

# A Relatively Simple Method for Calculating Mark-Houwink Parameters Using Basic Definitions

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**ABSTRACT:** A method for calculating Mark-Houwink parameters from intrinsic viscosity, size exclusion, and number- or weight-average molecular weight data using basic definitions was presented. Polydispersity is not an issue and no calibration curve is required as long as all of the aforementioned data are available. Results for polysty-

rene, cellulose acetate, and polymethylhydrosiloxane are discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3303–3309, 2009

**Key words:** Mark-Houwink constants; polydispersity; gel permeation chromatography; viscosity; molecular weight distribution

## INTRODUCTION

Size exclusion chromatography (SEC) is a quick and convenient method for estimating the molecular weight of a polymer sample. Unfortunately, it is an indirect method, so other types of data are required to determine the absolute molecular weight distribution. Direct comparison with standards is only possible if the test sample has the same composition. If not, a “universal calibration curve” is constructed from SEC and viscometry data. The latter are usually calculated from Mark-Houwink parameters, unless the SEC instrument is equipped with a differential viscometry detector.

This article outlines a method for calculating Mark-Houwink parameters from intrinsic viscosity, SEC, and number- or weight-average molecular weight data using basic definitions that accommodate polydisperse samples. Moreover, no calibration curve is required as long as all of the aforementioned data are available. Similar methods have been published, but the calculations associated with them are rather cumbersome.<sup>1–6</sup> The calculations presented herein can easily be performed on a spreadsheet.

The SEC chromatogram of a polydisperse polymer can be very broad. Accurate determination of the average molecular weight requires that the curve be divided into narrow intervals corresponding to elution volume or time. The height of the curve for a given interval is proportional to the weight of the components which were eluted during that interval. Since elution is influenced by polymer/solvent interac-

tions, the molecular weight for each interval must be corrected as follows to account for the intrinsic viscosity of the polymer.

$$J_i = [\eta]_i M_i \quad (1)$$

$J_i$ ,  $M_i$ , and  $[\eta]_i$  refer, respectively, to the hydrodynamic volume parameter, molecular weight, and intrinsic viscosity for interval  $i$ .<sup>7</sup> The natural logarithm of  $[\eta]_i$  varies linearly with the natural logarithm of  $M_i$ .

$$\ln[\eta]_i = \ln K + \alpha \ln M_i \quad (2)$$

The Mark-Houwink constants  $K$  and  $\alpha$  are derived from the slope and intercept of eq. (2). Substitution of eq. (1) into eq. (2) produces expressions for  $[\eta]_i$  and  $M_i$  in terms of  $J_i$ .

$$[\eta]_i = K^{\frac{1}{1+\alpha}} J_i^{\frac{\alpha}{1+\alpha}} \quad (3)$$

$$M_i = \left( \frac{J_i}{K} \right)^{\frac{1}{1+\alpha}} \quad (4)$$

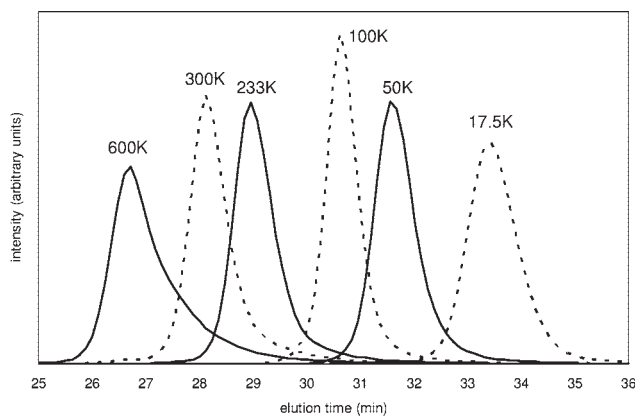
As the SEC curve represents the weight distribution for the sample, it is convenient to use the weight fraction  $w_i$  as the weighting factor for the calculation of average values.

$$\langle M_w \rangle = \sum_i w_i M_i = K^{-\frac{1}{1+\alpha}} \sum_i w_i J_i^{\frac{1}{1+\alpha}} \quad (5)$$

$$[\eta] = \sum_i w_i [\eta]_i = K^{\frac{1}{1+\alpha}} \sum_i w_i J_i^{\frac{\alpha}{1+\alpha}} = K \langle M_v \rangle^\alpha \quad (6)$$

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$\langle M_w \rangle$  and  $[\eta]$  refer, respectively, to weight-average values of molecular weight and intrinsic viscosity;  $\langle M_v \rangle$  refers to the viscosity-average molecular



**Figure 1** Size exclusion chromatograms for PS standards (Case 1). Nominal molecular weights are shown.

weight.<sup>7</sup> After some slight manipulation of its definition, the number-average molecular weight  $\langle M_n \rangle$  can also be expressed in terms of  $J_i$ .

$$\langle M_n \rangle = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{1}{\sum_i \frac{w_i}{M_i}} = K^{-\frac{1}{1+\alpha}} \left( \sum_i w_i J_i^{-\frac{1}{1+\alpha}} \right)^{-1} \quad (7)$$

The variable  $n_i$  refers to the number of moles of components which elute during interval  $i$ . According to the universal calibration principle, the plot of  $\ln J_i$  vs. elution time  $t_i$  is approximately linear for about 2 orders of magnitude for  $M$ .<sup>7</sup> Consequently, the relationship between  $J_i$  and  $t_i$  can be expressed as follows:

$$\ln J_i = m t_i + b \quad (8)$$

The parameters  $m$  and  $b$  refer, respectively, to the slope and intercept of the line. Substitution of eq. (8) into eqs. (5)–(7) allows expression of  $\langle M_n \rangle$ ,  $\langle M_w \rangle$ , and  $[\eta]$  in terms of  $t_i$ .

$$[\eta] = a_2 \sum_i w_i e^{a_1 t_i} \quad (9)$$

$$a_1 = \frac{\alpha m}{1 + \alpha} \quad (10)$$

$$a_2 = (K e^{ab})^{\frac{1}{1+\alpha}} \quad (11)$$

$$\langle M_n \rangle = \frac{a_4}{\sum_i w_i e^{a_3 t_i}} \quad (12)$$

$$\langle M_w \rangle = a_4 \sum_i w_i e^{-a_3 t_i} \quad (13)$$

$$a_3 = -\frac{m}{1 + \alpha} \quad (14)$$

$$a_4 = \left( \frac{e^b}{K} \right)^{\frac{1}{1+\alpha}} \quad (15)$$

Equations (9)–(15) are in a solvable format. According to eqs. (9), (12), and (13), plots of  $\langle M_n \rangle$  vs.  $(\sum_i w_i e^{a_3 t_i})^{-1}$ ,  $\langle M_w \rangle$  vs.  $\sum_i w_i e^{-a_3 t_i}$  and  $[\eta]$  vs.  $\sum_i w_i e^{a_1 t_i}$  are straight lines which pass through the origin. There are unique values of the constants  $a_1$  and  $a_3$  which satisfy these conditions; consequently, they may be determined by trial-and-error processes. The constants  $a_2$  and  $a_4$  are the slopes of the lines. Once  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$  have been determined,  $\alpha$ ,  $K$ ,  $m$ , and  $b$  can be calculated as follows:

$$b = \ln(a_2 a_4) \quad (16)$$

$$\alpha = -\frac{a_1}{a_3} \quad (17)$$

$$m = a_1 \left( \frac{1 + \alpha}{\alpha} \right) \quad (18)$$

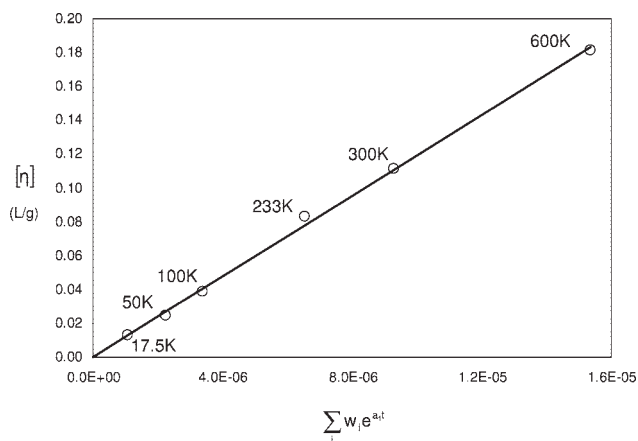
$$K = \frac{a_2}{a_4^\alpha} \quad (19)$$

The preceding set of equations will be used to calculate Mark-Houwink constants for the following two cases: (1) SEC, intrinsic viscosity, and number- or weight-average molecular weight data available for several samples; (2) a standard curve, plus intrinsic viscosity and SEC data for several samples.

**TABLE I**  
Results and Reference Values for Case 1: PS in THF Solvent

Nominal Molecular Weight <sup>a</sup>	[ $\eta$ ] (L/g)		$\langle M_n \rangle$		$\langle M_w \rangle$	
	By viscosity	Figure 2	By stoichiometry <sup>a</sup>	Figure 3	By LS <sup>a</sup>	Figure 4
600,000	0.1813	0.1830	610,000	612,000		
300,000	0.1110	0.1105	350,000	349,000		
233,000	0.0828	0.0779	220,000	215,000	254,000	253,000
100,000	0.0387	0.0404	100,000	95,400	93,050	96,500
50,000	0.0247	0.0269	50,000	54,900	53,700	53,400
17,500	0.0131	0.0129	17,500	20,400	20,400	18,400

<sup>a</sup> Waters Associates, Milford, MA; Polysciences.



**Figure 2** Plot used to determine  $a_1$  and  $a_2$  for PS standards (Case 1). Nominal molecular weights are shown.

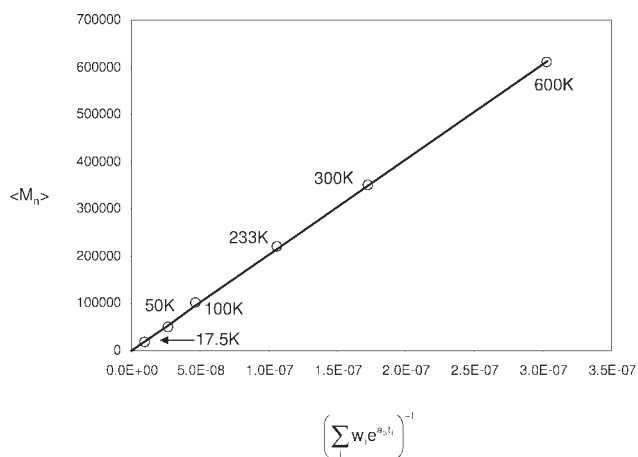
**EXPERIMENTAL**

**Polystyrene**

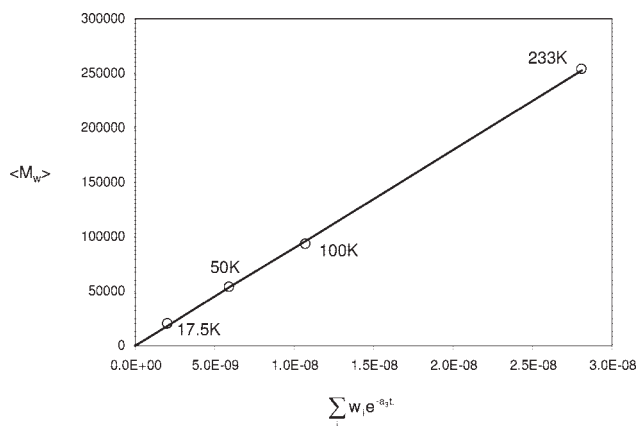
Polystyrene (PS) standards from Waters Special PS Standard Kit no. 25170 were used as received (Waters Associates, Milford, MA; Polysciences). SEC was performed at 35°C, using THF solvent on an Agilent 1100 Series HPLC equipped with Waters Styragel columns (HR2 and HR5), and a differential refractometer. The flow rate was set to 0.5 mL/min. Viscometry was performed on dilute solutions of the standards at 35°C using a Cannon size 1 Ubbelohde viscometer and THF solvent. Intrinsic viscosities were calculated from data collected below the critical concentration  $c^{**}$  at which the macromolecular coils start to contact.<sup>8</sup>

**Cellulose acetate**

Two commercial cellulose acetates (CAs) were used without further modification: Eastman product no.

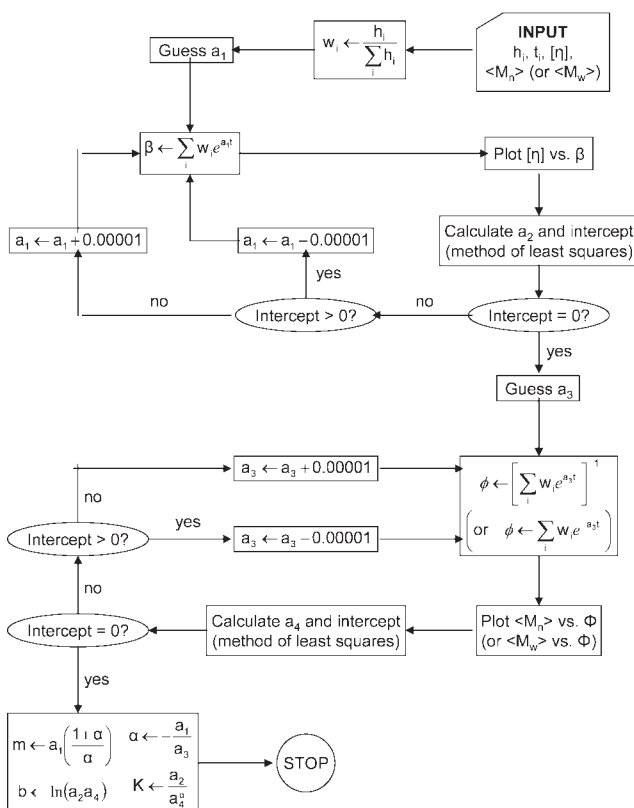


**Figure 3** Plot used to determine  $a_3$  and  $a_4$  for PS standards (Case 1 – stoichiometric data). Nominal molecular weights are shown.



**Figure 4** Plot used to determine  $a_3$  and  $a_4$  for PS standards (Case 1 – LS data). Nominal molecular weights are shown.

4650, ds ~ 2.5 (Eastman Chemical Company, Kingsport, TN) and Aldrich product no. 180955, ds ~ 2.5 (Aldrich Chemical Company, St. Louis, MO). A third CA sample was prepared by acid hydrolysis of cellulose triacetate (CTA; Eastman product CA-436-80S)<sup>9</sup>; the degree of substitution of this sample was determined to be  $2.44 \pm 0.12$  by the alkaline hydrolysis method (ASTM D 271). Three more samples were obtained by mixing the other samples. SEC was performed at 35°C, using THF solvent on an Agilent 1100 Series HPLC equipped with Waters



**Figure 5** Flow chart outlining the calculations for Case 1.

TABLE II  
Mark-Houwink Constants for PS, CA, PMHS, and Related Polymers

Polymer	Solvent	Temperature (°C)	10 <sup>3</sup> K (mL/g)	$\alpha$	Samples	$\langle M_n \rangle$ Range ( $\times 10^{-4}$ )	Methods
PS	THF	35	7.0	0.750	6	1.8–61.0	Stoichiometry, SEC, viscometry
PS	THF	35	15.5	0.686	4	1.8–23.3	LS, SEC, viscometry
Atactic PS <sup>13</sup>	THF	25	11.0	0.725	7	1–100	SEC
Atactic PS <sup>13</sup>	THF	25	14.0	0.70			LS
CA (ds ~ 2.5)	THF	35	34.4	0.713	6	2.3–4.6	SEC, viscometry
CA (ds = 2.5) <sup>13</sup>	THF	25	51.3	0.688	6	7–30	LS
PMHS	Toluene	35	10.1	0.620	9	0.14–1.4	SEC, viscometry
PDMS <sup>13</sup>	Toluene	25	13.6	0.69	13	0.26–63	VPO, LS
PDMS <sup>13</sup>	Toluene	35	12.5	0.703	8	1.7–90	LS
PDMS <sup>14</sup>	Toluene	30	21.5	0.650			

Styragel columns (HR2 and HR5), and a differential refractometer. The flow rate was set to 0.5 mL/min. Viscometry was performed on dilute solutions of the standards at 35°C using a Cannon size 1 Ubbelohde viscometer and THF solvent. Intrinsic viscosities were calculated from data collected below the critical concentration  $c^{**}$  at which the macromolecular coils start to contact.<sup>8</sup>

### Polymethylhydrosiloxane

Polymethylhydrosiloxane (PMHS) (Gelest product HMS-992) was separated into several fractions using the nonsolvent/solvent pair MeOH/CCl<sub>4</sub>.<sup>7,10,11</sup> The fractions were subsequently dried by rotary evaporation, and then characterized as soon as possible to avoid significant alcoholysis because of the presence of residual MeOH.<sup>12</sup> SEC was performed at 35°C using a Waters  $\mu$ Styragel 10-5A column and toluene solvent. The only detector for the system was a differential refractometer. Viscometry was performed on dilute solutions of the fractions at 35°C using an Ubbelohde viscometer and toluene solvent.

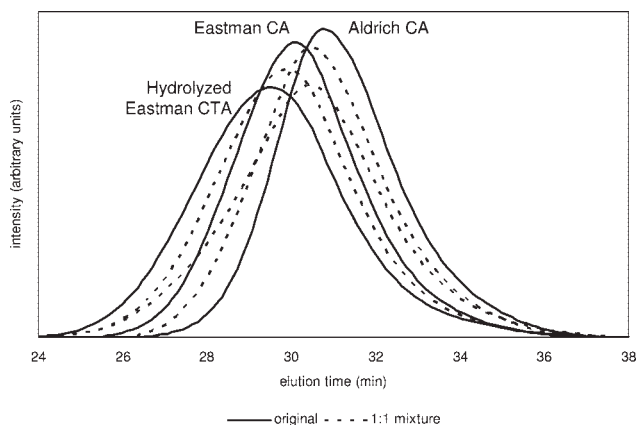


Figure 6 Size exclusion chromatograms for CA samples (Case 2).

## RESULTS AND DISCUSSION

### Case 1: SEC, intrinsic viscosity, and number- or weight-average molecular weight data available for several samples

Figure 1 shows the SEC chromatograms for various PS standards. The height of the curve for a given interval is proportional to the weight of the material represented by that interval; consequently, the curves were normalized as follows<sup>4,7</sup>:

$$w_i = \frac{h_i}{\sum_i h_i} \quad (20)$$

Table I lists intrinsic viscosity results from this study and the supplier's molecular weight data.  $\langle M_n \rangle$  had been determined by reaction stoichiometry and  $\langle M_w \rangle$  by light scattering (LS) (Water Associates, Milford, MA; Polysciences).

Figure 2 shows a plot of  $[\eta]$  vs.  $\sum_i w_i e^{a_1 t_i}$  that was initially constructed using a guess for the constant  $a_1$ . The constant  $a_1$  was varied until the intercept

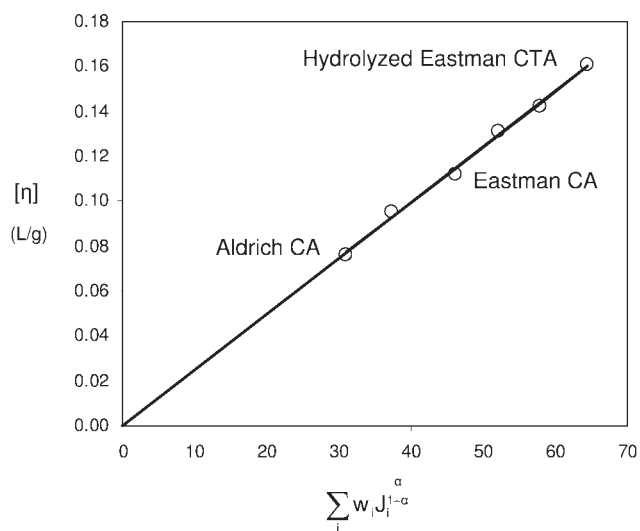


Figure 7 Plot used to determine  $\alpha$  and  $K$  for CA samples (Case 2).

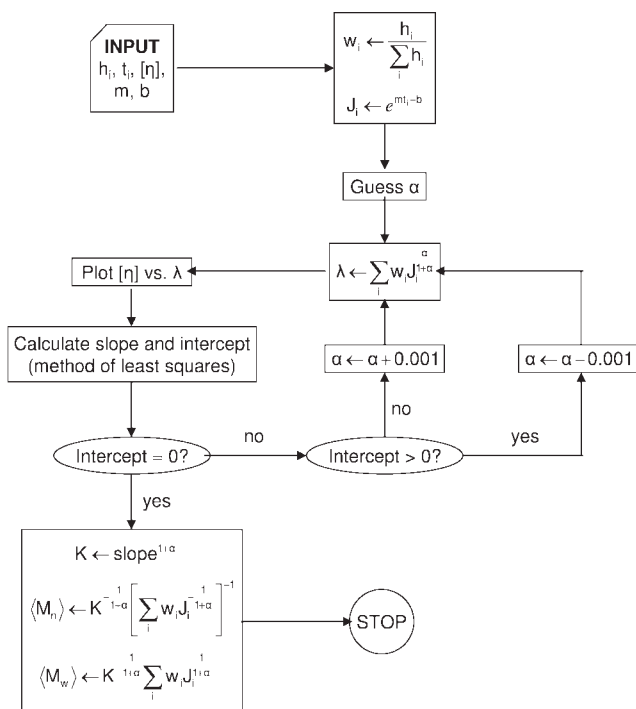
**TABLE III**  
Results for Case 2: CA

Sample ID	[η] (L/g)		$\langle M_n \rangle$	$\langle M_w \rangle$	Polydispersity
	Data	Regression			
Aldrich CA	0.0762	0.0770	22,800	53,100	2.33
1 : 1 Aldrich CA/Eastman CA	0.0952	0.0928	27,500	70,700	2.57
Eastman CA	0.1121	0.1146	37,700	96,300	2.55
1 : 1 Aldrich CA/hydrolyzed Eastman CTA	0.1313	0.1296	28,300	153,000	5.41
1 : 1 Eastman CA/hydrolyzed Eastman CTA	0.1420	0.1436	42,600	152,000	3.57
Hydrolyzed Eastman CTA	0.1608	0.1599	45,800	164,000	3.58

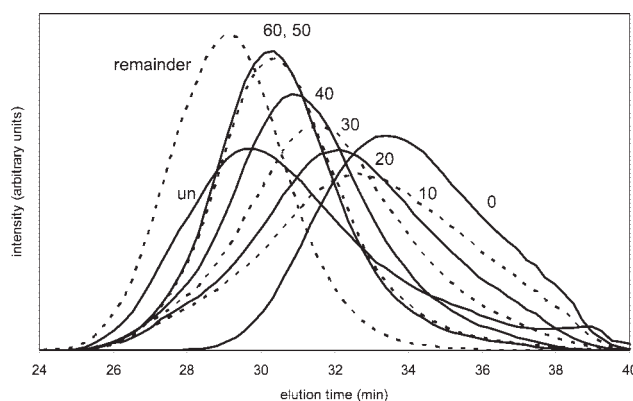
passed through the origin of the plot. The slope of this line is  $a_2$ , as stated by eq. (9). Similarly, Figures 3 and 4 shows the plots of  $\langle M_n \rangle$  vs.  $(\sum_i w_i e^{a_3 t_i})^{-1}$  and  $\langle M_w \rangle$  vs.  $\sum_i w_i e^{-a_3 t_i}$  that were initially constructed using a guess for the constant  $a_3$ . As before,  $a_3$  was varied until the intercept passed through the origin. The slopes of these lines are represented by  $a_4$ , as stated by eqs. (12) and (13). At this point,  $a_1, a_2, a_3,$  and  $a_4$  are known, so the Mark-Houwink constants  $K$  and  $\alpha$  can be calculated from eqs. (17) and (19). If desired,  $m$  and  $b$  can be calculated from eqs. (16) and (18); these values can be used to construct a "universal calibration curve" from eq. (8). Detailed calculations are outlined in Figure 5.

As shown in Table I, the calculated  $\langle M_n \rangle$  and  $\langle M_w \rangle$  values are very close to those reported by the supplier. Figures 3 and 4 show that the molecular

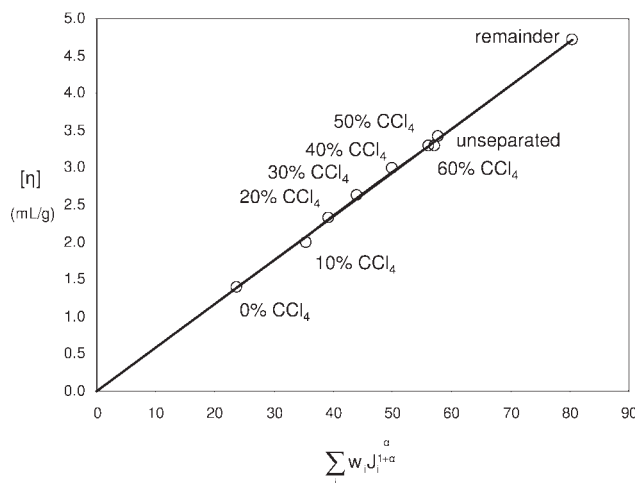
weight values are consistent with theory and with each other. The Mark-Houwink constants are listed in Table II, along with some representative values from literature (shaded rows). The small differences in the tabulated values may reflect the influence of temperature, molecular weight range, and method of data collection.



**Figure 8** Flow chart outlining the calculations for Case 2.



**Figure 9** Size exclusion chromatograms for PMHS fractions (Case 2), labeled with percentage of  $\text{CCl}_4$  used to form the second liquid layer.



**Figure 10** Plot used to determine  $\alpha$  and  $K$  for PMHS fractions (Case 2), labeled with percentage of  $\text{CCl}_4$  used to form the second liquid layer.

TABLE IV  
Results for Case 2: PMHS

Fraction	[ $\eta$ ] (L/g)		$\langle M_n \rangle$	$\langle M_w \rangle$	Polydispersity
	Data	Regression			
0% CCl <sub>4</sub>	0.00140	0.00139	1400	3200	2.3
10% CCl <sub>4</sub>	0.00200	0.00208	1800	6900	3.8
20% CCl <sub>4</sub>	0.00233	0.00231	2500	7800	3.1
30% CCl <sub>4</sub>	0.00263	0.00259	3200	9100	2.8
40% CCl <sub>4</sub>	0.00299	0.00294	4600	10,800	2.3
50% CCl <sub>4</sub>	0.00329	0.00329	6100	12,600	2.1
60% CCl <sub>4</sub>	0.00329	0.00336	6600	12,900	2.0
Remainder	0.00472	0.00472	13,500	21,900	1.6
Unseparated	0.00341	0.00339	3000	14,100	4.7

### Case 2: A standard curve, plus SEC and intrinsic viscosity data for several samples

Figure 6 shows the SEC chromatograms of several polydisperse CA samples. As in Case 1, the curves were normalized using eq. (20) to determine the  $w_i$  values. Because, neither number- nor weight-average molecular weight was known for any of these samples,  $m$  and  $b$  values were calculated from the PS data of Figures 2 and 3.  $J_i$  values were subsequently calculated using eq. (8). The Mark-Houwink constants for CA were determined from a plot of [ $\eta$ ] vs.  $\sum_i w_i J_i^{1/\alpha}$  which was initially constructed using a guess for  $\alpha$ ; this plot is shown in Figure 7. The constant  $\alpha$  varied until the intercept passed through the origin of the plot. The slope of this line is  $K^{1/\alpha}$ , as stated by eq. (6). At this point, both  $\alpha$  and  $K$  are known, so  $\langle M_n \rangle$  and  $\langle M_w \rangle$  can be calculated using eqs. (5) and (7); these values are listed in Table III. Detailed calculations are outlined in Figure 8.

Table III lists viscometry data, calculated values of  $\langle M_n \rangle$ ,  $\langle M_w \rangle$ , and polydispersity; the latter show that the fractions are very broad. The calculated values of  $K$  and  $\alpha$  are listed in Table II. These values are fairly close to the reference values of  $K$  and  $\alpha$ , calculated from data for monodisperse samples; the differences may reflect the influence of temperature, molecular weight range, and method of data collection.

Figure 9 shows the SEC chromatograms of a commercial PMHS which was separated into several polydisperse fractions using the solvent/nonsolvent pair MeOH/CCl<sub>4</sub>.<sup>7,10,11</sup> Figure 10 shows the corresponding [ $\eta$ ] vs.  $\sum_i w_i J_i^{1/\alpha}$  plot. Calculations were similar to those described for CA. The results are listed in Table IV. The designations "0% CCl<sub>4</sub>," "10% CCl<sub>4</sub>," etc., refer to the proportions of solvent/nonsolvent used to form a second liquid layer at particular stages in the separation process. The results show that the original polymer was systematically separated into a series of polymers, with narrower distributions in the range  $1400 \leq \langle M_n \rangle \leq$

13,500. According to the manufacturer's estimate,  $\langle M_n \rangle$  for the original polymer is approximately 2000, which is fairly close to the value 3000 obtained by this study. Mark-Houwink constants are listed in Table II. Literature values for PDMS (shaded rows) have been included for comparison, because no literature values for PMHS were found. The PMHS and PDMS values are very similar; the slight differences may reflect the influence of temperature, molecular weight range, method of collection, and in this case, structure.

### SUMMARY

Mark-Houwink parameters were calculated from SEC, intrinsic viscosity, and number- or weight average molecular weight data for several molecular weight series of polymers. No external calibration was necessary, when all of the aforementioned data were available. In fact, "universal calibration curves" could also be constructed from the same data. The method described herein relies exclusively on basic definitions that accommodate polymer distributions of any breadth and shape. Consequently, any molecular weight series of a given polymer can potentially be used as molecular weight standards. This represents a significant cost saving because monodisperse standards are often expensive to produce.

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