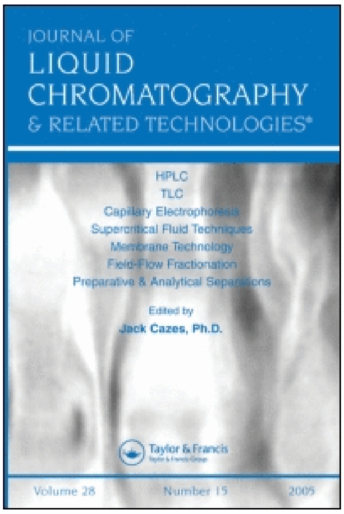

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COLD WALL TEMPERATURE EFFECTS ON THERMAL FIELD-FLOW FRACTIONATION

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ABSTRACT

Thermal field-flow fractionation is a powerful tool for separating and characterizing lipophilic polymers. The construction of calibration curves is required for converting retention data into molecular weight distributions because thermal diffusion of polymers in solution is not well understood. Retention behavior is determined by the physicochemical properties of the polymer and solvent and should be independent of and apply to any thermal field-flow apparatus. Among these properties is the effect of the cold wall temperature which has been studied in some detail and found to be very important in retention behavior. In addition, temperature effects on thermal diffusion have been measured.

INTRODUCTION

The ability of the various subtechniques of field-flow fractionation (FFF) to separate and characterize particles and macromolecules over a broad range is well established. The thermal field-flow fractionation (ThFFF) subtechnique has been primarily applied to lipophilic macromolecules up to 2 x 10^7 daltons, and also to particles in the submicron to micron range.

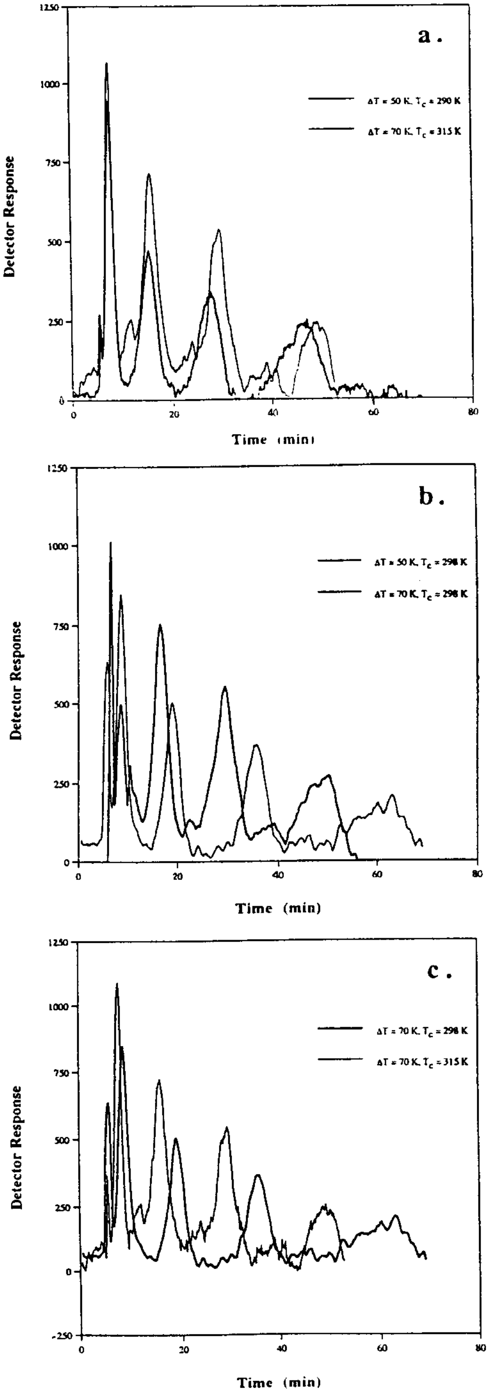
The physical parameters which operate in the other FFF subtechniques are well known, but the important parameter in ThFFF, thermal diffusion, is not well understood. Because of this, the use of ThFFF to characterize molecular weight distributions of polymeric samples requires the construction of a calibration curve obtained from well characterized standards of the polymer. Ideally, these standards are quite monodisperse, but the use of three or more well characterized broad standards has been shown to also provide good calibration curves.[1,2]

J. C. Giddings recently[3] suggested that calibration curves for one channel should be essentially transportable to all channels because the calibration curves depend on physicochemical properties of the polymer and solvent and not on the characteristics of the channel itself. If the proper parameters for a given polymer-solvent pair are measured in one channel, these parameters should hold in all channels. However, observed calibration curves by various workers in different laboratories, and even by the same person, have varied. Factors such as the cold wall temperature have not been carefully considered as contributing to the variation in calibration curves, although Brimhall et al.[4] examined temperature effects on the thermal diffusion coefficient, D_T.

Classical retention theory for FFF, considering an exponential concentration gradient across the channel and a parabolic velocity profile gives

$$R = \frac{V^0}{V_r} = 6\lambda\left(\coth\frac{1}{2\lambda} - 2\lambda\right) \qquad (1)$$

Figure 1 (right). Fractograms for a mixture of polystyrene standards in THF at different operating conditions in channel no. 21; a) the darker curve was obtained at $\Delta T = 50$ K, with $T_C = 290$ K, while the second curve was at $\Delta T = 70$ K, with $T_C = 315$ K; b) the ΔT values were the same as (a) but with $T_C = 298$ K in both fractograms; c) $\Delta T = 70$ K for both fractograms, but T_C was 298 K for the darker curve and 315 K for the second curve.


a.
ΔT = 50 K, T_c = 290 K
ΔT = 70 K, T_c = 315 K
Detector Response
1250
1000
750
500
250
0
0
20
40
60
80
Time (min)
b.
ΔT = 50 K, T_c = 298 K
ΔT = 70 K, T_c = 298 K
Detector Response
1250
1000
750
500
250
0
0
20
40
60
80
Time (min)
c.
ΔT = 70 K, T_c = 298 K
ΔT = 70 K, T_c = 315 K
Detector Response
1250
1000
750
500
250
0
-250
0
20
40
60
80
Time (min)

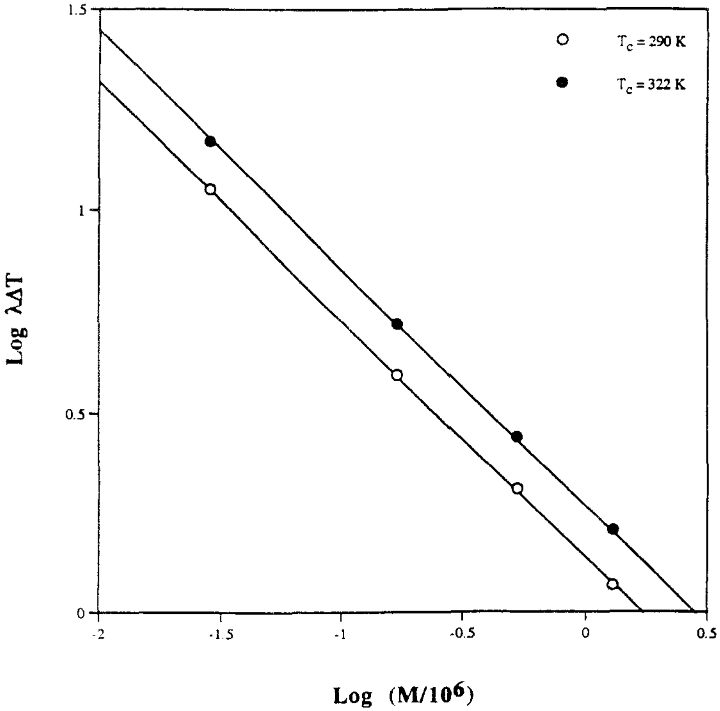


Figure 2. Calibration plots for polystyrene in THF showing the effect of T_C. Both plots were obtained at $\Delta T = 50$ K, with the open circles at $T_C = 298$ K and the filled circles with $T_C = 322$ K.

where V^0 is the channel or void volume, V_r is the sample (or peak) retention volume, and λ (for ThFFF) is

$$\lambda = \frac{D}{D_T \frac{dT}{dx} w} \approx \frac{D}{D_T \Delta T} \qquad (2)$$

where D is the ordinary diffusion coefficient of the polymer in the carrier solvent, $\frac{dT}{dx}$ is the temperature gradient, w is the channel thickness and ΔT is the difference in temperature between the hot and cold walls of the channel. In ThFFF, the retention equation must be modified because of the variation of

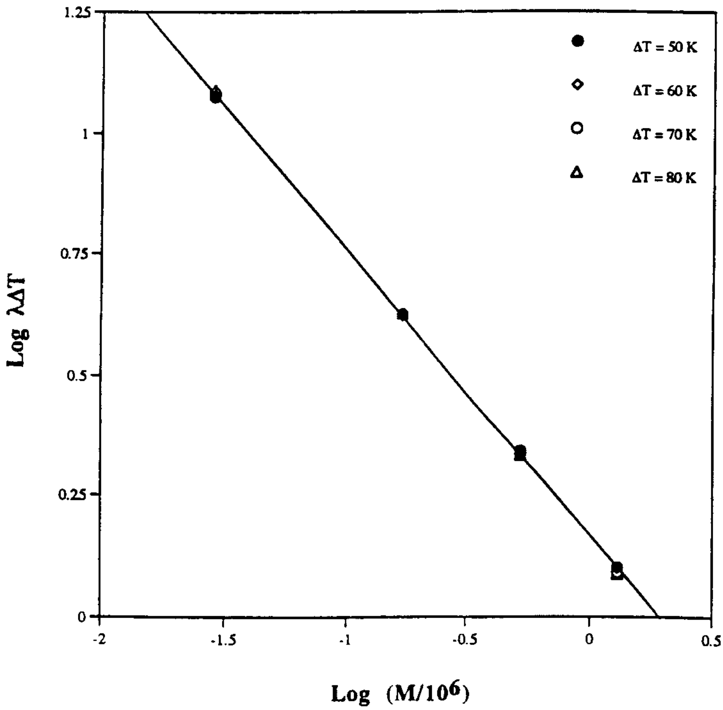


Figure 3. The effect of ΔT on the calibration plot for polystyrene in THF at $T_C = 298$, for ΔT values of 50, 60, 70 and 80 K.

viscosity of the solvent, η, and the thermal conductivity, κ, across the channel caused by the imposed temperature gradient

$$R = 6\lambda\left\{\nu + (1 + 6\lambda\nu)\left[\coth\frac{1}{2\lambda} - 2\lambda\right]\right\} \tag{3}$$

where ν depends on the carrier, ΔT, and the cold wall temperature T_C.[5]

The ordinary diffusion coefficient, D, for polymers is often given as:

$$D = AM^{-b} \tag{4}$$

where M is the molecular weight. Equation (2) is then rewritten as:

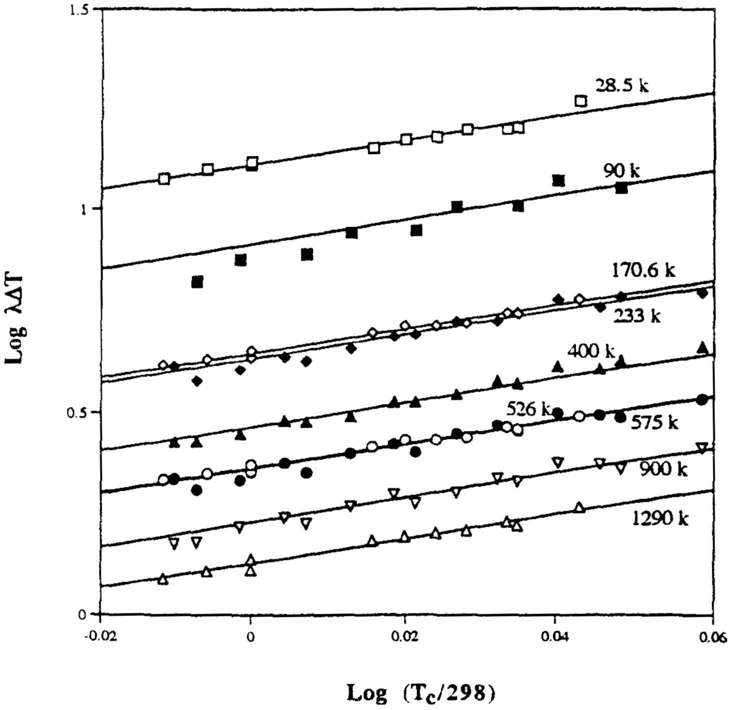


Figure 4. The effect of T_C on log $\lambda\Delta T$ for polystyrene in THF obtained from channels 15, 20, 21 and 22 with ΔT ranging from 30 to 70 K. Another sample series of five standards was also run which gave similar results but are not shown here. The slope of all the lines is 3.

$$\lambda\Delta T = \phi M^{-n} \tag{5}$$

where ϕ incorporates D_T and the nonmolecular weight-dependent portion of D, and n includes b and any molecular weight dependence of D_T. A calibration curve is obtained from:

$$\log \lambda\Delta T = \log \phi - n \log M \tag{6}$$

where the intercept gives log ϕ and the slope is n. In practice, to avoid extrapolation to M = 1, Eq (6) is modified to become:

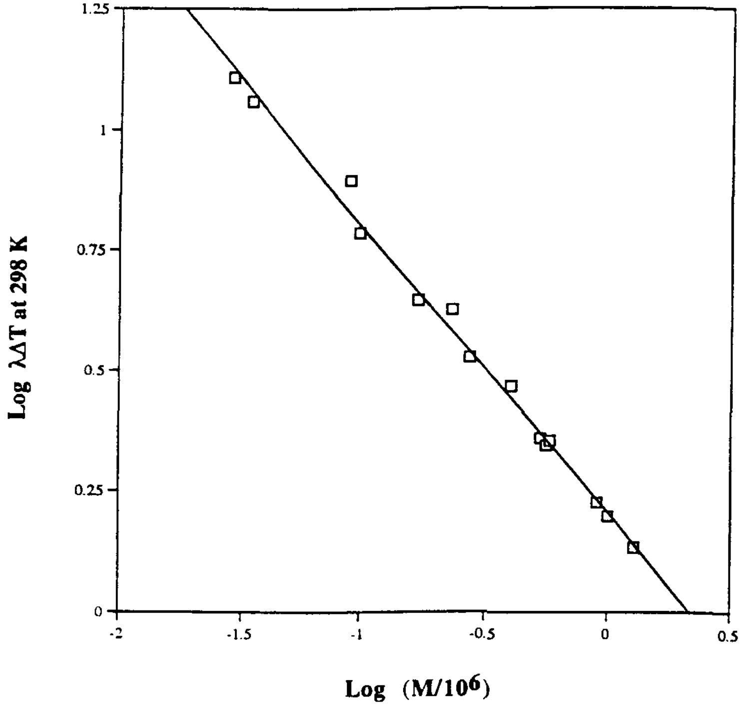


Figure 5. Values of log λΔT at 298 K obtained from Figure 4 and five additional standards give a calibration plot with a slope of -0.6.

$$\log \lambda \Delta T = \log \phi_6 - n \log \frac{M}{10^6} \qquad (7)$$

Changes in the velocity profile due to the temperature gradient across the channel are due primarily to changes in viscosity and to a lesser extent to the change in thermal conductivity (κ). Temperature corrections for η and κ are introduced in the v term in Equation (3).

However, other changes due to temperature are also present in ThFFF. Ordinary diffusion, D, is given by the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta\gamma} \qquad (8)$$

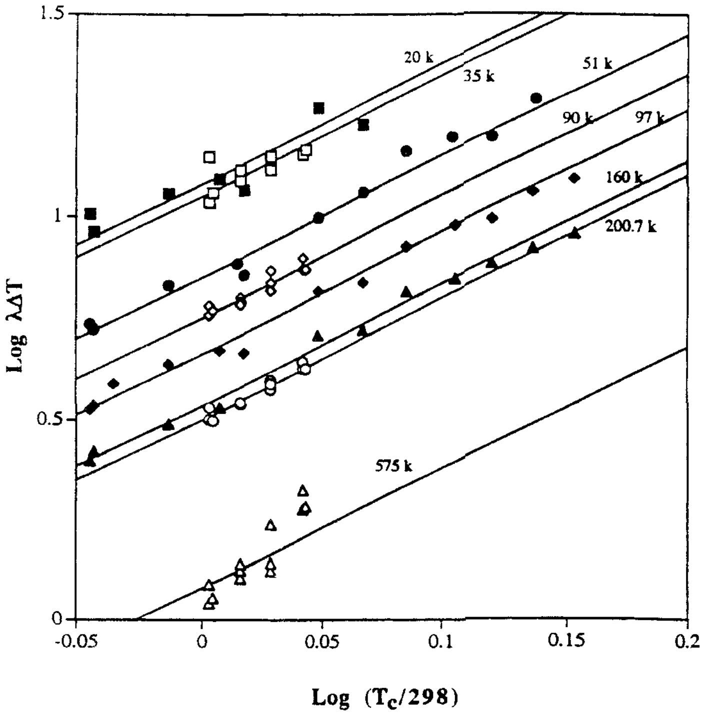


Figure 6. The effect of T_C on log $\lambda\Delta T$ for polystyrene in ethyl benzene from channels 5 (filled symbols) and 15 (open symbols) obtained 15 and 6+ years ago, respectively. The ΔT values varied from 40 K to 80 K. The slope of the lines is 3.

where k is Boltzman's constant, η is the viscosity of the solvent, and γ is the hydrodynamic radius of the molecule. Viscosity dependence on temperature can be expressed by[6]

$$\frac{1}{\eta} = a_0 + a_1T + a_2T^2 + a_3T^3 \qquad (9)$$

As mentioned above, the thermal diffusion coefficient, D_T, has also been shown to be temperature-dependent[4] with very little, if any, dependence on molecular weight.[4,7] Since the cold wall is the accumulating wall for most polymers, the cold wall temperature, T_c, will be an important, even a determining, factor in retention behavior.

Table 1

Channel Characteristics

Channel No.	Effective Channel Length, cm	Channel Breadth, cm	Channel Thickness, µm	Temp. Meas. Ports (Hot + Cold Wall)	Bar Thickness, cm
5	45	1.8	254	10	2.5
15	42	2	76	12	2.5
20	23.5	2	127	22	3.75
21	30.3	1.5	127	32	3.75
22	32.5	2.0	127	44	3.75

One of the sources of variation in calibration curve parameters obtained by different operators with different channels is probably due in part to differences in T_c. Over several years, several workers in our labortory have obtained data on cold wall effects. We present these observations as a necessary preliminary step towards developing the "Universal Calibration Curve" suggested by Giddings.

EXPERIMENTAL

Several channels were used in this study. The channel dimensions and characteristics are given in Table 1. Channels 20, 21 and 22 were designed to flatten the temperature profile along the channel length with ports for measuring temperature less than 2 cm apart. These three channels gave the most reproducible and consistent results because the temperature along the channel length was very uniform. The data from the very old channel 5 were obtained 15 years ago.

A variation in temperature in channel 15 has been observed to be as much as 4-6°C along the channel length and a similar variation would be expected from channel 5 but was not measured. The T_C was taken as the average cold wall temperature. Channels 20, 21 and 22 used 127 µm I.D. tubing for the inlet and outlet to minimize dead volume. Various sizes of tubing were used for the other channels. The heat exchangers in channels 20, 21 and 22 were modified to allow operation at colder T_C.

Table 2

Polystyrene Standards Characteristics

Supplier	M_n	M_w	M_p	M_w/M_n
Polymer Standards Services				
	32,600	33,500	34,300	1.03
	245,000	257,000	273,000	1.05
	536,000	546,000	556,000	1.02
	880,000	944,000	1,000,000	1.07
Polymer Laboratories				
	27,833	28,422	28,500	1.03
	165,683	169,246	170,600	1.03
	513,242	532,152	526,000	1.04
	1,203,119	1,253,827	1,290,000	1.05
Supelco				
		35,000		$\leq$1.06
		47,500		$\leq$1.06
		233,000		$\leq$1.06
		400,000		^{2}1.06
Pressure Chemical Co.				
		90,000		$\leq$1.06
		200,000		$\leq$1.05
		575,000		$\leq$1.06
		900,000		$\leq$1.06

Spacers to define the channel were made from Mylar, polyimide or Teflon-coated polyimide. The solvent or carrier was reagent or spectrograde tetrahydrofuran (THF), or reagent grade ethyl benzene. The linear polystyrene standards came from several sources and are listed in Table 2.

Temperature control and data collection were accomplished with in-house software and XT, 286 or Pentium computers. The runs were also monitored with an Omniscribe strip chart recorder (Houston Instruments). Channel flow was provided with a Spectra-Physics Isochrome (San Jose, CA) or an SSI-2 (FFFractionation, Salt Lake City, UT) metering pump. The THF effluent was

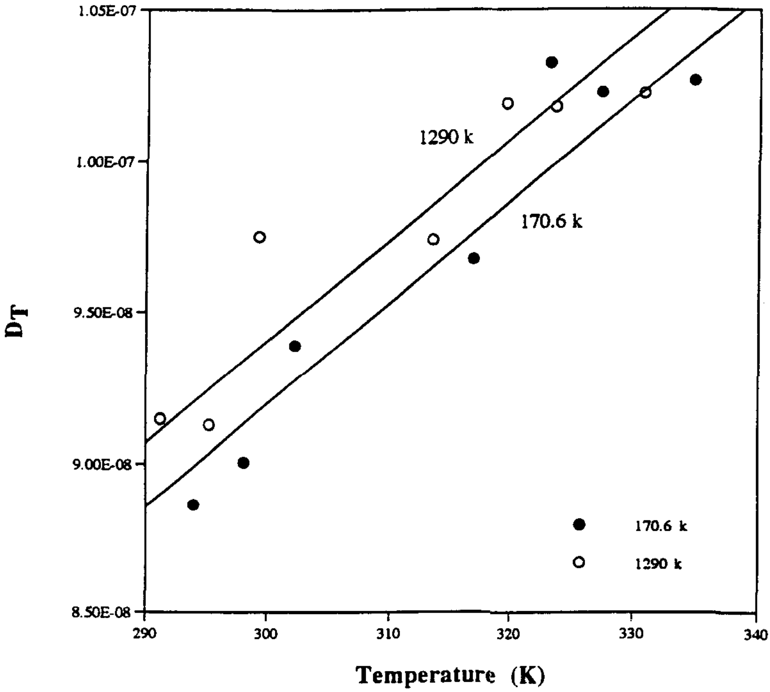


Figure 7. The dependence of D_T on temperature. The values of D_T were calculated at T_{cg} and show some molecular weight dependence. The lines were calculated from values of $\lambda\Delta T$ obtained from curve fitting the data shown in Figure 4.

monitored by an Applied Biosystems Model 757 (Ramsey, N.J.) or a Beckman Instruments Model 153 UV monitor. The ethyl benzene data utilized a Waters 401 Refractive Index detector (Milford, MA). Sample injections were made with a Rheodyne Model 7125 Sampling Valve (Cotati, CA), except for channel 22 which used an Alcott Model 718 autosampler (Norcross, GA).

The mass of sample injected varied from channel to channel. The injected masses in channels 5 and 15 were usually 10 μg or larger for each molecular weight standard in the sample mixture, while channel 20, 21 and 22 used 1 to 2 μg/each standard. Sample concentrations were ~1mg/mL of each standard for channels 5, 15, while channels 20, 21 and 22 used ~0.125 mg/mL.

Table 3

Coefficients for Estimating ν for THF

ΔT (K)	b_0 (x 10^1)	b_1 (x 10^3)	b_2 (x 10^6)	b_3 (x 10^8)
30	-4.235	1.551	-1.50	0.00
40	-5.3403	1.911	-1.805	0.00
50	-6.342	2.279	-2.145	0.00
70	-8.021	2.826	-2.581	0.00

Table 4

Coefficients for Estimating ν for Ethylbenzene

ΔT (K)	b_0	b_1 (x 10^3)	b_2 (x 10^6)	b_3 (x 10^8)
40	-2.255	16.49	-42.43	3.675
52	-1.580	7.660	-10.63	0.00
62	-1.386	6.622	-9.057	0.00
72	-1.280	6.158	-8.427	0.00
83	-1.081	5.141	-6.953	0.00

RESULTS AND DISCUSSION

The effect of T_C on retention is shown in Figure 1a, with two fractograms of polystyrene in THF with a large difference in both ΔT and T_C. The low ΔT (50 K) fractogram with low T_C (290 K) gave almost the same retention as the fractogram with a high ΔT (70 K) and T_C (322 K). At the same T_C, Figure 1b, the expected higher retention for the higher ΔT is obtained. The difference in retention caused by T_C at the same ΔT is illustrated in Figure 1c. The values of λ were calculated directly using Equation 3. The ν values were calculated using viscosity parameters given by Gunderson[6] and thermal conductivity parameters from Martin,[8] and can be very closely approximated over the temperature range studied from the empirical equation:

$$\nu = b_0 + b_1 T_c + b_2 T_c^2 + b_3 T_c^3 \qquad (10)$$

where values of the coefficients are given in Table 3 for THF and Table 4 for ethylbenzene.

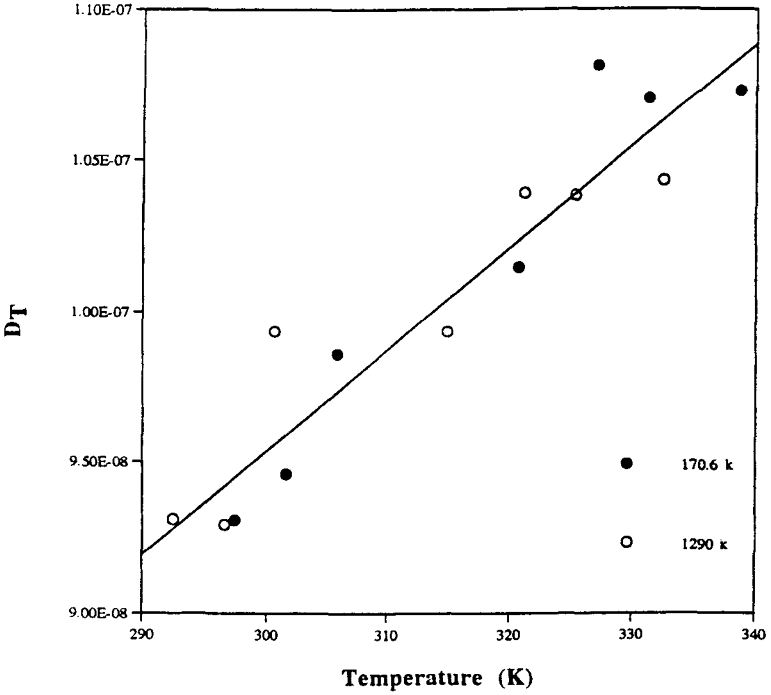


Figure 8. The dependence of D_T on temperature. The values of D_T were calculated at $T_{(xeq)}$ rather than T_{cg}. The lines were calculated from values of $\lambda\Delta T$ obtained from curve fitting the data in Figure 4.

The effect of T_c on the calibration plot is shown in Figure 2. The plots for different T_c values are linear and parallel. They have the same slope, *n*, but exhibit different values for $\log\phi_6$. When the same T_c is used with a range of ΔT values, the plots are essentially identical as illustrated in Figure 3. In the calibration function (Equation (7)), λ is multiplied by ΔT. As ΔT increases, λ decreases in value, with the product being very nearly constant, resulting in a calibration curve which is independent of ΔT.

Examining the effect of T_c on the values of $\lambda\Delta T$ by plotting $\log\lambda\Delta T$ versus $\log T_c/298$ (the division by 298 is in order to place the intercept within the data range) as shown in Figure 4, we obtain a series of plots for data from four channels, 15, 20, 21, and 22, for polystyrene in THF. Remarkably, the plots all exhibit a slope of 3.0 except for 90 k which were obtained on channel

15. The data shown were taken at several ΔT's ranging from 30 to 70 K but still fall on the same curve depending on molecular weight. The values of log $\lambda\Delta T$ obtained from the intercepts of the plots in Figure 4 are shown in Figure 5 as a calibration plot. The slope of this curve is -0.60. The data from channel 15 were obtained several years ago.

Data for polystyrene in ethyl benzene taken over 6 and 15 years ago on channels 15 and 5, respectively, are shown in Figure 6. Again, the value of the slopes is 3.0 for these data. The data for 575 k indicate a higher slope than the line shown with a slope of 3. These data were obtained using a refractive index detector which required larger sample amounts for detection than those used in the THF studies. The two channels are of a much older type where there may have been as much as 5° variation in temperature along the channel due to non-uniformity in the cartridge heaters, unlike channels 20, 21, and 22 which have a variation of only ± 0.5° over the channel length.

Using data for D at 297 K from the literature,[9] and using Equation (9) to calculate a value for η, the value for D at other temperatures may be estimated, assuming that γ has minimal changes over the temperature range being examined. With these values for D and the observed $\lambda\Delta T$ data, D_T can be determined using Equation (2). However, a problem exists for determining the temperature which should be used for calculating D and D_T. Using the classic approach, the temperature at the center of gravity, T_{cg}, would be used, where:

$$T_{cg} = \left\{ \frac{-1 + \left[1 + \lambda \frac{1}{\kappa}\frac{d\kappa}{dT} \Delta T \left(2 + \frac{1}{\kappa}\frac{d\kappa}{dT} \Delta T \right) \right]^{1/2}}{\frac{1}{\kappa}\frac{d\kappa}{dT}} \right\} \qquad (11)$$

When calculations of D and D_T are made at T_{cg} for polystyrene in THF, the results are shown in Figure 7 which indicate a slight molecular weight dependence of D_T. Martin, et al.[5] have suggested that T_{cg} is not the correct temperature to be used in ThFFF because the value of λ will not be constant across the channel due to the temperature gradient. Instead $T(x_{eq})$ should be used which is the temperature at the particular distance, s_{eq}, where the actual value of λ is the λ value calculated in the classical manner. The value of s_{eq} can be obtained from:

$$s_{eq} = 2\lambda - 2.2172(1+2v)\lambda^2 - 5.942(2-v)\lambda^3 \cdot \qquad (12)$$

Assuming the temperature gradient across the channel is linear, $T(x_{eq})$ can then be determined. When these temperatures are used to calculate D and D_T, the D_T values fall on almost the same curve even with a molecular weight difference of a factor of nearly 10, as shown in Figure 8. The change in D_T is 0.35% per degree in the range shown.

Ethyl benzene values for D_T were not calculated because of the lack of good values for D.

A compilation of the cold wall data for polystyrene in THF from channels 15, 20, 21 and 22 is given in the Appendix.

ACKNOWLEDGMENT

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APPENDIX

Summary of Cold Wall Data for Polystyrene in THF

Molecular Weight	ΔT	T_c (K)	R	λ
233000	30	291	0.565	0.137
		301	0.607	0.145
		311	0.651	0.162
		321	0.685	0.177
		331	0.715	0.192
		341	0.745	0.209
400000		291	0.43	0.089
		301	0.473	0.101
		311	0.514	0.112
		321	0.558	0.126
		331	0.587	0.135
		341	0.634	0.153
575000		291	0.36	0.072
		301	0.39	0.079
		311	0.428	0.088

(continued)

APPENDIX (continued)

Summary of Cold Wall Data for Polystyrene in THF

Molecular Weight	ΔT	T_c (K)	R	λ
		321	0.468	0.098
		331	0.49	0.104
		341	0.526	0.114
900000		291	0.265	0.05
		301	0.302	0.058
		311	0.338	0.066
		321	0.365	0.072
		331	0.39	0.078
		341	0.426	0.086
90000	40	293	0.649	0.167
		303	0.706	0.194
		313	0.75	0.221
		323	0.794	0.254
		333	0.823	0.281
233000		293	0.441	0.095
		303	0.485	0.106
		313	0.54	0.123
		323	0.588	0.139
		333	0.627	0.153
400000		293	0.332	0.067
		303	0.369	0.075
		313	0.405	0.084
		323	0.45	0.093
		333	0.49	0.106
575000		293	0.26	0.051
		303	0.288	0.056
		313	0.32	0.063
		323	0.354	0.071
		333	0.384	0.077
900000		293	0.202	0.038
		303	0.221	0.042
		313	0.247	0.047
		323	0.274	0.053
		333	0.298	0.057

APPENDIX (continued)

Summary of Cold Wall Data for Polystyrene in THF

Molecular Weight	ΔT	T_c (K)	R	λ
28500	50	290	0.745	0.237
		294	0.764	0.251
		298	0.772	0.257
		298	0.777	0.262
		309	0.802	0.283
		312	0.815	0.297
		315	0.82	0.301
		318	0.83	0.314
		322	0.832	0.314
		323	0.834	0.317
		329	0.869	0.37
90000		297	0.604	0.151
		307	0.663	0.175
		317	0.716	0.202
		327	0.766	0.234
170600		290	0.371	0.083
		294	0.386	0.086
		298	0.386	0.086
		298	0.398	0.09
		309	0.436	0.1
		312	0.451	0.104
		315	0.452	0.104
		318	0.457	0.105
		322	0.479	0.111
		323	0.479	0.111
		329	0.511	0.121
233000		297	0.382	0.081
		307	0.423	0.091
		317	0.481	0.106
		327	0.528	0.12
400000		297	0.279	0.056
		307	0.309	0.062
		317	0.343	0.07
		327	0.395	0.082
526000		290	0.206	0.043

(continued)

APPENDIX (continued)

Summary of Cold Wall Data for Polystyrene in THF

Molecular Weight	ΔT	T_c (K)	R	λ
		294	0.213	0.045
		298	0.216	0.045
		298	0.224	0.047
		309	0.249	0.052
		312	0.258	0.054
		315	0.26	0.054
		318	0.263	0.055
		322	0.278	0.058
		323	0.276	0.057
		329	0.296	0.062
575000		297	0.22	0.043
		307	0.255	0.05
		317	0.285	0.056
		327	0.319	0.063
900000		297	0.171	0.033
		307	0.192	0.037
		317	0.21	0.04
		327	0.244	0.047
1290000		290	0.121	0.025
		294	0.127	0.026
		298	0.128	0.026
		298	0.136	0.028
		309	0.152	0.031
		312	0.16	0.031
		315	0.159	0.032
		318	0.164	0.032
		322	0.17	0.034
		323	0.167	0.033
		329	0.184	0.037

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[†] Current address: TheraTech, 410 S. Chipeta Way, Salt Lake City, UT 84112.

[‡] Deceased: October 24, 1996.

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