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Part VI

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EVALUATION OF MOLECULAR WEIGHT FROM EQUILIBRIUM SEDIMENTATION

PART VI. EXPERIMENTAL VERIFICATION OF PREVIOUSLY PROPOSED REGULARIZATION-LINEAR PROGRAMMING TECHNIQUE WITH APPLICATION TO PBI

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task 734203, "Fundamental Principles Determining the Behavior of Macromolecules," with Dr. M. T. Gehatia (AFML/LNP) Project Scientist. The work was administered by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

The report covers research conducted from December 1970 to May 1971, and was submitted by the authors in May 1971.

This technical report has been reviewed and is approved.

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ABSTRACT

The relationships between the molecular weight distribution (MWD) of polymer in solution and concentrations (or concentration gradients) measured under conditions of ultracentrifugal equilibrium sedimentation can be expressed by the theory-oriented Fujita Equations. These equations, however, frequently constitute an "Improperly Posed Problem" in the Hadamard sense and, therefore, many attempts to infer MWD directly have failed by giving rise to unstable and unreliable solutions.

To combat this problem, new computation-oriented expressions have been developed in the Air Force Materials Laboratory. The new proposed method makes possible the MWD determination of a polymer from a single equilibrium sedimentation experiment. The authors have presented theoretical proof of the validity of this technique in a previous report, and here supporting experimental verification is provided. This was accomplished by investigating narrow linear polystyrene fractions to determine the MWD, and then by investigating MWD of a new sample created by combining these fractions. The results obtained by applying the newly developed method was in very good agreement with the MWD values known a priori. Thus, the theoretical as well as the experimental investigation successfully demonstrate the reliability of MWD determination by applying the new method.

This technique was then applied to data obtained for PBI in DMAC. The results show that an unusually large part of this polymer is of very low molecular weight. Follow-up to determine what effect this low molecular weight will have upon the use properties of PBI is planned.

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SECTION I

INTRODUCTION

In our previous works (References 1 through 4) a method was developed which makes it possible to determine a molecular weight distribution (MWD) from equilibrium sedimentation. Fujita developed formulas which express the MWD in the form of a function f(m) in the following way:

$$c(\xi)/c_o = \int_0^{m_{max}} \left[\frac{\lambda m e^{-\lambda m \xi}}{1-e^{-\lambda m}}\right] f(m)\, dm, \qquad (1)$$

or

$$-\frac{1}{c_o}\frac{dc(\xi)}{d\xi} = \int_0^{m_{max}} \left[\frac{\lambda^2 m^2 e^{-\lambda m \xi}}{1-e^{-\lambda m}}\right] f(m)\, dm \qquad (2)$$

where

m = the molecular weight

λ = a constant determined from the experiment

ξ $=(r_b^2 - r^2)/(r_b^2 - r_a^2)$

r = distance from the center of rotation

r_a = value of r at the meniscus

r_b = value of r at the bottom

c = concentration at ξ

c_0 = initial concentration

Equations 1 and 2 are special cases of Fredholm Integral Equations of the First Kind:

$$u(\xi) = \int_0^{m_{max}} K(\xi, m) f(m) dm. \qquad (3)$$

It has been shown that Fredholm Integral Equations of the First Kind frequently are Improperly Posed Problems (IPP) in the Hadamard sense (References 5 and 6). Also the Fujita Equations are IPPs and their inverse operations are unstable because to very small deviations of $u(\xi)$ may correspond uncontrollably large changes in f(m). Therefore, any direct approach to evaluate f(m) as an inverse operation of Equations 1 or 2 may lead to erratically oscillating curves. Such a trial has been done in our previous reports (References 7 and 8). A function f(m) has been arbitrarily assumed. By applying standard experimental conditions the functions $u(\xi)$ and $K(\xi,m)$ have been computed. Using these functions a distribution function $\overline{f}(m)$ has been calculated from an inverse operation. The so obtained $\overline{f}(m)$ fluctuated erratically and had nothing in common with the original f(m) function.

It has been theoretically proved that an approximate determination of MWD is possible by applying Tikhonov's regularization method (References 1 and 3). In such a case the Fredholm Integral Equation (Fujita Equations) will be modified in the following way:

$$b(m) = \int_0^{m_{max}} F(m, x) f(x) dx - A . \qquad (4)$$

Here

$$b(m) = \int_0^1 K(\xi, m)\, u(\xi)\, d\xi \tag{5}$$

$$F(m, x) = \int_0^1 K(\xi, m)\, K(\xi, x)\, d\xi \tag{6}$$

and

$$A = \alpha_2 \frac{d^4 f(m)}{dm^4} - \alpha_3 \frac{d^6 f(m)}{dm^6} \tag{7}$$

where α_2 and α_3 are numerical parameters. These parameters (sometimes only one of them) are chosen with the aid of a high speed digital computer in such a way that a $\overline{u}(\xi)$ function calculated from the determined $\overline{f}(m)$ function will be as close as possible to the original $u(\xi)$ function, or that the norm

$$\left[\int_0^1 \left\{\overline{u}(\xi) - u(\xi)\right\}^2 d\xi\right]^{\frac{1}{2}} = \| \overline{u}(\xi) - u(\xi) \| \tag{8}$$

is a minimum.

The technique of approximation replaces the integration in Equation 4 by a summation of discrete $\left\{f_k\right\}$ values. For different $\left\{m_n\right\}$ there will be a set of linear equations. The inverse matrix of this set will determine all values of a $\left\{f_k\right\}$ vector. The term A acts as a damping factor which reduces the oscillations, i.e., stabilizes the inverse operation.

With the help of Equation 4 very good results were obtained in case of an arbitrarily assumed symmetrical unimodal and symmetrical bimodal f(m). In case of an assymetrical bimodal and symmetrical trimodal distribution good results have been obtained after incorporating linear programing into Equation 4 (References 2 and 4).

As mentioned above, the proof of this method has been carried out only in a theoretical manner by the arbitrary choice of the function f(m). No experimental proof had been given, and therefore this method had not yet been fully checked under real experimental conditions. Therefore, the objective of the present work is to close this gap by creating an "a priori" known distribution and by determining it with the aid of Equation 4. This proof has been done by investigating linear polystyrene in cyclohexane at 35.0°C (the Ⓗ temperature).

SECTION II

EXPERIMENTAL

Fractionated linear polystyrene samples were obtained from Dr. G. E. Berry of the Mellon Institute, where the weight average molecular weight m_w of each fraction was estimated by applying viscosity technique.

Three of these fractions were individually investigated in the Air Force Materials Laboratory (AFML) by applying equilibrium ultracentrifugation and velocity sedimentation. Then these fractions were combined, and their relative weight concentrations were determined. The combined sample which will henceforth be called the "Polydisperse" (Sample P) was subjected to equilibrium centrifugation.

All samples were dissolved in spectral grade cyclohexane and measured at 35°C. The investigated fractions are shown in Table I.

TABLE I

THE INVESTIGATED FRACTIONS

Sample	Mellon Institute No.	m_w by Mellon Institute	Concentration (g Polymer (100g Solution)
A	1	5,270	0.49634
B	6	29,100	0.43441
C	16	114,200	0.52804
P	Combined 1, 6, and 16		0.44920

TABLE II

PREPARATION OF THE SAMPLE P (POLYDISPERSE)

Sample	Weight (gram)	Relative % Concentration
A	0.00665	56.9
B	0.00399	34.1
C	0.00108	9.0
Total	0.01172	100.0

TABLE III

THE CONDUCTED EXPERIMENTS

Sample	Velocity Sedimentation	Equilibrium Sedimentation		
	Angular Velocity (rpm)	Angular Velocity (rpm)	Duration of Experiment (hr)	Starting Angular Velocity (rpm)
A	40,000	16,000	48	16,000
B	40,000	10,000	74	10,000
C	40,000	4,800	72	5,600
P	———	10,000	104	10,000

In all cases the Schlieren angle was 65° and the length of the cells was 12 mm. The velocity experiments, however, were performed in a double sector Kel-F capillary synthetic boundary cell, and each equilibrium run was carried out using two separate cells, one with the solvent and one with solution. Each one was an aluminum, single sector, 4° cell.

The photographic plates obtained from each equilibrium experiment were processed and evaluated before the experiment was terminated. Only after such an equilibrium plot was reproducible, was the experiment terminated.

SECTION III

PROCESSING VELOCITY DATA

1. SEDIMENTATION CONSTANT (s)

The sedimentation constant for each sample has been determined by applying the Svedberg formula (Reference 9)

$$\log\left(r_{max}\right) = \text{const} + 0.4343\omega^2 s\, t_{exp} \tag{9}$$

Here ω is the angular velocity of the rotor, r_{max} is the radial distance of the moving boundary, and t_{exp} is an "experimental time" which is counted from any arbitrary $t_o = 0$.

From the plot of log (r_{max}) vs t_{exp} the sedimentation constant has been determined.

2. DIFFUSION CONSTANT (D)

The diffusion constant was determined from the highest $(\partial c/\partial r)$ ordinate, measured at different times by applying the following relationship (Reference 10)

$$\left(\frac{\partial c}{\partial r}\right)_{max} = H = \left(c_o\, e^{-2\beta t}\right) \Big/ \sqrt{4\pi D\alpha t} \tag{10}$$

where

$$\beta = s\omega^2 \text{ and } \alpha = \frac{1-e^{2\beta t}}{2\beta t} \text{ and D is the diffusion constant.}$$

Since

$$\alpha = 1 + \beta t + \frac{2}{3}\beta^2 t^2 \approx e^{\beta t} \tag{11}$$

one can derive the following approximate expression:

$$H^2 \approx \frac{c_o^2}{4\pi Dt}\, e^{-5\beta t} \tag{12}$$

Therefore,

$$\left(\frac{c_o}{H}\right)^2 \approx 4\pi Dt + \cdots \tag{13}$$

and

$$\left(\frac{H}{c_o}\right)^2 = \frac{\theta}{4\pi D} + \cdots, \quad \theta = \frac{e^{-5\beta t}}{t} \tag{14}$$

Equation 13 is correct if $t \to 0$. Therefore, by plotting the quantity $\left(\frac{C_o}{H}\right)^2$ appearing in Equation 13 vs t, one can obtain the slope $4\pi D$ for small t values. This method is not adequate to determine D. It can be used to find Δt, however, and transform the experimental time, t_{exp}, into the "true" time, t. Now with the aid of this true t the function $\theta = \frac{e^{-5\beta t}}{t}$ can be evaluated. The plot $\left(\frac{H}{C_o}\right)^2$ vs θ makes it possible to determine D from Equation 14.

3. DETERMINATION OF EXPERIMENTAL PARAMETERS

The ordinate Y measured on the photographic plates is related to the concentration gradient $\left(\frac{\partial c}{\partial r}\right)$ in the following way:

$$\frac{\partial c}{\partial r} = \frac{dc}{dn}\left(\frac{1}{a}\right) f g \tan(\phi)\, Y \tag{15}$$

where

a = the length of the cell

$\frac{dc}{dn}$ = the optical refractive index increment

ϕ = the Schlieren angle

f = the overall magnification factor equal in all directions

g = the additional optical magnification factor caused by the cylindrical lens and only in the direction of the gradient

Since in all experiments the same ϕ, $\frac{dc}{dn}$, a and g were applied, one can define the following constant:

$$G = \frac{g}{a} \frac{dc}{dn} \tan \phi \qquad (16)$$

and

$$\frac{\partial c}{\partial r} = f\,G\,Y \qquad (17)$$

Areas of several curves obtained from the same experiment were measured and denoted as A. Then an average A value was evaluated from several individual A_i values.

Such an area is proportional to the initial concentration c_o.

$$c_o = f^2\,G\,A \qquad (18)$$

From Equation 18 one can determine the constant G.

$$G = c_o / f^2 A \qquad (19)$$

Finally from Equations 17 and 19

$$\frac{\partial c}{\partial r} = \frac{f c_o}{f^2 A}\,Y \qquad (20)$$

or

$$\frac{\partial c}{\partial r} = F\,Y \qquad (21)$$

where

$$F = c_o/fA \tag{22}$$

The determination of the constant, f, is a routine matter for the ultracentrifugation technique. By applying the Svedberg Equation (References 11 and 12) one can determine the molecular weight

$$m = \left(\frac{RT}{1 - V\rho}\right)\left(\frac{s}{D}\right) \tag{23}$$

Here, m is the molecular weight, R is the gas constant, T is the temperature in °K, and $(1-V\rho)$ is the buoyancy factor.

SECTION IV

PROCESSING EQUILIBRIUM SEDIMENTATION DATA

1. STANDARD METHOD FOR HOMOGENEOUS FRACTIONS

The following formula was derived from Equation 2:

$$\frac{-dc(\xi)}{d\xi} = \frac{\lambda^2 m^2}{1 - e^{-\lambda m}} c_o e^{-\lambda m \xi} \tag{24}$$

or

$$\log\left(\frac{-dc(\xi)}{d\xi}\right) = \text{const} - 0.4343\lambda m\xi \tag{25}$$

Therefore, the plot $\log\left(\frac{dc(\xi)}{d\xi}\right)$ vs ξ leads to the determination of the molecular weight, m.

Since

$$\lambda = \frac{(1 - V\rho)\,\omega^2\,(r_b^2 - r_a^2)}{2RT} \tag{26}$$

Equation 25 can be modified:

$$\log\left(\frac{dc}{dr^2}\right) = \text{const} + (0.4343)\left(\frac{\omega^2}{2}\right)\frac{s}{D}\,r^2 \tag{27}$$

Here, the plot $\log\left(\frac{dc}{dr^2}\right)$ vs r^2 leads to the determination of s/D and therefore to the determination of m.

2. REGULARIZATION METHOD FOR MWD DETERMINATION

Finally all equilibrium experiments (Samples A, B, C, and P) were also evaluated with the aid of the newly derived Computational Equation for MWD Determination, Equation 4, incorporated into linear programing.

SECTION V

RESULTS

The results of all these experiments are presented according to the following grouping. First, all the results from the experiments associated with Sample A are presented. These results include the sedimentation constant, s, the diffusion constant, D, the weight average molecular weight obtained from the velocity experiment, the weight average molecular weight obtained from the equilibrium experiment, and finally the MWD using a fine molecular weight mesh so as to emphasize the full capabilities of the regularization-linear programing method. Second, the results for Sample B, third, the results for Sample C, and fourth, the results for Sample P are presented.

1. SAMPLE A

Using Equation 9, the sedimentation constant, s, is 1.33 sved. Upon using Equation 14 the diffusion constant is $D = 1.75 \times 10^{-6}$. As an auxiliary measurement, pycnometric data for polystyrene at 35°C yielded

$$\lim_{c \to 0} (1-V\rho) = 0.31.$$

This value was used for all subsequent evaluations. Applying Equation 14 with $RT/(1-V\rho) = 8.286 \times 10^{10}$ one obtains $m_w = 6300$ from the velocity data. The velocity data associated with this sample is given in Table IV. The equilibrium sedimentation data (see Table V) when evaluated using Equation 27 resulted in $m_w = 5600$. In addition this data was used as input for the regularization-linear programing computer program to determine the MWD. For $0 \leq m \leq 100{,}000$ the MWD for Sample A is given in Figure 1 with $\int f(m)dm = 0.569$.

2. SAMPLE B

Following the same procedure as that given above, s = 2.73 sved, $D = 5.50 \times 10^{-7}$ (for data see Table VI), m_w velocity = 41,000, m_w equilibrium = 36,700 (for data see Table VII) and the MWD with $15{,}000 \leq m \leq 100{,}000$ is given in Figure 2 with $\int f(m)dm = 0.341$.

3. SAMPLE C

Again following the procedure outlined for Sample A, s = 4.97 sved, $D = 3.16 \times 10^{-7}$ (for data see Table VIII), m_w velocity = 130,700, m_w equilibrium = 146,500 (for data see Table IX), and the MWD with $100{,}000 \leq m \leq 180{,}000$ is given in Figure 3 with $\int f(m)dm = 0.09$.

For comparison, the molecular weights of the above three samples determined by various methods are given in Table X.

4. SAMPLE P

This was the Polydisperse sample, the prepared "known" distribution of molecular weights. The purpose in choosing this particular distribution will become apparent when we discuss the MWD obtained for PBI in DMAC (see Section VI). This sample is a composite of Samples A, B, and C. The relative concentration for each sample is A (56.9%), B (34.1%), and C (9.0%). Because of these factors, the MWD for the previous samples were not normalized to unity. To span the entire molecular weight range $0 \leq m \leq 180{,}000$ and still keep a 41-point mesh (the computer program dimension statements prevented more points) the molecular weight interval, Δm, had to be increased. Then, to justifiably compare Samples A, B, C and P all four were evaluated with comparable molecular weight intervals. Naturally, as one would expect, the use of larger intervals, Δm resulted in more smoothening, i.e., less structure. The results of these computations are shown in Figure 4. Table XI contains the information for Sample P while Table XII presents the results for Samples A, B, and C. In Figure 4, $\int f(m)dm = 1$ for Sample P, and appropriately 0.569, 0.341, 0.09 for Samples A, B, and C, respectively.

SECTION VI

APPLICATION OF THE NEW METHOD FOR MWD DETERMINATION OF PBI

Poly-(5,5'bibenzimidazole 2,2'diyl,1,3-phenylene) was synthesized by Celenese Corp, Summit, New Jersey, in a melt reaction between diamenobenzidine (DAB) and the diphenyl ester of isophtalic acid. This sample is designated PBI-M. This PBI-M was purified as suggested by T. E. Helminiak (Reference 13) and dried in a vacuum oven at 120°C and 0.01 Torr (C.L. Benner, Reference 14). This sample is designated PBI-MPD (PBI-M purified and dried). Since the solute and the solvent are very hygroscopic , the solutions were stored in sealed containers under a blanket of nitrogen. If transferred they were continuously flushed with nitrogen.

PBI-MPD in DMAC solutions were investigated with the aid of a Spinco Analytical Ultracentrifuge Model E. Experiments were performed at 40° C and consisted of velocity (synthetic boundary) and equilibrium sedimentation types. Necessary auxiliary measurements were also made at 40° C. The data used for the present PBI computation (regularization-linear programing method) was the same as presented in Reference 7, labeled "experimental." The result of this evaluation can be seen in Figure 5 with the numerical tabulations given in Table XIII. Since this curve (Figure 5) was obtained before the artificial MWD (Sample P, Figure 4) was created, it should be immediately obvious that the research with polystyrene was initiated to substantiate the regularization-linear programing method which the authors have recently proposed (References 2 and 4).

SECTION VII

CONCLUSIONS

The importance of this presentation is threefold.

1. Three polystyrene fractions, which were expected to be pure and narrow, were investigated. Well known, well established experimental methods were applied to determine the molecular weight average of each fraction. By implementing such a procedure, the degree of confidence in the experimental techniques was established. The two experimental methods used were performed with the aid of an analytical ultracentrifuge. One method is called the velocity (or synthetic boundary) and the other sedimentation equilibrium. Even though the same instrument was used for each method, the theoretical basis for each is entirely different. After excellent comparison of the two methods, a polydisperse molecular weight distribution was constructed with these same fractions. The same experimental precautions used for the individual fractions, were now applied to the Polydisperse sample during a sedimentation equilibrium experiment.

2. Within the past year or two AFML has developed a mathematical procedure (References 1 through 4) for inferring the molecular weight distribution of a polymer in solution, given data obtained from a sedimentation equilibrium experiment at a single angular speed. Prior to this time a feasible solution to the mathematically improperly posed problem of inferring a molecular weight distribution from sedimentation equilibrium data had not been achieved. When the method of regularization was initially applied to this problem, all initial molecular weight

distributions which were investigated had been generated by use of a high speed digital computer, that is, numerical values analogous to experimental data were theoretically generated. In this report the mathematical procedure has been subjected to an actual experimental data test for the first time. To establish the utility of this mathematical procedure the molecular weight distributions (not just molecular weight average) for each fraction investigated were determined. Then the molecular weight distribution for the Polydisperse sample was determined. The fraction distributions were superimposed on the same graph as that of the Polydisperse sample (Figure 4). Naturally, the areas of each fraction were adjusted to the percent weight concentration in the Polydisperse sample. The two distributions, when compared in this manner, agreed extremely well.

The reliability of the mathematics used in inferring a distribution has now been established. In addition to vitiating the requirement of fractionating a polymer sample to determine its molecular weight distribution, the now available molecular weight distribution enables one to easily calculate the various molecular weight averages m_n, m_w. m_z, m_{z+1}, etc. The usefulness of these averages is discussed in various textbooks (References 15 through 19). Previously, experimental determination of molecular weight gave only an average value. These averages could then be related to features of the distribution curve. For example, some methods in effect count the number of molecules in a known mass of material. Through knowledge of Avogadro's number this information leads to the number average molecular weight (m_n) of the sample. For the distribution of molecular weights of typical polymers the number average lies near the peak of the curve or the most probable molecular weight. In other experiments the weight average molecular weight (m_w) results. Here the heavy molecules are favored in the averaging process. Finally the ratio m_w/m_n would be a measure of the polydispersity of the molecular weight distribution.

Another benefit in knowing the molecular weight distribution is evidenced in determining a viscosity average molecular weight. This viscosity average is quite often wrongly replaced by the weight average molecular weight, thus making the results from viscosity measurements less precise.

3. The molecular weight distribution for PBI-MPD (see Section VI and Figure 5) has been determined. Various moments such as m_n, m_w, m_z, m_{z+1} and their ratios have been computed. These results are presented in Table XIV. The major concern now is the reliability of a material such as PBI-MPD (Reference 2). Since the method (experimental and mathematical) has been proved, the next step is to obtain molecular weight distribution of PBI being used in applications in an attempt to determine whether or not a relationship between MPD and the reliability of the polymer material under use conditions can be elucidated.

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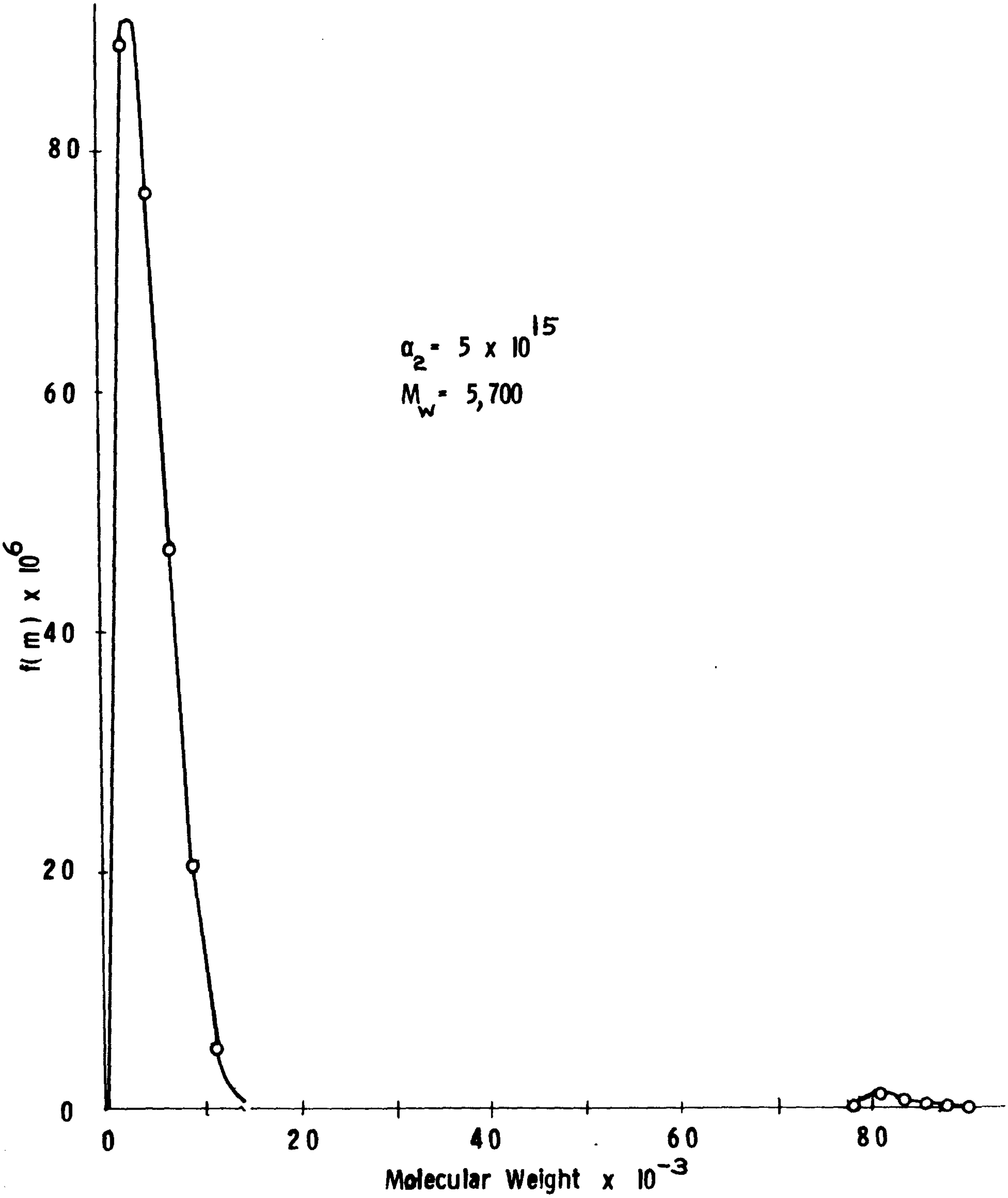

Figure 1. Molecular Weight Distribution for Sample A Using $0 \leq m \leq 100{,}000$, and $\Delta m = 2381$; $\int f(m)\,dm = 0.569$

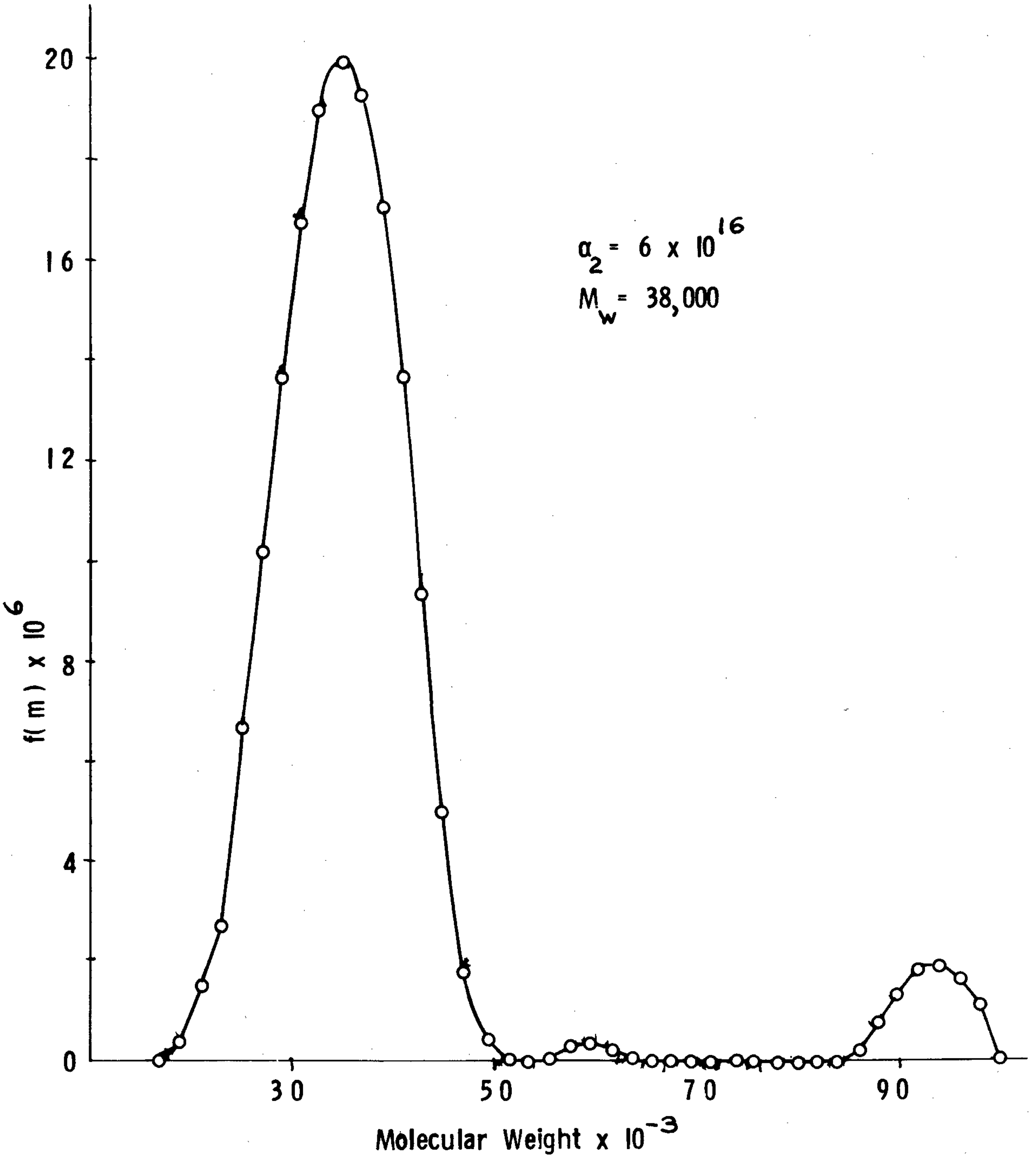

Figure 2. Molecular Weight Distribution for Sample B Using $15{,}000 \leq m \leq 100{,}000$, and $\Delta m = 2024$; $\int f(m)\,dm = 0.341$

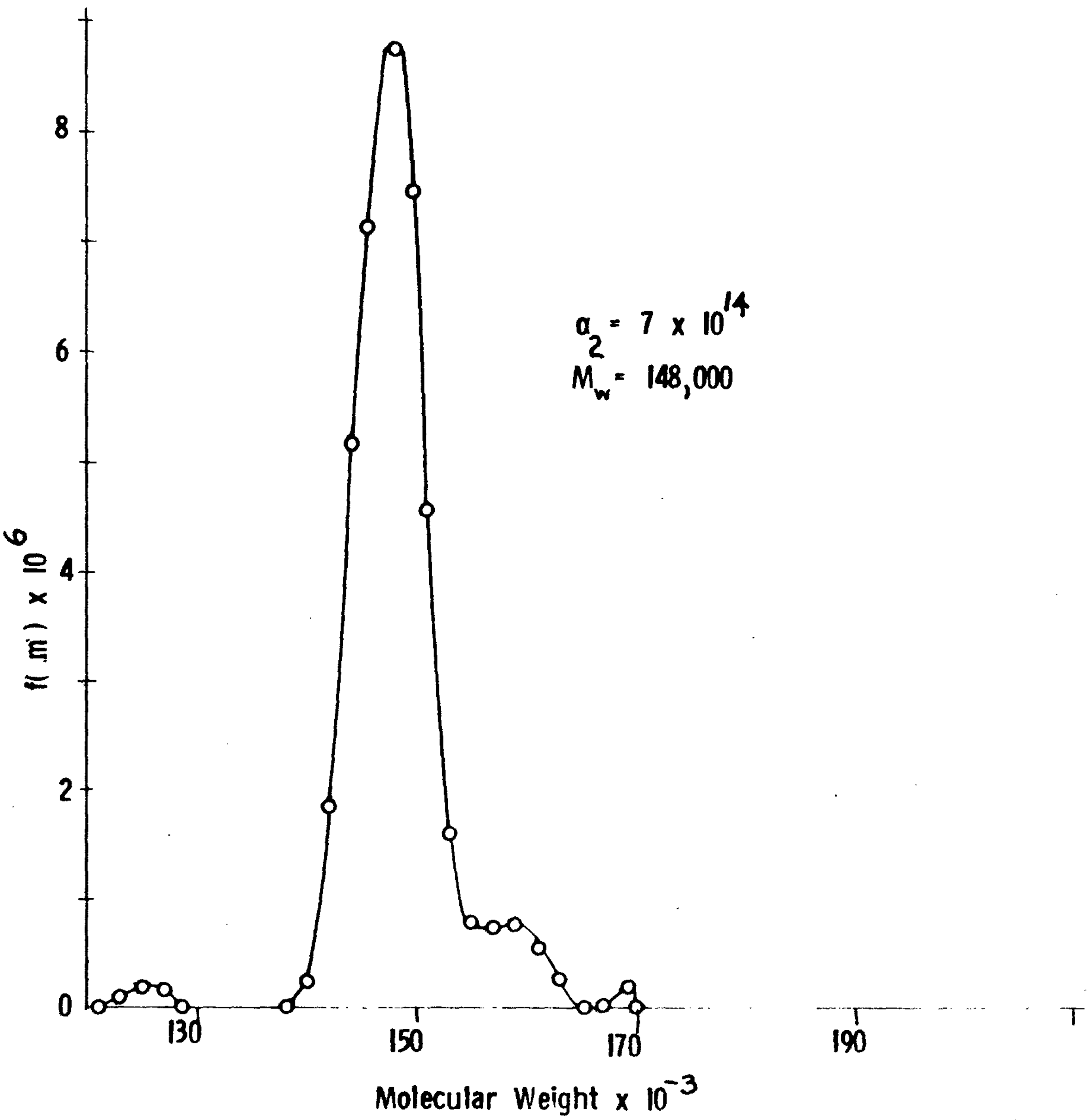

Figure 3. Molecular Weight Distribution for Sample C Using $100,000 \leq m \leq 180,000$, and $\Delta m = 1910$; $\int f(m)\,dm = 0.090$

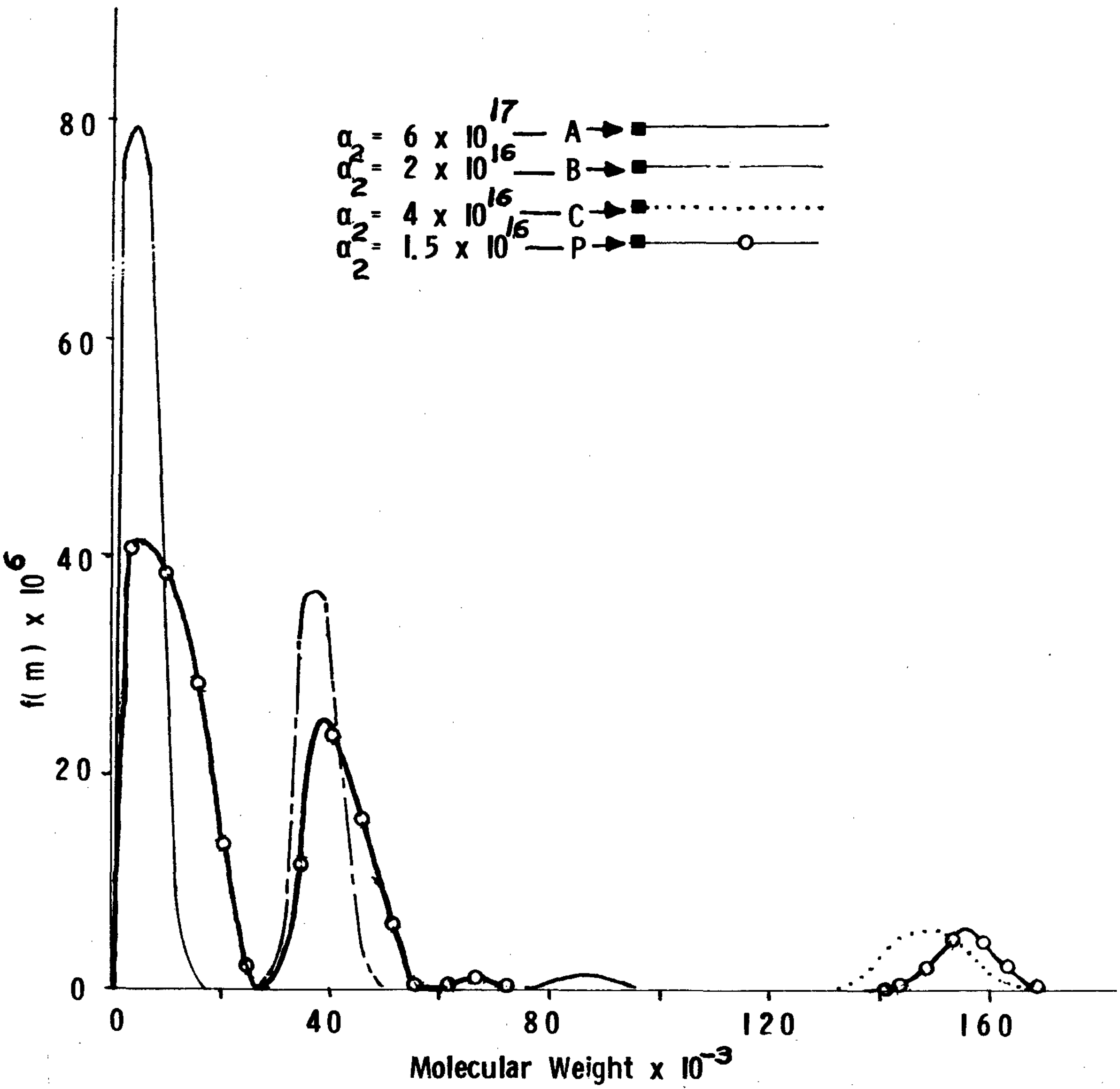

Figure 4. Molecular Weight Distribution for Sample P (Δm=5120) With a Superposition of the Molecular Weight Distributions for Samples A, B, and C (Δm=4286). In this case $\int f_p(m)\,dm = \int \left[f_A(m) + f_B(m) + f_C(m) \right] dm = 1$

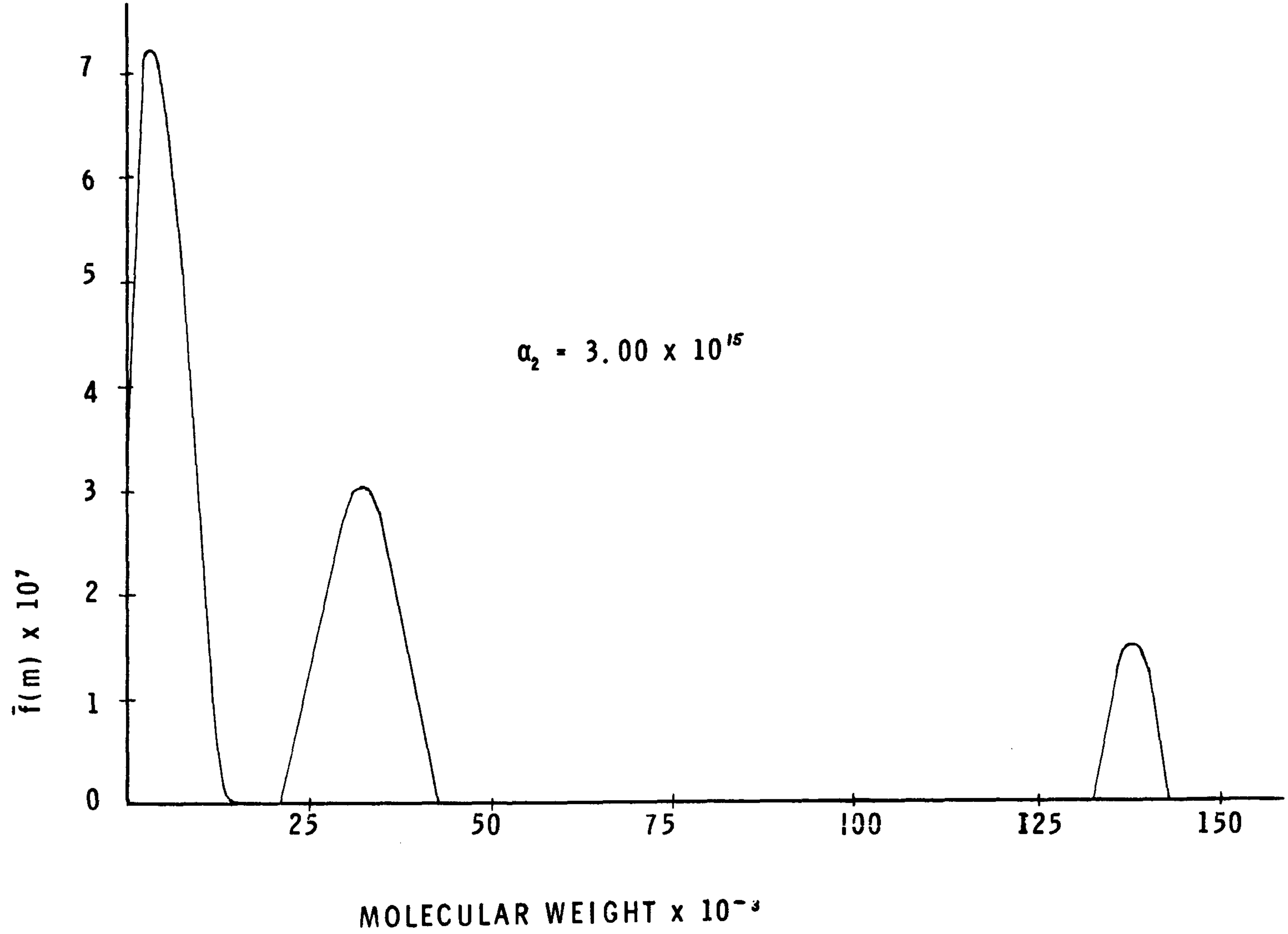

Figure 5. Molecular Weight Distribution of PBI (Purified and Dried) in DMAC at 40°C With the Distribution Normalized to Unity

TABLE IV

VELOCITY SEDIMENTATION DATA FOR SAMPLE A

No.	r_{max}	H	t_{exp} (sec)	$\frac{100}{H^2}$	$\theta \times 10^3$
1	6.7630	6.27	0	2.544	4.1554
2	6.7637	5.58	120	3.211	2.7661
3	6.7644	4.84	240	4.268	2.0717
4	6.7650	4.39	360	5.189	1.6550
5	6.7763	3.44	770	8.453	0.9785
6	6.7769	3.26	890	9.407	0.8734
7	6.7782	2.84	1130	12.391	0.7184
8	6.7809	2.68	1370	13.928	0.6096
9	6.7895	2.53	1610	15.630	0.5290
10	6.7868	2.37	1850	17.790	0.4669
11	6.7941	2.24	2090	19.920	0.4177
12	6.8027	2.10	2330	22.680	0.3776
13	6.8073	2.10	2570	22.680	0.3444
14	6.7974	1.95	2810	26.320	0.3164
15	6.8126	1.90	3050	27.780	0.2925

$H = 1.05233\,Y$
$f = 0.06611$
$\omega^2 = 1.755 \times 10^7$
$s = 1.33 \times 10^{-13}$
$D = 8.5 \times 10^{-5}$
$M_w = (8.286 \times 10^{10}) \left(\frac{s}{D}\right)$
$t_o = 240$ sec

TABLE V

EQUILIBRIUM SEDIMENTATION DATA FOR SAMPLE A

No.	r (cm)	U_{exp} (ξ)	m	f(m) x 10^6	U_{calc} (ξ)
1	7.1941	3.209	2,381	89.071	3.165
2	7.1720	2.490	4,762	76.422	2.428
3	7.1500	1.962	7,143	46.878	1.939
4	7.1280	1.622	9,524	20.477	1.610
5	7.1059	1.406	11,905	5.121	1.386
6	7.0839	1.252	14,286	0.000	1.229
7	7.0619	1.068	16,667	0.000	1.117
8	7.0398	1.009	19,048	0.000	1.034
9	7.0178	0.959	21,429	0.000	0.970
10	6.9957	0.910	23,810	0.000	0.919
11	6.9737	0.871	26,190	0.000	0.876
12	6.9517	0.839	28,571	0.000	0.840
13	6.9296	0.807	30,952	0.000	0.808
14	6.9076	0.783	33,333	0.000	0.780
15	6.8856	0.760	35,714	0.000	0.753
16	6.8635	0.737	38,095	0.000	0.729
17	6.8415	0.708	40,476	0.000	0.706
18	6.8194	0.680	42,857	0.000	0.684
19	6.7974	0.660	45,238	0.000	0.663
20	6.7754	0.640	47,619	0.000	0.643
21	6.7533	0.617	50,000	0.000	0.624
22	6.7313	0.599	52,381	0.000	0.606
23	6.7093	0.581	54,762	0.000	0.589
24	6.6872	0.563	57,143	0.000	0.572
25	6.6652	0.542	59,524	0.000	0.556
26	6.6432	0.531	61,905	0.000	0.541
27	6.6211	0.517	64,286	0.000	0.526
28	6.5991	0.506	66,667	0.000	0.511
29	6.5770	0.490	69,048	0.000	0.497
30	6.5550	0.476	71,429	0.000	0.484
31	6.5330	0.460	73,810	0.000	0.471
32	6.5109	0.449	76,190	0.000	0.459
33	6.4889	0.436	78,571	0.000	0.447
34	6.4669	0.422	80,952	1.1906	0.435
35	6.4448	0.411	83,333	0.814	0.423
36	6.4228	0.401	85,714	0.232	0.414
37	6.4007	0.388	88,095	0.228	0.403
38	6.3787	0.372	90,476	0.000	0.393
39	6.3567	0.358	92,857	0.000	0.383
40	6.3346	0.352	95,238	0.000	0.374
41	6.3126	0.345	97,619	0.000	0.365

$r_b^2 - r_a^2 = 14.1006$

$r_a = 6.13630$

$\int f(m)dm = 0.569$

$$\xi = \frac{r_b^2 - r^2}{r_b^2 - r_a^2}$$

TABLE VI

VELOCITY SEDIMENTATION DATA FOR SAMPLE B

No.	r_{max}	H	t_{exp} (sec)	$\frac{100}{H^2}$	$\theta \times 10^3$
1	6.6507	6.7454	0	2.1978	1.6430
2	6.6546	6.6086	120	2.2897	1.3651
3	6.6586	5.2617	360	3.6121	1.0180
4	6.6685	4.8618	600	3.7922	0.8098
5	6.6771	4.3987	840	5.1682	0.6709
6	6.6817	4.0620	1080	6.0606	0.5718
7	6.6969	3.7358	1320	7.1654	0.4974
8	6.6983	3.5779	1560	7.8119	0.4396
9	6.7049	3.3990	1800	8.6558	0.3934
10	6.7115	3.2622	2040	9.3967	0.3556
11	6.7207	3.1570	2280	10.0331	0.3241
12	6.7412	2.8623	2760	12.2055	0.2746
13	6.7571	2.6519	3240	14.2187	0.2376
14	6.7723	2.5466	3720	15.4202	0.2088
15	6.7987	2.3362	4680	18.3217	0.1669

$H = 1.05233\ Y$

$f = 0.06611$

$\omega^2 = 1.755 \times 10^7$

$s = 2.729 \times 10^{-13}$

$D = 5.373 \times 10^{-7}$

$M_w = (8.286 \times 10^{10}) \left(\frac{s}{D}\right)$

$t_o = 600$ sec

TABLE VII

EQUILIBRIUM SEDIMENTATION DATA FOR SAMPLE B

No.	r (cm)	U_{exp} (ξ)	M	f(m) x 10^6	U_{calc} (ξ)
1	7.1412	4.426	17,024	0.000	4.296
2	7.1191	3.899	19,048	0.344	3.871
3	7.0971	3.440	21,071	1.520	3.498
4	7.0751	3.049	23,095	3.668	3.169
5	7.0530	2.814	25,119	6.658	2.878
6	7.0310	2.592	27,143	10.159	2.621
7	7.0089	2.390	29,167	13.716	2.392
8	6.9869	2.199	31,190	16.831	2.187
9	6.9649	2.017	33,214	19.029	2.004
10	6.9428	1.841	35,238	19.938	1.840
11	6.9208	1.711	37,262	19.308	1.692
12	6.8988	1.582	39,286	17.142	1.558
13	6.8767	1.450	41,310	13.658	1.437
14	6.8547	1.320	43,333	9.358	1.327
15	6.8326	1.246	45,357	5.046	1.227
16	6.8106	1.158	47,381	1.831	1.136
17	6.7880	1.081	49,405	0.425	1.053
18	6.7665	1.002	51,429	0.000	0.977
19	6.7445	0.927	53,452	0.000	0.908
20	6.7225	0.863	55,476	0.012	0.844
21	6.7004	0.802	57,500	0.259	0.785
22	6.6784	0.749	59,524	0.293	0.731
23	6.6564	0.699	61,548	0.219	0.681
24	6.6343	0.646	63,571	0.088	0.635
25	6.6123	0.597	65,595	0.000	0.593
26	6.5902	0.556	67,619	0.000	0.554
27	6.5682	0.516	69,643	0.056	0.517
28	6.5462	0.477	71,667	0.002	0.484
29	6.5241	0.444	73,690	0.000	0.452
30	6.5021	0.413	75,714	0.000	0.423
31	6.4801	0.382	77,738	0.000	0.396
32	6.4580	0.358	79,762	0.066	0.371
33	6.4360	0.332	81,786	0.000	0.348
34	6.4139	0.305	83,810	0.000	0.326
35	6.3919	0.286	85,833	0.255	0.306
36	6.3699	0.266	87,857	0.753	0.287
37	6.3478	0.248	89,881	1.340	0.270
38	6.3258	0.233	91,905	1.788	0.253
39	6.3038	0.217	93,929	1.897	0.238
40	6.2817	0.196	95,952	1.603	0.224
41	6.2597	0.182	97,976	1.125	0.210

$r_b^2 - r_a^2 = 13.219$

$r_a = 6.1694$

$\int f(m)\,dm = 0.341$

$$\xi = \frac{r_b^2 - r^2}{r_b^2 - r_a^2}$$

TABLE VIII

VELOCITY SEDIMENTATION DATA FOR SAMPLE C

No.	r_{max}	H	t_{exp} (sec)	$\frac{100}{H^2}$	$\theta \times 10^3$
1	6.6586	9.58	0	1.09	1.290
2	6.6685	8.89	120	1.27	1.107
3	6.6718	8.42	240	1.41	0.967
4	6.6804	8.00	360	1.56	0.858
5	6.6850	7.58	480	1.74	0.771
6	6.6983	7.31	600	1.87	0.698
7	6.7049	6.84	720	2.14	0.638
8	6.7115	6.79	840	2.17	0.587
9	6.7247	6.16	1080	2.64	0.504
10	6.7512	5.42	1560	3.40	0.391
11	6.7776	4.95	2040	4.08	0.317
12	6.8074	4.47	2520	5.00	0.265
13	6.8391	4.16	3000	5.78	0.226
14	6.8669	3.89	3480	6.62	0.197
15	6.8967	3.63	3960	7.58	0.173

$H = 1.05233\ Y$

$f = 0.06611$

$\omega^2 = 1.755 \times 10^7$

$s = 4.97 \times 10^{-13}$

$D = 3.152 \times 10^{-7}$

$M_w = (8.286 \times 10^{10})\ (\frac{s}{D})$

$t_o = 750$ sec

TABLE IX

EQUILIBRIUM SEDIMENTATION DATA FOR SAMPLE C

No.	r (cm)	U_{exp} (ξ)	M	f(m) x 10^6	U_{calc} (ξ)
1	7.1632	0.7290	101,900	0.000	0.7376
2	7.1412	0.6808	103,810	0.000	0.6882
3	7.1191	0.6384	105,710	0.000	0.6422
4	7.0971	0.5955	107,620	0.000	0.5995
5	7.0751	0.5577	109,520	0.000	0.5597
6	7.0530	0.5227	111,430	0.000	0.5226
7	7.0310	0.4897	113,330	0.000	0.4882
8	7.0089	0.4582	115,240	0.000	0.4560
9	6.9896	0.4284	117,140	0.000	0.4261
10	6.9649	0.4006	119,050	0.000	0.3983
11	6.9428	0.3744	120,950	0.000	0.3723
12	6.9208	0.3514	122,860	0.100	0.3482
13	6.8988	0.3289	124,760	0.198	0.3256
14	6.8767	0.3090	126,670	0.162	0.3046
15	6.8547	0.2902	128,570	0.000	0.2850
16	6.8326	0.2708	130,480	0.000	0.2667
17	6.8106	0.2540	132,380	0.000	0.2497
18	6.7886	0.2388	134,290	0.000	0.2338
19	6.7665	0.2241	136,190	0.000	0.2189
20	6.7445	0.2095	138,100	0.000	0.2050
21	6.7225	0.1953	140,000	0.245	0.1921
22	6.7004	0.1817	141,900	1.864	0.1800
23	6.6784	0.1707	143,810	5.162	0.1687
24	6.6564	0.1608	145,710	7.117	0.1582
25	6.6343	0.1503	147,620	8.774	0.1483
26	6.6123	0.1398	149,520	7.475	0.1391
27	6.5902	0.1304	151,430	4.592	0.1305
28	6.5682	0.1205	155,240	1.595	0.1225
29	6.5462	0.1100	157,140	0.765	0.1149
30	6.5241	0.1037	159,050	0.741	0.1079
31	6.5021	0.0969	160,950	0.772	0.1013
32	6.4806	0.0906	162,860	0.589	0.0951
33	6.4580	0.0854	164,760	0.258	0.0894
34	6.4360	0.0796	166,670	0.000	0.0840
35	6.4139	0.0733	168,570	0.000	0.0790
36	6.3919	0.0681	168,570	0.189	0.0742
37	6.3699	0.0628	170,485	0.000	0.0697
38	6.3478	0.0587	172,380	0.000	0.0656
39	6.3258	0.0550	174,295	0.000	0.0617
40	6.3038	0.0518	176,190	0.000	0.0580
41	6.2817	0.0508	178,105	0.000	0.0545

$r_b^2 - r_a^2 = 13.559$

$r_a = 6.1495$

$\int f(m)\,dm = 0.090$

$$\xi = \frac{r_b^2 - r^2}{r_b^2 - r_a^2}$$

TABLE X

COMPARISON OF WEIGHT AVERAGE MOLECULAR WEIGHTS

Measured by	Technique Used	M_w of Samples		
		A	B	C
Mellon Institute	Viscosity	5,200	29,100	114,200
AFML/LNP	Velocity Sedimentation	6,300	42,100	130,700
AFML/LNP	Equilibrium Sedimentation Svedberg-Pederson Method	5,600	36,700	146,500
AFML/LNP	Equilibrium Sedimentation Regularization-Linear Prog with $\Delta m \approx 1500$	5,700	38,000	148,100
AFML/LNP	Equilibrium Sedimentation Regularization-Linear Prog with $\Delta m \approx 5000$	7,100	37,700	148,600

TABLE XI

EQUILIBRIUM SEDIMENTATION DATA AND
MOLECULAR WEIGHT DISTRIBUTION FOR SAMPLE P

No.	r (cm)	U_{exp} (ξ)	M	f(m) x 10^6	U_{calc} (ξ)
1	7.1677	19.053	5,119	41.123	19.101
2	7.1479	15.112	10,238	38.378	15.272
3	7.1280	12.774	15,357	28.136	12.357
4	7.1082	9.959	20,476	13.496	10.125
5	7.0884	8.487	25,595	21.419	8.404
6	7.0685	7.032	30,714	10.708	7.068
7	7.0487	6.105	35,833	11.278	6.022
8	7.0289	5.101	40,952	23.448	5.195
9	7.0090	4.503	46,071	15.828	4.536
10	6.9892	3.984	51,190	5.875	4.004
11	6.9694	3.637	56,310	0.650	3.570
12	6.9495	3.291	61,429	0.000	3.212
13	6.9297	2.962	66,548	0.610	2.913
14	6.9099	2.693	71,667	0.000	2.661
15	6.8900	2.468	76,786	0.000	2.445
16	6.8702	2.312	81,905	0.000	2.259
17	6.8504	2.156	87,024	0.000	2.096
18	6.8305	1.992	92,143	0.000	1.953
19	6.8107	1.819	97,262	0.000	1.826
20	6.7909	1.715	102,380	0.000	1.712
21	6.7710	1.593	107,500	0.000	1.609
22	6.7512	1.481	112,620	0.000	1.516
23	6.7314	1.403	117,740	0.000	1.431
24	6.7115	1.299	122,860	0.000	1.354
25	6.6917	1.273	127,980	0.000	1.283
26	6.6719	1.169	133,100	0.000	1.217
27	6.6520	1.126	138,210	0.000	1.156
28	6.6322	1.083	143,330	0.000	1.100
29	6.6124	1.039	148,450	2.031	1.047
30	6.5925	0.979	153,570	4.584	0.999
31	6.5727	0.953	158,690	4.938	0.953
32	6.5529	0.892	163,810	1.931	0.911
33	6.5330	0.866	168,930	0.000	0.871
34	6.5132	0.840	174,050	0.000	0.834
35	6.4934	0.823	179,170	0.000	0.799
36	6.4735	0.797	184,290	0.000	0.766
37	6.4537	0.779	189,400	0.000	0.735
38	6.4339	0.736	194,520	0.000	0.707
39	6.4140	0.701	199,640	0.000	0.679
40	6.3942	0.676	204,760	0.000	0.654
41	6.3744	0.650	209,880	0.000	0.629

$\int f(m)\,dm = 1.00$

$r_b^2 - r_a^2 = 13.477$

$r_a = 6.1562$

$$\xi = \frac{r_b^2 - r^2}{r_b^2 - r_a^2}$$

TABLE XII

MOLECULAR WEIGHT DISTRIBUTION OF SAMPLES A, B, AND C

No.	M	$f_A(m) \times 10^6$	$f_B(m) \times 10^6$	$f_C(m) \times 10^6$
1	4,286	79.275	0.000	0.000
2	8,571	46.942	0.000	0.000
3	12,857	4.875	0.000	0.000
4	17,143	0.000	0.000	0.000
5	21,429	0.000	0.000	0.000
6	25,714	0.000	0.000	0.000
7	30,000	0.000	1.534	0.000
8	34,286	0.000	27.726	0.000
9	38,571	0.000	35.972	0.000
10	42,857	0.000	14.193	0.000
11	47,143	0.000	0.148	0.000
12	51,429	0.000	0.000	0.000
13	55,714	0.000	0.000	0.000
14	60,000	0.000	0.000	0.000
15	64,286	0.000	0.000	0.000
16	68,571	0.000	0.000	0.000
17	72,857	0.000	0.000	0.000
18	77,143	0.000	0.000	0.000
19	81,429	0.719	0.000	0.000
20	85,714	0.934	0.000	0.000
21	90,000	0.014	0.000	0.000
22	94,286	0.000	0.000	0.000
23	98,571	0.000	0.000	0.000
24	102,860	0.000	0.000	0.000
25	107,140	0.000	0.000	0.000
26	111,430	0.000	0.000	0.000
27	115,710	0.000	0.000	0.000
28	120,000	0.000	0.000	0.000
29	124,290	0.000	0.000	0.000
30	128,570	0.000	0.000	0.000
31	132,860	0.000	0.000	0.000
32	137,140	0.000	0.000	1.261
33	141,430	0.000	0.000	3.547
34	145,710	0.000	0.000	5.018
35	150,000	0.000	0.000	5.005
36	154,290	0.000	0.000	3.724
37	158,570	0.000	0.000	1.931
38	162,860	0.000	0.000	0.514
39	167,140	0.000	0.000	0.000
40	171,430	0.000	0.000	0.000
41	175,710	0.000	0.000	0.000

$\int f_A(m)\,dm = 0.569$

$\int f_B(m)\,dm = 0.341$

$\int f_C(m)\,dm = 0.090$

TABLE XIII

EQUILIBRIUM SEDIMENTATION DATA AND
MOLECULAR WEIGHT DISTRIBUTION FOR PBI-MPD

No.	r (cm)	U_{exp} (ξ) x 10^3	M	f(m) x 10^7	U_{calc} (ξ) x 10^3
1	7.1860	48.18	13,333	7.197	47.41
2	7.1632	41.67	16,667	4.855	43.25
3	7.1404	37.81	20,000	2.137	39.54
4	7.1176	34.84	23,333	0.000	36.25
5	7.0948	32.38	26,667	0.000	33.32
6	7.0720	30.02	30,000	0.000	30.70
7	7.0492	28.08	33,333	1.145	28.37
8	7.0264	26.16	36,667	2.314	26.28
9	7.0035	24.57	40,000	2.901	24.41
10	6.9807	22.96	43,333	2.547	22.72
11	6.9579	21.48	46,667	1.343	21.21
12	6.9351	20.22	50,000	0.000	19.85
13	6.9123	19.14	53,333	0.000	18.61
14	6.8895	18.12	56,667	0.000	17.50
15	6.8667	17.14	60,000	0.000	16.49
16	6.8439	16.33	63,333	0.000	15.57
17	6.8211	15.41	66,667	0.000	14.74
18	6.7983	14.63	70,000	0.000	13.97
19	6.7754	13.92	73,333	0.000	13.28
20	6.7526	13.36	76,667	0.000	12.64
21	6.7298	12.68	80,000	0.000	12.05
22	6.7070	12.00	83,333	0.000	11.51
23	6.6842	11.54	86,667	0.000	11.01
24	6.6614	11.01	90,000	0.000	10.55
25	6.6386	10.58	93,333	0.000	10.12
26	6.6158	10.08	96,667	0.000	9.73
27	6.5930	9.68	100,000	0.000	9.35
28	6.5702	9.21	103,333	0.000	9.01
29	6.5473	8.89	106,667	0.000	8.69
30	6.5245	8.53	110,000	0.000	8.39
31	6.5017	8.32	113,333	0.000	8.11
32	6.4789	7.92	116,667	0.000	7.84
33	6.4561	7.67	120,000	0.000	7.59
34	6.4333	7.41	123,333	0.000	7.35
35	6.4105	7.20	126,667	0.000	7.13
36	6.3877	6.95	130,000	0.000	6.92
37	6.3649	6.73	133,333	0.000	6.72
38	6.3421	6.51	136,667	1.191	6.52
39	6.3192	6.29	140,000	1.365	6.34
40	6.2964	6.07	143,333	0.000	6.17
41	6.2736	5.89	146,667	0.000	6.00

$r_a = 6.0455$

$r_b^2 - r_a^2 = 15.0908$

$$\xi = \frac{r_b^2 - r^2}{r_b^2 - r_a^2}$$

TABLE XIV

VARIOUS MOMENTS AND RATIOS
OF MOMENTS COMPUTED FOR
PBI-MPD

Designation	Value
M_n	22,200
M_w	36,500
M_z	70,200
M_{z+1}	108,800
M_w/M_n	1.64
M_z/M_w	1.92
M_{z+1}/M_z	1.55

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PART VI. EXPERIMENTAL VERIFICATION OF PREVIOUSLY PROPOSED REGULARIZATION-LINEAR PROGRAMING TECHNIQUE WITH APPLICATION TO PBI

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13. ABSTRACT

Experimental verification of the solution associated with the mathematically improperly posed problem of inferring a molecular weight distribution from equilibrium sedimentation data has been achieved. This was accomplished by investigating narrow linear polystyrene fractions and then superimposing these fractions to create a known molecular weight distribution.

It has been shown that the previously proposed regularization-linear programing technique used to infer a molecular weight distribution produces a reliable solution. This technique was then applied to data obtained for PBI in DMAC. The results show that an unusually large part of this polymer is of very low molecular weight. How this low molecular weight will affect the strength and reliability of PBI should warrant further investigation.

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