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High Temperature Thermal Field-Flow Fractionation for the Characterization of Polyethylene

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ABSTRACT

A thermal field-flow fractionation device has been constructed in which the cold wall can be held above 100°C. The apparatus is described. Preliminary results are given which illustrate the retention of polyethylene and polypropylene. Details are provided of preliminary experiments intended to determine the molecular weight averages and molecular weight distribution of a National Bureau of Standards polyethylene sample, SRM 1484. The lack of monodisperse, well-characterized calibration standards is considered a major problem. Nonetheless, good agreement is found with published values for number average and weight average molecular weight.

INTRODUCTION

Thermal FFF is that subtechnique of FFF which uses a temperature gradient as the effective field (1-5). The temperature gradient, acting through the phenomenon of thermal diffusion, induces components within a carrier to migrate toward the hot or the cold wall of the system. The thickness of the layer formed at the wall, and the migration rate controlled by this thickness, depends

on the chemical nature and molecular weight of the component and on the chemical nature of the carrier.

Thermal diffusion is a weak effect, especially when its forces are compared to those of electrical origin. However, thermal gradients can be effectively used in FFF by virtue of 1) the general way in which FFF magnifies separation effects, and 2) the possibility of using very high temperature gradients, in some cases approaching 10^4 °C/cm. Thermal FFF is presently the most effective subtechnique for the analytical separation and characterization of synthetic nonpolar polymers.

Initially polystyrene was studied by thermal FFF because of the availability of many well characterized and narrow molecular weight standards (6,7). Other materials that have been studied include asphaltenes and crude oils (8); polyisoprene, polytetrahydrofuran, and polymethylmethacrylate (9). Work involving other polymers has been hindered by the lack of well characterized standards and the necessity of finding an appropriate solvent for each polymer.

This paper reports the applicability of FFF to a more difficult polymer class: high molecular weight polyolefins. These polymers lack favorable solubility characteristics and require minimum temperatures of around 100°C for reasonable solubility levels.

For difficult polymers such as the polyolefins, thermal FFF offers the advantages over size exclusion chromatogaphy (SEC) of less shear degradation of the sample because of the uniform flow and lack of extensional shear. The open FFF channel is less susceptible to clogging by gel formation. Thermal FFF also avoids the problems inherent in some packed columns of swelling and channeling of packing caused by the heating and cooling cycles that occur with operation at elevated temperatures.

This paper involves an extrapolation of previous methodology in order to characterize polyethylene and related polymers. A major difficulty of this study was the modification of a typical apparatus to operate at elevated temperatures where polyethylene

is tractable. Since a significant temperature drop (~25-100°C) must be superimposed on the minimum (cold-wall) temperature of approximately 100°C, the device must operate at temperatures of fairly high magnitude. This paper reports the construction and operation of a high temperature device for this purpose.

Other problems encountered include finding a sufficient number of characterized samples to form a calibration curve and dealing with the considerable polydispersity of the calibration samples.

THEORY

In FFF as in chromatography, the degree of solute retention can be measured by the retention ratio R, which is defined as the elution time (or volume) of a nonretained substance divided by the elution time (or volume) of the solute of interest. Parameter R can also be thought of as the velocity of the solute V divided by the average velocity of the carrier solution $\langle v \rangle$

$$R = V^o/V_r = V/\langle v \rangle \qquad (1)$$

In this equation, V^o is the void volume of the channel or, equivalently, the elution volume of a nonretained peak and V_r is the elution volume of the solute which is retained.

The expression for R in the normal situation of a parabolic flow profile in the channel is

$$R = 6\lambda[\coth(1/2\lambda) - 2\lambda] \qquad (2)$$

where λ is a basic retention parameter related to the strength of coupling of the field and the solute. The nature of λ in thermal FFF will be described shortly.

For highly retained solutes, which migrate with a small R, Equation 2 approaches the limiting form

$$R = 6\lambda \qquad (3)$$

In thermal FFF, the assumption of a parabolic profile is not quite correct. The variation of the temperature across the width of the channel causes the viscosity of the carrier to be nonuniform. Viscosity ordinarily decreases with increasing temperature, and is thus greatest at the cold wall. This affects the flow velocity profile by shifting the maximum velocity from the center to a position somewhat closer to the hot wall (10,11).

If the viscosity η is assumed to depend on temperature T as $\eta = \eta_o \exp(B/T)$, then through various simplifying assumptions we arrive at the following limiting expression for R when R is small

$$R = 6\lambda(1 - \beta/6) \qquad (4)$$

where $\beta = B\ T/T_c^2$ and T_c is the cold wall temperature. Equation 4 replaces Equation 3 by its allowance for viscosity variation.

In order to determine how retention depends on molecular weight, we now examine the λ term. A good approximation for λ in thermal FFF is given by (11)

$$\lambda = [(\alpha/T + \gamma)\ \Delta T]^{-1} \qquad (5)$$

where γ is the coefficient of thermal expansion, T is the absolute temperature, and α is the thermal diffusion factor given by

$$\alpha = D'T/D \qquad (6)$$

in which D' is the thermal diffusion coefficient and D is the ordinary diffusion coefficient. By ignoring the change in thermal conductivity with temperature, we have introduced a small error into Equation 5 (12), but since ΔT is constant for all runs, the percentage error remains constant and drops from consideration.

Combining Equations 5 and 6 and neglecting γ, we get a simple expression for the retention parameter in terms of diffusion coefficient and field strength ΔT

$$\lambda = D/D'\Delta T \tag{7}$$

the diffusion coefficient for dilute polymer solutions varies with weight average molecular weight, M_w, as $1/(M_w)^a$, where $0.5 \leq a \leq 1$ (13). The change in the thermal diffusion coefficient with molecular weight is small and can be assumed to be negligible (11,12, 14). For fixed operating conditions, ΔT and β are constant. By substituting the diffusion coefficient dependancies into Equation 7 and combining all the constant terms into one, we arrive at the dependance of λ on molecular weight

$$\lambda = \text{constant}/M_w^a \tag{8}$$

In the case of high retention, Equation 8 can be substituted into Equation 4 to yield

$$R = 6\lambda(1 - \beta/6) = CM_w^{-a} \tag{9}$$

where C is a constant. This relationship has been well substantiated for polystyrene (11,12) where $0.55 \leq a \leq 0.60$. From Equations 1 and 9 we find that elution volume ($= V^o/R$) increases with increasing molecular weight, a trend opposite to that in size exclusion chromatography.

EXPERIMENTAL

The thermal FFF apparatus used for this work can be divided into two major parts for descriptive purposes: 1) the basic column system consisting of the channel and the heat transfer bars forming the channel walls and 2) the auxiliary equipment required for

temperature control, detection, channel pressurization, and sample injection. While we have used standard equipment for part 1), we have extensively redesigned part 2), the auxiliary equipment, in order to accommodate polymers like polyethylene which require high temperatures in order to get the polymer into solution.

The basic column system used here has been described previously (5,11,15). It was made by clamping two polished chrome plated copper bars together over a thin Mylar spacer. The metal bars form the top and bottom faces of the channel. The top bar has a hole drilled along its longitudinal axis into which heater rods were inserted as a heat source. The bottom bar was internally chambered to accommodate the flow of coolant which acts as a heat sink. The separation channel was formed by cutting out a 2.5 cm by 47 cm area with tapered ends from a 0.025 cm thick Mylar film. The outlet and inlet tubes enter the channel from the hot wall. The void volume of the channel was 2.55 ml.

The ancillary apparatus required a number of major modifications, in part because of the low solubility of the polyethylene. The usual method of regulating the temperature of the cold wall by adjusting the flow rate of tap water was inadequate for the present case in which the cold wall's temperature had to be maintained near 100°C (instead of the usual 20°C) to prevent precipitation of the sample.

A closed coolant circulation system was designed where the liquid to vapor phase transition was used as the heat absorbing mechanism to regulate the temperature of the cold wall. The desired temperature was selected by using a regulating valve to control the pressure inside the cooling system. This resulted in a stable, uniform temperature along the length of the channel. Water was used for this study, but in other studies alternate coolants have been used to obtain different cold wall temperature ranges.

For the present study, the coolant was preheated to 95°C and the circulation rate controlled so that only a small amount of coolant was vaporized. The coolant was recovered by passing it

through a condenser which drained into a reservoir to form a closed loop. A diagram of the system is shown in Figure 1.

For this study, the hot wall temperature was held at 193°C and the cold wall temperature at 107°C for a "field strength" of 86±1°C.

Since the separation channel had to be operated above the boiling point (121°C) of the carrier (tetrachloroethylene) at atmospheric pressure, the channel was pressurized to 15 atmospheres to supress boiling by restricting the flow at the outlet with a metering valve (Nupro Co.). A trap which cooled the carrier solution was placed between the detector and metering valve to precipitate the polymer and avoid clogging of the valve.

A Dupont-Wilks-Miran I IR detector (E.I. duPont Co.) was used in these experiments. A new cell was built to withstand the pressure of the carrier solution. The windows consisted of 25 mm diameter, 3.0 mm thick sapphire discs which were placed on either side of a 0.050 inch (0.127 mm) thick stainless steel disc with a 1/16 by 1/2 inch slot milled into its center. Inlet and outlet tubes were silver soldered into the ends of the slot in the stainless steel disc. This cell unit (consisting of windows, teflon gaskets, and stainless steel disc) was clamped between two teflon pads in a stainless steel cell holder which was built to accommodate two small heater rods and a thermocouple. The detector monitored absorbance at 3.42 μm (2925 cm^{-1}) wavelength.

Samples were injected with a six port sample injection valve (Valco Instrument Co.) fitted with a 20 μl sample loop. This injector valve, as well as the detector cell and all connecting tubing up to the trap before the outlet, was maintained at a temperature between 100 and 110°C by means of electrical heating tapes in order to prevent the precipitation of the samples and the clogging of the system.

Temperatures were measured with copper-constantan thermocouples with an ice bath reference. Temperatures were recorded on the chart using the second channel of the chart recorder.

A Model M-6000A pump (Waters Associates) was used to move the carrier solution at a flow rate of 5.0 ml/hr. A two pen

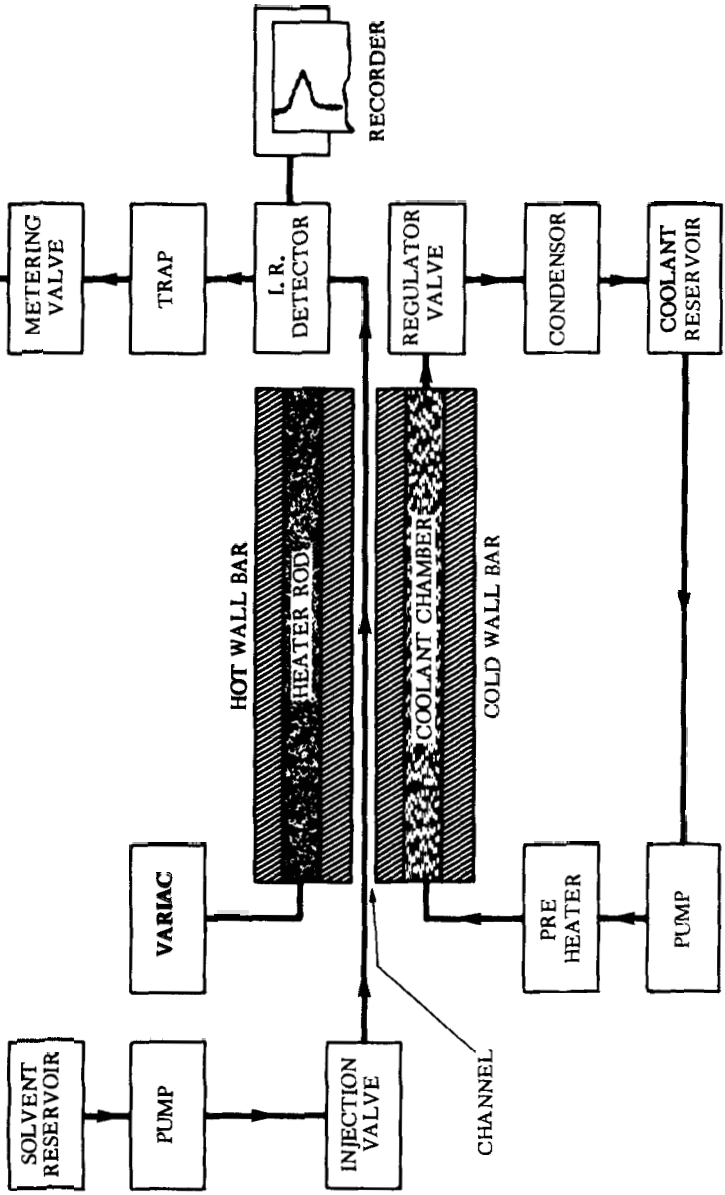

FIGURE 1. Block Diagram of the Thermal FFF Apparatus showing modifications in coolant systems for high "cold wall" temperature operation.

Omniscribe chart recorder (Houston Instruments) was used to record the fractograms and monitor the temperature.

The carrier solution was reagent grade tetrachloroethylene (C_4Cl_4) (MCB) with 100 ppm 3,5-di-tert-butylcatechol (Aldrich) added as an antioxidant. Polymers included two samples of uncharacterized low density polyethylene (Kodak, Aldrich) for setting experimental parameters. The samples used for calibration standards are listed in Table 1 (1-7) along with their number average molecular weights, weight average molecular weights, polydispersities and sources. NBS SRM 1484 high density polyethylene was used to assess the accuracy of the technique. The samples were prepared by adding 0.5% (weight/volume) of the polyethylene to the carrier solution and heating at 90°C for 1 to 2 hours in closed containers.

RESULTS AND DISCUSSION

Preliminary runs with two uncharacterized polyethylene samples (Kodak, Aldrich) were used to prove the applicability of the technique and to determine optimum operating conditions. Figure 2 shows a plot of retention ratio R versus temperature drop ΔT for these two samples. Since the degree of retention was not high but increased as expected with ΔT, it was decided that the best retention and selectivity could be obtained if the experiments were run at the highest possible ΔT value compatible with the polymer and the channel materials. For this purpose we used a hot wall temperature T_h = 193°C and a cold wall temperature T_c = 107°C, yielding $\Delta T = 86 \pm 1$°C. Any higher T_h led to spacer degradation and solder joint failures in the channel and any lower T_c led to insufficient sample dissolution. We note that polymers normally accumulate at the cold wall, reducing their exposure to the high temperature near the hot wall which could lead to excessive degradation.

TABLE 1

Polyethylene Samples used as Calibration Standards in this Study, Including Source, Molecular Weight Data, and Polydispersity.

Sample	Source	M_n	M_w	Polydispersity
1	DuPont	18,300	53,100	2.90
2	DuPont	25,000	89,000	3.56
3	NBS	94,600	119,200	1.26
4	NBS	4,500	5,500	1.22
5	NBS	125,000	158,000	1.26
6	NBS	-	200,000	-
7	Pressure Chem. Co.	20,900	41,600	1.99

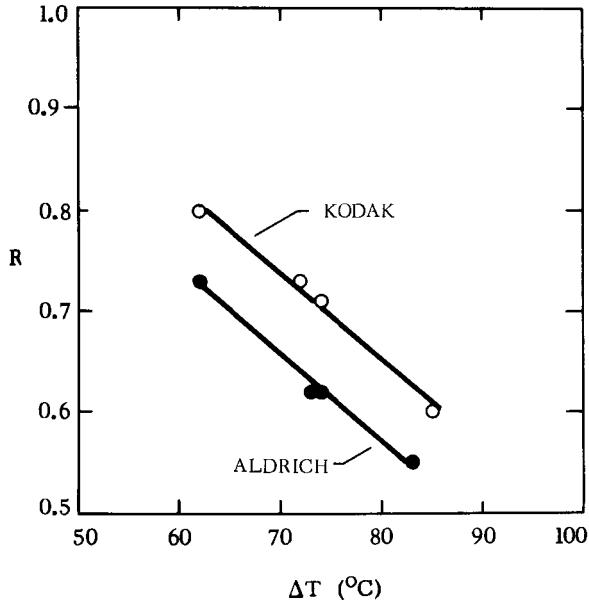

FIGURE 2. Plot of retention ratio R as a function of field strength ΔT for two uncharacterized low density polyethylene samples.

It was observed that after a sample had been heated for 4 to 6 hours prior to injection, its fractogram consisted of a peak whose variance was two to three times greater than the original variance. This was attributed to sample degradation. Thus, when the variance began to get abnormally large, the sample was discarded and a fresh solution prepared.

As part of the preliminary work, two samples of polypropylene (Hercules Pro-Fax 6801 and 6701) were run. These samples were reported to have molecular weights M_w of 780,000 and 635,000, respectively, with rather large polydispersities, M_w/M_n = 7.95 and 9.58, in that order. With a temperature drop ΔT of 77°C and a cold wall temperature of 107°C, both of these samples showed weak but measurable retention, R = 0.72. The fractograms for the two samples were reproducible and distinctive from each other despite nearly identical overall retention. The identical retention values may result from the poor resolution of materials with low retention or from inexact characterization and thus errors in the reported M_w values.

We note that the polypropylene samples do not exhibit retention levels as high as those of polyethylene. Thus, we calculate that the retention of polypropylene of M_w ~700,000 is comparable (adjusting for differences in ΔT) to that of polyethylene having a M_w of only ~50,000.

The next series of experiments consisted of the fractionation of the characterized samples listed in Table 1 in order to obtain a calibration curve. These samples were run without adding a void peak marker (i.e. a nonretained component) to avoid error due to the overlap of the sample peak with the void peak. The void volume was measured separately before each sample injection by injecting a blank containing n-dodecane as a void peak marker.

Figures 3 and 4 show fractograms for sample 1 from Table 1 (M_w = 53,100) and for NBS polyethylene SRM 1484 (M_w = 119,600), respectively. We note that the peak shapes for the two polymer samples are quite different, reflecting different molecular weight distributions. The broadness of the peaks is due to the high

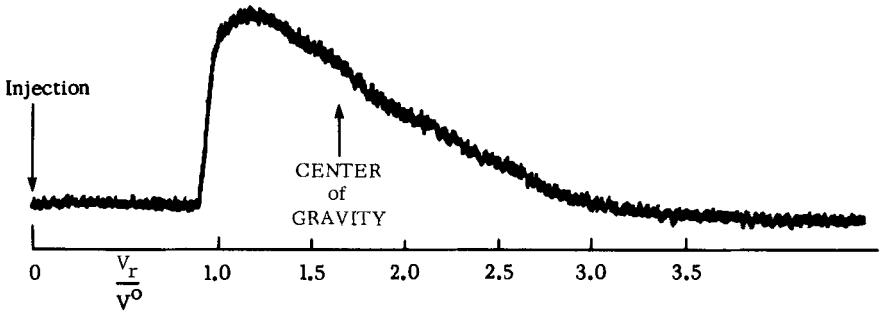

FIGURE 3. Thermal FFF fractogram for polyethylene sample number 1 from Table 1 (M_w = 53,100). Experimental conditions: flow rate = 5.0 ml/hr, cold wall temperature = 107°C, hot wall temperature = 193°C, void volume V^o = 2.55 ml.

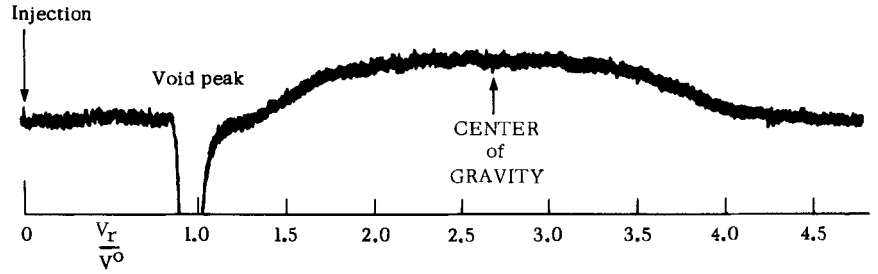

FIGURE 4. Thermal FFF fractogram for NBS polyethylene SRM 1484 (M_w = 119,600). Experimental conditions are the same as those for Figure 3.

selectivity of FFF compared to SEC (16,17) and the attendant ability of FFF to fractionate the individual components over a considerable elution volume range.

Since the relevant viscosity and diffusion parameters are unknown for the present system of solvent and polymer, no attempt has been made to construct a calibration curve from theory. Instead, we have relied on empirical calibration using polymer samples from various sources as shown in Table 1. Unfortunately, these have been characterized by different methods of varying accuracy. All samples except numbers 1 and 2 are polymer frac-

tions. Furthermore, the samples are all rather polydisperse with a polydispersity (M_w/M_n) ranging from 1.22 to 3.56.

In order to construct the calibration curve,the center of gravity of each peak was found; this value was used to calculate the retention ratio R. For a polydisperse sample producing a broad peak, particularly with some material eluting near the void peak, one would not expect the center of gravity of the peak to occur at exactly the position representing the true weight average molecular weight because elution volume is not linear in molecular weight. However, the center of gravity was choosen as a better approximation than the peak center or peak maximum. It is doubtful if more accurate procedures are presently justified considering the uneven quality of the standard materials.

Calculations were made to determine whether Equations 8 and 9 would serve as the basis for a calibration curve. Figure 5 shows two plots using log-log coordinates, the lower of which would be

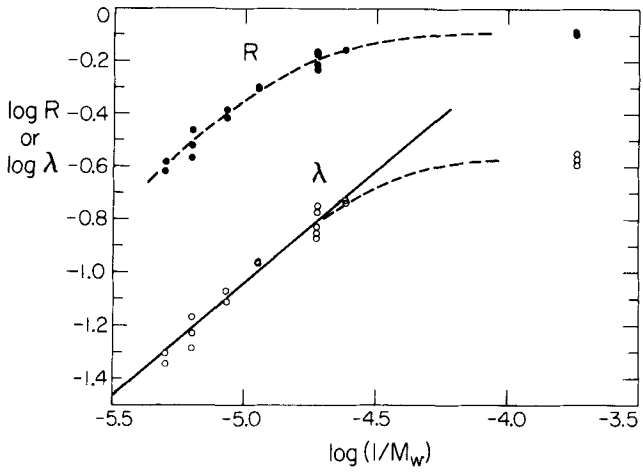

FIGURE 5. Plots of log R (solid circles) and log λ (open circles) as functions of log ($1/M_w$). λThe straight line is the least square fit of the log λ data for the six highest molecular weight samples. The samples used for this plot are described in Table 1. Each point represents one experimental run.

linear if Equation 8 were applicable over the entire experimental range and the upper of which would be linear if equation 9 were valid.

The λ value for each point of the lower plot was found by iteration using a temperature corrected R versus λ expression appearing as Equation 17 of an earlier paper (11). The B values needed for the dependence of viscosity on temperature were obtained from Reid, Prausnitz, and Sherwood (18).

It is observed that data for the six highest molecular weight samples fall on a fairly straight line in the log λ - log M_w plot. The slope of 0.85 indicates that the best value of $\underline{a}$ in Equation 8 equals 0.85, a value considerably higher than those in the 0.55-0.60 range characteristic of polystyrene.

The low molecular weight sample does not appear to follow the trend established by the other samples. However, when the probable error is taken into account for this sample, the discrepancy is understandable. The error for this low molecular weight material has three major contributions. First an error of, say, 10% in R in this low retention region produces an error in λ of 50%, while the relative error in λ for the more retained samples is about the same as the error in R. Second, the uncertainties in R are themselves larger for poorly retained samples, in this case approximately 10% as opposed to about 3% or less for the samples of higher retention. This error is due to the nature of the numerical integration procedure used to determine R.

The third source of uncertainty lies in the assumption that the center of gravity of the peak corresponds to the weight average molecular weight. This assumption works very poorly in the low molecular weight (low retention) region of the calibration curve.

The plot of log R versus log $(1/M_w)$ is a curved line with the low molecular weight sample once again abnormally low. The considerable curvature in the log R - log $(1/M_w)$ plot is not altogether unexpected since we are working with fractions of only moderate retention (R = 0.25 - 0.8) whereas Equation 9 is based on the lim-

iting form for high retention. Since this line is not straight, we conclude that Equation 9 is a poor approximation, especially in the low molecular weight region, and should not be used in the present case to form a calibration curve. Thus, we are left to rely on an empirical calibration curve. The retention data shown on a linear plot (see Figure 6) fit well to a quadratic equation of the form

$$M_w = 318{,}600 - 592{,}900\ R + 264{,}500\ R^2 \qquad (10)$$

with a standard error of 9,200.

The major contributions to scatter in the individual data points in Figure 6 are temperature fluctuations and errors in the measurement of retention volumes. A fluctuation of $\pm 1^{\circ}C$ gives rise to a change in R of about ±0.01. The measurement of retention and void volumes and the calculational procedure used result normally in an error in R of ±3%. For a typical sample with a molecular weight of ~120,000 and a retention ratio of 0.4, the above effects would give an estimated error of ±8,500 in molecular weight.

National Bureau of Standards polyethylene SRM 1484 was characterized to test the accuracy of the calibration curve given by Equation 10 and shown in Figure 6, and to test the efficacy of the FFF method. The weight average molecular weight of SRM 1484 was calculated using the formula

$$M_w = \frac{\Sigma M_i h_i}{\Sigma h_i} \qquad (11)$$

and the number average molecular weight was calculated by using

$$M_n = \frac{\Sigma h_i}{\Sigma h_i / M_i} \qquad (12)$$

where h_i is the detector response at each point and M_i is the molecular weight from the calibration curve at that point. The results of two runs, together with the NBS values, appear in Table

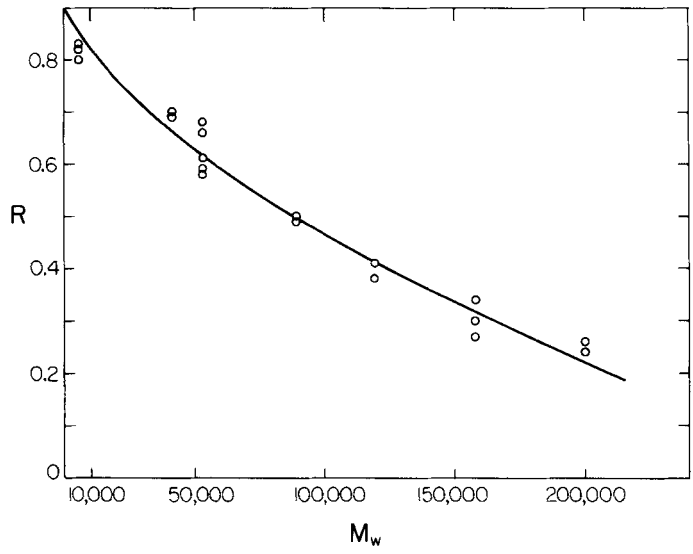

FIGURE 6. Plot of retention ratio R as a function of weight average molecular weight M_w of calibration standards (Table 1). Each point represents one run. The solid line is the calibration curve, Equation 10, determined by the method of least squares.

TABLE 2

Weight Average and Number Average Molecular Weights for National Bureau of Standards SRM 1484 obtained in Two Thermal FFF Runs in Comparison to Values Reported by NBS.

Method	M_n	M_w
FFF (1)	106,000	122,000
FFF (2)	110,000	127,000
NBS	100,500	119,600

2. The discrepancies with NBS values of between 2 and 10% lie within the range expected considering the questionable calibration standards and some experimental and calculational error. The data from the first run listed in Table 2 and shown in Figure 4 were also used to determine a molecular weight distribution. This result is shown in Figure 7.

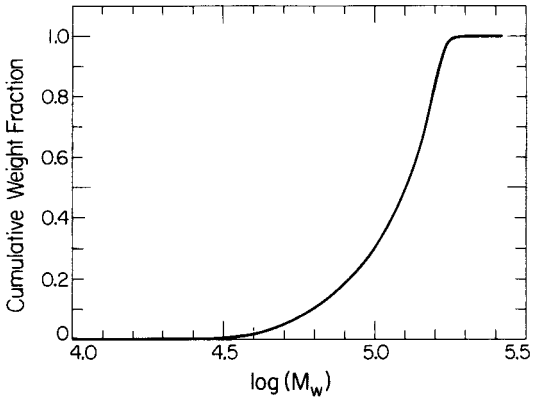

FIGURE 7. The cumulative molecular weight distribution curve for NBS polyethylene sample SRM 1484 determined from the fractogram shown in Figure 4. The experimental results for this run were M_w = 122,000 and M_n = 106,000. The NBS values are M_w = 119,600 and M_n = 100,500.

CONCLUSIONS

This study shows that polyethylene, and to a lesser degree polypropylene, are subject to retention, fractionation, and characterization in thermal FFF equipment modified for high temperature use. Retention levels (especially for polypropylene) are considerably below those for most other polymers when compared at the same levels of molecular weight and temperature drop. It is unclear whether this situation would improve with other carrier liquids. However, since retention (and thus resolution) increases with molecular weight, and since the most difficult characteriza-

tion problems occur for high molecular weight polyolefins, it is likely that thermal FFF could be quickly adapted to practical use in high molecular weight polyolefin analysis.

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