

subjected to flash chromatography (silica gel, hexane : ether=15 : 1) to give 184 mg (92%) of **9b**.

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## Study of Equivalent Retention among Different Polymer-Solvent Systems in Thermal Field-Flow Fractionation

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An equivalent retention has been experimentally observed in thermal field-flow fractionation (ThFFF) for different polymer-solvent systems. It is shown that iso-retention between two sets of polymer-solvent systems can be obtained by adjusting the temperature difference ( $\Delta T$ ) according to the difference in the ratio of ordinary diffusion coefficient to thermal diffusion coefficient. This method uses a compensation of field strength ( $\Delta T$ ) in ThFFF at a fixed condition of cold wall temperature. It is applied for the calculation of molecular weight of polymers based on a calibration run of different standards obtained at an adjusted  $\Delta T$ . The polymer standards used in this study are polystyrene (PS), polymethylmethacrylate (PMMA), and polytetrahydrofuran (PTHF). Three carrier solvents, tetrahydrofuran (THF), methylethylketone (MEK) and ethylacetate (EtAc) were employed. Though the accuracy in the calculation of molecular weight is dependent on the difference in the slope of  $\log \lambda$  vs.  $\log M$  which is related to Mark-Houwink constant  $a$ , it shows reasonable agreement within about 6% of relative error in molecular weight calculation for the polymer-solvent systems having similar a value.

### Introduction

Thermal field-flow fractionation (ThFFF) is useful for the separation and molecular weight characterization of polymers.<sup>1-6</sup> It utilizes a temperature gradient as an external field to induce thermal diffusion of polymers and this allows polymers to be separated by the differences in their ordinary diffusion coefficients.<sup>3</sup> Retention of polymers in ther-

mal FFF is controlled by an applied field strength given by temperature gradient which is also adjustable. Separation in thermal FFF like other FFF techniques is carried out in an open channel which is treated as unique advantage for the study of polymers since the possibility of sample adsorption or degradation can be minimized.<sup>6</sup>

For the calculation of molecular weight and molecular weight distribution (MWD) of polymers in thermal FFF, a calibration is required with narrow standards having an identical chemical composition to analyte to be charac-

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terized since retention of polymers in thermal FFF is dependent on  $D/D_T$  in which  $D$  is an ordinary diffusion coefficient (solute-solvent related) and  $D_T$  is thermal diffusion.<sup>6-8</sup> However, it is currently difficult to obtain calibration standards for every needs and this limits thermal FFF for the wide application of MWD measurement despite its broad potential for polymer analysis. A few attempts have been made to use rather a universal way of calibration method. Kirkland *et al.* have tried an universal calibration for ThFFF by plotting  $\log(S_0M)$  vs retention time.<sup>9</sup> Here  $S_0$  is the Soret coefficient  $S_0 = D_T/D$  and  $M$  the molecular weight of polymer. Gao *et al.* tried similar method for obtaining an universal calibration by plotting the retention data obtained at a number of polymer-solvent pairs vs  $D_T(KM^{a+1})^{-1/3}$ .<sup>10</sup> In order to utilize these methods for the MW calculation, both require a complete set of data on specific polymer-solvent systems such as  $D_T$ , Mark-Houwink constants  $K$  and  $a$  from literatures. Due to the difficulty in finding these parameters, those universal calibration methods can only be used with known polymer-solvent systems.

In this work, we have evaluated the possibility of calculating the molecular weight of polymers from a calibration obtained with a different polymer-solvent system that are run at different field strength ( $\Delta T$ ) in ThFFF. By adjusting the field strength in proportion to the difference in the ratio of  $D/D_T$  data experimentally obtained from ThFFF for both polymer standards and analyte, it is found that an equivalent retention can be observed for a various sets of polymer-solvent systems.

### Theory

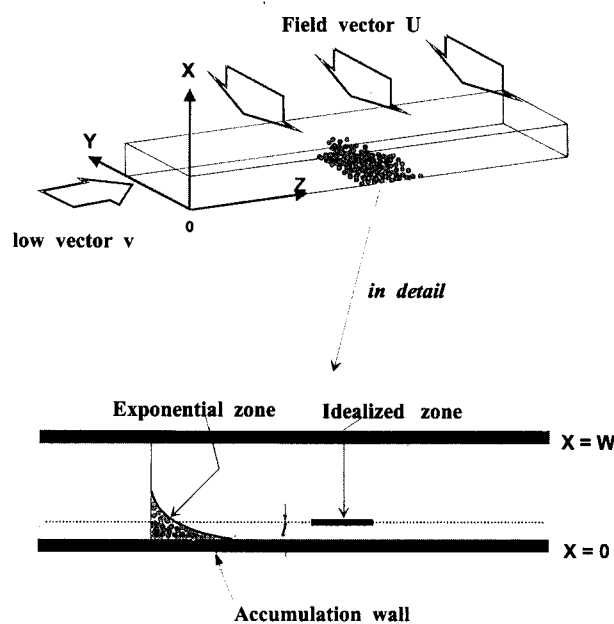
In ThFFF, each molecular species assumes a unique characteristic layer thickness within the channel. The distribution of molecules in the steady-state layer is of an exponential form (Figure 1) The layer thickness is expressed in a dimensionless form,  $\lambda = l/w$ , where  $l$  is the effective thickness of the layer and  $w$  is the channel thickness. In FFF, retention ratio,  $R$  is defined as the channel void volume ( $V^0$ ) divided by the retention volume ( $V_r$ ) and is generally expressed by

$$R = \frac{t^0}{t_r} = \frac{V^0}{V_r} = 6\lambda \left[ \coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right] \quad (1)$$

where  $t^0$  is the void time which is the passage time of a non-retained component through a FFF channel and  $t_r$  is the retention time of a sample component. In ThFFF, Eqn. (1) needs to be modified to account for the asymmetry of the channel flow caused by the temperature gradient and attendant viscosity change across the channel.<sup>11</sup> The dimensionless parameter  $\lambda$  is the measure of the separation efficiency in ThFFF as is experimentally related to the retention time  $t_r$  of a sample component. The relationship of  $\lambda$  to the corresponding transport coefficients is given by

$$\lambda = \frac{D}{wD_T(DT/dx)} \cong \frac{D}{D_T \cdot \Delta T} \quad (2)$$

where  $dT/dx$  is the temperature gradient across the channel and  $D$ ,  $D_T$  are the ordinary and thermal diffusion coef-



**Figure 1.** Vector profile in FFF and concentration profile of an exponential zone.

ficients, respectively, of the polymer-carrier solvent system. It can be seen that the ratio,  $D/D_T$  is the determining factor for the solute retention parameter  $\lambda$ .

**Iso-Retention Concept.** When one observes the retention of polymers having two different chemical compositions in an identical carrier liquid by ThFFF under the same temperature difference ( $\Delta T$ ), they will show different retentions since their retention behaviors are determined by the difference in thermal diffusions.<sup>12</sup> The different thermal diffusion of unlike polymers will differentially drive them into the different equilibrium positions against the channel wall and thus they elute at different retention times. However, if the polymers of different compositions having an identical MW can be placed at the same equilibrium height by a proper means, they will migrate at the same retention time. This can be approximately achieved by the adjustment of  $\Delta T$  for one polymer-solvent system inversely proportional to the ratio of diffusion coefficient to thermal diffusion coefficient for another polymer-solvent system. In this case, there exists difficulties in practical work since the variation of the polymer viscosity by temperature change may alter the ordinary diffusion of polymers and the influence of polymer structures may become a significant factor in the retention of polymers in ThFFF. However, if these contributions are somehow kept minimum by selecting a proper solvent, the following approximation can be tried. When a polystyrene standard is run at any arbitrary  $\Delta T$  in ThFFF, the value of  $D/D_T$  at a solvent used can be experimentally obtained from the observed retention data as Eqn. (2). The parameter  $\lambda$  for two different polymers of an identical MW can be set as constant by adjusting the  $\Delta T$  in such a way to compensate the difference in the  $D/D_T$  between the two polymers. For the two different polymer-solvent systems denoted as A and B, retention for two identical molecular weight of polymers can be adjusted the same if the following condition is met as

$$\frac{(D/D_T)_A}{\Delta T_A} = \frac{(D/D_T)_B}{\Delta T_B} \quad (3)$$

The simple rearrangement of Eqn. (3) is written as

$$\Delta T_B = \frac{(D/D_T)_B}{(D/D_T)_A} \Delta T_A \quad (4)$$

$\Delta T_B$  is the new field strength where two different polymers of an identical MW have the same retention. For obtaining above  $\Delta T_B$ ,  $D/D_T$  values must be determined. These values in two systems can be determined from the literatures or ThFFF experimental data. The latter was used in this study due to the difficulty in finding these values in various conditions. Using the approximate equation of retention parameter,  $\lambda \cdot \Delta T = D/D_T$ , Eqn. (4) is expressed by

$$\Delta T_B = \frac{(\lambda \cdot \Delta T)_B}{(\lambda \cdot \Delta T)_A} \Delta T_A \quad (5)$$

As the values on the right side of equation are easily obtained from experiment,  $\Delta T_B$  can be determined. In the same way,  $\Delta T$  can be measured under identical polymer in different solvents and different polymers in different solvent systems.

**Molecular Weight Calibration Curve.** The diffusion coefficient  $D$  is inversely proportional to the viscosity,  $\eta$ , of the carrier solution, intrinsic viscosity ( $[\eta]$ ) of polymer, and molecular weight ( $M$ ) of polymers according to the relationship with Stokes-Einstein equation as<sup>10</sup>

$$D = \frac{RT}{6\pi\eta N} \left[ \frac{10\pi N}{3[\eta]M} \right]^{1/3} \quad (6)$$

where  $T$  in thermal FFF is considered as  $T_{cg}$ , the temperature at the center of gravity of a sample zone, and the intrinsic viscosity  $[\eta]$  is proportional to the MW of polymer with the relationship of the Mark-Houwink (M-H) constants  $K$  and  $a$  by

$$[\eta] = KM^a \quad (7)$$

Thus, the combined equation for the retention parameter  $\lambda$  is obtained by inserting Eqns. (6) and (7) into Eqn. (2)

$$\lambda = \frac{A}{D_T \eta (KM^{a+1})^{1/3} \Delta T} \quad \text{where } A = \frac{RT_{cg}}{6\pi\eta N} \left[ \frac{10\pi N}{3} \right]^{1/3} \quad (8)$$

The logarithmic form of Eqn. (8) is given by

$$\log \lambda = - \left( \frac{a+1}{3} \right) \log M + \log \left( \frac{A}{K^{1/3} \cdot D_T \cdot \Delta T} \right) \quad (9)$$

In the plot of  $\log \lambda$  vs.  $\log M$ , M-H constant  $a$ ,  $K$  and thermal diffusion coefficient,  $D_T$ , are determined from the intercept and slope, respectively. However, studies are focused with the observation of an equivalent retention of polymer standards and coincidence of calibration curves composed at different polymer-solvent systems after a proper adjustment of  $\Delta T$ . This is based on the difference in experimental  $D/D_T$  values measured under different polymers in identical solvent, identical polymer in different solvents, and different polymers in different solvent systems.

## Experimental

Thermal FFF system utilized in this work is a Model T 100 ThFFF Polymer Fractionator from FFFractionation, LLC (Salt Lake City, UT). The ThFFF channel and the system configuration are the same as described in an earlier work.<sup>3</sup> Two different channels are used with a breadth of 1.5 cm for most runs and with 1.3 cm for PS-THF(II) and PTHF-ETAc systems. Both channels have a length of 46.5 cm and a thickness of 0.0127 cm. The void volumes for the two channels are calculated from the passage time of benzene. The carrier liquid is delivered to the channel by using a M-6000A HPLC pump from Waters Associates (Milford, MA). A flow rate used throughout the works is maintained at 0.12 mL/min. Eluted samples are detected with a Shodex RI-71 RI (refractive index) detector from Showa Denko K. K. (Tokyo, Japan) and the detector signal is transferred to a PC by using an FFF data analysis software version 2.0 from FFFractionation, LLC.

Polymer standards used in this work are polystyrene (PS), polymethylmethacrylate (PMMA), and polytetrahydrofuran (PTHF). The molecular weights and polydispersity data provided by the manufacturer are listed in Table 1. Solvents for the sample preparation are the same as the carrier solvents used for thermal FFF operation. Samples are prepared with the concentration of about 2 mg/mL for PS and 3 mg/mL for both PMMA and PTHF and filtered with sample clarification kit having pores of 0.45  $\mu$ m for the removal of particulates. A volume of 15  $\mu$ L of each sample (about 30-45  $\mu$ g) is injected individually by using a Rheodyne 7125 injector with a 20  $\mu$ L sample loop. For the carrier solvents, HPLC grade tetrahydrofuran (THF), methylethylketone (MEK), and ethylacetate (ETAc) are used. These solvents are selected for the good dissolution of polymer standards and for the purpose of detecting a large difference in RI values. For example, MEK is selected for PMMA sample due to the big difference in RI values from PS-THF system. Carrier solvents are degassed by sonication prior to the use. In this study, five different polymer-solvent systems are investigated by varying  $\Delta T$  from 25 to 50 K at a cold wall temperature fixed at 318 K.

## Results and Discussion

**Temperature Compensation between Different Polymers at an Identical Solvent.** For the initial evaluation of the iso-retention concept in thermal FFF, retention of two sets of polymer standards (PS and PMMA) is first examined in an identical solvent (MEK) at a fixed

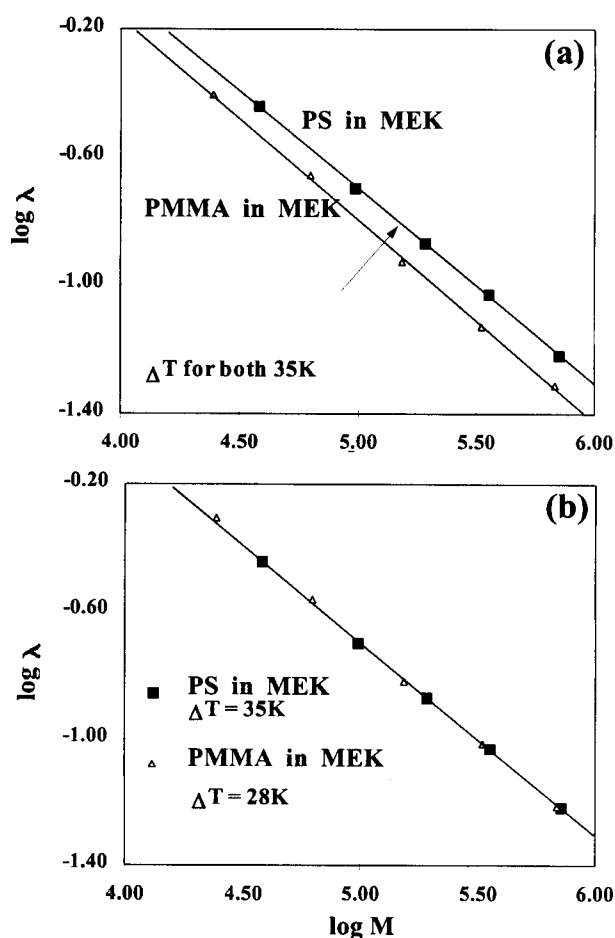
**Table 1.** Polymer standards used in this work

	PS	PMMA	PTHF
Supplier	Tosoh Corp.	Polymer Laboratories	Polymer Laboratories
MW/ (polydispersity)	37,900(1.01)	24,300(1.06)	35,500(1.06)
	96,400(1.01)	62,600(1.06)	67,500(1.04)
	190,000(1.04)	153,700(1.04)	99,900(1.08)
	355,000(1.02)	333,000(1.06)	282,300(1.08)
	706,000(1.05)	685,000(1.10)	547,000(1.35)

$\Delta T$  and  $T_c$ . Since the two standards are different in their chemical compositions, they should have different thermal diffusion and this leads them eluted at different retention time scale in thermal FFF. Figure 2(a) shows the plot of  $\log \lambda$  versus  $\log M$  for both polymer standards in MEK obtained at  $\Delta T=35$  K and  $T_c=318$  K. The two calibration curves are nearly parallel to each other with slopes of  $-0.63$  for PMMA and  $-0.61$  for PS. Based on these measurements, the  $\Delta T$  adjustment is applied to PMMA-MEK system for the equivalent retention of both PS-MEK and PMMA-MEK system. The  $D/D_T$  values of PS-MEK pair are calculated for each standard from the experimental measurements of  $\lambda$  values. The values for PMMA-MEK system are obtained from its own calibration curve by recalculating  $D/D_T$  for each MW corresponding to PS standards. From the ratio of  $D/D_T$  values for the two pairs, an adjusted  $\Delta T$  is calculated by using Eqn. (5) and all of these data are listed in Table 2(A). The resulting  $\Delta T$  value for PMMA-MEK system is calculated as an average of 27.7 K which is expected to be equivalent to  $\Delta T=35.0$  K for PS-MEK system. In the calculation of an adjusted  $\Delta T$ , there is an alternate way to calculate it more systematically: expected  $\lambda$  values of each MW of PMMA which can be calculated from PS-MEK calibration curve are plotted with  $D/D_T$  values obtained from

PMMA-MEK system and then the slope of this regression is treated as  $1/\Delta T$  in which relationship can be found in Eqn. (2). However in this work, a simple calculation of an average  $\Delta T$  is used throughout. The real experimental  $\Delta T$  is adjusted as 28 K by rounding off. The retention data for PMMA obtained at an adjusted field strength are plotted in Figure 2(b). The straight line is the linear regression of PS standards and the triangle symbols represent the data for PMMA at the same solvent by changing the  $\Delta T$  as 28 K. Data show a good agreement to the PS calibration curve illustrated in Figure 2(b). The relative errors in experimental  $\lambda$  values of PMMA-MEK system from the PS-MEK calibration curve are 0.2-4.1% which seems to be acceptable. By using the PS-MEK calibration curve, MW of PMMA standard is recalculated from the retention measurements. Table 2(B) shows the comparison between the certified MW of PMMA (measured by GPC) and the calculated data in which the deviation appears to be less than 5% except the lowest MW sample. From the initial evaluation, it is shown that the slight difference in the  $T_c$ , temperature at the center of gravity, for both polymer systems is not seriously altering the retention when the cold wall temperature is fixed throughout the runs. Apparently, from this simple adjustment it is likely to obtain the MW distribution of unknown polydisperse PMMA sample with PS standards alone without leaning to PMMA standards.

**Temperature Compensation between an Identical Polymer Sample at Different Solvents.** Similar tests are made with an identical polymer standards by using different solvents. When a series of PMMA standards are run at MEK and at THF, retention behaviors at both sol-



**Figure 2.** (a) Plots of  $\log \lambda$  vs.  $\log M$  of PS-MEK and PMMA-MEK obtained at  $\Delta T=35$  K and (b) data points of PMMA-MEK obtained at an adjusted  $\Delta T=28$  K are superimposed over the PS-MEK calibration plot.

**Table 2.** A) Experimental  $D/D_T$  values for each polymer-solvent system and adjusted  $\Delta T$  values for PMMA standard (corresponding MW) of which retention is equivalent to PS-MEK system obtained at  $\Delta T=35$  K. B) Calculated MW of PMMA in MEK by using the calibration curve of PS in MEK. All runs are fixed at  $T_c=318$  K

MW of PS standards	$D/D_T^*$ (PS-MEK)	$D/D_T^{**}$ (PMMA-MEK)	$[D/D_T]_{\text{PMMA-MEK}} / [D/D_T]_{\text{PS-MEK}}$	$\Delta T(K)^1$ for PMMA-MEK
37,900	12.72	10.35	0.8134	28.5
96,400	7.067	5.750	0.8137	28.5
190,000	4.764	3.748	0.7864	27.5
650,000	3.284	2.530	0.7703	27.0
706,000	2.132	1.640	0.7691	26.9

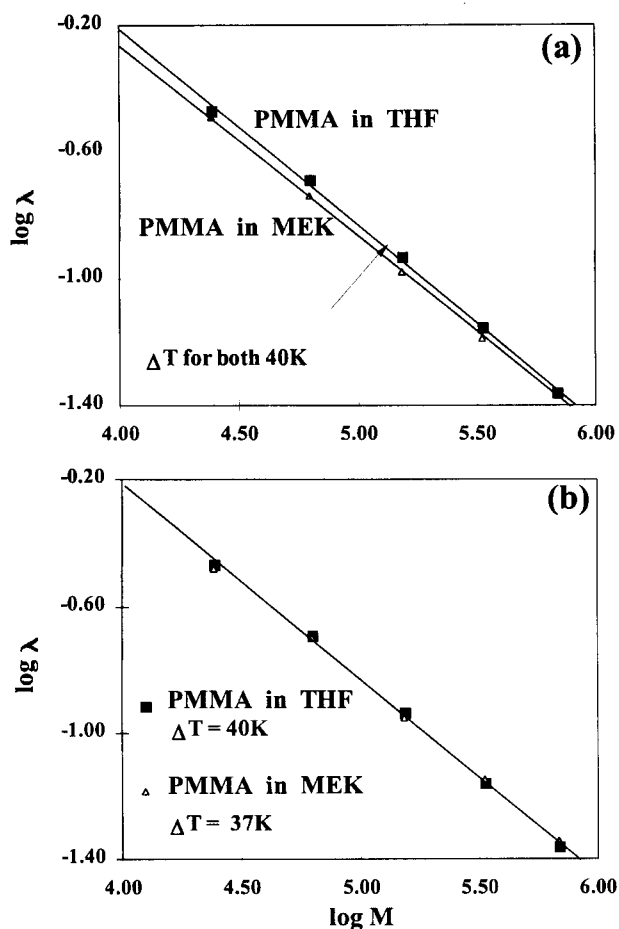
\*values are obtained at  $\Delta T=35$  K. \*\*calculated from the PMMA-MEK calibration curve at corresponding MW obtained at  $\Delta T=35$  K. <sup>1</sup>adjusted  $\Delta T$  for PMMA-MEK system.

B)

MW of PMMA*	Calculated MW**	Deviation (%)
24,300	22,800	6.2
62,600	59,700	4.6
153,700	157,000	2.2
333,000	332,000	0.30
685,000	704,000	2.8

\*GPC results in toluene. \*\*FFF results from PS-MEK calibration.

vents appear as clearly different in Figure 3(a). The thermal field employed in these runs is  $\Delta T=40$  K at a fixed  $T_c=318$  K. Since the values of the Mark-Houwink constant  $a$  for PMMA on both solvents are similar (about 0.72) each other at 25 °C from the literature,<sup>13</sup> the two calibration curves are nearly parallel each other and the compensation of field strength can be made with a minimized risk in correlation of one curve to the other. According to the previous calculation procedure, field strength of PMMA-MEK system is adjusted as being equivalent to that of PMMA-THF system. The experimental data are listed in Table 3(A). The calculation of an adjusted  $\Delta T$  for PMMA-MEK system is done similarly to the above work as 37.4 K. The experimental data obtained in MEK at  $\Delta T=37$  K by rounding off are superimposed over the PMMA-THF calibration curve and are expressed as triangles in Figure 3(b). The correlation seems to be agreeable with the relative errors of 1.0-6.7% between the data at two different solvents. The calculated MW of PMMA standards from the calibration curve obtained at THF are within 4% of relative differences except the sample of a smallest MW (about 12%). The relatively large difference arises from the difficulties in measuring the accurate retention time of the small MW polymer sample since the eluting peak of standard 24 K overlaps with the void peak.



**Figure 3.** (a) Plots of  $\log \lambda$  vs.  $\log M$  of PMMA-THF and PMMA-MEK obtained at  $\Delta T=40$  K and (b) data points of PMMA-MEK obtained at an adjusted  $\Delta T=37$  K are superimposed over the PMMA-THF calibration plot.

While this compensation procedure is applied to the case of polymer-solvent systems having similar values of constant  $a$  of M-H constants, it is not appropriate to simply utilize this concept to the polymer-solvent systems having large difference in values of M-H constant  $a$ .

**Temperature Compensation between Different Polymers at Different Solvents.** Based on the preliminary tests at the above, the iso-retention concept is extended to the totally different polymer-solvent systems. Figure 4(a) shows the calibration curves of PS-THF(I) and of PMMA-MEK systems obtained at  $\Delta T=50$  K with a fixed  $T_c=318$  K. The field adjustment is applied for PMMA-MEK system by decreasing the temperature difference ( $\Delta T$ ). The calculation of adjusted  $\Delta T$  for PMMA-MEK system results as 34.9 K and the related data are listed in Table 4. The measured  $\lambda$  values for PMMA-MEK system obtained at  $\Delta T=35$  K in real experiments are represented as open triangles on the calibration curve of PS-THF(I) system obtained at  $\Delta T=50$  K in Figure 4(b). Since the slopes of the original calibration curves are clearly different each other as  $-0.60$  and  $-0.69$  from the bottom, there is a deviation in fitting PMMA-MEK data onto the PS-THF calibration curve. Calculation of PMMA molecular weight using PS-THF(I) calibration curve shows relatively large differences (in maximum 12%) since the slopes of the two calibration curves are clearly different each other.

A more reliable work has been obtained with the correlation of PTHF-ETAc to PS-THF(II) system. These two systems are run first at  $\Delta T=30$  K and the retention data are

**Table 3.** A) Experimental  $D/D_T$  values for PMMA-MEK and PMMA-THF systems and adjusted  $\Delta T$  values for PMMA-MEK system (corresponding MW) of which retention is equivalent to PMMA-THF system obtained at  $\Delta T=40$  K. B) Calculated MW of PMMA in MEK by using the calibration curve of PMMA in THF. All runs are fixed at  $T_c=318$  K.

A)

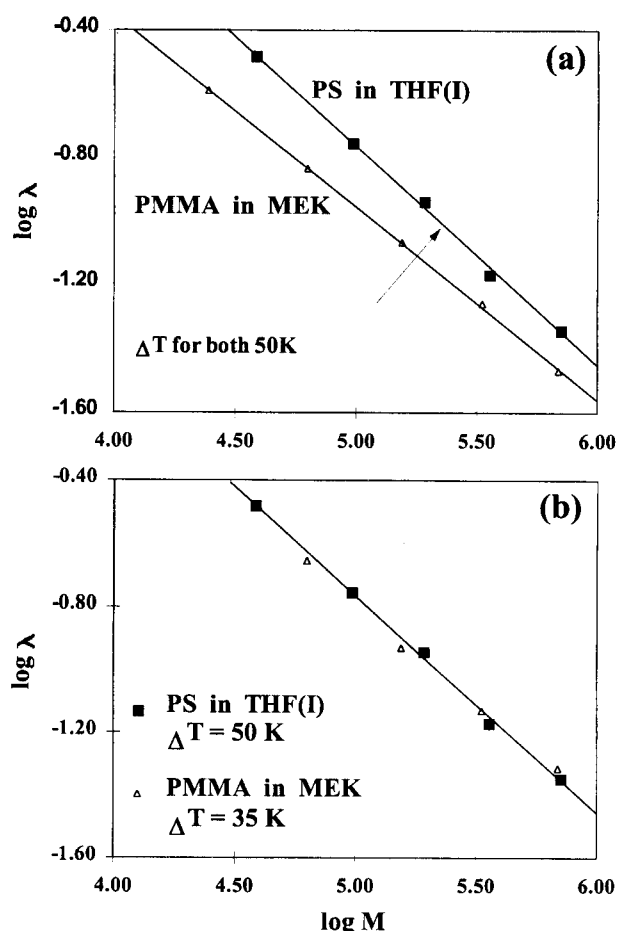
MW of PMMA standards	$D/D_T^*$ (PMMA-THF)	$D/D_T^{**}$ (PMMA-MEK)	$[D/D_T]_{\text{PMMA-MEK}} / [D/D_T]_{\text{PMMA-THF}}$	$\Delta T$ (K) <sup>1</sup> for PMMA-MEK
24,300	13.62	12.96	0.9521	38.1
62,600	8.192	7.296	0.8906	35.6
153,700	4.660	4.172	0.8953	35.8
333,000	2.789	2.572	0.9224	36.9
685,000	1.750	1.767	1.0094	40.4

\*values are obtained from PMMA-THF curve at  $\Delta T=40$  K. \*\*calculated from the PMMA-MEK calibration curve at each corresponding MW at  $\Delta T=40$  K. <sup>1</sup>adjusted  $\Delta T$  for PMMA-MEK system.

B)

MW of PMMA*	Calculated MW**	Deviation (%)
24,300	27,200	12
62,600	60,800	2.9
153,700	156,000	1.5
333,000	322,000	3.3
685,000	672,000	1.9

\*GPC results in toluene. \*\*FFF results from PMMA-THF calibration.



**Figure 4.** (a) Plots of  $\log \lambda$  vs.  $\log M$  of PS-THF(I) and PMMA-MEK obtained at  $\Delta T=50$  K and (b) data points of PMMA-MEK obtained at an adjusted  $\Delta T=35$  K are superimposed over the PS-THF(I) calibration plot.

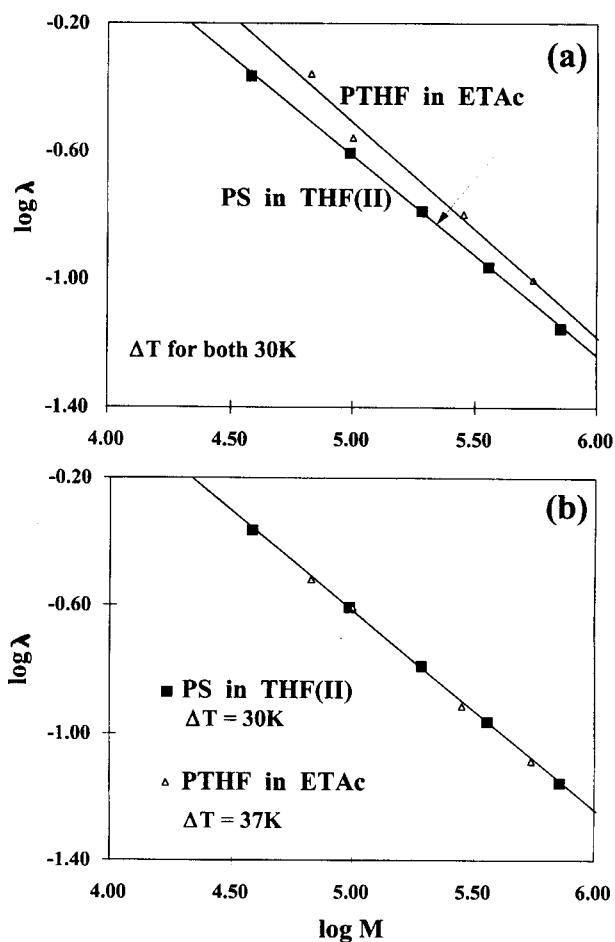
**Table 4.** A) Experimental  $D/D_T$  values for PMMA-MEK and PS-THF (I) systems and adjusted  $\Delta T$  values for PMMA-MEK system (corresponding MW) of which retention is equivalent to PS-THF system obtained at  $\Delta T=50$  K. B) Calculated MW of PMMA in MEK by using the calibration curve of PS in THF (I). All runs are fixed at  $T_c=318$  K

MW of PS standards	$D/D_T^*$ (PS-THF (I))	$D/D_T^{**}$ (PMMA-MEK)	$[D/D_T]_{\text{PMMA-MEK}} / [D/D_T]_{\text{PS-THF(I)}}$	$\Delta T(K)^1$ for PMMA-MEK
96,400	8.835	5.642	0.6386	31.9
190,000	5.765	3.746	0.6497	32.5
355,000	3.393	2.571	0.7579	37.9
706,000	2.273	1.698	0.7470	37.3

\*values are obtained at  $\Delta T=50$  K. \*\*calculated from the PMMA-MEK calibration curve at each corresponding MW at  $\Delta T=50$  K. <sup>1</sup> adjusted  $\Delta T$  for PMMA-MEK system.

MW of PMMA*	Calculated MW**	Deviation (%)
62,600	69,800	12
153,700	173,000	12
333,000	337,000	1.1
685,000	620,000	9.4

\*GPC results in toluene. \*\*FFF results from PS-THF (I) calibration.



**Figure 5.** (a) Plots of  $\log \lambda$  vs.  $\log M$  of PS-THF(II) and PTHF-ETAc obtained at  $\Delta T=30$  K and (b) data points of PTHF-ETAc obtained at an adjusted  $\Delta T=37$  K are superimposed over the PS-THF(II) calibration plot.

plotted in Figure 5(a). The slopes of the two curves are  $-0.62$  and  $-0.67$  from the bottom. In this case, run condition of PTHF-ETAc system is adjusted by raising  $\Delta T$  to 37 K so that retention of PTHF-ETAc system is equivalent to that of PS-THF(II) system. The resulting MW calculation of PTHF based on PS-THF(II) calibration shows at most 6% in relative error in Table 5.

## Conclusion

In the present study, we have evaluated the possibility of obtaining an equivalent retention by adjusting field strength ( $\Delta T$ ) in ThFFF. While the iso-retention concept using temperature adjustment appears to work for the given polymer-solvent systems in this study, it somehow bears limitations to apply as a universal way since the Mark-Houwink constant  $a$  significantly affect the accuracy in the calculation of MW of polymers. In the present work, it has been found that a relatively large difference (about 15%) in the slopes of calibration curves propagated to maximum 12% of uncertainty in the calculation of molecular weight. However the current approach may be considered as useful if a good solvent is selected to provide a comparable slope of calibration. If the Mark-Houwink constant  $a$  values between

**Table 5.** A) Experimental  $D/D_T$  values for PTHF-ETAc and PS-THF (II) systems and adjusted  $\Delta T$  values for PTHF-ETAc system (corresponding MW) of which retention is equivalent to PS-THF (II) system obtained at  $\Delta T=30$  K. B) Calculated MW of PTHF in MEK by using the calibration curve of PS in THF. All runs are fixed at  $T_c=318$  K

A)

MW of PS standards	$D/D_T^*$ (PS-THF (II))	$D/D_T^{**}$ (PTHF-ETAc)	$[D/D_T]_{\text{PTHF-ETAc}} / [D/D_T]_{\text{PS-THF(II)}}$	$\Delta T(\text{K})^{\dagger}$ for PTHF-ETAc
96,400	7.509	9.531	1.269	38.1
190,000	4.944	6.036	1.221	36.6
355,000	3.300	3.969	1.203	36.1
706,000	2.109	2.499	1.186	35.5

\*values are obtained at  $\Delta T=30$  K. \*\*calculated from the PTHF-ETAc calibration curve at each corresponding MW at  $\Delta T=30$  K. <sup>†</sup> adjusted  $\Delta T$  for PTHF-ETAc system.

B)

MW of PTHF*	Calculated MW**	Deviation (%)
67,500	70,100	3.9
99,900	95,900	4.0
282,300	299,000	5.9
547,000	569,000	4.0

\*GPC results in toluene. \*\*FFF results from PS-THF (II) calibration.

any two polymer-solvent systems differ by 7% (from 0.7 to 0.65), the difference would result in 3.5% error in the slopes of calibration curve,  $(a+1)/3$ , which will reduce the error in the calculation of molecular weight. Since the present study is solely based on the experimental data of a given set of polymer-solvent systems by ThFFF, comparison of experimental  $D/D_T$  between two different polymer-solvent systems would be more realistic than it is relied on the comparison of those values from the literature. The concept of an equivalent retention would require more

precise tabulations of parameters  $D_T$ ,  $K$ , and  $a$  by ThFFF or by other experiments if it is potentially used for the MW calculation of unknowns.

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