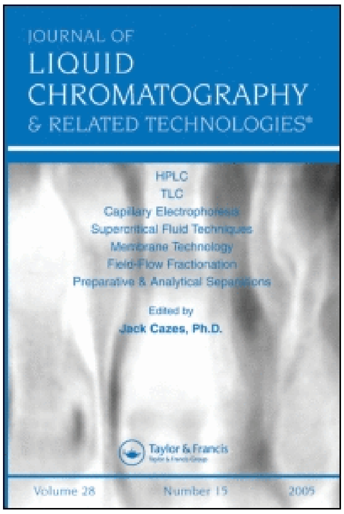

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K. Wang[a]; H. Huang[a]; J. Sheng[a]
[a] Beijing Research Institute of Chemical Industry Hepingli, Beijing, People's Republic of China

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DETERMINATION OF THE MARK-HOUWINK EQUATION PARAMETERS AND THEIR INTERRELATIONSHIP

Wang Keqiang, Huang Honghong, Sheng Jianfang

Beijing Research Institute of Chemical Industry
Hepingli, Beijing
People's Republic of China

ABSTRACT

This paper presents a trial and error method for determining the optimal values of k and *a* of the Mark-Houwink equation using polymers with different intrinsic viscosities ([η]) and molecular weight distribution (MWD) as standards. The values of k and *a* for polystyrene, EP-copolymer, polypropylene, polyethylene, polyvinylchloride, and polycarbonate, etc., have been determined with this method. The relative errors of the resultant [η] are below 6%, 4% or 3%. The viscosity-average molecular weight (M_v) of polystyrene standards agrees well with those of Pressure Chemical Co.; the weight- and number-average molecular weights of EP-copolymer coincide with that measured by using the low angle laser light scattering KMX-6 and the Knauer membrane osmometer, respectively. Thus, the method possesses high precision and can be applied to polymers with a wide range of molecular weight (MW) and molecular weight distribution (MWD).

At the same time, the linear relationship between log k and α was found falling within the range of experimental error. The computer program for calculating the optimal values of k and α has been used on the computer associated with the GPC instrument in Beijing University of Chemical Industry.

INTRODUCTION

Gel permeation chromatography (GPC) is a relative method of determining MW for polymers. In principle, either a standard with narrow MWD or one with precisely known broader MWD should be used to calibrate the GPC columns in the determination of the MW and MWD for a given sample. However, it is difficult and expensive to prepare such standards. Thus, Benoit[1] has proposed a universal calibration method which GPC experiments have shown to be valid for widely different species. One, therefore, can calculate the weight- and number-average MW and MWD from the universal calibration curve if the Mark-Houwink relationship ($[\eta] = kM^{\alpha}$) for the particular polymer-solvent pair is known. In the case of this being unknown, the narrow fractions obtained from the fractionation method are usually used to determine the values of k and α; so far, however, the values of k and α measured by different authors appear to differ widely,[2,3] presenting, thereby, difficulties in citing the values of k and α from the literature. Now, we present a trial and error method for determining the optimal values of k and α of the Mark-Houwink parameter with the application of the GPC universal calibration curve, using polymers with different $[\eta]$ and MWD as standards, and further study the relationship between k and α within the range of experimental error.

EXPERIMENTAL

Reagents

o-Dichlorobenzene: analytical reagent; trichloromethane: chemically pure.

Intrinsic Viscosity

Intrinsic viscosities were, respectively, measured in ODCB at 135°C or 90°C and in trichloromethane (chloroform) at 25°C, using Ubbelohde viscometers with flow rates exceeding 100 sec. For some of the data, the required extrapolation to zero concentration was made according to measurements obtained from five concentrations. For others, however, only a single measurement was made and the Cheng's equation[4] was employed for calculating the intrinsic viscosity. No significant difference was found to exist between the results ohtained from the two methods as far as the same sample was concerned.

Gel Permeation Chromatography

The instrument employed for measuring the GPC data was a Waters GPC Model 200 with Styragel-packed columns. The instrument was either of five-column assembly (l0E3, l0E4, l0E5, l0E6 and l0E7 angstroms) or four column assembly (10E3, l0E4, l0E6 and l0E7 angstroms). To minimize the effect of solution concentration on the results, the columns were connected in series according to the order of small to large permeation limit. The determination of GPC data was made at 135°C and 90°C, as well as at 25°C, in ODCB or trichloromethane solvents; the polymer solution concentration was 0.17-0.24%; the flow rate was 1 mL/min.

In order to minimize error, the polymer solution, after determination of intrinsic viscosity, was divided into four parts which were then separately injected into the GPC instrument. Thus, four GPC chromatograms were obtained for each sample. These were then individually normalized. The average value

$$\frac{1}{4}\sum_{j=1}^{4}\left(H_i / \sum_{i=1}^{n} H_i\right)_j = W_i$$

of the normalized height of the i-th count was taken (Hi /ΣHi).

Determination of k and α

Weiss[5] has proposed that the k and α of the Mark-Houwink equation may be determined by using two polymers having relatively broad MWD with different intrinsic viscosities. The procedure is as follows. As J represents [η]M, i represents the i-th species, and t represents the total count intervals, then

$$J_i = [\eta]_i M_i \tag{1}$$

$$[\eta]_i = k^{1/(1+\alpha)} J_i^{\alpha/(1+\alpha)} \tag{2}$$

$$[\eta] = k^{1/(1+\alpha)} \sum_{i=1}^{t} w_i J_i^{\alpha/(1+\alpha)} \tag{3}$$

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\sum_{i=1}^{t_1} w_{1i} J_i^{\alpha/(1+\alpha)}}{\sum_{i=1}^{t_2} w_{2i} J_i^{\alpha/(1+\alpha)}} \tag{4}$$

where w_i and $[\eta]_i$ are, respectively, the weight-fraction and the intrinsic viscosity of the i-th species. Therefore, using w_i's from the GPC chromatogram, J_i's from the universal calibration curve, and $[\eta]$ determined by viscometry, one can solve for α and k from equations (4) and (3), respectively, and ultimately calculate weight- and number-average molecular weights according to the definition for MW of polymer. Our experiments have shown that the calculated α and k from data based on samples 1 and 2 might not be appropriate for other samples due to polydispersity of polymer MW and errors in viscosity determination and GPC data. Therefore, we employ a number of samples with broad distribution, having different $[\eta]$ and MWD for determining the optimal values of α and k by means of a trial and error method. This procedure consists of two steps. In the first step, let

$$\left| \left(\frac{[\eta]_1}{[\eta]_2} - \frac{\sum_{i=1}^{t_1} w_{1i} J_i^{\alpha/(1+\alpha)}}{\sum_{i=1}^{t_2} w_{2i} J_i^{\varepsilon/(1+\alpha)}} \right) \bullet \frac{[\eta]_2}{[\eta]_1} \times 100 \right| \le u \qquad (0 < u \le 7) \tag{5}$$

The range of the exit criterion u is given according to the accuracy of the GPC determination. After the determination of the intrinsic viscosity ($[\eta]_d$), GPC chromatogram, and universal calibration curve using polystyrene standards, the value α (denoted as $\alpha_{(0)}$) can be calculated through iteration with a computer from equation (5) with given values of u. By substituting $\alpha_{(0)}$, the intrinsic viscosity and GPC data of samples from sample 1 to sample n into equation (3), we can calculate the k values of all samples. Thus, k values of n samples are obtained, which are represented by $k_{(0,y)}$, y = 1, 2, 3.....n. Since $\alpha_{(0)}$ is obtained from the inequality (5), $k_{(0,y)}$ values are not equal to each other; the difference may be great in some cases. Thus, several average values of k are further taken: $k_{(0,5)} = (k_{(0,1)} + k_{(0,2)} + \cdots k_{(0,n)}/n$ and $k_{(0,4)} = (k_{(0,1)} + k_{(0,2)} + k_{(0,3)}/3$ as well as $k_{(0,3)} = (k_{(0,1)} + k_{(0,2)} /2$ (the values of the variables can be reset in a computer program). However, the sequence of calculating k-average values can not be reversed (the same holds true below). We take five values of k corresponding to $\alpha_{(0)}$) only, that is, $k_{(0,1)}$, $k_{(0,2)}$, $k_{(0,3)}$, $k_{(0,4)}$, and $k_{(0,5)}$, where $k_{(0,3)}$, $k_{(0,4)}$, and $k_{(0,5)}$ are the average values of k. Thus, the five values of k may be represented with $k_{(0,j)}$, j=1,2....5. The values of α (denoted as α_1) can then be calculated through iteration from equation (6) with given values of z:

$$\left|\left([\eta]_3 - k_{(0,4)}^{1/(1+\alpha}\sum_{i=1}^{t_3} w_{3i} J_i^{\alpha/(1+\alpha)}\right)/[\eta]_3 \times 100\right| \le z \qquad (0 \le z \le 7) \quad (6)$$

The range of the exit criterion z are also given according to the accuracy of GPC determination. By substituting $\alpha_{(1)}$ and experimental data of n samples, one by one, into equation (3), the k values of all samples can be calculated, which are represented with $k_{(1,y)}$, y = 1,2,......n. Similarly, several average values of k are taken: $k_{(1,5)} = (k_{(1,1)} + k_{(1,2)} + \ldots\ldots + k_{(1,n)})/n$ and $l_{(1,4)} = k_{(1,1)} + k_{(1,2)} + k_{(1,3)})/3$. Thus, we have five values of k, i.e., $k_{(1,1)}$, $k_{(1,2)}$, $k_{(1,3)}$, $k_{(1,4)}$, $k_{(1,5)}$. At the same time, we take the average of $\alpha_{(0)}$ and $\alpha_{(1)}$ to obtain $\alpha_{(2)}$ and, subsequently, $k_{(2,1)}$, $k_{(2,2)}$, $k_{(2,3)}$, $k_{(2,4)}$, and $k_{(2,5)}$. In this manner, 15 groups of values of α and k are obtained which are, respectively, the corresponding values of $a_{(i)}$ and $k_{(ij)}$, i = 0, 1, 2; j =1,2.....5. Finally, the corresponding values of $a_{(i)}$ and $k_{(i,j)}$ of each group are used to calculate the intrinsic $[\eta]_c$ from equation (3). The relative error $[\eta]_{er}$ between $[\eta]_c$ and the measured value of the intrinsic viscosity $[\eta]_d$ determined by viscometry of each sample, as well as the standard deviation

$$\sigma = \sqrt{\sum_{i=1}^{n}\left([\eta]_c - [\eta]_d\right)_i^2 / n}$$

(where n is the number of samples) are calculated. The foregoing procedure is repeated assuming new values of u and z and, if necessary, exchanging the

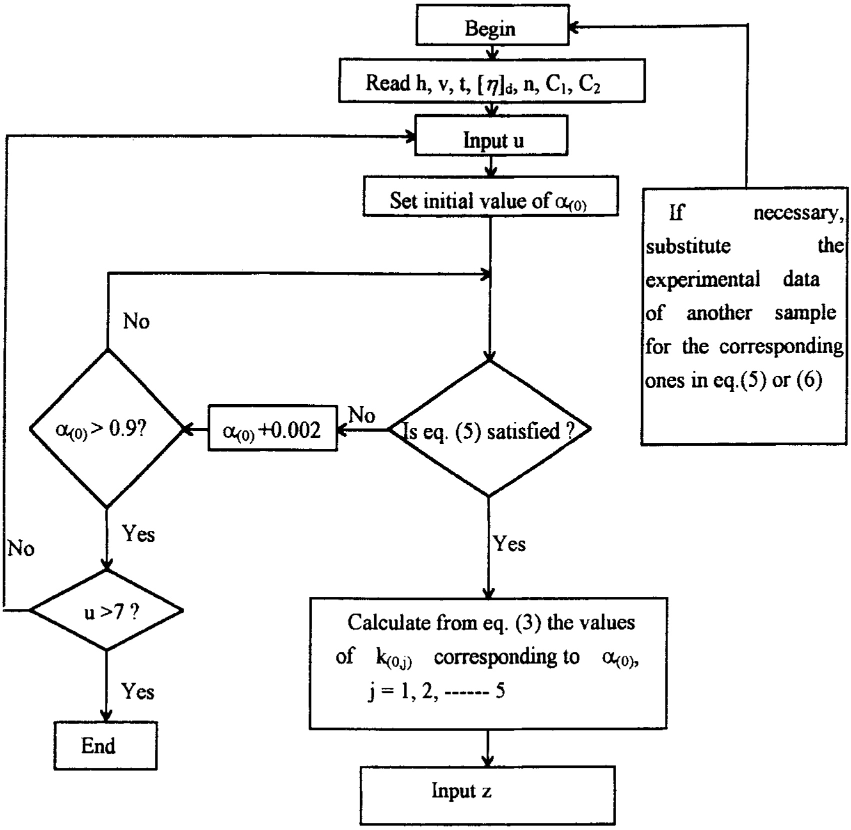

Figure 1a. Flow diagram of iterative calculation. h = height of interval from baseline; v = elution volume (count number); t = total count intervals; $[\eta]_d$ =intrinsic viscosity of sample; n = number of samples; C_1 and C_2 are the intercept and slope of the universal calibration curve.

experimental data of sample 3 in equation (6) with that of sample 1 or sample 2 in equation (5) or, alternatively, substituting the experimental data of another sample for the corresponding ones in (5) or in (6). Calculate as before using a computer until the accumulation of sufficient data. The flow diagram for the iteration calculation is presented in Figures 1a and 1b. On the basis of the relative error of $[\eta]$ and their standard deviation, a number of groups of α and the corresponding k falling within the range of allowable error of experiment can be selected, since there exist a number of k corresponding to any one value of α.

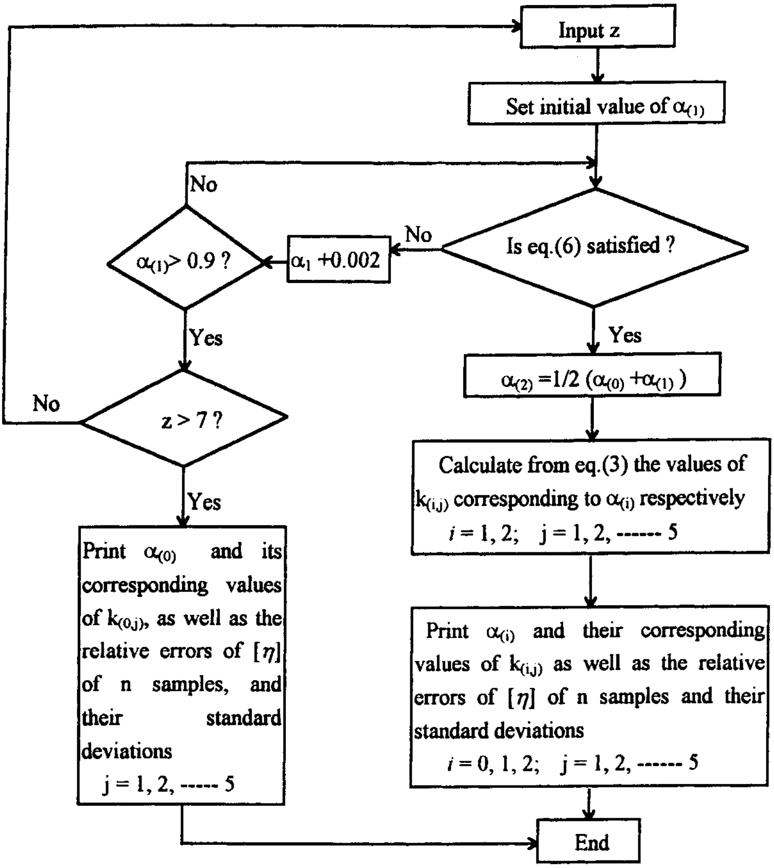

Figure 1b. Flow diagram of iterative calculation. (See Fig. 1a).

In the second step, with respect to the same group of α and k, keep α constant and let values of k increase within the above selected range by a constant pace, and calculate the standard deviation σ with another computer program. The k value can be selected on the basis of the minimum σ value, and the relative error $[\eta]_{er}$ of each sample can be calculated.

The rest of the groups of k and their corresponding α are treated with the same method as above. All the minimum σ values are compared with each other, and a group of optimal values of α and k can be determined on the basis of the minimum σ.

If one use the same polymer standards with narrow distribution to calibrate the GPC columns, then, $[\eta] = k\sum_{i=1}^{t} w_i M_i^{\alpha}$, where w_i and M_i can be obtained from the GPC chromatogram and the calibration curve. The procedures for determining α and k values are the same as the universal calibration method .

This computer program for calculating the optimal values of k and α has been used with the computer associated with the GPC instrument.

RESULTS AND DISCUSSION

Accuracy of the Result

The GPC columns were calibrated with polystyrene standards provided by Pressure Chemical Co. (Pittsburgh, PA, USA). Determination of the values of α and k (ODCB, 135 °C or 90 °C; trichloromethane, 25 °C) for polystyrene (PS), polypropylene (PP), polyethylene (PE), EP-copolymer (EP), polyvinylchloride (PVC) and polycarbonate (PC), etc., was performed with the foregoing method. The optimal values of α and k for PS, PP, PE, PVC, and PC are given in Table 1. As for EP-copolymer, because the k value bears a relationship to EP compositions, the optimal values of α and k were not obtained. However, the following empirical formula has been established, which is within the range of experimental error:[6]

$$\text{Log } k = \text{Log}(5.755 + 4.65C_3) - 5.75\alpha \quad (\text{ODCB, } 135°\text{C}) \qquad (7)$$

where C_3 is the propylene content, in mol%, in the EP-copolymer. They are primarily applicable to EP-copolymer with propylene contents in the range of 30-55 mol%, and α can take any value between 0.73 and 0.755. The $[\eta]$ and MW values of polymers measured with GPC on the basis of the foregoing method agreed well with those which resulted from other methods, as shown in Tables 2, 3, and 4. It can be seen, from Table 2, that the values of viscosity-average MW (M_v) for PS agree well with those provided by Pressure Chemical Co. At the same time, it can be inferred, from Table 3, that the relative errors $[\eta]_{er}$ between $[\eta]_c$ and $[\eta]_d$ of PS are below 6%. In addition, the relative error $[\eta]_{er}$ of PP, PVC, and PC are, respectively, below 5%, 4%, and 3%.

Table 1

Optimal Value of α and k for Some Polymers

Sample	α	k x 10^4	Solvent	Temp. (°C)
PS	0.74	0.82	ODCB	135
PS	0.715	1.33	ODCB	90
PP	0.73	1.80	ODCB	135
PE	0.72	3.973	ODCB	135
PVC	0.735	1.94	ODCB	90
PC	0.575	0.156	trichloromethane	25

Table 2

Viscosity-Average Molecular Weight of PS

Data From	M_v x 10^{-4}					
Pressure Chem Co.	0.92	4.74	11.1	23.3	38.8	234
GPC, 135°C	0.80	4.63	11.8	26.0	42.3	231.7
GPC, 90°C	1.0	4.46	10.6	24.4	35.9	227

Table 3

Relative Error Between $[\eta]_c$ and $[\eta]_d$ of PS

Sample	M_v x 10^{-4}	M_w/M_n	$[\eta]_{er}$ (%)
WG1	26.5	4.20	-3.91
F-108	15.2	2.09	0.11
F-114	25.0	1.80	0.56
F-99	24.1	2.02	3.43
PS-3	11.8	1.02	-1.74
PS-4	26.0	1.05	-2.20
PS-5	42.3	1.10	4.56
PS-6	65.8	1.10	-5.40
PS-7	231.7	1.21	0.09

Table 4

Comparison of Data from GPC and Absolute Methods

Sample	k x 10^4	α	$(M_n)_{GPC}$ x 10^{-4}	$(M_n)_{osm}$ x 10^{-4}	Rel. %	$(M_w)_{GPC}$ x 10^{-4}	$(M_w)_{LLS}$ x 10^{-4}	Rel. %
ZK-11(1)-3 (C_3=49.5 mol%)	2.04	0.735	29.9	29.8	0.33	63.3	62.3	1.6
ZK-11(1)-4 (C_3=53.9 mol%)	1.90	0.735	13.9	13.0	7.0	23.8	---	---

Moreover, it can be seen, from Table 4, that the number- and weight-average MW of EP-copolymer determined by GPC basically agree with those measured by low angle laser light scattering KMX-6 and Knauer membrane osmometer, respectively. It can be seen from the above that the method described in this paper possesses high precision and can applied to polymers with a wide range of MW and MWD.

Relationship Between k and α

So far, k and α values for a particular polymer-solvent pair reported in the literature differed with different authors.

So far, k and α values for a particular polymer-solvent pair reported in the literature have differed with different authors.[2,3] This might be due to differences in polydispersity and MW range of polymer standards, the methods employed for the determination, and errors in measurement. Van Krevelen[7] noted that different authors obtained different results for $[\eta] = 6.76 \times 10^{-4}M^{0.55}$ and $[\eta] = 4.10 \times 10^{-5}M^{0.735}$ from the Mark-Houwink equation for the polyvinylpyrolidone - water system with, however, the calculated values of MW falling within the permissible range of experimental error. Moreover, a linear relationship between log k and α could be ultimately established by rearranging. Cervenk[8] found that the k and α values for linear polyethylene - 1,2,4-trichlorobezene system, determined by different authors, differed significantly ($1.5 \times 10^{-3} \geq k \geq 3.23 \times 10^{-4}$; $0.735 \geq \alpha \geq 0.60$, at 135°C). Though a basically linear relationship between log k and α could be found in this case, it was difficult to select a pair of k and α that was most suitable to the polymer in question. Therefore, we set out to investigate further into the relationship between k and α. We treated the values of k and α, obtained from our previous experiments, with the least squares method. The linear relationships between log k and α for different polymers obtained are shown below,

PS $\log k = 0.3757 - 6.03\alpha$ (8)
$r = -0.99974,\ 0.70 \le \alpha \le 0.76$ (ODCB, 135°C)

$\log k = 0.7073 - 6.433\alpha$ (9)
$r = -0.99996,\ 0.69 \le \alpha \le 0.75$ (ODCB, 90°C)

PP $\log k = 0.403 - 5.682\alpha$ (10)
$r = 0.99996,\ 0.695 \le \alpha \le 0.775$ (ODCB, 135°C)

PE $\log k = -0.610 - 3.876\alpha$ (11)
$r = -0.9999,\ 0.705 \le \alpha \le 0.74$ (ODCB, 135°C)

PVC $\log k = -0.0899 - 4.93\alpha$ (12)
$r = -0.99986,\ 0.71 \le \alpha \le 0.75$ (ODCB, 90°C)

PC $\log k = -01636 - 4.598\alpha$ (13)
$r = 0.99998,\ 0.55 \le \alpha \le 0.62$ (trichloromethane, 25°C)

where r is the linear correlation coefficient. As is obvious from the values of r, equations (8) through (13) all possess good linearity, within the range of experimental error. It is well known that the precision of the Waters 200 GPC at high temperature is below 5-7%. Therefore, as the $[\eta]_{er}$ values are restricted within the precision range of GPC, any pair of α and k obtained from equations (8) to (13) in the range of the individual α values noted under the equations can generally meet the requirement of experiment. A comparison of the values of k corresponding to α for PS and PP calculated from equations (8) and (10) (ODCB, 135°C), respectively, with that reported in the literature, is shown in Table 5. It can be seen from Table 5 that, except for a few individual cases, most of the values for k corresponding to α basically agreed with those reported in the literature. When the k and α values of PS from literature in Table 5 were further treated with the least squares method to obtain the following relationship:

PS $\log k = 0.0063 - 5.502\alpha$ (14)
$r = -0.9997,\ 0.69 \le \alpha \le 0.75$ (ODCB, 135°C)

Table 5

Comparison of Data from This Paper with That Reported in the Literature

Sample	α	k x 10^4 Value From This Paper	k x 10^4 Value From Literature	Lit. Ref.
PS	0.606	5.27	4.57	9
	0.693	1.57	1.51	10
	0.70	1.42	1.38	3
	0.715	1.159	1.156	11
	0.75	0.732	0.736	12
PP	0.704	2.53	2.67±0.09	13
	0.707	2.43	2.40±0.09	13
	0.78	0.94	1.0	2
	0.78	0.94	1.30	3

it was found that the values of k calculated from equations (8) and (14), respectively, were quite close to each other when α took any value between 0.69 and 0.75. Moreover, the range of α values in equation (14) basically falls within that required by equation (8).

It can be seen, from the above results, that the parameters k and α of the Mark-Houwink equation have much elasticity. For a particular polymer - solvent pair system, though the values of k and α given by different authors were different, it would be rather safe to cite, directly, any pair of them.

However, it should be pointed out that errors greater than 30% do exist in some cases. In order to obtain optimal k and α, especially when the values are not available in the literature, the method described in this paper may provide a simple, rapid, and reliable solution.

Moreover, as the calibration standards for GPC columns are taken from the polymers themselves (about five to eight standards would be enough), information on MW and MWD can be obtained at the same time.

CONCLUSION

Optimal values of k and α of the Mark-Houwink equation, applicable to a broad range of MW and MWD, can be obtained by the trial-and-error method described in this paper, using polymers of different intrinsic viscosities and broad MWD as standards. The measurement of MW and MWD is further facilitated by the application of the GPC universal calibration technique. Besides, the method is inexpensive and fast as compared with the classical method. At the same time, the corresponding computer program can be directly applied to any computer associated with gel permeation chromatography.

We have also proven that log k is a good linear function of α. However, for any particular polymer–solvent system, only the k that is calculated on the basis of values of α selected from a particular range can meet the requirements of the experiment.

At the same time, the obtained values of k corresponding to α for PS and PP (ODCB, 135°C) determined by the method coincide basically with most of those reported in the literature. Generally speaking, except for a few cases, there would be no problem in directly citing the values of k and a reported in the literature.

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