

# Grid Search as Applied to the Determination of Mark–Houwink Parameters

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**ABSTRACT:** This article demonstrates the applicability of the algorithm of grid search to the determination of Mark–Houwink (MH) parameters. In the existing methods, the determination of MH parameters involves the use of linear or nonlinear regression. In the cases of using the algorithm of grid search to solve the linear regression problem for the determination of MH parameters, the values of the MH parameters obtained by the grid search method are the same as those obtained by the linear regression method, while in the cases when some nonlinear regression methods have to be used in the existing methods, using the algorithm of grid search can determine the parameters much more easily and accurately than using any nonlinear regression methods. In addition, the grid search method is very easy to understand and execute, and the accuracy of the results can be exhibited by the value of the least-square function. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 481–487, 2000

**Key words:** grid search algorithm; global optimization; Mark–Houwink parameters; molecular weight

## INTRODUCTION

In the existing methods, Mark–Houwink (MH) parameters are determined by both linear- and nonlinear regression methods. If there are several molecular weight monodispersed samples of a polymer available, the MH parameters of the polymer (in a certain kind of solvent at a certain temperature) can be determined accurately by the linear regression method. The monodispersed samples of a few kinds of polymers, such as polystyrene, can be obtained by well-controlled ionic polymerizations, while that of other polymers can only be obtained by fractionating polydisperse samples of the polymers. Due to the difficulty in the fractionation, methods using polydisperse samples directly to determine the MH parameters

through treating GPC data of the samples have been developed.<sup>1–6</sup> In these methods, nonlinear regression algorithms have to be applied. Although the equipment of the coupling of a high-pressure gel permeation chromatograph and the “Ouano”-type continuous viscometer developed by Lesec et al. can be used for the determination of MH parameters by linear regression and the characterization of other properties of a polymer,<sup>7,8</sup> it has not been equipped in most laboratories and the viscosities determined with this equipment are not as accurate as with a well-designed Ubbelohde-type viscometer.

In fact, the linear regression method or the nonlinear regression method determines the MH parameters through minimizing the least-square function,  $f(k, \alpha) = \sum_{i=1}^n (y_i^{\text{exp}} - y_i^{\text{cal}})^2$  (where  $k, \alpha$  are MH parameters;  $n$ , the number of the samples;  $y_i^{\text{cal}}$  and  $y_i^{\text{exp}}$ , the values of molecular weight or intrinsic viscosity or another quantity calculated and measured, respectively; and  $y_i^{\text{cal}}$ , also

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the function of  $k$  and  $\alpha$ ), which is built according to the least-square principle, since the least-square principle supposes that the real values of the MH parameters,  $k^{\text{real}}$  and  $\alpha^{\text{real}}$ , correspond to the least value of  $f(k, \alpha)$ . When a linear regression is involved, there is only one minimum value of  $f(k, \alpha)$ , and this minimum value is also the least value of the  $f(k, \alpha)$  and can be easily found by a linear regression method. When nonlinear regression is involved, there are many minimum values of  $f(k, \alpha)$ , and the least value, namely, the global minimum, of  $f(k, \alpha)$  is usually very difficult to find. In this case, the parameters determined by existing methods are strongly dependent on the initial values of  $k, \alpha$  one inputs to start the nonlinear regression. Therefore, the accuracy of the MH parameters determined by the nonlinear regression methods is not assured. Besides, the procedure of the calculation by nonlinear regression is rather complex and difficult to execute.

The algorithm of grid search, also called the exhaustive search, is a most dependable global optimization algorithm. It is often ignored because it is, in most cases, very time-consuming. But, in this case, according to the reasonable ranges and any possible requirement of the precision of the  $k, \alpha$  values, one can divide the phase space, which is defined as the set of points bounded by the minimum and maximum values of  $k, \alpha$ , of the function into no more than  $10^8$  grid points, as will be detailed later. Calculating the values of the function at each grid point and choosing one grid point at which the value of the function is the global minimum, namely, the global minimum point, will take no more than 1 h. The  $k, \alpha$  values at the global minimum point are  $k^{\text{real}}, \alpha^{\text{real}}$ , according to the least-square principle. So, the MH parameters can be determined more accurately and easily than in any of the nonlinear regression methods. Also, the linear regression method used to determine the MH parameters can be replaced by it as well.

In this article, we present the application of grid search to the determination of the MH parameters of two polymer systems, polystyrene (PS) in toluene at 25°C and poly(methyl methacrylate) (PMMA) in benzene at 25°C, to demonstrate the applicability of the method proposed.

## EXPERIMENTAL

### Materials

Samples of both PS and PMMA were obtained by radical polymerization of styrene and MMA in

benzene at 60°C using azodiisobutyronitrile as the initiator. The amount of the initiator was controlled in order to acquire samples with different molecular weight. All the reagents and the polymer samples obtained were purified by a standard method. The polymer samples were used without being further fractionated.

### Measurements of Relative Viscosities

Five different concentrations of each of the samples of PS in toluene and PMMA in benzene were measured at  $25 \pm 0.1^\circ\text{C}$  with a Ubbelohde-type viscometer. The intrinsic viscosity of each sample was evaluated by linear extrapolation using the Huggins equation:

$$\frac{\eta_{\text{sp}}}{c} = [\eta] + k_h[\eta]^2c$$

### GPC Measurements

A Waters Model 244 GPC-LC chromatograph connected with  $10^3$ ,  $10^4$ , and  $10^5$  Å  $\mu$ -Styragel columns in series was used. The detector was a Waters Model 440 ultraviolet absorption meter at the wavelength of 254 nm. The injection volume was 200  $\mu\text{L}$  and the detection response was collected and recorded by a Waters Model 730 microprocessor. The flow rate was kept at 1.0 mL/min at 25°C. Toluene was used as the elution solvent for the measurement of the PS, and benzene, for the measurement of PMMA. The column set was calibrated by standard PS samples provided by Department of Polymer Science, Nanjing University, P.R. China.

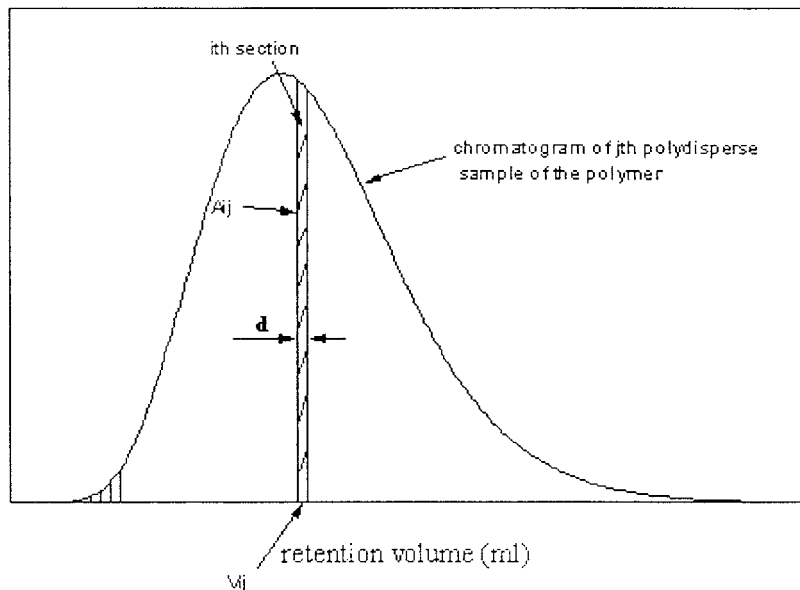
## RESULTS AND DISCUSSION

### Using the Grid Search Method to Replace Nonlinear Regression Method to Determine MH Parameters

The GPC chromatograms and the intrinsic viscosities of a series of polydisperse samples of the polymer system, for example, PS in toluene at 25°C or PMMA in benzene at 25°C, are measured. Then, each of the chromatograms is divided into  $n$  sections with the same width as indicated in Figure 1.

According to

1. The universal calibration principle,  $\text{Log}([\eta_i]M_i) = A - BV_i$  ( $[\eta_i]$  is the intrinsic viscosity of  $i$ th section;  $M_i$  and  $V_i$ , the viscosity-average molecular weight and the



**Figure 1** Division of a GPC chromatogram.

- retention volume of  $i$ th section; and  $A$  and  $B$ , the intercept and the slope of the line  $\text{Log}([\eta_i]M_i)$  vs.  $V_i$ ; the values of  $A$  and  $B$  are obtained from the calibration of the columns set by the standard PS samples for the polymer system to be determined),
2. The MH equation,  $[\eta_i] = k \times M_i^\alpha$  ( $k$  and  $\alpha$  are MH parameters), and
  3. The formula  $[\eta]^\text{cal} = \sum_{i=1}^n A_i \times [\eta_i]$  ( $A_i$  is the area fraction of  $i$ th section in the chromatogram, and it approximates the weight fraction of  $i$ th component of the sample;  $n$ , the number of sections into which the chromatogram were divided; and  $[\eta]^\text{cal}$ , the intrinsic viscosity calculated according to the GPC chromatogram of the sample),

the calculated intrinsic viscosity of  $j$ th sample and the least-square function can be formulated as a function of the MH parameters  $k$  and  $\alpha$ :

$$[\eta]_j^\text{cal} = k^{1/(1+\alpha)} \sum_{i=1}^n A_{i,j} \times 10^{(A-B \times V_{i,j}) \times \alpha / (1+\alpha)} \quad (1)$$

$$\begin{aligned} f(k, \alpha) &= \sum_{j=1}^m (1 - [\eta]_j^\text{cal} / [\eta]_j^\text{exp})^2 \\ &= \sum_{j=1}^m (1 - ([\eta]_j^\text{exp})^{-1} \times k^{1/(1+\alpha)} \\ &\quad \sum_{i=1}^n A_{i,j} \times 10^{(A-B \times V_{i,j}) \times \alpha / (1+\alpha)})^2 \quad (2) \end{aligned}$$

$j$  is the ordinal number of the  $j$ th sample;  $m$ , is the number of the polydisperse samples;  $[\eta]_j^\text{exp}$ , intrinsic viscosity of the  $j$ th sample; and  $A_{i,j}$  and  $V_{i,j}$ , area fraction or weight fraction and the retention volume of  $i$ th section of  $j$ th sample. The reciprocal of  $[\eta]_j^\text{exp}$ ,  $1/[\eta]_j^\text{exp}$  is used as the weight factor of  $j$ th sample.

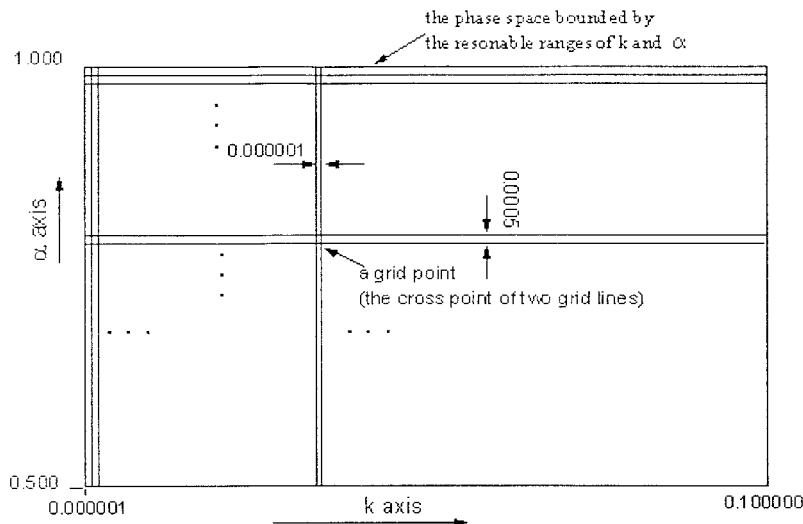
Thereby, the determination of the MH parameters is to find the  $k, \alpha$  values where the value of the least-square function  $f(k, \alpha)$  is the least. This is a problem of optimization, which can be expressed as

$$f(k, \alpha)^\text{least} = f(k^\text{real}, \alpha^\text{real})$$

$$1 \times 10^{-6} \leq k \leq 0.100000$$

$$0.500 \leq \alpha \leq 1.000 \quad (3)$$

From eq. (2), we can see that this is a nonlinear optimization problem. There are many local minimum values of the function  $f(k, \alpha)$ . If one of the local optimization algorithms, such as the Gauss-Newton method, the Marquardt<sup>9</sup> method, and some other Newton-based methods,<sup>10,11</sup> which are usually applied to the nonlinear simulating problems, are used to solve this problem, the  $k, \alpha$  values obtained will be strongly dependent on the initial values of  $k, \alpha$  one inputs to start the optimization. The  $k, \alpha$  values that we eventually get will change with the variation of the initial values. Therefore, the accuracy of the results cannot be assured. Besides, the procedures of applying



**Figure 2** Determination of the grid points according to the reasonable ranges and precision of  $k, \alpha$  values.

the nonlinear optimizations involve the differential of the function, so it is very complicated to be implemented. Although there are a few kinds of newly developed global optimization algorithms, such as the simulated annealing algorithm<sup>12</sup> and the genetic algorithm,<sup>13</sup> which have exhibited great efficiency in finding the global minimum of a function, they are futile when applied to this problem.

The grid search algorithm determines the MH parameters very accurately and conveniently according to eq. (2) following the steps described below:

1. Divide the phase space, which is defined to be the set of points bounded by the minimum and maximum values of  $k, \alpha$ , into the grid points as indicated in Figure 2. In Figure 2, the reasonable ranges of  $k$  and  $\alpha$  are 0.000001–0.1 and 0.5–1, respectively. The distance between two neighboring grid points along the direction of the  $k$  axis is 0.000001 and that along the direction of the  $\alpha$  axis is 0.0005; the precision of the values of  $k$  and  $\alpha$  are thus determined. The total number of the grid points is  $1 \times 10^8$ .
2. Calculate the values of  $f(k, \alpha)$  according to eq. (2) at each of all the grid points.
3. Compare the values of  $f(k, \alpha)$  and choose the global minimum point at which  $f(k, \alpha)$  is the global minimum [the least value of  $f(k, \alpha)$ ].
4. The  $k, \alpha$  values at the global minimum point are the values of  $k^{\text{real}}$  and  $\alpha^{\text{real}}$ .

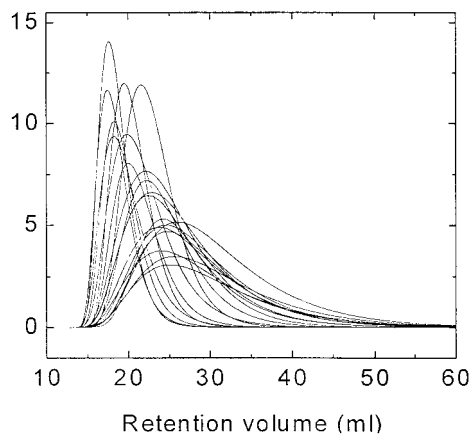
The calculation can be completed on a personal computer in no more than 1 h. Also, this calculation program can be available to all the cases when MH parameters are to be determined with this method.

Among the most completely studied polymer systems are two random polymer systems, which are PS in toluene at 25°C and PMMA in benzene at 25°C. In this article, these two polymer systems are selected to exhibit the applicability of this method through comparing the values of the MH parameters obtained by this method with those in ref. 14.

GPC chromatograms of 20 polydisperse samples of PS in toluene at 25°C are shown in Figure 3, and their intrinsic viscosities are listed in Table I. The molecular weights of the samples range from 70,000 to 800,000.

Each of the chromatograms of 20 polydisperse PS was divided into 40 sections according to the dispersed data points recorded by the GPC instrument, and the weight fraction of each section in the respective chromatogram was calculated. In eq. (2),  $A$  and  $B$  for the GPC condition of PS in toluene at 25°C were determined to be 12.48 and 0.182, respectively, by the standard PS samples.  $m$  is 20 and  $n$  is 40 and the values of  $A_{ij}, V_{ij}$  ( $i = 1, 2, \dots, 40; j = 1, 2, \dots, 20$ ) were recorded in a data file for the calculation of  $f(k, \alpha)$ .

Finally, the values of  $f(k, \alpha)$  at the global minimum point,  $f(k, \alpha)^{\text{least}} = f(k^{\text{real}}, \alpha^{\text{real}})$ , was calculated to be  $3.32 \times 10^{-4}$ , and  $k^{\text{real}}$  and  $\alpha^{\text{real}}$  were determined to be 0.01339 and 0.715, respectively. The  $k^{\text{real}}, \alpha^{\text{real}}$  values are quite close to the one of



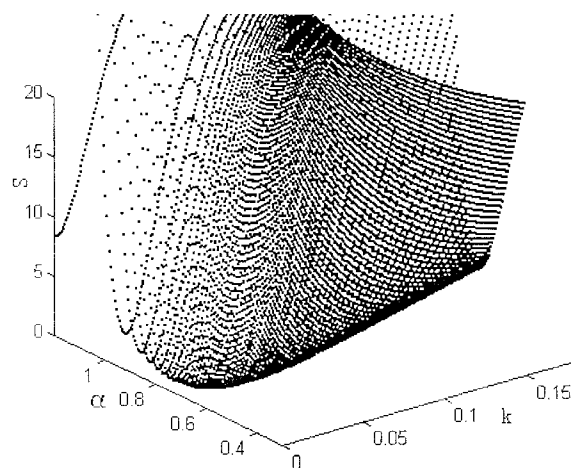
**Figure 3** GPC chromatograms of PS in toluene at 25°C.

nine pairs of  $k$  and  $\alpha$  values, which are 0.0134 and 0.71, respectively, reported in ref. 14.

The points where the values of  $f(k, \alpha)$  are less than 30 are shown in Figure 4. All the local minimum points [where the values of  $f(k, \alpha)$  are less than 1.5] are presented in Figure 5. In Figures 4 and 5, a lowest point, namely, the global minimum point, can be seen.

It is shown in Figures 4 and 5 that there are many local minimum points in the phase space, and among the local minimum points are many high barriers. Hence, it is very difficult for any other algorithm to find the global minimum point.

The MH parameters of the polymer system of PMMA in benzene at 25°C were also determined by this method. The GPC chromatograms of 11



**Figure 4** Values of objective function  $f(k, \alpha)$  for PS in the phase space,  $f(k, \alpha) \leq 30$ .

polydisperse samples of PMMA were measured, and their intrinsic viscosities are listed in Table I. The constants,  $A$  and  $B$ , for the GPC system using benzene as the elution solvent were determined to be 12.17 and 0.181, respectively, by standard PS samples. The procedure for the determination of the MH parameters of the system is similar to that of PS in toluene at 25°C. The three-dimensional graph of grid points, at which the values of  $f(k, \alpha)$  of this system are less than 30, versus  $f(k, \alpha)$ , and the graph of the local minimum points versus  $f(k, \alpha)$  are similar to those of Figures 4 and 5, respectively. The  $k^{\text{real}}$ ,  $\alpha^{\text{real}}$  values of the PMMA system determined according to the global minimum point are 0.00753, 0.755, close to one of

**Table I** Intrinsic Viscosities and the Respective Viscosity-average Molecular Weight of the Samples of PS and PMMA

Sample No.	Intrinsic Viscosity	Molecular Weight	Sample No.	Intrinsic Viscosity	Molecular Weight
PS1	42.41	74,467	PS16	85.40	198,212
PS2	135.39	377,618	PS17	57.65	114,403
PS3	59.65	120,010	PS18	137.84	387,199
PS4	201.55	658,749	PS19	56.31	110,719
PS5	235.15	817,246	PS20	50.43	94,880
PS6	194.81	628,123	PMMA1	14.71	47,003
PS7	52.07	99,222	PMMA2	25.46	102,277
PS8	82.94	190,281	PMMA3	65.16	387,831
PS9	71.10	153,404	PMMA4	77.03	491,745
PS10	46.47	84,645	PMMA5	30.49	132,110
PS11	239.43	838,155	PMMA6	18.20	63,540
PS12	100.99	250,615	PMMA7	17.76	61,369
PS13	78.18	175,174	PMMA8	14.62	46,592
PS14	156.76	463,515	PMMA9	11.14	31,672
PS15	39.85	68,264			



four pairs of the  $k, \alpha$  values of the PMMA system reported in ref. 14, which are  $k = 0.00724$ ,  $\alpha = 0.76$ .

Moreover, plot  $\alpha$  versus  $\log(k)$  at the local minimum points of these two polymer systems will yield two straight lines. In addition, there are nine pairs of  $k, \alpha$  values for PS in toluene at 25°C and four pairs of  $k, \alpha$  values for PMMA in benzene at 25°C reported in ref. 14. As is shown in Figure 6, all these  $k, \alpha$  values are, correspondingly, distributed very close to the lines.

### Using the Grid Search Method to Solve a Linear Regression Problem for the Determination of MH Parameters

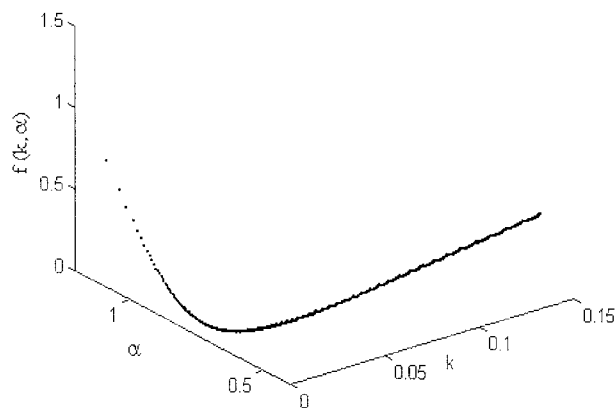
The grid search can also be used as an alternative for linear regression in the determination of the MH parameters by treating the least-square equation directly. When the molecular weights of several monodisperse samples of a polymer and their intrinsic viscosity have been measured, the least-square equation built for determining the  $k, \alpha$  values can be formulated as

$$f(k, \alpha) = \sum_{i=1}^m \{\text{Log}([\eta]_i^{\text{cal}}) - \text{Log}([\eta]_i^{\text{exp}})\}^2$$

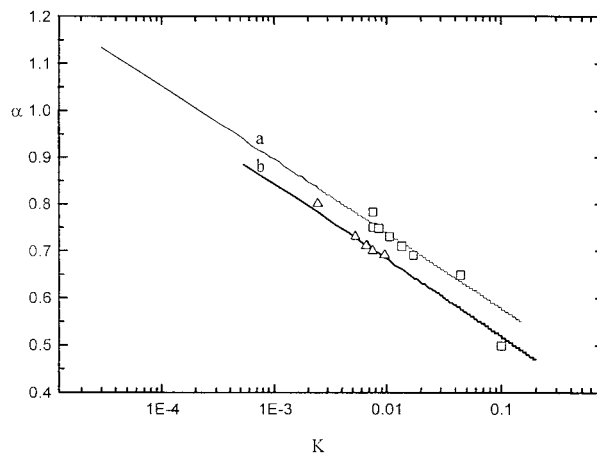
$$= \sum_{i=1}^m \{\text{Log}(k \times M_i^\alpha) - \text{Log}([\eta]_i^{\text{exp}})\}^2 \quad (4)$$

where  $M_i$  is the molecular weight of the  $i$ th sample, and  $m$ , the number of the samples. The problem of the optimization can be thus expressed as

$$f(k, \alpha)^{\text{least}} = f(k^{\text{real}}, \alpha^{\text{real}})$$



**Figure 5**  $f(k, \alpha)$ ,  $k$ , and  $\alpha$  values at local minimum points of the objective function for PS,  $f(k, \alpha) \leq 1.5$ .



**Figure 6** Comparison of  $k, \alpha$  values reported in the *Polymer Handbook*<sup>14</sup> with  $k, \alpha$  values at the local minimum points for the PS system and the PMMA system, respectively: (line a) drawn according to  $k, \alpha$  values in the minimum points of objective function  $S$  for PS; (line b) drawn according to  $k, \alpha$  values in the minimum points of objective function  $S$  for PMMA; (□) data points representing the  $k, \alpha$  values reported in the literature<sup>2</sup> for PS in toluene at 25°C; (△) data points representing the  $k, \alpha$  values reported in the literature<sup>2</sup> for PMMA in acetone at 25°C.

$$0.000001 \leq k \leq 0.100000$$

$$0.500 \leq \alpha \leq 1.000 \quad (5)$$

As an example, the data reported in the literature<sup>15</sup> were treated with the grid search. The procedures are the same as those described above. The  $k, \alpha$  values in the global minimum point are  $5.43 \times 10^{-4}$  and 0.715, respectively, that is, the same values as the results reported in the literature.

With the development of polymer science, the number of new kinds of polymers synthesized has increased continuously and rapidly. Owing to the difficulty in the fractionation of the polymer samples, the MH parameters of a very large number of the polymer systems have not been reported as yet. The method proposed here can help to determine the MH parameters of these polymers.

It is worthwhile to mention here that the MH parameters can be determined by linear regression using the data of the weight-average molecular weight or number-average molecular weight to approximate the viscosity-average molecular weight of the polydisperse polymer samples as in the literature<sup>15</sup>; in most cases, it can only be thought of as an approximate approach and may give rise to considerable errors in the MH parameters acquired.

## CONCLUSIONS

All the linear regression and the nonlinear regression methods used to determine the MH parameters can be replaced by the grid search method. First, this method can serve as an alternative for the linear regression method; the results obtained by this method are the same as those obtained by linear regression. Second, in the cases when some nonlinear regression methods have to be used, the grid search method can determine the MH parameters more easily and more accurately.

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