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## A Method for Determining Molecular Weights of Block Copolymers by Gel Permeation Chromatography

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A theory is given for determining the molecular weights of block copolymers from the experimental elution volume in GPC. Interaction effect between a sample of block copolymer and a column packing material as well as the size effect are separately considered for the first time applying the partial exclusion mechanism proposed by Dawkins. The molecular weight determination shows 6% standard-deviation from the molecular weights measured by an osmometric method for eight block copolymers, which is much more improved result than other methods, *e.g.*, the universal plot method (13 %) and the Runyon's method (12 %). The reason which explains the better result is that our theory takes into account the interaction effect correctly.

### Introduction

Gel permeation chromatography (GPC) is one of the most useful tools for characterizing molecular weight distributions of polymeric substances. One of the major separation

mechanisms of GPC is a size exclusion, but the other mechanisms should be considered to explain the proper elution behavior of polymer samples. Particularly, for copolymers which have heterocomponents in a single molecule, such as block and graft copolymers, the situation is more complicated.

In spite of this complexity, efforts to obtain molecular weights of block copolymers by GPC were made by many authors,<sup>1-4</sup> because of its simplicity and its easy availability. Benoit and coworkers<sup>1</sup> proposed the "universal plot method," Runyon and coworkers<sup>2</sup> proposed a weighted-average interpolation method. Their methods both use two kinds of standard homopolymers which constitute the block copolymer. But their methods are lack of the consideration of the elution mechanism of the block copolymers, especially, the interaction effect between the block copolymer and the column packing material in GPC was neglected. For homopolymer cases, Dawkins<sup>5,6</sup> considered the interaction using Eq. (1)

$$V_e = V_0 + k_d k_p V_i \quad (1)$$

where,  $V_e$  is the elution volume,  $V_0$  and  $V_i$  are the void volume (mobile phase volume) and the solvent volume in the pore of the packing material (stationary phase volume), respectively;  $k_d$  is the distribution coefficient for size, and  $k_p$  is that for interaction between the sample and the packing material. If  $k_p = 1$ , there is no interaction, and the separation mechanism is completely a size exclusion. In the case of  $k_p \neq 1$ , Eq. (1) tells the so-called partial exclusion mechanism, *i.e.*, it considers the interaction effect as well as the size effect.

In this paper, we extended the chromatographic equation, Eq. (1), to block copolymers, and introduced the idea that the interaction between a component polymer in a block copolymer and the packing material in a GPC is different from the interaction of the other component polymer. For simplicity, we incorporated the idea of the random phase approximation<sup>7-10</sup> for the morphology of a block copolymer in a dilute solution. Using this model we developed a theory for determining the molecular weights of block copolymers  $M_{bl}$  by using GPC. Our results of  $M_{bl}$  obtained for several block copolymers were compared with other results obtained by using different assumptions from ours. Our results were better than others'.

### Theoretical

A given block copolymer which has composition  $\omega$  for one component, has its own size in solution. In a dilute solution, this size is the hydrodynamic volume,  $V_h$ . Consider the two component homopolymers of A and B which have the same size as the block copolymer in the same solvent. Then, these three polymers have the same  $k_d$  which appears in Eq. (1). But the interactions of the two homopolymers with a packing material (*i.e.*, the  $k_p$ 's) are different, and they have different elution volumes in the GPC chromatogram according to Eq. (1). The interaction of the block copolymer with the packing material will be in between the interactions of the two homopolymers. Assuming that the interaction is linearly dependent on  $\omega$ , we may write Eq. (2),

$$k_{pbl} = \omega k_{pA} + (1-\omega) k_{pB} \quad (\text{at a given } k_d) \quad (2)$$

where,  $k_{pbl}$ ,  $k_{pA}$  and  $k_{pB}$  are the  $k_p$ 's of the block copolymer, A and B component homopolymers, respectively,  $\omega$  is the volume fraction of component A of the block copolymer.

From Eqs. (1) and (2), we obtain

$$\begin{aligned} V_{ebi} &= V_0 + k_d [\omega k_{pA} + (1-\omega) k_{pB}] V_i \\ &= \omega (V_0 + k_d k_{pA} V_i) + (1-\omega) (V_0 + k_d k_{pB} V_i) \\ &= \omega V_{eA} + (1-\omega) V_{eB} \quad (\text{at a given } k_d) \quad (3) \end{aligned}$$

where,  $V_{ebi}$ ,  $V_{eA}$  and  $V_{eB}$  are the elution volumes of the block copolymer, the homopolymers of A and B, respectively,  $V_0$  and  $V_i$  are constants for a column. Equation (3) indicates that  $V_{ebi}$  is in between  $V_{eA}$  and  $V_{eB}$ .

We can measure  $V_{ebi}$  for a block copolymer by a GPC. In order to determine the molecular weight of the block copolymer, we need to know the values of  $V_{eA}$  and  $V_{eB}$  of the homopolymers having the same hydrodynamic volume  $V_h$  as the block copolymer. For this purpose, we make two curves, a plot of  $\log V_h$  vs.  $V_e$  for each standard homopolymer, where the  $V_h$  value is calculable by using experimental data obtained at given  $V_e$  (see the Calibration Curve part). The plots for the two homopolymers yield usually two lines over a given range of  $V_e$ . Figure 1a is a schematic representation of the plots for the standard polymers A and B. The dotted line in between the A and B lines in Figure 1a is the locus of such a point  $f_i$ , which divides the chord  $a_i b_i$  passing through point  $f_i$  in parallel to the  $V_e$  axis in the ratio  $(1-\omega)/\omega$ , where the length of  $a_i f_i$  is  $(1-\omega)l$  whereas the length of  $f_i b_i$  is  $\omega l$ ,  $l$  being the length of the chord. That is the dotted line represents the curve of  $\log V_h$  vs.  $V_e$  for block copolymers of composition of  $\omega$  since every point on the curve satisfies Eq. (3), and represents the elution volume  $V_{ebi}$  and the hydrodynamic volume  $V_{hbi}$  of the block copolymer.

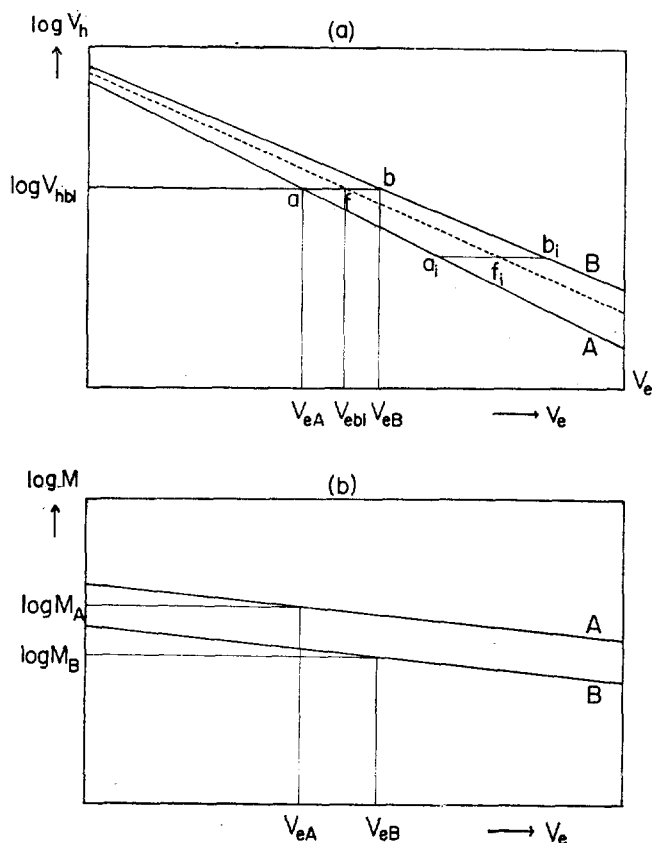
At point  $V_{ebi}$  on the  $V_e$  axis, a line parallel to the  $\log V_h$  axis is drawn which crosses the dotted curve at  $f$ . Through the latter a chord  $ab$  parallel to the  $V_e$  axis is drawn. The  $V_e$  values corresponding to points a and b are  $V_{eA}$  and  $V_{eB}$ , respectively. The  $V_{eA}$  and  $V_{eB}$  are the values at which the standard homopolymers have the same values of  $V_h$  with the block copolymer as shown in Figure 1a.

In Figure 1b, the plots of  $\log M$  vs.  $V_e$  are schematically shown where  $M$  is the molecular weight of a homopolymer measured by osmometry. Lines A and B in Figure 1b are for the homopolymers of A and B, respectively. The two lines are parallel for the first approximation, which is true experimentally. By using the chromatographic equation,  $V_e = a' \log M + b'$  (where  $a'$  and  $b'$  are constants for a polymer sample with a given column), one obtains from Eq. (3),

$$\log M_{bl} = \omega \log M_A + (1-\omega) \log M_B \quad (4)$$

where  $M_{bl}$ ,  $M_A$  and  $M_B$  are the molecular weights of the block copolymer, A and B component homopolymers, respectively. By using Figure 1b, one can obtain the molecular weights  $M_A$  and  $M_B$  corresponding to the above-mentioned elution volumes  $V_{eA}$  and  $V_{eB}$ , respectively (see Figure 1b). Then, the molecular weight  $M_{bl}$  of the block copolymer is calculated from Eq. (4).

Equation (4) is similar to Runyon *et al.*'s equation,<sup>2</sup> but the physical meaning is quite different. In our theory, the polymers having molecular weights  $M_{bl}$ ,  $M_A$  and  $M_B$  in Eq. (4) have the same hydrodynamic volume  $V_h$  (*i.e.*, the same



**Figure 1.** a. Schematic representation of  $\log V_h$  vs.  $V_e$  plot. The dotted line between the two lines for homopolymers A and B is for the block copolymers of composition  $\omega$ . b. Schematic representation of  $\log M$  vs.  $V_e$  plot. The values of  $\log M_A$  and  $\log M_B$  corresponding to  $V_{eA}$  and  $V_{eB}$ , respectively, are obtained from the figure.

$k_d$ ). On the other hand, the above mentioned polymers have the same elution volume  $V_e$  in Runyon *et al.*'s equation.

### Calibration Curves

We applied our theory to the data of Ho-Duc and Prud'homme.<sup>11</sup> Table 1 shows the experimental data<sup>11</sup> of polystyrene (PS), polyisoprene (PI) standard homopolymers and block copolymers (PS-PI, PS-PI-PS). We have drawn two different calibration curves as shown in Figures 2 and 3, *i.e.*, the curves of  $\log V_h$  vs.  $V_e$  and  $\log M$  vs.  $V_e$  for the two standard homopolymers. Here the data in Table 1 were utilized, and the hydrodynamic volume  $V_h$  was calculated from Eq. (5),

$$V_h = \frac{40M[\eta]10^{24}}{N_a} \quad (5)$$

which was derived from the Einstein equation  $[\eta] = \eta_0(1 + 2.5\phi)$ ,  $N_a$  being the Avogadro number. In Eq. (5),  $[\eta]$  is expressed in units of  $dl \cdot g^{-1}$  and  $V_h$  in  $(\text{\AA})^3$ . Figure 2 shows the  $\log V_h$  vs.  $V_e$  plots for PS and PI. Two lines are drawn for the two standard polymers using the linear-least-square method. The point of the highest  $V_h$  of the standard PS samples deviates so much that we dropped it from the least square. The point does not fall into our calibration range, and by shortening the range of calibration the theory is applicable with more precision. (Many authors reported an S

**TABLE 1: Molecular Weight, Intrinsic Viscosity and Elution Volume at the GPC Peak Maximum**

Sample	$\omega^a$	$M_n \times 10^{-5b}$	$[\eta]_{35}^c$ (dl/g)	$V_e$ (ml) <sup>c</sup>
PS	1.00	0.49	0.278	129.7
		0.96	0.452	23.1
		1.64	0.663	118.1
		3.92	1.24	105.3
		7.73	2.02	95.6
		17.8	3.68	87.5
PI	0	1.49	1.22	114.0
		2.26	1.68	108.1
		3.19	2.18	103.5
PS-PI	0.38	0.95	0.654	119.8
	0.40	2.21	1.19	109.1
	0.38	8.8	3.60	92.5
	0.21	0.581	0.512	126.3
	0.20	5.3	3.20	97.5
PS-PI-PS	0.50	1.5r	0.826	114.0
	0.49	5.1	2.26	97.9
	0.32	1.96	1.23	111.6

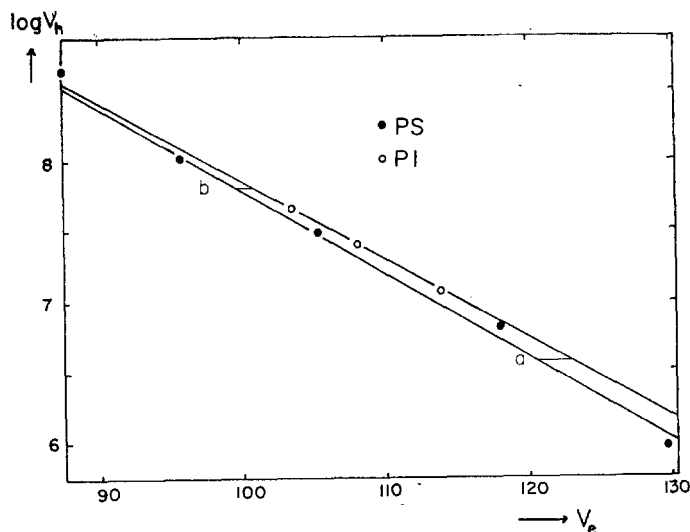
<sup>a</sup> Volume fraction of PS recalculated from Ho-Duc's original data<sup>11</sup> using the densities 1.05 and 0.913 for PS and PI, respectively; <sup>b</sup> Measured by osmometry; <sup>c</sup> Elution volume at the peak maximum of the GPC.

shaped curve deviating from the linearity over the high and low  $V_h$  regions in the  $\log V_h$  vs.  $V_e$  plot.)<sup>12,13</sup>

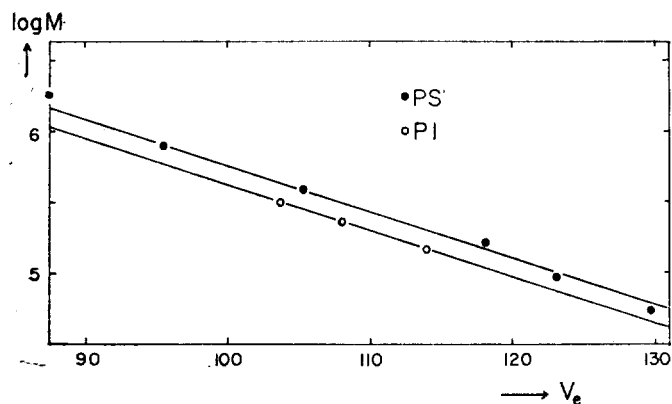
We can see from Figure 2 a finite elution-volume difference between PI and PS at a given hydrodynamic volume. PI interacts more strongly than PS with the silica beads (Porasil) which was used in this experiment, thus PI retards the elution. This explains the fact that  $V_{epi} > V_{eps}$  at a given  $V_h$  in Figure 2.

Another calibration curve, the plot of  $\log M$  vs.  $V_e$  is shown in Figure 3. Two standard curves are nearly parallel like in Tung's treatment.<sup>14</sup>

The two lines PS and PI in Figure 2 correspond, respectively, to the two lines A and B in the schematic drawing Figure 1a, and the lines PS and PI in Figure 3 correspond to the A and B lines in Figure 1b, respectively. The calibration



**Figure 2.** The  $\log V_h$  vs.  $V_e$  plot for the PS and PI standards.  $V_h$  in  $(\text{\AA})^3$  and  $V_e$  in ml units. The straight lines are drawn by a linear least square method.



**Figure 3.** The  $\log M$  vs.  $V_e$  plot for the PS and PI standards.  $V_e$  in ml units. The straight lines are drawn by a linear least square method.

curves in Figures 2 and 3 are used to obtain the molecular weights of block copolymers  $M_{bl}$  by a GPC according to the principle mentioned in the theoretical part.

### Results

For each block copolymer, the hydrodynamic volumes calculated by various methods are shown in Table 2. It is advisable here to make some remarks on the universal plot method.<sup>1</sup> It uses the relation,  $M_{bl}[\eta]_{bl} = M_{ps}[\eta]_{ps}$ , if  $V_{ebi} = V_{eps}$ , polystyrene (abbreviated as ps or PS) being taken as a standard material. If polyisoprene (pi or PI) is taken as a standard polymer, the relation is written as  $M_{bl}[\eta]_{bl} = M_{pi}[\eta]_{pi}$ . One may note that if the relation for the universal plot method holds, then the relation  $V_{hbl} = V_{hps}$  follows from Eq. (5). By substituting this  $V_{hbl}$  to Eq. (5), we can calculate back  $M_{bl}$ . This is the essential point for determining the molecular weight  $M_{bl}$  by the universal plot method. By a similar method, but taking PI as a standard polymer, we can also calculate  $M_{bl}$  by the universal plot method.

The  $V_{hps}$  and  $V_{hpi}$  in Table 2 are the hydrodynamic volumes calculated by the universal plot method taking PS and PI as a standard material, respectively, where the experimental data in Table 1 were utilized. The  $V_{hc}$  in Table 2 is the hydrodynamic volume calculated from our theory using elution volumes of block copolymers  $V_{ebi}$  at the GPC peak maximum (see Table 1). Here  $V_{hc}$  corresponds to the hydrodynamic volume of the block copolymer  $V_{hbl}$  at point f in Figure 1a. The  $V_{hexp}$  is the quantity calculated from the experimental data in Table 1 of a block copolymer by using Eq. (5). Thus the  $V_{hexp}$  has no concern with GPC experiments. The intrinsic viscosity  $[\eta]$  and the molecular weight  $\bar{M}_n$  which are used in the calculation of  $V_{hexp}$ , are averaged values over the molecular weight distribution. On the other hand, the quantities of  $V_{hps}$ ,  $V_{hpi}$  and  $V_{hc}$  are not the average quantities over molecular weights, but the quantities which are related to the GPC peak maximum.

The molecular weights of a block copolymer  $M_{bl}$  in the fourth and fifth columns in Table 3 are calculated from Eq. (5) by using  $V_{hps}$  and  $V_{hpi}$  in Table 2, respectively. The  $M_{bl}$  in the last column is the molecular weight calculated from the data in Table 1 by the authors by using Runyon *et al.*'s

**TABLE 2: Hydrodynamic Volumes of the Block Copolymers Calculated by Various Methods**

Sample	$\omega^a$	$\log V_{hps}^b$	$\log V_{hpi}^c$	$\log V_{hc}^d$	$\log V_{hexp}^e$
PS-PI	0.38	6.6r	6.67	6.71	6.62
	0.40	7.7	7.35	7.32	7.24
	0.38	8.25	8.26	8.26	8.32
	0.21	6.25	6.40	6.37	6.30
	0.20	7.96	7.99	7.98	8.05
PS-PI-PS	0.50	6.98	7.08	7.03	6.93
	0.49	7.93	7.97	7.95	7.88
	0.32	7.12	7.21	7.18	7.20

<sup>a</sup> Volume fraction PS recalculated from Ho-Duc's original data<sup>11</sup> using the density 1.05 for PS and 0.913 for PI; <sup>b</sup> Obtained from the universal plot method (PS standard); <sup>c</sup> Obtained from the universal plot method (PI standard); <sup>d</sup> Obtained from our method. <sup>e</sup> Calculated from Eq. (5) by using the experimental data<sup>11</sup> of block copolymers shown in Table 1.

method.<sup>2</sup> The  $M_{bl}$  in the sixth column is the molecular weight calculated by our method by using the data in Table 1. In Table 3, the ratios of  $M_{bl}/\bar{M}_n$  are shown where  $\bar{M}_n$  is the number-averaged molecular weight determined by an osmometry. The standard-deviations from unity  $\sigma$  are also shown in Table 3. Table 3 shows that our method for determining  $M_{bl}$  is far better than the other methods (see Table 3). The better results of our method indicate that the interaction plays an important role in GPC.

In Table 3, the  $M_{bl}$  in the seventh column is obtained by the following procedure: (i) the hydrodynamic volume of a block copolymer  $V_{hexp}$  shown in Table 2 is utilized. (ii) using this hydrodynamic volume  $V_{hexp}$ , we carried out exactly the same procedure as that described in the theoretical part to find the molecular weight of the block copolymer  $M_{bl}$ . According to Table 3, the standard deviation of  $M_{bl}/\bar{M}_n$ , where  $M_{bl}$  were obtained by the abovementioned procedure, is  $\sigma = 0.03$ . The superb result is due to the fact that, in process (i), we used the  $V_{hexp}$  calculated from Eq. (5) by using the molecular weight  $\bar{M}_n$  obtained by osmometry. But the good result of  $\sigma = 0.03$  shows in one side that our method for determining  $M_{bl}$  is correct.

### Discussion

(1) *Separation of the Size and Interaction Effects.* We have tried to separate the interaction effect from the size effect by considering Eq. (1) at a constant  $k_d$  which determines the size effect. Then, the elution volumes for polymers  $V_e$  are determined only by the interaction parameters  $k_p$  according to Eq. (1). We consider segments a and b in between the PS and PI lines as depicted in Figure 2. Segment a is equal to  $(\Delta V_e)_a$ , the difference in the  $V_e$ 's of PS and PI, whereas segment b equals  $(\Delta V_e)_b$ . One notes that the  $(\Delta V_e)_a$  is due to the difference in the  $k_p$ 's of PS and PI of small molecules (*i.e.*, small  $V_h$ ) in accordance of Eq. (1) whereas  $(\Delta V_e)_b$  is due to the  $k_p$  difference for larger molecules (*i.e.* larger  $V_h$ ). One also notes that  $(\Delta V_e)_a > (\Delta V_e)_b$ , this means that the interaction between PI and the packing material is larger than that between PS and the packing material, this effect

**TABLE 3: The Ratios of Molecular Weights of the Block Copolymers Calculated by Various Methods to the Osmometric Molecular Weights**

Sample	$\omega^a$	$\bar{M}_n^b \times 10^{-5}$	$M_{bl}^c/\bar{M}_n$	$M_{bl}^d/\bar{M}_n$	$M_{bl}^e/\bar{M}_n$	$M_{bl}^f/\bar{M}_n$	$M_{bl}^g/\bar{M}_n$
PS-PI	0.38	0.95	1.06	1.40	0.91	1.03	1.16
	0.40	2.21	1.07	1.21	1.05	0.99	1.11
	0.38	8.8	0.85	0.87	0.94	0.99	0.94
	0.21	0.581	0.90	1.27	1.01	1.01	1.11
	0.20	5.3	0.81	1.07	1.01	1.06	1.02
PS-PI-PS	0.50	1.54	1.13	1.42	1.05	1.01	1.18
	0.49	5.1	1.12	1.11	1.11	1.00	1.16
	0.32	1.96	0.83	1.02	0.95	1.02	1.02
			0.13 <sup>h</sup>	0.25 <sup>h</sup>	0.06 <sup>h</sup>	0.03 <sup>h</sup>	0.12 <sup>h</sup>

<sup>a</sup> Volume fraction of PS recalculated from the original data<sup>11</sup> using the density 1.05 for PS and 0.93 for PI; <sup>b</sup> Obtained by osmometry; <sup>c</sup> Obtained by the universal plot method (PS standard); <sup>d</sup> Obtained by the universal plot method (PI standard); <sup>e</sup> Obtained by our method; <sup>f</sup> Obtained by our method, but the  $V_h$  was obtained from Eq. (5) by using experimental data in Table 1; <sup>g</sup> Obtained by Runyon et al.'s method<sup>2</sup>; <sup>h</sup> Standard-deviation from unity $\sigma$ .

being pronounced when the size of the molecule is small. This fact indicates that interaction effect is more pronounced in small-size block copolymers. A similar results were reported Dawkins<sup>5</sup> for homopolymers from the calculations of  $k_p$ 's for various sizes.

(2) *Errors in the Determination of Molecular Weights.* In our method of molecular weight determination, there are two sources of errors which come from experiment. There is a finite scattering in the plots of  $\log V_h$  vs.  $V_e$  for homopolymers because of the experimental errors in  $[\eta]$  and  $\bar{M}_n$  which enter in the calculation of hydrodynamic volumes  $V_h$  [Eq. (5)]. Because of the uncertainty in the plots of  $\log V_h$  vs.  $V_e$ , from which the  $M_{bl}$  determination follows, some errors are introduced in the latter (see the Theoretical part). Another source of errors is the molecular weight distribution of block copolymers in a GPC chromatogram. The molecular weight calculated from our theory is not an averaged value but a value at the GPC peak maximum of a block copolymer, since we took  $V_{ehl}$  at the GPC peak maximum. The fluctuation of hydrodynamic volumes as shown in Figure 2 reflects the source of random errors which will appear in the determination of  $M_{bl}$ .

Let us consider the molecular weight distribution effect more in detail. If the molecular weight distribution is very sharp, the ratio  $M_{bl}/\bar{M}_n$  approaches unity since the polydispersity ( $\bar{M}_w/\bar{M}_n$ ) is unity. According to the Ho-Duc and Prud'homme,<sup>11</sup> the samples of block copolymers have the polydispersity smaller than 1.1. In Table 3, which was obtained from the data of Ho-Duc and Prud'homme, the results in the sixth column were obtained by our method from the  $V_e$  value at the GPC peak maximum. It shows that  $\sigma=0.06$ , i.e., the standard deviation from  $M_{bl}/\bar{M}_n=1$  is less than 10% in a good agreement with the polydispersity data of Ho-Duc and Prud'homme.

Concerned with the standard deviation  $\sigma$  listed in Table 3, it may be necessary to add some remarks on the  $\sigma$ 's of the other methods. One notes from Table 3 that the universal plot method shows a large uncertainty depending on the choice of a standard material. The standard deviation  $\sigma$  is 0.13 and 0.25 for the PS and PI standard, respectively. We can see the maximum 42% of error in the PI standard. The

result of Runyon et al.'s method of calculation gives  $\sigma=0.12$ , which is still larger than 10%. Tung<sup>14</sup> also reported the standard deviations of the universal plot method (PS standard) and of the Runyon et al.'s method by using the experimental data of Ho-Duc and Prud'homme;<sup>11</sup> according to him,  $\sigma=0.26$  for the universal plot method (PS standard), and  $\sigma=0.14$  for Runyon et al.'s method. Tung's  $\sigma=0.26$  for the universal plot method is larger than our value ( $\sigma=0.13$ ), this may be due to the difference in handling the experimental data.

(3) *On the Random Phase Approximation.* There were many discussions on the morphology of a block copolymer in a dilute solution for a recent few years. One of the arguments is that unlike segments in a block copolymer rarely overlap.<sup>15,16</sup> The other is that they overlap to a great extent and form a random phase morphology.<sup>7-10</sup> In the former case, it is hardly imagined that the shape of the block copolymer is a spherical form. Recently, various experimental methods, such as small angle X-ray scattering,<sup>9</sup> light scattering,<sup>7,10</sup> neutron scattering,<sup>8</sup> etc., were applied to study the morphology of block copolymers. According to these investigations, the radius of gyration of a component polymer is much larger than that of the homopolymer of the same molecular weight, which is a strong evidence of random phase morphology of a block copolymer. That is, in a block copolymer (the component polymer A enlarges its size to admit the segments of polymer B, vice versa, thus making the phases of segments of A and B intermingle randomly. The shape of the block copolymer with such random phase will be a sphere-like form. Thus, we can apply Eq. (5) to block copolymers, since Eq. (5) was derived from Einstein's viscosity equation for hard spheres. We also note that Eq. (2), which expresses  $k_p$  for a block copolymer by a linear combination of  $k_p$ 's of component polymers A and B, is applicable only when the block copolymer has a random phase morphology, i.e., if the phases of polymers A and B are separated in a block copolymer Eq. (2) is not applicable.

By applying our theory to diblock and triblock copolymers we obtained satisfactory results, i.e., Eqs. (2) to (4) are well applied to both copolymers. We could not notice any significant difference in the results of the diblock and triblock

copolymers (see Table 3). This fact also justify the random phase approximation for block copolymers.

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## Calculation of Thermodynamic Properties Through the Use of two New Analytical Expressions for the Partition Function of the Morse Oscillator

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The entropy and heat capacity are calculated for the Morse oscillator model in order to test the quality of the partition function recently deduced by two of us. It is found that these analytical expressions are more reliable than the usually accepted one and give better results in the calculation of thermodynamic properties.

### 1. Introduction

The calculation of thermodynamic properties in statistical mechanics is usually made through known or estimated structural and spectroscopic parameters, by means of the analytical expression for the partition function of the system under consideration. Usually, the rigid rotor-harmonic oscillator model is unsatisfactory, so it is necessary to use more realistic models. The Morse potential is generally chosen as a model of a one-dimensional anharmonic oscillator<sup>1</sup>. The partition function corresponding to this model can be calculated exactly in a numerical way, because there is only a finite number of energy eigenvalues<sup>2,3</sup>.

However, in the study of certain physical-chemistry properties, it is mandatory to take recourse to analytical expressions for the partition function, even though they give only approximate results. For instance, isotope effects on the equilibrium constants are of theoretical and experimental interest in connection with isotope separation. It has been suggested that in the approximation of the harmonic

oscillator-rigid rotator the isotopic mass dependence of the dissociation equilibrium constant of diatomic molecules changes sign at high temperatures<sup>2</sup>. It is necessary to calculate molecular partition function which is customarily done in the framework of the Born-Oppenheimer approximation. The rotation-vibration energy levels can be calculated by direct integration of the Schrödinger equation so that precise partition functions are available by numerical summation of Boltzmann factors<sup>4</sup>.

For a qualitative discussion numerical partition functions are not well suited, so that analytical partition functions are necessary for the general discussion of the effect mentioned above. Unfortunately, analytical expressions can only be found in certain approximations.

The usual way to obtain those approximate analytical expressions consists in taking into account the partition function of the Morse oscillator:

$$Q(N, u) = A(u) \sum_{n=0}^N \exp(-u(n - n(n+1)\chi)) \quad (1)$$