# Procedure for Evaluation of the Mark–Houwink Constants

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## Synopsis

An iterative procedure for evaluation of the Mark–Houwink constants, using the GPC universal calibration principle and the extended $[\eta]$–$M$ relationship, is described. The procedure is recommended for newly prepared polymers of unknown average molecular weights. An example is given for bisphenol C-2 polycarbonate.

## INTRODUCTION

Well-characterized standards of narrow molecular weight distribution (MWD) are hardly available for newly prepared polymers. Therefore, conventional direct methods for determination of $K$ and $a$ constants of the Mark–Houwink equation

$$[\eta] = K\overline{M}_v{}^a \tag{1}$$

where $[\eta]$ is the intrinsic viscosity and $\overline{M}_v$ is the viscosity average molecular weight $(M)$, are not applicable. However, the constants $K$ and $a$ can be evaluated from broad MWD samples, using gel permeation chromatography (GPC) and viscometric (VIS) measurements and the universal calibration principle. Several procedures for this purpose have been described.[1-12] The two-sample procedure of Weiss and Cohn-Ginsberg[1] is particularly convenient for a newly prepared polymer, since $\overline{M}_n$ and $\overline{M}_w$, and any other specific demands are not required. The application of Weiss–Cohn-Ginsberg procedure reveals, however, that a broad spread of different pairs of $K$ and $a$ values is obtained, although $M$ averages calculated for different $K$–$a$ pairs are not significantly different.[10,12] Thus the correct $K$ and $a$ values are arbitrarily chosen[3,10] or are felt to be suitable.[3] Recently the relation between $K$ and $a$ in the form of semilogarithmic equation[13,14]

$$\log K = C - Ba \tag{2}$$

where $C$ and $B$ are constants, has been applied to find the reliable $K$–$a$ pair.[12] The constants $C$ and $B$ are, however, not known for a newly prepared polymer, since they have to be just calculated from a set of $K$ and $a$ values for several solvents.

In this paper a procedure for evaluation of $K$ and $a$ constants is proposed, where merely GPC data and values of $[\eta]$ for several samples of any MWD are required. The GPC universal calibration principle[15] and the three-var-

iable extended $[\eta]$—M relationship[16] are applied, and then the results are treated statistically.

## CALCULATION PROCEDURE

The following *initial data* are required.
(1) Data for the reference polymer:
    (a) the reference calibration function in the form of polynomial

$$\log M = \sum_{k=0}^{n} A_k V^k \tag{3}$$

where $A_k$ represents the coefficients of calibration polynomial and $k$ is the degree of polynomial;
(b) the constants $K_R$ and $a_R$ of the Mark–Houwink equation, eq.(1), for the reference polymer.
Usually polystyrene (PS) is used as the reference polymer, but any other polymer may be used, if $A_k$, $K_R$, and $a_R$ are known.
(2) An initial pair of $K_0$ and $a_0$ for a new polymer, which can be:
    (a) arbitrarily chosen,
    (b) taken for theta conditions with $a_0 = 0.5$ and $K_0$ calculated from group contributions,[13] or
    (c) taken from any other preliminary data, e.g., obtained from approximate methods described by Ambler[3] or by Coll and Gilding.[17]
(3) Experimental data for a new linear polymer:
    (a) GPC chromatograms for several samples in a GPC solvent, i.e., the function

$$h_i = f(V_i) \tag{4}$$

where $h_i$ is the chromatogram height at the elution volume $V_i$;
    (b) $[\eta]$ for several samples in a GPC solvent;
    (c) $[\eta]$ for several samples in any other solvent.
*K and a values for a GPC solvent* are calculated by the iterative procedure:
(4) The viscosity average $M$, $\overline{M}_{vGPC}$, and the ratio $q = \overline{M}_w/\overline{M}_n$ are calculated from GPC data. Thus, the calibration polynomial for a new polymer is calculated, using the reference calibration polynomial, $K_R$ and $a_R$ for the reference polymer, and $K_0$ and $a_0$ for a new polymer. The following relation is applied:

$$\log M = \frac{1}{1 + a_j} \log \frac{K_R}{K_j} + \frac{1 + a_R}{1 + a_j} \sum_{k=0}^{n} A_{kR} V^k \tag{5}$$

where subscript $R$ denotes the reference data and $j$ is the number of the iteration step ($j = 0$ for the initial step). The relation given by eq. (5) can easily be derived using the universal calibration principle,[15] i.e.,

$$M_j[\eta]_j = M_R[\eta]_R$$

which can be written as

$$K_j M_j^{a_j+1} = K_R M_R^{a_R+1}$$

since $[\eta] = KM^a$, or in the logarithmic form

$$\log K_j + (a_j + 1) \log M_j = \log K_R + (a_R + 1) \log M_R$$

Hence

$$\log M_j = \frac{1}{a_j + 1} \log \frac{K_R}{K_j} + \frac{a_R + 1}{a_j + 1} \log M_R$$

Substituting eq.(3) for the reference data, we obtain

$$\log M_j = \frac{1}{a_j + 1} \log \frac{K_R}{K_j} + \frac{a_R + 1}{a_j + 1} \sum_{k=0}^{n} A_{kR} V^k \tag{5a}$$

Equation (5a) is commonly used for recalculations of GPC calibration polynomials for different solvents. The M averages are obtained from the known relations

$$\overline{M}_n = 1/\Sigma(w_i/M_i) \tag{6a}$$

$$\overline{M}_{v\mathrm{GPC}} = \left(\Sigma w_i M_i^a\right)^{1/a} \tag{6b}$$

$$\overline{M}_w = \Sigma w_i M_i \tag{6c}$$

(5) A new pair of $K_j$ and $a_j$ values is calculated from the experimental $[\eta]$ values for a GPC solvent and obtained $\overline{M}_{v\mathrm{GPC}}$ values, using the extended $[\eta]$—$M$ relationship[16] written as

$$[\eta] = K\overline{M}_x^a q^{a_{px}} \tag{7}$$

where subscript $x$ denotes the type of $M$ average, i.e., the number $(x = n)$, viscosity $(x = v)$, or weight $(x = w)$ averages, respectively, $q = \overline{M}_w/\overline{M}_n$ is the polydispersity degree, and $a_{px}$ is the polydispersity exponent. Thus, for $\overline{M}_x = \overline{M}_{v\mathrm{GPC}(j-1)}$ and $q = q_{j-1}$, constants $K = K_j$, $a = a_j$, and $a_{px} = a_{pvj}$ are obtained. $K_j$ and $a_j$ values are immediately used in the next iteration step instead of the previous $K_{j-1}$, $a_{j-1}$ pair. $K_{j-1}$ and $a_{j-1}$ values are applied as the reference data for calculation of a new calibration polynomial in the $j$th iteration step. The iterative procedure is repeated until $K_j = K_{j-1}$ and $a_j = a_{j-1}$ is obtained for $j = N$ within an assumed accuracy, i.e.,

$$|K_j - K_{j-1}| \leqslant \delta_0 \tag{8a}$$

and

$$|a_j - a_{j-1}| \leqslant \delta_1 \qquad (8b)$$

where $\delta_0$ and $\delta_1$ are the required differences between the calculated values of $K$ and $a$, respectively.

(6) The auxiliary data are calculated at each iteration step:

  (a) the viscosity average $M$, $\overline{M}_{v\mathrm{VIS}}$, for all samples considered, using eq. (1), $K_j$, $a_j$, and $[\eta]$ in a GPC solvent;

  (b) the ratio

$$g_v = \overline{M}_{v\mathrm{GPC}}/\overline{M}_{v\mathrm{VIS}} \qquad (9)$$

for each sample, and the mean value of $g_v$, $\overline{g}_v$, standard deviation $\sigma$ and variation coefficient $s = \sigma/\overline{g}_v \, 100\%$. If the convergence conditions, eqs. (8), are satisfied, the final $K_N$ and $a_N$ values are checked by the polydispersity exponent $a_{pv}$ of the $[\eta]$—$M$ relationship, eq. (7), (cf. also Ref. 16) and by the mean value of $g_v$ . Since $a_{pv}$ and $\overline{g}_v$ should be equal to zero and unity, respectively, the following reliability conditions can be written:

$$|a_{pvN}| \leqslant \delta_2 \qquad (10a)$$

and

$$|\overline{g}_v - 1| \leqslant \delta_3 \qquad (10b)$$

where $\delta_2$ and $\delta_3$ are the required differences between the calculated and theoretical values of $a_{pv}$ and $\overline{g}_v$, respectively. The polydispersity exponent of eq. (7) is given by the relation

$$a_{px} = 0.5a(a - \epsilon)$$

for log-normal MWD, where $\epsilon$ is the exponent of $M$ in the integral form of average $\overline{M}_x$ definition

$$\overline{M}_x^{\epsilon} = \int_0^{\infty} M^{\epsilon} w(M) \, dM$$

For $\overline{M}_v$ we have $\epsilon = a$; therefore, $a_{pv} = 0$ (cf. Ref. 16). Also, for other types of MWD the polydispersity exponent for $\overline{M}_v$, $a_{pv}$ is equal to zero. The ratio $g_v$ , given by eq. (9), is equal to unity for linear polymers, since $\overline{M}_{v\mathrm{GPC}} = \overline{M}_{v\mathrm{VIS}}$ for linear polymers (cf. also Refs. 16 and 18).

   If the reliability conditions, eqs. (10), are satisfied, the obtained $K_N$ and $a_N$ constants are correct, as well as the coefficients $A_{kN}$ of GPC calibration polynomial. Otherwise, the experimental data should be reconsidered. The correction of calibration polynomial in the range of low $M$[21] should also be considered.

The iteration procedure is shown in Figure 1 in the form of flow sheet convenient for computer programming.
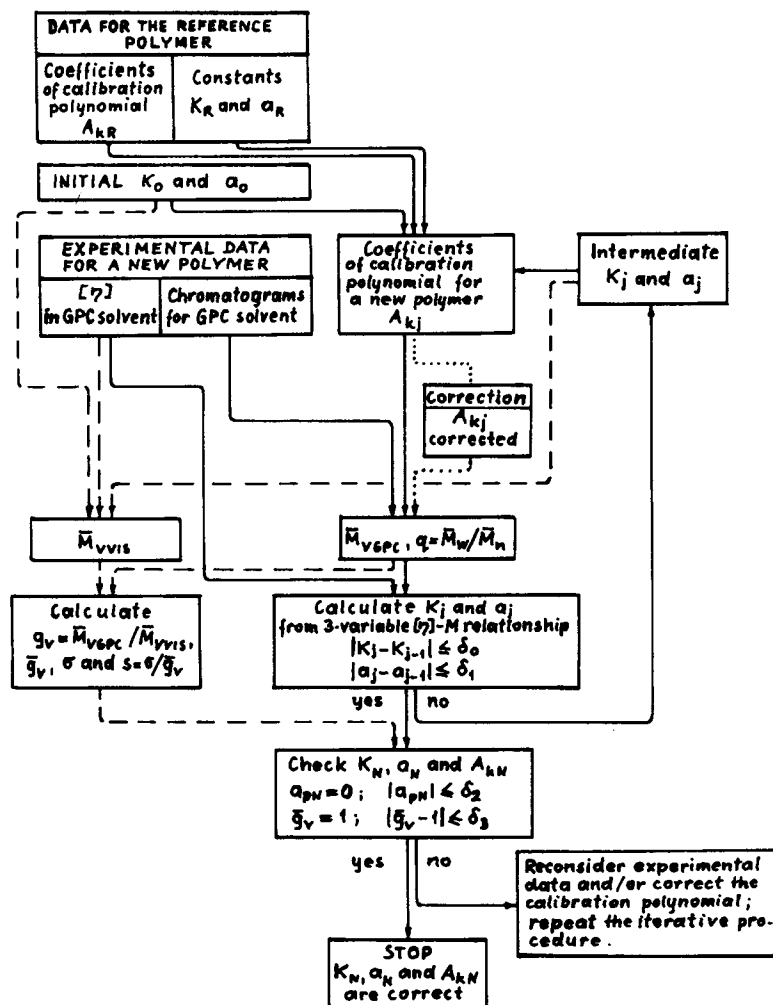
Fig. 1.   Flow sheet for simultaneous calculation of $K$ and $a$ constants and coefficients $A_k$ of GPC calibration polynomial.

(7) *K and a values for a non-GPC solvent.* Once the GPC calibration polynomial is established for a GPC solvent, $[\eta]$ data for any other solvent can be combined with $\bar{M}_w$ and $q$ values from GPC, using eq. (7). Thus obtained $K$ and $a$ constants are checked again with eq. (7) using $\bar{M}_{vGPC}$ for a given value of $a$, and with eqs. (8) and (10).

## EXPERIMENTAL

Bisphenol C-2 polycarbonate (CPC), i.e., polycarbonate from 1,1-dichloro-2,2-bis(4-hydroxyphenyl) ethylene of the formula
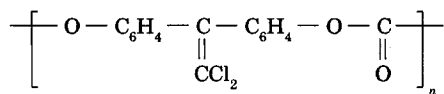
was used as a new polymer. CPC was prepared in our Institute by the interfacial polycondensation method[19] and then fractionated. Ten fractions of linear CPC* were characterized by their GPC chromatograms and $[\eta]$ values obtained at 25°C in tetrahydrofuran (THF) as a GPC solvent, as well as by $[\eta]$ values measured at 25°C in chloroform and in methylene chloride. A Waters Associate Model 200 Chromatograph and a Hewlett-Packard Model 5901B Autoviscometer were used for GPC/VIS measurements, respectively. Both $\eta_{sp}/c = f(c)$ and $\ln \eta_r/c = f(c)$ relationships were used for evaluation of $[\eta]$ at $c = 0$ by linear regression equations, where $c$ is the concentration of CPC in solution ranging from 0.004 to 0.012 g/cm³. Then the mean values of $[\eta]$ were calculated (shown in Table I) with maximum errors not exceeding $\pm 1.63\%$. Calculations were performed in parts, using a Hewlett-Packard Model 9810A Calculator with statistical and special GPC programs. Bisphenol A polycarbonate (APC) was used as the reference polymer with $K_R = 3.89 \times 10^{-2}$ cm³/g and $a_R = 0.70$ for THF.[18,20] The fourth degree calibration polynomial was earlier checked and corrected in the range of low $M$ for APC–THF GPC system.[18,21]

## RESULTS AND DISCUSSION

Results of GPC/VIS measurements are shown in Table I and Figure 2. A linear plot of $[\eta]$ vs. $V_{max}$, where $V_{max}$ is the elution volume corresponding to the maximum chromatogram height, is obtained for each solvent in the considered ranges of $[\eta]$. It can serve as an additional verification of $[\eta]$ measurements. The sequence of $[\eta]$ results, i.e., $[\eta]_{THF} > [\eta]_{CHCl_3} > [\eta]_{CH_2Cl_2}$, is the same as for 85/15 CPC/APC copolymer.[22] Data for APC in THF are also included in Figure 2 for comparison. Chromatograms of all CPC fractions were unimodal, without low $M$ or high $M$ tails.

* Fractions of CPC were prepared by Dr. A. Dems, Institute of Synthetic Fibres, Technical University of Lód'z, Poland, and kindly supplied to the author.

TABLE I
GPC/VIS Measurements of Polycarbonate Samples

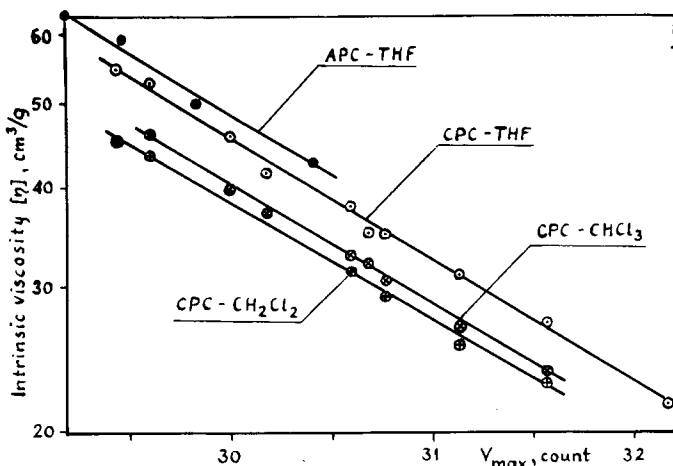| Polycarbonate | Sample no. | GPC measurements $V_{max}$ (counts) | Intrinsic viscosity $[\nu]$ (cm³/g) at 25°C | | |
| --- | --- | --- | --- | --- | --- |
| | | | THF | CHCl₃ | CH₂Cl₂ |
| CPC | 1 | 32.17 | 21.7 | — | — |
| | 2 | 31.57 | 27.2 | 23.9 | 23.1 |
| | 3 | 31.14 | 31.2 | 26.9 | 25.6 |
| | 4 | 30.76 | 35.1 | 30.9 | 29.5 |
| | 5 | 30.68 | 35.2 | 32.4 | — |
| | 6 | 30.59 | 37.9 | 33.2 | 31.8 |
| | 7 | 30.17 | 41.5 | 37.0 | — |
| | 8 | 30.00 | 46.0 | 39.9 | — |
| | 9 | 29.61 | 53.3 | 46.4 | 43.5 |
| | 10 | 29.44 | 55.0 | — | 45.7 |
| APC | 1 | 30.40 | 43.0 | — | — |
| | 2 | 29.83 | 50.3 | — | — |
| | 3 | 29.47 | 59.6 | — | — |
| | 4 | 29.20 | 63.1 | — | — |

Fig. 2.  Intrinsic viscosity [$\eta$] vs. elution volume of chromatogram peak $V_{max}$: (◯) CPC–THF; (⊗) CPC–CHCl$_3$; (⊕) CPC–CH$_2$Cl$_2$; (●) APC–THF systems.

Two runs of calculations, according to the above-described iterative procedure, have been performed: (A) with the initial $K_0 = 3.89 \times 10^{-2}$ cm$^3$/g and $a_0 = 0.70$ for CPC in THF, taken according to the point (2a) of the calculation procedure. Thus $K_0$ and $a_0$ are assumed to be the same as $K$ and $a$ for APC–THF system[18,20]; (B) with the initial $K_0 = 17.75 \times 10^{-2}$ cm$^3$/g and $a_0 = 0.50$ for CPC in THF. Thus theta conditions are assumed, according to the point (2b) of the calculation procedure, where $K_0$ is calculated from group contributions.[13] The following criteria were assumed: $\delta_0 = 10^{-4}$ cm$^3$/g and $\delta_1 = 10^{-3}$ for convergence, eqs. (8), and $\delta_2 = 0.03$ and $\delta_3 = 0.02$ for reliability, eqs. (10). As a result of the iterative procedure, similar $K_N$ and $a_N$ values have been obtained in both runs A and B (see Table II). The criteria for the coefficients of polydispersity in eq. (7), $a_{pnN} > 0$ and $a_{pwN} \leqslant 0$ (cf. Refs. 16 and 23) are satisfied and indicate the log-normal MWD of CPC fractions (Table II). The convergence of the procedure is shown in Figure 3. Thus, four to eight iteration steps are needed, depending on the assumed initial $K_0$ and $a_0$ values, i.e., depending on the difference between assumed and expected $K$ and $a$ values, respectively. Coefficients $A_{kN}$ of GPC calibration polynomial have simultaneously been obtained for CPC–THF system (see Fig. 1 and Table III). Therefore, the mean values of $K_N = 4.40 \times 10^{-2}$ cm$^3$/g and $a_N = 0.673$ for CPC in THF at 25°C have been obtained from $\overline{M}_{vGPC}$ data (Table II), as well as the mean values of $A_{kN}$ (Table III), within maximum errors of 0.71%, 0.15%, and 0.03%, respectively. Then the molecular characteristics of CPC samples have also been obtained (see Table IV). The range of $\overline{M}_w$ from $10^4$ to $4.3 \times 10^4$ g/mol is relatively narrow one, but it covers the $M$ of CPC used for injection moulding materials. $K$ and $a$ values for chloroform and methylene chloride at 25°C have been obtained from eq. (7), using the measured values of [$\eta$] (Table I) and the values of $\overline{M}_w$ from Table IV. Then the results have been verified with $\overline{M}_{vGPC}$ for a given value of $a$. Thus we have $K = 3.84 \times 10^{-2}$ cm$^3$/g and $a = 0.672$ for chloroform at 25°C, and $K = 4.50 \times 10^{-2}$ cm$^3$/g and $a = 0.651$ for methylene chloride at 25°C. The coefficients of eq.

TABLE II
Final Results of Calculations for CPC in THF: Coefficients of Three-Variable $[\eta]$–$M$ Relationship

| | For $\bar{M}_{uGPC}$ | | | For $\bar{M}_n$ | | | | For $\bar{M}_w$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $K_N \times 10^2$ (cm³/g) | $a_N$ | $a_{puN}$ | $\bar{g}_v$ | $K_N \times 10^2$ (cm³/g) | $a_N$ | $a_{pnN}$ | $K_N \times 10^2$ (cm³/g) | $a_N$ | $a_{pwN}$ |
| Run A: $N=4$ | 4.366 | 0.673 | −0.027 | 1.019 | 4.412 | 0.671 | 0.567 | 4.356 | 0.672 | −0.106 |
| Run B: $N=8$ | 4.427 | 0.672 | −0.028 | 1.014 | 4.350 | 0.673 | 0.566 | 4.425 | 0.671 | −0.101 |
| Mean values | 4.397 | 0.673 | −0.028 | 1.017 | 4.381 | 0.672 | 0.567 | 4.391 | 0.672 | −0.104 |
| Max. relative error (%) | 0.71 | 0.15 | 3.57 | 0.29 | 0.71 | 0.15 | 0.18 | 0.80 | 0.15 | 2.88 |
| Theoretical values, for log-normal MWD[a] | | | 0 | 1 | | | 0.562 | | | −0.110 |
| Difference | | | −0.028 | 0.017 | | | 0.005 | | | 0.006 |
| Relative error (%) | | | −2.8 | 1.7 | | | 0.9 | | | 5.5 |

[a] Calculated for $a_N = 0.672$ from relations $a_{pnN} = 0.5a_N(a_N+1)$ and $a_{pwN} = 0.5a_N(a_N-1)$. Cf. Ref. 16; see also text following eq. (10b).
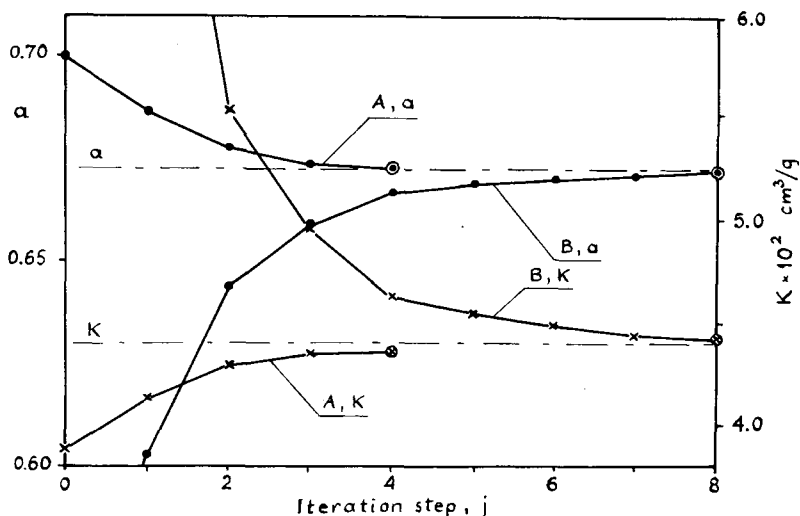
Fig. 3.   Convergence of iterative procedure for constants $K$ and $a$: (A) run A; (B) run B; (●) for values of $a$; (x) for values of K.

(7) obtained from $\overline{M}_{v\text{GPC}}$ data are compared with those obtained from $\overline{M}_n$ and $\overline{M}_w$ (see Table V). It is evident that they agree with each other, respectively.

Other data on $K$ and $a$ values for CPC are not available from the published papers. As a matter of fact, Factor and Orlando[22] reported [$\eta$] measurements of 85/15 CPC/APC copolymer; however, their values of $K = 3.34 \times 10^{-4}$ cm$^3$/g and $a = 1.22$ for the copolymer seem to be unreliable (their result is based on $\overline{M}_n$ which is not recommended for determination of $K$ and $a$,[24] and only three samples were taken for the regression equation). Studies of Dems on $K$ and $a$ of CPC were not published in details; only $K = 9.83 \times 10^{-2}$ cm$^3$/g and $a = 0.614$ for CH$_2$Cl$_2$ at 20°C were mentioned.[25] Differences from our values for CH$_2$Cl$_2$ at 25°C are too high to be explained only by the difference in temperature of measurements.

The reliability of our results depends, of course, on the measurements of [$\eta$] and on GPC data. We offer, however, the reasonable means for verification both [$\eta$] and GPC measurements. They are $a_{pv} = 0$ for eq. (7) (cf. Refs. 16 and 23), $g_v = 1$ for each linear sample (cf. Refs. 16,18,23), and $\overline{g}_v = 1$ for a set of linear samples (this work).

TABLE III
Final Results of Calculations for CPC in THF: Coefficients of Fourth Degree Calibration Polynominal

|  | $A_0 \times 10^{-1}$ | $A_1 \times 10^0$ · | $A_2 \times 10$ | $A_3 \times 10^3$ | $A_4 \times 10^5$ |
|---|---|---|---|---|---|
| Run A: $N = 4$ | 5.6301 | −5.1641 | 2.0305 | −3.7406 | 2.6360 |
| Run B: $N = 8$ | 5.6328 | −5.1672 | 2.0317 | −3.7428 | 2.6376 |
| Mean values | 5.6315 | −5.1657 | 2.0311 | −3.7417 | 2.6368 |
| Relative error (%) | 0.025 | 0.031 | 0.030 | 0.029 | 0.030 |

TABLE IV
Molecular Characteristics of CPC Samples

| Sample no. | $\bar{M}_n$ | $\bar{M}_w$ | $q = \bar{M}_w/\bar{M}_n$ | THF | | CHCl$_3$ | | CH$_2$Cl$_2$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\bar{M}_{vVIS}$ | $g_v = \bar{M}_{vGPC}/\bar{M}_{vVIS}$ | $\bar{M}_{vVIS}$ | $g_v = \bar{M}_{vGPC}/\bar{M}_{vVIS}$ | $\bar{M}_{vVIS}$ | $g_v = \bar{M}_{vGPC}/\bar{M}_{vVIS}$ |
| 1 | 8212 | 10470 | 1.27 | 10035 | 1.01 | — | — | — | — |
| 2 | 12095 | 14941 | 1.24 | 14037 | 1.03 | 14383 | 1.00 | 14569 | 0.99 |
| 3 | 14551 | 18160 | 1.25 | 17211 | 1.02 | 17150 | 1.02 | 17061 | 1.02 |
| 4 | 15160 | 21831 | 1.44 | 20503 | 1.01 | 21079 | 0.98 | 21212 | 0.97 |
| 5 | 17461 | 22533 | 1.29 | 20590 | 1.05 | 22620 | 0.96 | — | — |
| 6 | 18872 | 23472 | 1.24 | 22980 | 0.99 | 23456 | 0.97 | 23805 | 0.95 |
| 7 | 20487 | 28400 | 1.39 | 26297 | 1.03 | 27560 | 0.98 | — | — |
| 8 | 24259 | 32424 | 1.34 | 30643 | 1.01 | 30835 | 1.01 | — | — |
| 9 | 29782 | 40437 | 1.36 | 38141 | 1.01 | 38600 | 1.00 | 38519 | 1.00 |
| 10 | 30548 | 43089 | 1.41 | 39962 | 1.03 | — | — | 41552 | 0.98 |
| Mean value of $g_v$, $\bar{g}_v$ | | | | | 1.02 | | 0.99 | | 0.99 |
| Standard deviation $\sigma$ | | | | | 0.0166 | | 0.0207 | | 0.0243 |
| Variation coefficient $s = 100\sigma/\bar{g}_v$ (%) | | | | | 1.63 | | 2.09 | | 2.45 |

Note: the values of $\bar{M}_{vVIS}$ were calculated from eq. (1), using $K = 4.40 \times 10^{-2}$ cm$^3$/g and $a = 0.673$, $K = 3.84 \times 10^{-2}$ cm$^3$/g and $a = 0.672$, and $K = 4.50 \times 10^{-2}$ cm$^3$/g and $a = 0.651$ obtained at 25°C for THF, CHCl$_3$, and CH$_2$Cl$_2$, respectively (this work).

TABLE V
Coefficients of Three-Variable $[\eta]$–$M$ Relationship for CPC

| Solvent | Temper-ature (°C) | Coefficients | Values of coefficients for different $\overline{M}_x$ from GPC measurements | | | Mean values | Max. relative error (%) |
|---|---|---|---|---|---|---|---|
| | | | For $\overline{M}_{v\,GPC}$ (basic) | For $\overline{M}_n$ | For $\overline{M}_w$ | | |
| THF | 25 | $K_N \times 10^2$ (cm³/g) | 4.40 | 4.38 | 4.39 | 4.39 | 0.23 |
| | | $a_N$ | 0.673 | 0.672 | 0.672 | 0.672 | 0.15 |
| | | $a_{pxN}$ | −0.028 | 0.567 | −0.104 | — | — |
| | | correlation $r^2$ | 0.9985 | 0.9984 | 0.9985 | — | — |
| CHCl₃ | 25 | $K_N \times 10^2$ (cm³/g) | 3.84 | 3.80 | 3.81 | 3.82 | 0.52 |
| | | $a_N$ | 0.672 | 0.673 | 0.672 | 0.672 | 0.15 |
| | | $a_{pxN}$ | 0.020 | 0.611 | −0.057 | — | — |
| | | correlation $r^2$ | 0.9954 | 0.9945 | 0.9952 | — | — |
| CH₂Cl₂ | 25 | $K_N \times 10^2$ (cm³/g) | 4.50 | 4.39 | 4.44 | 4.44 | 1.35 |
| | | $a_N$ | 0.651 | 0.653 | 0.652 | 0.652 | 0.15 |
| | | $a_{pxN}$ | 0.020 | 0.588 | −0.064 | — | — |
| | | correlation $r^2$ | 0.9966 | 0.9960 | 0.9965 | — | — |

## CONCLUSIONS

The described iterative procedure, based on the three-variable $[\eta]$—M relationship, offers reliable values of $K$ and $a$ constants of the Mark–Houwink equation and simultaneously the GPC calibration for polymer samples of unknown $M$ averages. Merely GPC chromatograms and $[\eta]$ measurements are needed for several samples. Experimental errors of GPC/VIS measurements can be estimated by the statistical treatment of data.

The criterion of reliability of $K$ and $a$ values is $a_{pvN} = 0$; the calculated value of $a_{pvN} \times 100$, i.e., the deviation from $a_{pvN} = 0$, can be used as a measure of this reliability.

The criterion of reliability of GPC calibration is $\overline{g}_v = 1$ for a GPC solvent, as well as for other solvents; the variation coefficient $s = 100\sigma/\overline{g}_v$ is a measure of this reliability.

The described procedure has been applied to bisphenol C-2 polycarbonate (CPC) and the following values of $K$ and $a$ at 25°C have been obtained:

$K = 4.40 \times 10^{-2}$ cm³/g    and    $a = 0.673$    for THF
$K = 3.84 \times 10^{-2}$ cm³/g    and    $a = 0.672$    for chloroform
$K = 4.50 \times 10^{-2}$ cm³/g    and    $a = 0.651$    for methylene chloride

The reliability measures are $a_{pvN} \times 100$ equal to 2.8%, 2.0%, and 2.0%, and the variation coefficient $s$ equal to 1.63%, 2.09%, and 2.37% for THF, chloroform, and methylene chloride, respectively.

## References

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