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Determination of Thermal Diffusion Coefficients for Polydisperse Polymers and Microgels by ThFFF and SEC−MALLS

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ABSTRACT: A new method combining thermal field-flow fractionation (ThFFF) and SEC−MALLS is proposed for the measurement of the thermal diffusion coefficient D_T for polydisperse polymeric samples. This method should greatly increase the range of applicability of ThFFF for characterization of block copolymers and also for studies of thermal diffusion, an interesting phenomenon not yet well understood. ThFFF is one of only a few techniques (e.g., thermal diffusion forced Rayleigh scattering) that can determine D_T values of polymers. The values of D_T can be used to reflect the surface composition of block copolymer molecules as reported in recent studies. Currently, the value has been measured with ThFFF based on the sample peak maximum method, which can introduce errors when the sample has a broad MW distribution. The method proposed here measures D_T by taking all digitized points in the entire sample peak into consideration, and has been tested with polystyrene, poly(*tert*-butylstyrene), and some copolymer microgels. Preliminary results are presented and discussed.

Introduction

Several studies on thermal diffusion of polymers and copolymers using several methods[1] including thermal FFF (ThFFF) have been carried out in recent years. Schimpf et al.[2] used ThFFF to obtain values of D_T for several copolymer samples having different types of molecular architecture and with different ratios of the two parent monomers. Their study found that for random copolymers, D_T values can be described by a weighted average of the D_T values of the corresponding homopolymers, whereas for block copolymers, D_T values reflect the type and ratio of polymer on the outermost sphere of the copolymer molecules in contact with the surroundings. These findings indicate that ThFFF has the potential to become a very powerful technique for studying copolymers, especially for surface characterization.

If the value of the concentration diffusion coefficient D is determined by some independent method (e.g. size exclusion chromatography (SEC) or dynamic light scattering (DLS)), the thermal coefficient D_T can be obtained from ThFFF data using the equation[2−10]

$$\lambda = \frac{D}{D_T \Delta T} \tag{1}$$

where λ = retention parameter and ΔT = the temperature difference between the hot and cold plates in the ThFFF channel, and D is given by the commonly used empirical relationship

$$D = AM^{-b} \tag{2}$$

where M = molecular weight, and A and b are constants at least over limited ranges of M.

For more accurate results, the apparent field S can be used instead of D_T when the variation in thermal conductivity (κ) with temperature $d\kappa/dT$ is taken into account.[11−13] Equation 1 then becomes

$$\lambda = \frac{D}{SD_T} \tag{3}$$

where

$$S = \Delta T + \frac{1}{\kappa_c}\frac{d\kappa}{dT}\frac{(\Delta T)^2}{2} \tag{4}$$

The above equations may be utilized with narrow MW standards if λ is determined at the peak maximum of the sample peak. While narrowly dispersed samples can be readily handled by these methods (i.e. SEC, DLS, ThFFF) to provide D and D_T values, polydisperse samples remain a difficulty because of the dependence of D on MW. Another approach requires prefractionation of the polydisperse sample (e.g., using preparative SEC) to produce a series of relatively narrow MW subsamples for analysis.[14] However, such a procedure is tedious and would further complicate the measurement process. Due to these drawbacks, studies of thermal diffusion by ThFFF to date have generally been limited to narrowly dispersed polymeric samples. Therefore, the application of ThFFF for the measurement of D_T for polydisperse polymer samples would be very desirable.

In this paper, a new approach for the determination of thermal diffusion coeffficients for polydisperse samples will be introduced. For polydisperse samples that have known A and b constants, the thermal coefficient D_T can be extracted directly from their ThFFF fractograms. For samples for which A and b are unknown, a multiangle laser light scattering detector is employed on-line with a SEC system (SEC−MALLS) to produce the constants

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A and b (from $D = AM^{-b}$), as well as the weight average molecular weight M_w for the polydisperse sample. The constants can then be put into ThFFF equations to extract the value of D_T. The methodology was tested with the polystyrene−tetrahydrofuran system. D_T values so-obtained were compared with D_T values obtained from the peak maximum method using narrow standards. The proposed method was then applied to poly(*tert*-butylstyrene) (PtBS) and some block copolymer microgel polydisperse samples dissolved in tetrahydrofuran (THF). Preliminary results only from this latter work are presented.

Theory

Thermal FFF. An expression for M_w for use in ThFFF has been derived by Nguyen and Beckett as[15,16]

$$M_w = \frac{I_t \sum h_i (S\lambda_i)^{-1/}b}{\sum h_i} \tag{5}$$

where h_i and λ_i are the height of the detector signal above the baseline and the retention parameter respectively at the digitized ith point and

$$I_t = \Phi^{1/}b \tag{6}$$

where

$$\Phi = \frac{A}{D_T} \tag{7}$$

Rearrangement of eq 5 gives

$$I_t = \frac{M_w \sum h_i}{\sum h_i (S\lambda_i)^{-1/b}} \tag{8}$$

therefore

$$\Phi^{1/b} = \left(\frac{A}{D_T}\right)^{1/b} = \frac{M_w \sum h_i}{\sum h_i (S\lambda_i)^{-1/b}} \tag{9}$$

thus the expression for D_T becomes

$$D_T = A \left(\frac{\sum h_i (S\lambda_i)^{-1/b}}{M_w \sum h_i} \right)^{b} \tag{10}$$

According to eq 10, if A and b are available from an independent source, D_T can be determined from the ThFFF fractogram data of a polydisperse sample of known M_w.

The accurate application of these equations assumes that D_T is independent of molecular weight and that its concentration dependence can be neglected in dilute solution.

SEC with On-Line MALLS (SEC−MALLS). For polydisperse polymeric samples A and b may be determined with an SEC system equipped with on-line MALLS and concentration sensitive detectors. At the same time M_w for the sample can be measured accurately.[17,18]

In MALLS−SEC the empirical equation

$$\log M_i = \mathbf{x} - \mathbf{y} V_{e_i} \tag{11}$$

is often used to express the relationship between MW and retention volume along an elution chromatogram.[19] Thus a plot of log M_i vs V_{e_i} will be a straight line. Each polymer type will have different $\mathbf{x}$ and $\mathbf{y}$ values and hence be represented by a different line. The slope of the line, $\mathbf{y}$, indicates the compactness of the polymer molecule.[20] It should be noted that since eq 11 assumes a linear relationship between log M and V_e, therefore, the method is not applicable for polymer systems for which this relationship does not hold. Such deviations may occur if the polymer interacts with the column stationery phase, which may be indicated by a tailing of the SEC peak.

Taking the logarithm of both sides of eq 2 gives

$$\log D_i = \log A - b \log M_i \tag{12}$$

Combining eqs 11 and 12 gives

$$\log D_i = \mathbf{C}_1 + \mathbf{C}_2 V_{e_i} \tag{13}$$

where

$$\mathbf{C}_1 = \log A - b\mathbf{x} \tag{14}$$

and

$$\mathbf{C}_2 = b\mathbf{y} \tag{15}$$

According to eq 13 a plot of log D_i vs V_{ei} yields a straight line with slope $\mathbf{C}_2$ and y-intercept $\mathbf{C}_1$. Combining the Stokes−Einstein equation

$$D = \frac{kT}{6\pi\eta r_h} \tag{16}$$

where r_h = the hydrodynamic radius of the molecule, η = the viscosity of the solvent, k = the Boltzmann constant, and T = the sample temperature (K).

Using the universal calibration concept from Benoit et al.[21]

$$\log([\eta]M) = a' - b' V_e \tag{17}$$

where $M[\eta]$ is the hydrodynamic volume and a' and b' are universal constants applicable for all polymers when used in the same SEC column; it follows that for a given solvent, values of $\mathbf{C}_2$ and $\mathbf{C}_1$ are the same for all polymers. This arises provided we can assume that at a given SEC elution volume V_{e_i} all polymers have the same hydrodynamic radius r_h and, as D is a function of r_h, that polymer molecules with the same value of D_i coelute. Caution should be taken when polymers that have a rodlike shape are used, as the universal calibration line was reported to deviate from the expected linear relationship for such samples.[22]

D_i, $\mathbf{C}_1$, $\mathbf{C}_2$ may be obtained from SEC−MALLS as follows. We start by using polystyrene (PS) for which the constants A_{PS} and b_{PS} are known; an SEC chromatogram is run with either some monodisperse MW standards or a broad sample with a MALLS detector. From these SEC data, a plot of log M_{PS_i} vs V_{ePS_i} will provide the values of the constants $\mathbf{x}_{PS}$ and $\mathbf{y}_{PS}$. Then constants $\mathbf{C}_1$ and $\mathbf{C}_2$ can be calculated by eqs 14 and 15.

As $\mathbf{C}_1$ and $\mathbf{C}_2$ are now available, constants A and b for any polydisperse unknown sample (designated by subscript unk) can be obtained from its SEC−MALLS data. Since in SEC−MALLS, the plot of log M_{unk_i} vs $V_{e_{unk i}}$ provides $\mathbf{x}_{unk}$ and $\mathbf{y}_{unk}$ from which A_{unk} and b_{unk}

can be calculated by

$$b_{\mathrm{unk}} = \frac{\mathbf{C}_2}{\mathbf{y}_{\mathrm{unk}}} \tag{18}$$

$$A_{\mathrm{unk}} = 10^{(\mathbf{C}_1 + b_{\mathrm{unk}}\mathbf{x}_{\mathrm{unk}})} \tag{19}$$

Equations 18 and 19 are the rearranged forms of eqs 15 and 14, respectively. Once A_{unk} and b_{unk} have been found, the normal diffusion coefficient D_{unk_i}, corresponding to any MW, may be calculated.

Experimental Section

Instrumentation and Run Conditions. Thermal FFF. The ThFFF channel, model T100 from FFFractionation Inc., Salt Lake City, UT, was used for this study. The ThFFF channel dimensions were 20.9 mm in breadth, 47 cm tip to tip length, and 0.127 mm in thickness, which gave a geometric void volume of 1.15 mL. The experimentally measured void volume had a value of 1.13 mL; this value was used for calculation in the following section. The postcolumn dead volume was 0.034 mL. This channel was different from that used previously for the development of ThFFF calibration methods using broad polystyrene standards (see Nguyen and Beckett).[16]

The pump used was an LDC Milton Roy Constametric III and the UV detector was a Waters model 480 set at a wavelength of 254 nm. A back-pressure regulator was connected to the detector outlet to prevent the solvent boiling. The flow rates were measured by an in-house flow meter comprising an electronic balance (model FX300 from AND) which continuously monitors the mass of solvent from the outlet of the detector. The chart recorder used was from ICI Instruments Model no. DP600.

The thermal gradient field control and data acquisition were achieved using programs supplied by FFFractionation Inc., Salt Lake City, UT, and an Epson PCe computer. The program FFF.EXE, supplied by FFFractionation Inc., was used for adjusting the baseline and removal of the void peak. Fractograms were digitized when needed using a Hewlett-Packard plotter and the GRAPHPAD software package. Analysis of the fractogram data was achieved using in-house programs.

A 20 μL sample was introduced onto the channel through a Rheodyne six-way loop injection valve. A ΔT value of 40 K was employed. The sample was relaxed for 1 min. The field strength (i.e., the temperature difference between the hot and cold plates of the channel) was held constant. The detector response was recorded on a chart recorder and collected in digitized form on a PC computer for later processing using in-house programs.

Microgel samples and the corresponding parent polymers were dissolved in HPLC grade THF and were run at a field strength of 40 K, and the temperature at the cold wall T_c was maintained at 25 °C. Each sample was run with the flow rate as given in Table 2. D_T was calculated using an in-house program.

SEC−MALLS. In the SEC system, a series of two 10^3 Å, two 10^4 Å, and one 10^5 Å Ultrastyragel columns from Waters was used for the separation of the polymers in THF. The differential refractometer (DRI) was a Waters model 401. The columns were calibrated using a series of polystyrene standards supplied by Waters. The MALLS instrument model DAWN F was from Wyatt Technology Corp., Santa Barbara, CA. ASTRA and EASI software packages from Wyatt Technology Corp., were used for analysis of light scattering data. DRI was used to determine the refractive index increment dn/dc for the polymeric samples. Data for conventional SEC with the DRI were analyzed with the Baseline software package from Waters. HPLC grade THF was used without any further treatment. The solvent was pumped with a Waters HPLC pump at a flow rate of 1.00 mL/min.

Table 1. Molecular Weight (M_p = Peak Maximum, M_w = Weight Average, and M_n = Number Average) and Polydispersity (μ) Details for Six Narrowly Dispersed Polystyrene Standards As Supplied by the Manufacturer and Their Corresponding Values of Retention Parameter, λ, and D_T (cm^2 s^{-1} K^{-1}) in THF[a]

std	M_p (kDa)	M_w (kDa)	M_n (kDa)	μ	λ (corrected)	D_T ($\times 10^7$)
N1	46	43	42	1.03	0.204	1.12
N2	92	85	80	1.05	0.140	1.09
N3	217	213	209	1.02	0.079	1.19
N4	440	427	417	1.03	0.050	1.24
N5	827	810	785	1.03	0.033	1.31
N6	1310	1260	1200	1.04	0.025	1.36
					av	1.22

[a] ThFFF data (λ) were obtained at ΔT = 40 K, T_c = 20 °C, and corrected for non parabolic channel flow and variation in thermal conductivity across the channel.

Table 2. Details of Number and Weight Average MWs (M_n and M_w) and the Polydispersity (μ) Given by the Suppliers (Dow and Pressure Chem. Co.) for Four Polydisperse Polystyrene Standards, the Flow Rates Employed in ThFFF Runs, and Their Corresponding Values of D_T (cm^2 s^{-1} K^{-1}) in THF[a]

std	M_n (kDA)	M_w (kDa)	μ	flow rate (mL/min)	D_T ($\times 10^7$)
B1		100	1.5[b]	0.130	1.18
B2	100	250	2.5	0.138	1.15
B3		498	<1.2	0.180	1.21
B4		1000	1.2[b]	0.130	1.42
				av	1.24

[a] ThFFF data were obtained at ΔT = 40 K, T_c = 20 °C, and corrected for nonparabolic channel flow and variation in thermal conductivity across the channel. [b] Measured by SEC−MALLS.

Materials. For comparison of D_T values obtained using the peak maximum method with those obtained from the proposed method for polydisperse samples, fractograms of the six narrow and four broad polystyrene standards discussed in Nguyen and Beckett[16] were reused. The narrow MW polystyrene standards were supplied by Polymer Standards Services, Mainz, Germany. MW information for these standards is indicated in Table 1. The broad MW polystyrene samples from different sources were used for the studies of the calibration method. Details of their nominal MW values given by the suppliers together with the flow rates of ThFFF runs are indicated in Table 2. All sample solutions were made up to 1−2 mg/mL in spectrophotometry or HPLC grade tetrahydrofuran (THF), which was also the carrier solvent.

When the method was applied to copolymer microgel samples, two homopolymers, polystyrene and poly(*tert*-butylstyrene) (PtBS), and four microgels composed of different parent monomer ratios were used. The polystyrene sample had a M_w of 100 kDa specified by the supplier. PtBS and microgel samples were synthesized according to the method described by Funke et al.[23,24] The microgel samples were the products of the polymerization processes when either divinylbenzene (DVB) or a mixture of DVB and styrene in different ratios was added into a living PtBS solution. The polymerization processes were carried out in heptane; details of the synthesis were described in Pille et al.[20] These synthesized polymer and microgels were characterized by SEC−MALLS which showed that PtBS is randomly coiled and flexible while the microgels were compact and highly cross-linked. The method of synthesis suggested that the microgels should be internally cross-linked.[20,21,24] Weight average MW and polydispersities of these samples were also determined by SEC−MALLS. For polystyrene the dn/dc value used in the light scattering calculations was from literature which is 0.185 mL/

g.[25] The d*n*/d*c* value of other samples were determined with the DRI detector, details of the measurements of d*n*/d*c* are described in Pille et al.[26]

Results and Discussion

Comparison of D_T Values Obtained for Polystyrene. ThFFF runs of the six narrow and four broad polystyrene standards previously used in the calibration paper (Nguyen and Beckett)[16] were reused as mentioned. The same *A* and *b* constants from the literature ($A = 3.861 \times 10^{-4}$; $b = 0.571$)[8,27] were employed for both narrow and broad standards. We neglect the small temperature decrease through the thin sample cloud.

For the peak maximum method with narrow standards, D_T was calculated from eq 3, which on combining with eq 2 and rearranging gives

$$D_T = \frac{A}{\lambda S M^b} \tag{20}$$

where *S* is obtained from eq 4. The D_T values obtained for these six narrow polystyrene standards are shown in Table 1. For the broad polystyrene samples, values of D_T were obtained using the new method (eq 10) and are summarized in Table 2.

It is apparent that the average value of D_T obtained from the new method was almost identical to that from the conventional method using the peak maximum of ThFFF runs with narrow standards. This confirms the applicability of ThFFF in measurements of D_T for polydisperse samples using eq 10.

The small systematic change in D_T in Tables 1 and 2 may be due to a number of factors.

(a) First is errors in the *A* and *b* values from the literature that in turn yield errors in the calculated D_T values.[28]

(b) If the gradient of the calibration line is truly not equal to *b* then this could indicate that there is genuinely a small dependence of D_T on MW. For example if D_T were to vary according to

$$D_T = \mathrm{A}_T M^{\beta'} \tag{21}$$

We obtain using eqs 2, 3, and 21

$$S\lambda = \frac{A}{A_T M^{(b+\beta')}} \tag{22}$$

or

$$\log S\lambda = \log \frac{A}{A_T} - (b + \beta') \log M \tag{23}$$

Since the experimental gradient is 0.636 we would then deduce a small but significant influence of MW on D_T according to the expression

$$D_T = \frac{A}{A_T} M^{0.065} \tag{24}$$

This is an interesting observation which needs further consideration but it is beyond the scope of this work. As the effect is relatively small and this work presents only preliminary work on the determination of D_T, it will not be considered further.

(c) Perhaps there are experimental errors of unknown origin which cause systematic errors resulting in the gradient of the calibration line log $S\lambda$ vs log *M* to deviate from *b*. Alternatively Martin et al.[29] have suggested that the deviations in *b* can be explained by simplifications made in the theoretical calculations.

Table 3. Summary of d*n*/d*c*, M_w, and μ Values for Polystyrene, PtBS, and Microgel Samples Together with the Flow Rate Used for Each Sample in ThFFF Runs[a]

sample	d*n*/d*c*	M_w (kDa)	μ	flow rate (mL/min)
PS	0.185	100	1.5[b]	0.192
PtBS	0.140	740	1.28	0.205
M7-7-2	0.155	385	2.84	0.192
M8-9-2	0.161	720	3.02	0.120
M11-9-2	0.161	96.3	2.10	0.120
M12-9-2	0.166	1521	2.27	0.120

[a] Abbreviations: PS = polystyrene, PtBS = poly(*tert*-butylstyrene). [b] Measured by SEC−MALLS.

Table 4. Summary of the Quantity of Monomers *tert*-Butylstyrene (tBS), Styrene (ST), and Divinylbenzene (DVB) and the Resultant Ratio of ST and DVB Monomers Used in the Synthesis of Microgel Samples[a]

sample (microgel)	tBS ($\times 10^2$ mol)	ST ($\times 10^3$ mol)	DVB ($\times 10^3$ mol)	ST:DVB (mole ratio)
M7-7-2	1.46		5.92	
M8-9-2	1.46	8.74	2.17	4:1
M11-9-2	1.42	13.7	1.65	8:1
M12-9-2	1.35	21.9	2.63	8:1

[a] Abbreviations: tBS = *tert*-butylstyrene, ST = styrene, and DVB = divinylbenzene.

It should be noted here that overloading effects were checked and found to have an insignificant effect. The value of *b* obtained for PS−THF for this ThFFF system was consistent and was always around the value of 0.64. A slight increase in T_H along the channel was observed, therefore an investigation into the effects on D_T of the increase in either Δ_T or T_c down the channel was carried out and was found to be negligible.

Finally, we note that although the above trend in D_T with *M* will be important for the accurate characterization of D_T it does not affect the MW calibration procedures developed in Nguyen and Beckett[16] since the experimental calibration plots are linear.

Measurement of D_T for Some Polydisperse Polymers and Microgels. The new method was applied to determine D_T for polydisperse samples of polystyrene (for comparison), PtBS, and a series of microgels. Refractive index increment (d*n*/d*c*), weight average MW and polydispersities of these samples are summarized in Table 3. Table 4 summarizes the ratios of parent monomers present in each microgel sample. Constants *A* and *b* for PtBS and the microgels are unknown. SEC−MALLS was used to provide these constants as described in the Theory section.

Determination of *A* and *b* Using SEC−MALLS. Values of $A = 3.861 \times 10^{-4}$ and $b = 0.571$ for polystyrene in THF obtained from the literature[8,27] were used to construct the calibration line described by eq 12. From SEC−MALLS runs constants **x** and **y** in eq 11 were found to be 9.829 and 0.132, respectively, for polystyrene−THF (log *M* vs V_e as shown in Figure 1). The slope $\mathbf{C}_2$ and *y*-intercept $\mathbf{C}_1$ of the calibration line in eq 13 are 7.567×10^{-2} and -9.026, respectively. These values were then used to determine *A* and *b* values for PtPS and microgels using eqs 18 and 19 as outlined in the Theory section.

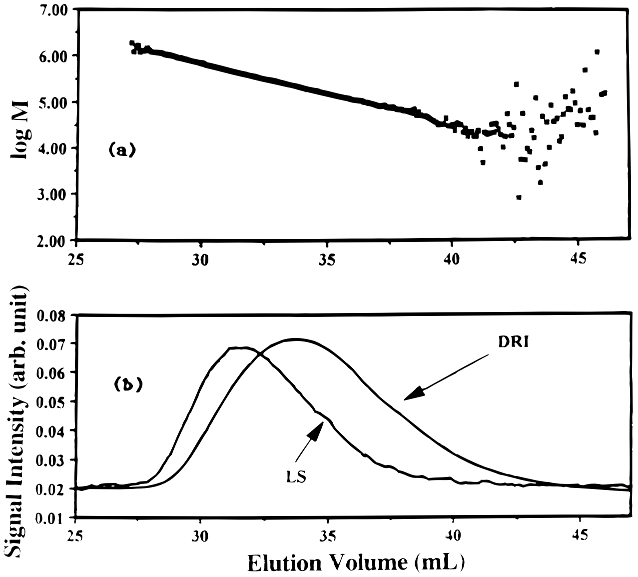

Figure 1. (a) Plot of log M vs elution volume V_e obtained from SEC−MALLS system. From this plot, constants **x**, **y**, and also molecular weight averages are obtained. (b) SEC chromatograms obtained from a MALLS and a concentration sensitive detector (DRI) for a polystyrene sample.

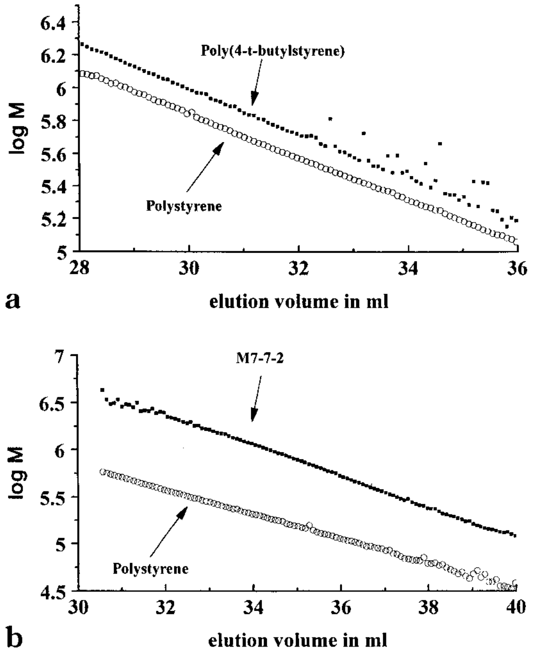

Figure 2. Plots of log M vs V_e for the PtBS sample (a) and for the microgel sample (M7-7-2) (b) compared with that of polystyrene, illustrating the difference in **x** and **y** and hence the compactness of these samples. PtBS and polystyrene have similar values of **x** and **y** since they both have linear random coiled molecular configurations.

SEC−MALLS calibration lines for PtBS and one of the microgels (M7−7−2) are shown in Figure 2, the line obtained for polystyrene is also plotted for comparison. This figure shows that the molecules of the microgels are much more compact than that of polystyrene, which is a little less compact compared with the molecules of PtBS.

The **x** and **y** values from SEC−MALLS runs and the *A* and *b* values calculated from the calibration lines for PtBS and all the microgels are tabulated in Table 5. These results showed that the *A* and *b* values of PtBS are similar to those of polystyrene, while they are quite different from those of the microgels. The **x** and **y** values in eq 11 provide information on the compactness of the polymers. Higher values of **x** and **y** indicate that the molecule is more compact.[20] Table 5 shows that almost all of the microgels are more compact than the parent homopolymers PtBS and polystyrene. The *b* values imply that they have a molecular conformation between that of a dense sphere ($b = {}^1/_3$) and a linear random coil (*b* from 0.5 to 0.6), with the exception of sample M11-9-2. In Table 5, values of *A* and *b* for polystyrene are from the literature, and used in the SEC calibration step to obtain the constants $\mathbf{C}_1$ and $\mathbf{C}_2$.

Table 5. Values of x, y, *A*, and *b* from SEC−MALLS Data Analysis for Polystyrene, PtBS, and Microgel Samples[a]

sample[b]	x	y	A ($\times 10^4$)	b
PS	9.829	0.132	3.861[c]	0.571[c]
PtBS	10.10	0.137	3.680	0.553
M7-7-2	11.50	0.160	2.587	0.473
M8-9-2	11.45	0.159	2.568	0.475
M11-9-2	10.26	0.133	6.369	0.568
M12-9-2	11.45	0.161	2.331	0.471

[a] Polystyrene was used for calibration of the SEC column. [b] Abbreviation: PS = polystyrene; PtBS = poly(*tert*-butylstyrene). [c] From literature.

Determination of Thermal Diffusion Coefficient Using ThFFF. The values of *A* and *b* in Table 5 were then used to calculate D_T for each sample from their ThFFF digitized fractograms using eq 10. Samples of polystyrene, PtBS, and the microgels were run under identical run conditions, as described in the Experimental Section. Fractograms of these samples are shown in Figure 3. Values of D_T for all samples are summarized in Table 6 along with their M_w obtained from SEC−MALLS.

This method provided a D_T value of 0.87×10^{-7} cm^2 s^{-1} K^{-1} for the polystyrene−THF combination. This value had a deviation of −13% from the literature value (1.0×10^{-7} cm^2 s^{-1} K^{-1}).[8] (However, D_T values reported by different workers range from 0.87×10^{-7} to 1.107×10^{-7} cm^2 s^{-1} K^{-1}.[5,8−10]) The thermal diffusion coefficient D_T of PtBS was found to be 0.83×10^{-7} cm^2 s^{-1} K^{-1}. This value is close to that of polystyrene since they have similar *A*, *b*, and ThFFF retention data. The difference between the D_T values for the broad polystyrene standard (M_w = 100 kDa) reported in Table 6 and those reported Table 2 is unknown at this stage, except for the fact that they were obtained using different ThFFF channels (spacers) as mentioned in the Experimental Section.

The values of D_T for all microgel samples were very similar despite their having different molecular weights, M_w, and compositions (i.e. ratios of parent monomers). Surprisingly, these D_T values were up to 25% lower than that of either polystyrene or PtBS, which were the component blocks in the copolymer microgels.

Previous studies on copolymers showed that D_T of copolymer samples possessed intermediate values between those of parent polymers. These studies were carried out on random and block copolymers which had both linear and star-shaped configurations.[2] The low D_T values obtained here for microgel samples are not understood at this stage. Since either *tert*-butylstyrene (tBS) or styrene blocks were expected to be on the outer region of the microgel molecular core,[20,21,24] a D_T value close to that of the two component polymers was expected. This may be due to the fact that the microgel molecules have structural configurations different from

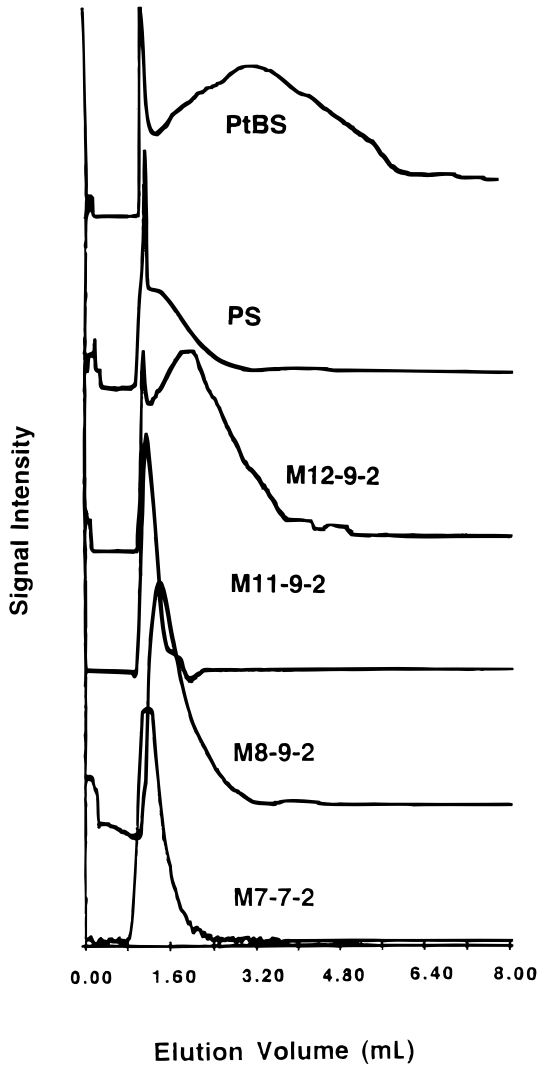

Figure 3. ThFFF fractograms for polydisperse PS, PtBS, and four microgel samples at $\Delta T = 40$ K and $T_c = 25$ °C. The flow rate for each sample was indicated in Table 2

Table 6. D_T Values (cm^2 s^{-1} K^{-1}) for PS, PtBS, and Microgel Samples Obtained from ThFFF

sample	M_w (kDa)	D_T ($\times 10^7$)
PS	100	0.87
PtBS	740	0.83
M7-7-2	385	0.66
M8-9-2	720	0.67
M11-9-2	96.3	0.68
M12-9-2	1521	0.68

those of the linear parent polymers. The microgels are cross-linked and more compact, having molecular conformations between spherical and linear random coil as indicated by the SEC−MALLS analysis. The limitation of the SEC universal calibration method for characterizing this type of samples (e.g., cross-linked copolymer microgels) may introduce errors since these molecules are not linear random coils. However, Pille and Solomon[20] have found that the molecular shapes of these microgels are not rodlike. In addition previous research from different workers reported satisfactory results for similar highly branched, cross-linked copolymer microgel systems using the universal calibration method.[30,31] Further study is required on the thermal diffusion of microgels so that meaningful conclusions can be made regarding these results.

Conclusion

In recent years ThFFF has provided much useful information on the thermal diffusion phenomenon not previously available. However, current measurements of the thermal diffusion coefficient D_T, as well as of constants A and b used in the calculation, have been based on the peak maximum method. This method tends to limit the measurements to narrowly dispersed samples.

The new method discussed in this work, which was developed to measure D_T for polydisperse samples, should broaden the applicability of ThFFF to include a much wider range of polymeric samples. This method promises to become a powerful tool for studies of the thermal diffusion phenomenon and surface characterization of copolymers, since it introduces a simple way to obtain thermal diffusion coefficient data for polymers and copolymers for which only broad molecular weight samples are available.

The method was tested with the polystyrene−THF system. Excellent agreement was achieved between the values of D_T obtained by the new broad standard method and those measured by the conventional peak maximum method with narrow standards.

The method was then applied to polydisperse PtBS, PtBS−DVB copolymer, and PtBS−ST−DVB terpolymer microgel samples. It has been suggested that D_T reflects the type of polymer on the outer region of the solvated polymer molecule, in which case this measurement could provide valuable information about the architecture of the microgel particles. However, in this case the polystyrene and PtBS polymers had almost identical thermal diffusion coefficients. The D_T values of the microgel samples were found to be up to 25% below those of polystyrene and PtBS. Further study is required before definite conclusions can be drawn about the thermal diffusion of microgels and the effects of the structure of the microgel molecule.

References and Notes

(1) Rossmanith, P.; Kohler, W. *Macromolecules* **1996**, *29*, 3203−3211.
(2) Schimpf, M. E.; Giddings, J. C. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2673−2680.
(3) Giddings, J. C.; Caldwell, K. D.; Myers, M. N. *Macromolecules* **1976**, *9*, 106−112.
(4) Brimhall, S. L.; Myers, M. N.; Caldwell, K. D.; Giddings, J. C. *J. Polym. Sci.: Polym. Phys. Ed.* **1985**, *23*, 2443−2456.
(5) Gunderson, J. J.; Giddings, J. C. *Macromolecules* **1986**, *19*, 2618−2621.
(6) Song, K.-C.; Kim, E.-K. Chung, I.-J. *Korean J. Chem. Eng.* **1986**, *3* (2), 171−175.
(7) Schimpf, M. E.; Giddings, J. C. *Macromolecules* **1987**, *20*, 1561−1563.
(8) Schimpf, M. E.; Giddings, J. C. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1317−1332.
(9) Gao, Y.; Chen, X. In *Study on the Universal Calibration for Thermal Field-Flow Fractionation*; Proceedings of the 1st International Symposium of FFF, Park City, UT, June, 1989; Paper no. 2.
(10) Antonietti, M.; Briel, A.; Tank, C. *Acta Polym.* **1995**, *46*, 254−260
(11) Gunderson, J. J.; Caldwell, K. D.; Giddings, J. C. *Sep. Sci. Technol.* **1984**, *19* (10), 667−683.
(12) Schimpf, M. E.; Williams, P. S.; Giddings, J. C. *J. Appl. Polym. Sci.* **1989**, *37*, 2059−2076.
(13) van Asten, A. C.; Boelens, H. F. M.; Kok, W. Th.; Poppe, H.; Williams, P. S.; Giddings, J. C., *Sep. Sci. Technol.* **1994**, *29*, 513−533.
(14) van Asten, A. C.; van Dam, R. J.; Kok, W. Th.; Tijssen, R.; Poppe, H. *J. Chromatogr., Part A* **1995**, *703* (1 & 2), 245−263.
(15) Nguyen, M.; Beckett, R. *Polym. Intl.* **1993**, *30*, 337−343.

(16) Nguyen, M.; Beckett, R. *Sep. Sci. Technol.* **1996**, *31*, 291−317.

(17) Wyatt, P. J. *J. Liq. Chromatogr.* **1991**, *14*, 2351−2372.

(18) Martin, M.; Hes, J. *Sep. Sci. Technol.* **1984**, 19, 685−707.

(19) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.

(20) Pille, L.; Solomon, D. H. *Macromol. Chem. Phys.* **1994**, *195*, 2477−2489.

(21) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753−759.

(22) Dubin, P. L.; Principi, J. M. *Macromolecules* **1989**, *22*, 1891−1896.

(23) Funke, W.; Okay, O. *Macromolecules* **1990**, *23*, 2623−2628.

(24) Okay, O.; Funke, W. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 583−587.

(25) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989.

(26) Pille, L.; Jhingran, A. G.; Capareda, E. P.; Solomon, D. H. *Polymer* **1996**, *37*, 2459−2464.

(27) Schaefer, D.; Han, C. C. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenvin Press: New York, 1985.

(28) Nguyen, M. New Calibration Methods for Use in Characterization of Polydisperse Polymeric Samples with Field- Flow Fractionation. Ph.D. Thesis, Monash University, Victoria, Australia, 1995; pp 160−162.

(29) Martin, M.; van Batten, C.; Hoyos, M. *Anal. Chem.* **1997**, *69*, 1339−1346.

(30) Siochi, E. J.; DeSimone, J. M.; Hellstern, A. M.; McGrath, J. E.; Ward, T. C. *Macromolecules* **1990**, *23*, 4696−4706.

(31) Lang, P.; Burchard, W.; Wolfe, M. S.; Spinelli, H. J.; Page, L. *Macromolecules* **1991**, *24*, 1306−1314.

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