy, NY, 1988
17 Mahmud, F., Atiqullah, M., Jarrah, N. and Hussain, I. *Eur. Polym. J.* 1992, **28**, 1039
18 Collins, E. A., Bares, J. and Billmeyer, F. W., Jr, 'Experiments in Polymer Science', Wiley, New York, 1973
19 Dennis, J. E., Jr and Schnabel, R. B. 'Numerical Methods for Unconstrained Optimization and Nonlinear Equations', Prentice-Hall, Englewood Cliffs, NJ, 1983
20 UMING/DUMING, IMSL Math/Library, IMSL Inc., 1989
21 Ambler, M. R. and Mate, R. D. *J. Polym. Sci. (A-1)* 1972, **10**, 2677