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SOME SOLUTION PROPERTIES OF POLY(5, 5' BIBENZIMIDAZOLE 2, 2'-DIYL, 1, 3-PHENEYLENE)

CHARLES L. BENNER
University of Dayton Research Institute

TECHNICAL REPORT AFML-TR-70-7

February 1970

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

FOREWORD

This report was prepared by the University of Dayton Research Institute under contract AF 33615-69-C-1385. The work was initiated under Project 7340 "Nonmetallic and Composite Materials", Task 734004 "New Organic and Inorganic Polymers". This work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Systems Command with Mr. J. M. Kelble, MAN, acting as project engineer.

This report covers work conducted between October 1964 and March 1969. This report was released by the author November 1969.

This technical report has been reviewed and is approved.

R. T. Schwartz

R. T. SCHWARTZ, Chief
Nonmetallic Materials Division

ABSTRACT

Some solution property measurements have been made on two samples of Poly(5, 5' bibenzimidazole, 2, 2'-diyl, 1, 3-phenylene). Fractions were obtained from these samples by using a solvent--non-solvent system (DMAC-hexane). Intrinsic viscosities were determined for both whole samples and fractions in various solvents. Osmometry measurements have been made on the samples in DMAC at 37°C. Several problems concerning sample solubility, concentration determination, and coloration of the solutions have been encountered.

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SECTION I

INTRODUCTION

The aromatic heterocyclic polybenzimidazoles (PBI) represent a class of new high temperature polymers that exhibit good thermal stability and retain mechanical properties at high temperature. These desirable properties have caused this type polymer to be considered for aircraft, aerospace vehicle, and extreme evnironment applications. Therefore, it is of interest to determine the physical properties of these polymers in order to more completely characterize this new macromolecular material. As part of the physical property of this polymer, a study of solution properties was begun.

This technical report presents the solution property data that has been obtained on several samples of poly(5, 5' bibenzimidazole-2, 2' diyl-1, 3 phenylene). Since the sole purpose of this undertaking was to acquire characterization data for this polymer type, no attempt is made to interpret the data. The correlation and interpretation of the data will appear elsewhere[1].

SECTION II

DISCUSSION

INTRINSIC VISCOSITY AS A FUNCTION OF SOLVENT

The intrinsic viscosity of a sample of poly(5, 5' bibenzimadazole-2, 2' diyl-1, 3 phenylene) (PBI) obtained from Celanese Corporation and designated PBI-C was determined in several solvents to determine the effect of solvent on the intrinsic viscosity of the sample. The solvents were N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and N-methylpyrolidone (NMP).

The solutions were made up by dissolving 1.5 grams of the sample in 100 cc of each of the four solvents. The solutions were then filtered to remove the insoluble portion of the sample. The viscosities, an original concentration plus four dilutions, were run in a Cannon-Ubbelohde dilution viscometer which was thermostated at 30°C ± 0.01° in a water bath. The data were reduced and plotted as $\eta sp/C$ and $\ln \eta r/C$ and extrapolated to zero concentration. Since a portion of the PBI was insoluble, the make-up concentration could not be used in the calculations, so solids were determined on the solutions both initially and at the conclusion of the experiment. They were not in good agreement, so only the final concentration values were used in the calculation since they were more dilute and less likely to retain solvent on drying. The results are shown in Table I.

TABLE I

Intrinsic Viscosity of PBI-C as a Function of Solvent

SOLVENT	$[\eta]$ (dl/gm)
DMF	0.53
DMAC	0.69
DMSO	0.71
NMP	0.65

VISCOSITY OF PBI f(LiCl)

On occasion, a sample of PBI-M would fail to dissolve in DMAC for reasons still unexplained. It was suggested that the addition of a salt to the DMAC would effect solubility[2]. The addition of 5 percent LiCl caused the samples to readily dissolve. A series of intrinsic viscosities were run with varying amounts of LiCl in the DMAC to determine what effect, if any, it would have on the intrinsic viscosity. Four PBI solutions were made up with DMAC containing 0.1%, 0.5%, 1%, 2.5%, LiCl (gm/cc). Data were obtained in the normal manner using the solvent containing the respective concentrations of LiCl for each viscosity. The intrinsic viscosities are shown in Table II. A sample of PBI-M was also run in DMSO in order to obtain a comparison of intrinsic viscosities in different solvents.

TABLE II

Intrinsic Viscosity of PBI-M in DMAC as a Function of LiCl Concentration

Percent LiCl	$[\eta]$ (dl/gm)
-0-	0.79
0.1	1.50
0.5	1.21
1.0	1.16
2.5	1.07
DMSO	0.69

VISTEX INTRINSIC VISCOSITIES

Since both PBI and DMAC are known to be hygroscopic, viscosity data were obtained to determine the effect that water has on intrinsic viscosity. The "vistex" method was used to calculate the viscosity data[3]. This "vistex" technique requires that viscosity data be obtained as a function of water content. The calculation of data assumes that the effect of water will be simply additive to the solution flow times. If this be so, then deleting the contribution of the water should yield an intrinsic viscosity that is independent of the initial water content. If not, then it can be assumed that the water is effecting the viscosity behavior of the solute.

Four solutions were made up by dissolving 1.5 grams PBI-C in 100 ml of DMAC and adding 1% water to two of the solutions. The other two had no water added, but contained a small amount that they had absorbed from the air.

They were filtered and flow times were taken in a Cannon-Ubbelodhe dilution viscometer which was thermostated in a water bath at 30°C ± 0.01°. The data were obtained as an original concentration and four dilutions.

The first set of intrinsic viscosities were run on one dry solution and one solution containing 1% water. The water-containing solution was diluted with DMAC containing 1% water and the dry solution was diluted with dry DMAC.

The second set was run on the other dry solution and the other solution containing water. The dilutions were made with dry DMAC for both the wet and the dry solution.

A portion of each of the four solutions was withdrawn at both the beginning and at the completion of the experiment. These samples, as well as original solvent and final solvent, were sealed in bottles and sent out for a Karl Fisher water determination[4]. From these data the amount of water in the original solution and each of the dilutions are calculated. Using these data and a plot of solvent flow times (DMAC) versus percent water, the flow times are corrected to give data for dry solvent and dry solutions. These data are plotted as $\eta sp/C$ and $\ln \eta r/C$ versus concentration.

The concentrations were determined from solids. As before, the original and final solids were not in good agreement so the final solids data were used since they are less likely to retain solvent. The results are shown in Table III.

TABLE III

Vistex Calculation of Intrinsic Viscosity of PBI-C

	vistex cal.[c]	non-vistex cal.[c]
dry sample run 1	0.61	0.61
wet sample run 1	0.68	0.64
dry sample run 2	0.65	0.65
wet sample run 2	0.64	0.72

SOLIDS DRYING TECHNIQUE

Good solids data were very difficult to obtain because of solvent retention by the sample during the drying process. Two experiments were designed in connection with this problem[5]. One technique involved precipitating the PBI by adding a non-solvent to the solids solution. The other was a long term drying procedure to determine the length of time required to come to constant weight.

In the first experiment 10 ml of a 0.5% PBI-C in DMAC was pipetted into each of four previously weighed bottles. Then the bottles were reweighed; next 10 mls toluene were added to the first bottle, 10 mls water were added to the second bottle, 10 mls carbon tetrachloride were added to the third bottle, and the fourth bottle did not have a non-solvent added to it. The bottles were placed in a drying oven at 105°C until all of the liquid had evaporated; then they were placed in a vacuum oven and further dried with weighings being taken on subsequent days. Table IV shows the results.

TABLE IV

Concentration of PBI-C with Various Non-solvent

Non-Solvent Added	con$^{\underline{c}}$ (gm/100gm)
No non-solvent	0.5772
Toluene	0.5803
H_2O	0.5672
CCL_4	0.5748
Make Up	0.5

There is no significant improvement in the concentration data with the addition of non-solvents to the solids. This is partly due to the fact that the non-solvents evaporate before the solids become dry and therefore the PBI goes back into solution. All the concentrations are approximately 12% greater than the make up concentration.

A 1% PBI-C in DMAC solution was made up after first drying the PBI at 200°C for 18.5 hrs to remove any water or other volatiles contained in the sample. DMAC was added and the flask was heated to 80°C for 68 hrs; then approximately 10 cc of the solution was filtered into each of four previously weighed weighing bottles. Two of these bottles were placed in a drying oven at 80°C with the temperature gradually being raised to 120°C, and evaporated to dryness before being placed in the vacuum oven. The other two were placed directly into the vacuum oven and evaporated to dryness at 80°C under a vacuum of 300 ± 50 mm Hg. The oven-dried bottles were then placed in the vacuum oven and all four were heated to 200°C under a vacuum of approximately 0.1 mm Hg. The samples were removed from the oven, placed in a dessicator to cool, weighed and returned to the vacuum oven until they came to constant weight. This required 40 days and even though the solids finally came to a constant weight the concentrations were 5.2% higher than the make up concentration. The agreement among the samples is 1%. The results are shown in Table V.

TABLE V

Concentration of PBI-C after Drying

Technique Used	Cons (gm/100gm)
Make Up	1.1495
Vac Oven	1.2182
Vac Oven	1.2083
Drying Oven	1.2047
Drying Oven	1.2068

DETERMINATION OF CONCENTRATION BY SPECTROPHOTOMETRIC METHODS

The inability to completely remove solvents from PBI by evaporation techniques without some degree of polymer degradation has led to the search for a method of concentration determination that is more accurate than the evaporation method. One possibility is the use of absorbance measurements.

For this experiment, the solutions were prepared from a master solution of 3.4% Celanese PBI-C in DMAC. One ml of solution was pipetted into a volumetric flask and weighed. It was then diluted to 50 mls with DMAC and reweighed. The concentration was calculated on a weight/weight basis. One ml of this diluted solution was again diluted to 50 mls with DMAC using the previously stated method. The solutions for the measurements were made from this solution by weighing out from 1 to 5 mls and diluting with the appropriate amount of DMAC. It should be noted that the concentration can be expressed as grams solute/grams solvent or gm solute/gm solution. Since there will be a slight difference in concentration depending upon which value is used, the concentrations were converted to the proper units during the dilution calculations. The final concentration values are expressed in gm solute/gm solvent. The final concentrations are in the range of 10^{-6} gm solute/gm solvent; therefore, care must be taken in making the dilutions.

The absorbance of each concentration was determined with a Beckman model DK-2A spectrophotometer. A base line was determined with DMAC in both the solvent and sample cells. This base line value was subtracted from the values that were obtained for the solutions. The region scanned was from 360 mμ to 330 mμ with a peak in absorbance at 347 mμ ± 2 mμ. The absorbance of each solution at 347 mμ minus the base line reading at 347 mμ was plotted against concentration.

Each solution in two series of five solutions was measured three times over a period of about two weeks and the average absorbance calculated. The data are shown in Table VI.

TABLE VI

Absorbance of PBI-M

1st series

Solution	1st	2nd	3rd	Avg.	Con $\frac{c}{-}$ $\frac{\text{gm solute}}{\text{gm solvent}}$ x10^6
I	0.874*	0.819	0.811^x	0.835	5.431
II	0.331*	0.311	0.313^x	0.318	2.096
III	0.185	0.190	---	0.188	1.234
IV	0.096	0.097	0.091	0.095	0.622
V	0.045	0.045	0.046	0.045	0.321

TABLE VI (cont'd)

2nd series

Solution	1st	2nd	3rd	Avg.	Con $c - \frac{\text{gm solute}}{\text{gm solvent}} \times 10^6$
A	1,014^{o}	0.925	0.955	0.965	6.364
B	0.344	0.326	0.324	0.331	2.162
C	0.184	0.178	0.179	0.180	1.182
D	0.097	0.095	0.096	0.096	0.621
E	0.051	0.046	0.048	0.048	0.320

* both base line and curves noisy
x meniscus low
o 0.5-1.5A scale

The consistency of the measurements was determined by dividing absorbance by concentration, and comparing these values. (See Table VII).

TABLE VII

Absorbance Divided by Concentration

1st series

Solution	1st	2nd	3rd
I	0.1609	0.1508	0.1493
II	0.1579	0.1483	0.1493
III	0.1498	0.1539	
IV	0.1544	0.1560	0.1463
V	0.1401	0.1401	0.1432

2nd series

Solution	1st	2nd	3rd
A	0.1593	0.1453	0.1500
B	0.1591	0.1508	0.1499
C	0.1557	0.1506	0.1514
D	0.1560	0.1528	0.1544
E	0.1594	0.1438	0.1500

Avg. 0.1513

The variation from the average value was approximately ± 3%. Dilution errors, incomplete rinsing of the cells, dirty cells, concentration changes, water absorption, and improper adjustment of the instrument could account for these deviations. The reproducibility of repeated measurements on the same solution averaged ±1.1%. The deviations could be caused by the aforementioned errors with the exception of dilution, since the same solution was used for each determination.

SAMPLE PURIFICATION

A portion of a large sample of fiber grade poly(5,5' bibenzimidazole, 2,2' diyl- 1,3 phenylene)[6] designated PBI-M was purified in order to obtain a sample which was completely soluble. The procedure involved refluxing the sample in DMAC for 3 days to dissolve all of the soluble portion of the sample[7]. The solution was filtered several times through a coarse sintered glass filter, then several times through a medium, and finally through a fine porosity several times. It was then precipitated in methyl ethyl ketone (MEK) and filtered through a buchner funnel with a fine porosity teflon filter in place. The precipitate was washed with a liter of MEK to remove any remaining DMAC followed by 100 ml aliquots of 80%/20%, 60%/40%, 40%/60%, 20%/80% mixtures of MEK/methanol (MEOH). Next it was washed with a liter of methanol followed by washes with 100 ml aliquots of 80%/20%, 60%/40%, etc. mixture of MEOH/ether, and finally with a pint of pure ether. The sample was placed in a vacuum oven and dried at 120°C and 0.01 Torr. A sample of PBI-C was also purified by this method.

Comparative intrinsic viscosities were run on three samples of PBI-M. They are PBI-M (sample as-received from Celanese), PBI-M2 (sample purified by the above procedure), PBI-M2 TGA 300 (sample of PBI-M2 dried to 300°C on a thermobalance with a weight loss of 0.37%)[8]. The three samples were made up to approximately 1% concentration in DMAC. Data for each solution were obtained in the Cannon-Ubbelodhe dilution viscometer, thermostated @ 35°C ± 0.01°C, as an orig. con $\underline{c}$ plus three dilutions. The concentrations were determined by taking solids on the solutions and using data from the final solids for the calculations.

The results are shown in Table VIII.

TABLE VIII

Comparative Intrinsic Viscosities
(purified samples)

Sample	$[\eta]$ dl/gm	k'
PBI-M	0.59	0.415
PBI-M2	0.68	0.450
PBI-M2 TGA 300	0.71	0.465

EVALUATION OF PURIFICATION TECHNIQUES

A 50 gram sample of PBI-M was placed in a round bottom flask and refluxed for 48 hours with a liter of DMAC. An additional liter was added and refluxing continued another 24 hours. After the solution had cooled to room temperature, it was filtered through a coarse sintered glass filter, then through a medium, and finally through a fine. The filters were rinsed with an additional 500 ml DMAC bringing the total volume to 2500 mls. The solution was brought to turbidity by adding 1600 cc MEK to it. At this point the sample was divided into 2 five-gram and one 40 gram portions. Precipitation was accomplished by adding the mixture to 12 liters of stirring MEK. The large sample was purified by washing the filtered precipitate with a liter of MEK, followed by mixtures of MEK and MEOH with increasing amounts of MEOH, then with a liter of MEOH, mixtures of MEOH and ether, and finally with 1 pint of pure ether. It was then placed in the vacuum oven and dried at 120°C. This sample was designated as PBI-M7A. The second sample was washed as described above except with MEK, MEOH, and benzene as the solvents. It was then freeze-dried. The sample designation is PBI-M7B. The third sample was handled similarly to the other two with the solvents being MEK, MEOH, ether, and benzene. This sample, designated PBI-M7C, was also freeze dried.

The samples were then dried on a high vac line up to 300°C[9] to determine which sample had retained the least solvent. The results are shown in Table IX.

TABLE IX

Percent Weight Loss of PBI-M

SAMPLE	PERCENT WEIGHT LOSS
PBI-M7A	5.37
-M7B	10.58
-M7C	11.57

NUMBER AVERAGE MOLECULAR WEIGHT OF PBI-M2

A number average molecular weight measurement was made on a sample of PBI-M2. The measurement was made with a Mechrolab High Speed Membrane Osmometer equipped with a 37°C single set temperature probe and a 600 grade gel cellophane membrane. The membranes were conditioned by allowing them to stay a minimum of four hours in each of the following solvent mixtures: 75% water (W)-25% isopropyl alcohol (A), 25%W-75%A, A1, A2, A3, 75%A-25%DMAC, 50%A-50%DMAC, 25%A-75%DMAC, DMAC 1, DMAC 2, DMAC 3. They were then degassed in a vacuum oven for a few minutes and cut to size. The instrument was assembled with a membrane and solvent which also had been degassed.

Four concentrations ranging from 0, 10% to 0.25% were dissolved in DMAC. They were thermostated at approximately 38°C in a water bath located near the instrument. This was done to reduce the time necessary for the solutions to reach temperature equilibrium in the instrument. The solvent was run first to establish a reference value. The sample stack was then washed three times with 0.2 ml of solution with the third rinse being left in the instrument and allowed to come to equilibrium. The process was repeated for each of the four solutions.

The solutions showed some diffusion which necessitated plotting the log of the solution head (h) as a function of time and extrapolating to zero time. These values were taken to be the true solution heads. Typical data are shown in Figure 1. The value of π was then calculated from equation 1, plotted as $\frac{\pi}{c}$ vs c, and extrapolated to zero concentration. (See Figure 2).

$$\pi = \rho \, (h \text{ soln} - h \text{ solv}) \tag{1}$$

Where h soln is the value of h at time zero, h solv is the solvent head and ρ is the solvent density at the elevator temperature. The number average molecular weight is calculated from equation 2.

$$\overline{M_n} = \frac{RT}{\left(\frac{\pi}{c}\right)_{c = 0}} \tag{2}$$

Solids were taken on the solutions, but give a value which seems too high. Since PBI-M2 is completely soluble and DMAC has a low evaporation rate, the make up concentrations probably give more reliable concentration data. Using the make up concentration data the number average molecular weight for PBI-M2 is 15,000.

FRACTION PURIFICATION

Seven fractions were obtained from a sample designated PBI-M4[10]. Each fraction was handled essentially the same way during the purification process

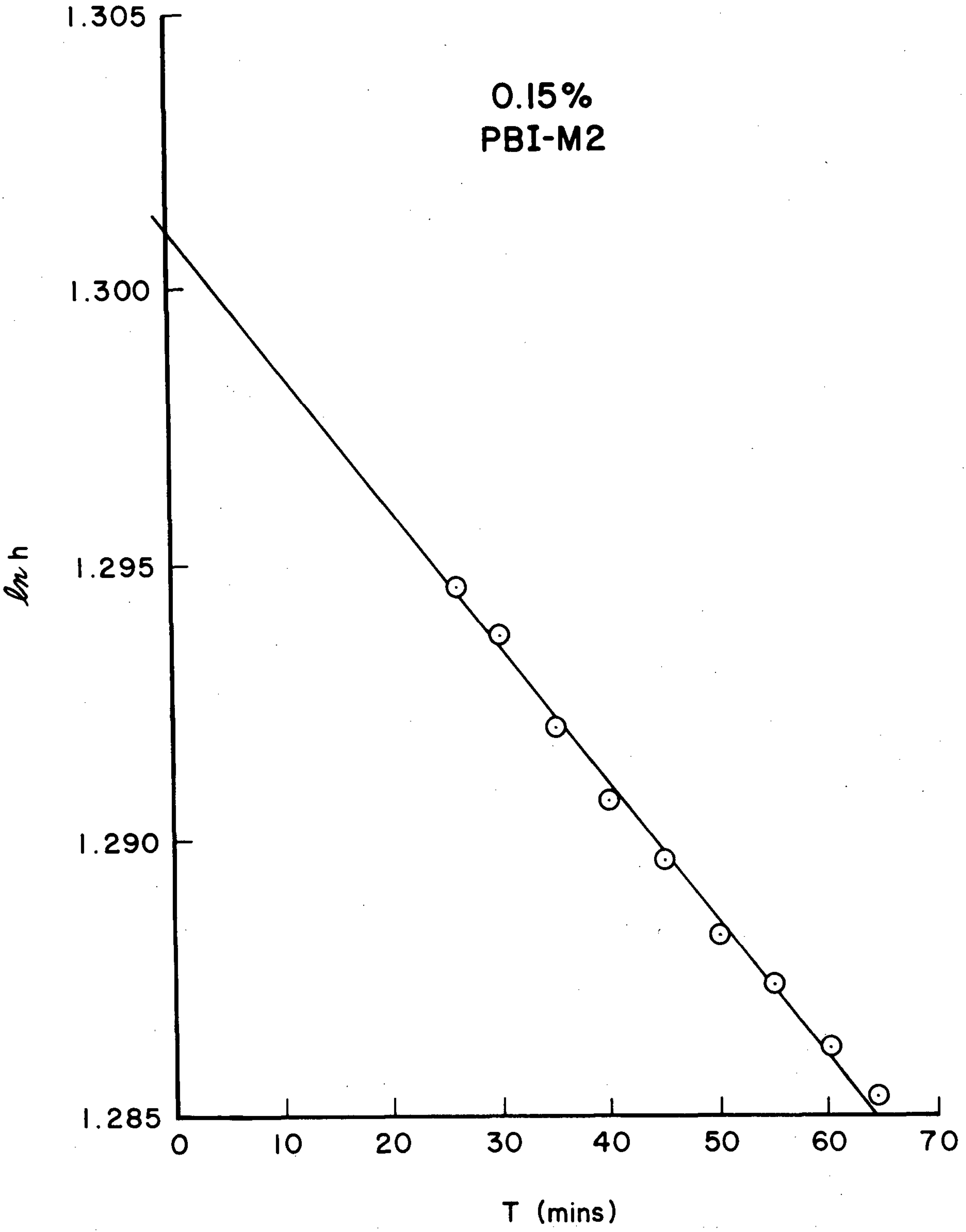

Figure 1. Typical extrapolation of ln of solution pressure head versus time after injection of sample.

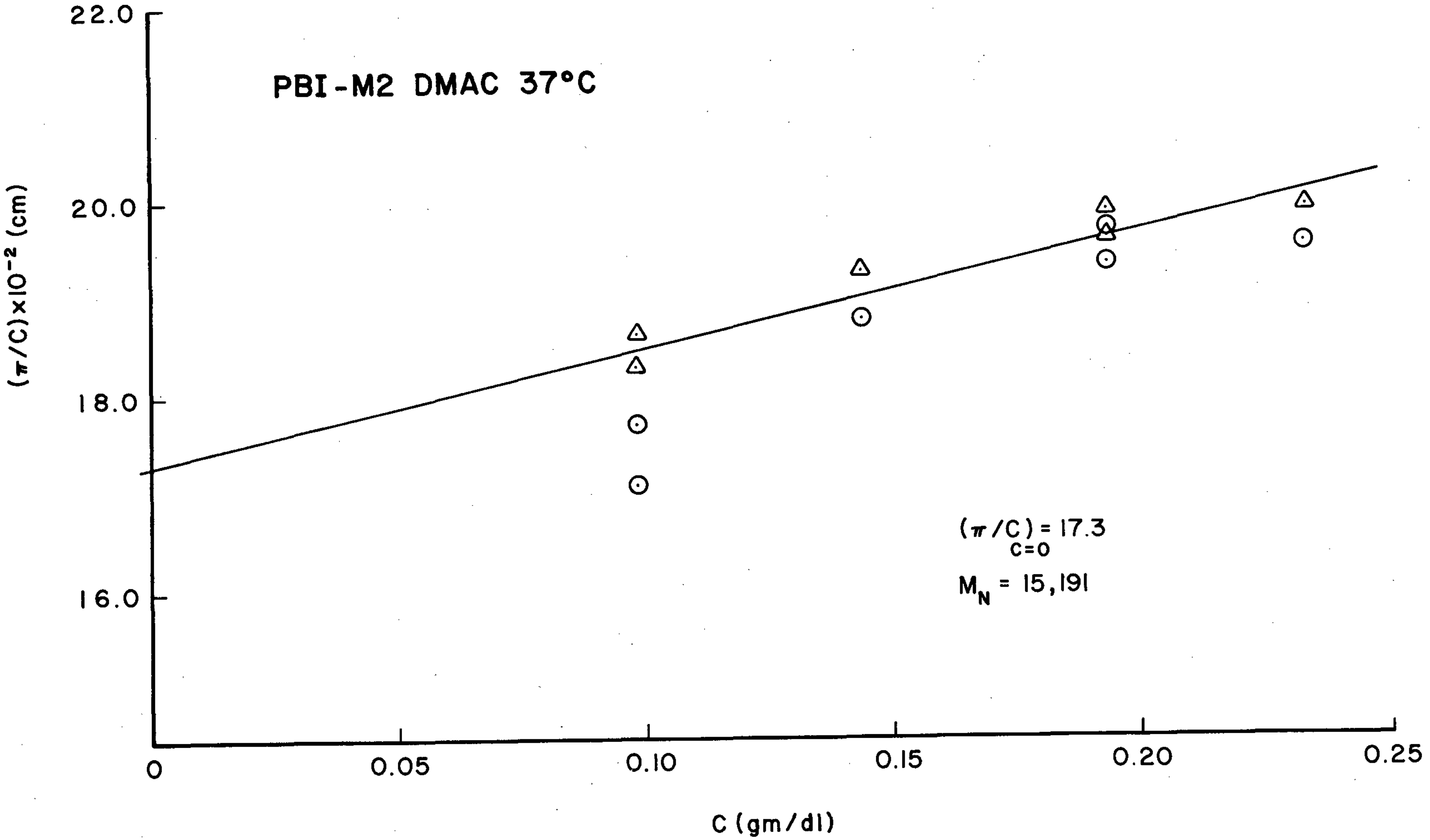

Figure 2. Osmotic pressure, PBI-M2 in DMAC at 37°C. π/C versus concentration.

except for a few changes in technique necessitated by difficulties. The first fraction was filtered through a coarse, a medium, and a fine sintered glass filter to remove any insoluble portion of the sample. The volume was then reduced by vacuum distillation. It did not precipitate as expected when it was added to a beaker of stirring methyl ethyl ketone (MEK), A small amount of methanol (MEOH) was added to the solution to effect the precipitation. The solution was then filtered through a Buchner filter with the precipitate being retained by a Whatman number 42 filter disc. The sample dried out before it could be washed with MEK and was dried in the vacuum oven several days before attampting to redissolve it. Not all of the sample was soluble, so it was reprecipitated with the possibility of it being completely soluble after it was dried. Again the precipitate dried out and was placed in DMAC to redissolve it. It still was not soluble even with the addition of a saturated lithium chloride solution. Fraction 1 was approximately 0. 6 grams and was not used for any of the measurements. Fraction 2 was filtered the same as Fraction 1 and its volume reduced under vacuum before precipitation. It precipitated as expected when it was added to the stirring MEK. It was then filtered through the Buchner funnel, washed with MEK, and dried overnight before being redissolved in DMAC. It was precipitated again, filtered, washed with MEK, but dried out during the process and would redissolve only when LiCl was added to the solution. In order to get all of the LiCl out of the solution, the sample was again precipitated in MEK, filtered with the Buchner filter and Whatman number 42 filter paper, washed with a large quantity of MEK and dried in a vacuum oven. The weight of the fraction was 2. 3 grams. Fraction 3 was filtered and the volume reduced as described for Fraction 1. Some filter paper stuck to the sample when it was dried after being precipitated and an attempt to redissolve it gave a very turbid solution with some insoluble particles. It was precipitated in MEK in an attempt to obtain a readily soluble fraction. It was redissolved and filtered through an extra coarse, a coarse, and a medium filter in an attempt to remove any turbidity caused by very small chunks of filter paper that might be in the solution. It was then precipitated in methanol, filtered and dried. On being dissolved, the solution still exhibited a turbidity which disappeared when 15 mls of a 7. 5% LiCl solution was added. It was then precipitated in MEK from the solution containing LiCl, washed with MEK, and dried in the vacuum oven. After being handled several times the fraction weight was 4. 9 grams. Fraction 4 was filtered through a coarse, medium, and fine sintered glass filter and the volume was reduced before being precipitated in MEOH. After being filtered through the Buchner funnel and washed with MEOH, it was dried in the vacuum oven. The weight of it was 4. 4 grams. Fraction 5 was not filtered prior to precipitation because there was a large amount of insoluble material which was thought to be PBI with hexane trapped in it, in the bottom of the flask. The volume was reduced under vacuum and most of the insolubles dissolved. It was then precipitated in MEK, collected on a Whatman number 42 filter disc and washed with MEK. The fraction weighed 8. 6 grams and was completely soluble except for some particles which appeared not to be polymer. Fraction 6 also had a large amount of insoluble material in the flask. An attempt to dissolve the insoluble portion by adding a large amount of DMAC failed and the volume was then reduced and, as with Fraction 5, the sample completely dissolved. It was then precipitated in MEK, filtered through the Buchner funnel, washed with MEK, and dried in the vacuum oven. The weight of Fraction 6 was 3.9 grams. The last fraction (Fraction 7) contained a large amount of hexane. The volume was reduced and the sample handled the same way as Fraction 6. The weight of this fraction was 6 grams.

After the fractions were purified by the above procedure, intrinsic viscosity and osmometry measurements were made on the fractions.

For the viscosity measurements each fraction was dissolved in DMAC with concentrations decreasing with increasing molecular weight. Solvent flow times plus the original concentration and three dilutions were run for each fraction. The flow times were obtained in a number 50 Cannon-Ubbelodhe dilution viscometer which was thermostated at 30°C ± 0.01°C in a water bath. The data were then reduced to $\ln \eta r/C$ and plotted versus concentration (See Figure 3). The plots were extrapolated to zero concentration with the intercept giving $[\eta]$ and the slope yielding k' as calculated from equations 1 and 2.

$$1. \quad -\beta' = \frac{\text{slope}}{[\eta]^2}$$

$$2. \quad k' = 0.5 - \beta'$$

Fraction 3 data are meaningless since it contained LiCl.

Next four concentrations of fractions 2, 4, 5, and 6 were dissolved in DMAC and number average molecular weights were obtained from osmometry data which was obtained with the Mechrolab High Speed Membrane Osmometer. The data were reduced to $\sqrt{\pi/c}$ versus c. (See Figure 4). Squaring $\sqrt{\pi/c}$ extrapolated to zero concentration and using the equation

$$\overline{M}n = \frac{RT}{\left(\frac{\pi}{c}\right)_{c = 0}}$$

the number average molecular weights were calculated. There was some diffusion of Fraction 6 which required measuring the solution head (h soln) as a function of time and extrapolating log h soln to zero time at injection of sample. Since Fraction 6 exhibited diffusion no attempt was made to make measurements on Fraction 7. None of the other fractions showed diffusion. Data for Fraction 3 are missing. This fraction contained LiCl as evidenced by the extremely rapid diffusion rate when the solution was placed in the osmometer, therefore, the measurement was not made. The results are shown in Table X.

TABLE X

Intrinsic Viscosity and Number Average Molecular Weight (PBI-M4)

Fraction	[η] dl/gm	$\pi/C \times 10^{-2}$	$\overline{Mn} \times 10^{-4}$
2	1.41	6.20	4.239
3	--	--	--
4	0.76	17.46	1.505
5	0.67	21.23	1.238
6	0.58	23.93	1.098
7	0.46	--	--

FRACTIONATION OF PBI-M5 and M6

Two samples (PBI-M5 and M6) were fractionated in the same manner with the intention of combining those fractions having similar viscosities. The combined fractions would be further fractionated to give large fractions with homogeneous molecular weights. The general procedure was to thermostat a solution of PBI-M at 61°C; then add enough hexane to cause turbidity. After removing the flask from the bath and allowing the sample to stand at room temperature, an excess amount of hexane was added and the temperature was raised back to 61°C where the flask was allowed to stand for several days until the fraction had completely separated. The supernatant liquid was then drawn off by vacuum into another flask and more hexane was added to this solution. The flask was again thermostated in the water bath at 61°C until the subsequent fraction had precipitated. The procedure was repeated until the next to the last fraction was removed from solution. For the last fraction, the volume of the remaining solution was reduced by evaporation under vacuum; the polymer was precipitated, washed, and freeze-dried in the same manner as the previous fractions. Each fraction was dissolved in DMAC; then benzene was added until the benzene to DMAC ratio was 1.3 to 1. This mixture was pipetted into enough pure benzene to make the benzene to DMAC ratio 10 to 1. The fractions were washed with a liter of pure benzene, freeze-dried, and finally dried in a vacuum oven.

PBI-M5 was obtained by combining several solutions which were made up by refluxing a sample of PBI-M in DMAC for 3 days followed by filtering through sintered glass filters of coarse, medium, and fine porosity. PBI-M6 was obtained by taking a large sample of PBI-M and attempting to dissolve it at room temperature in DMAC which had been previously dried over molecular sieves. After the sample showed no signs of dissolving even after being allowed to stand for one week; it was refluxed for one week, then filtered through coarse, medium, and fine sintered glass filters to remove any insoluble material.

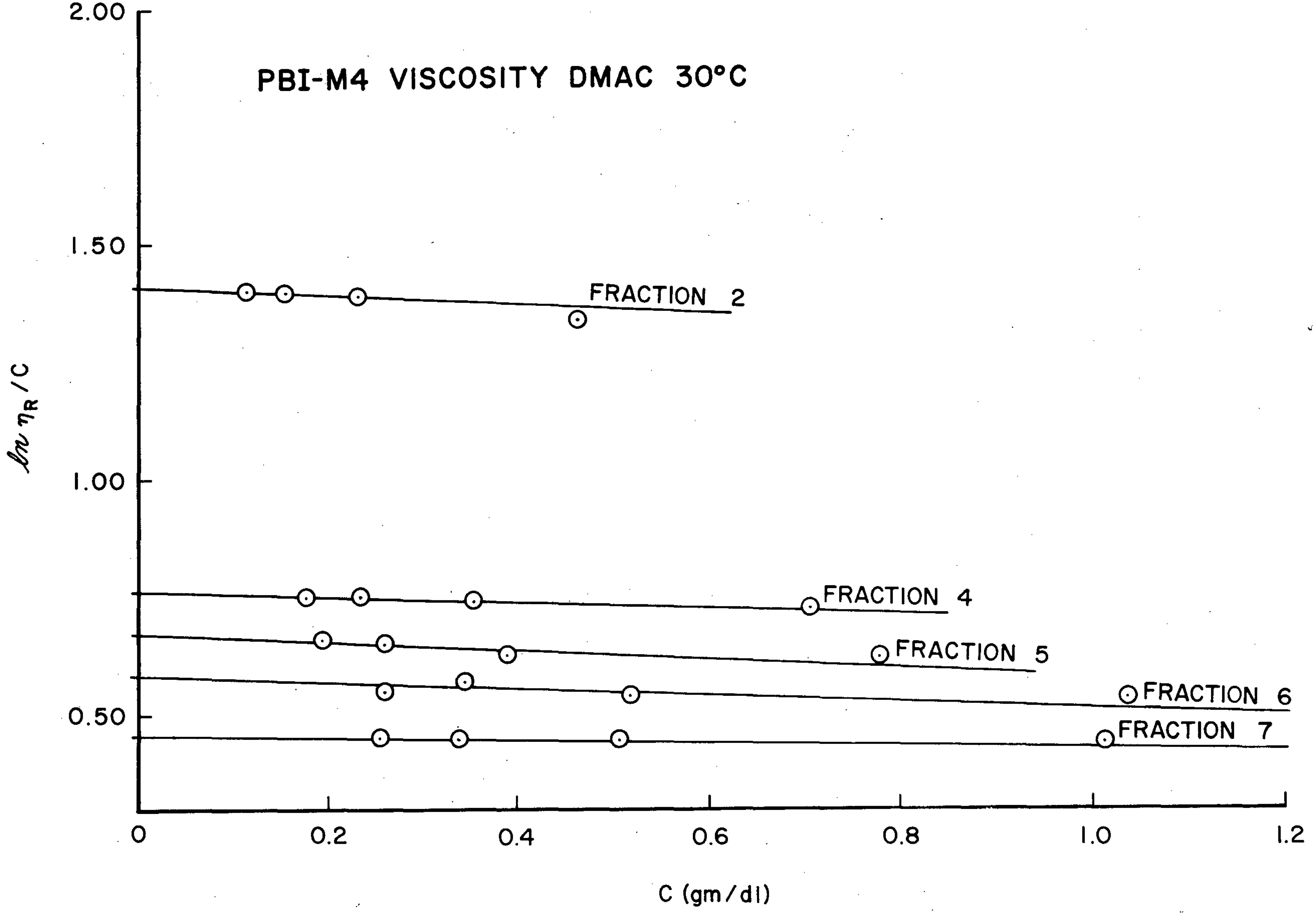

Figure 3. Intrinsic viscosity, PBI-M4 fractions in DMAC at 30° C. $\ln \eta_r / C$ versus concentration.

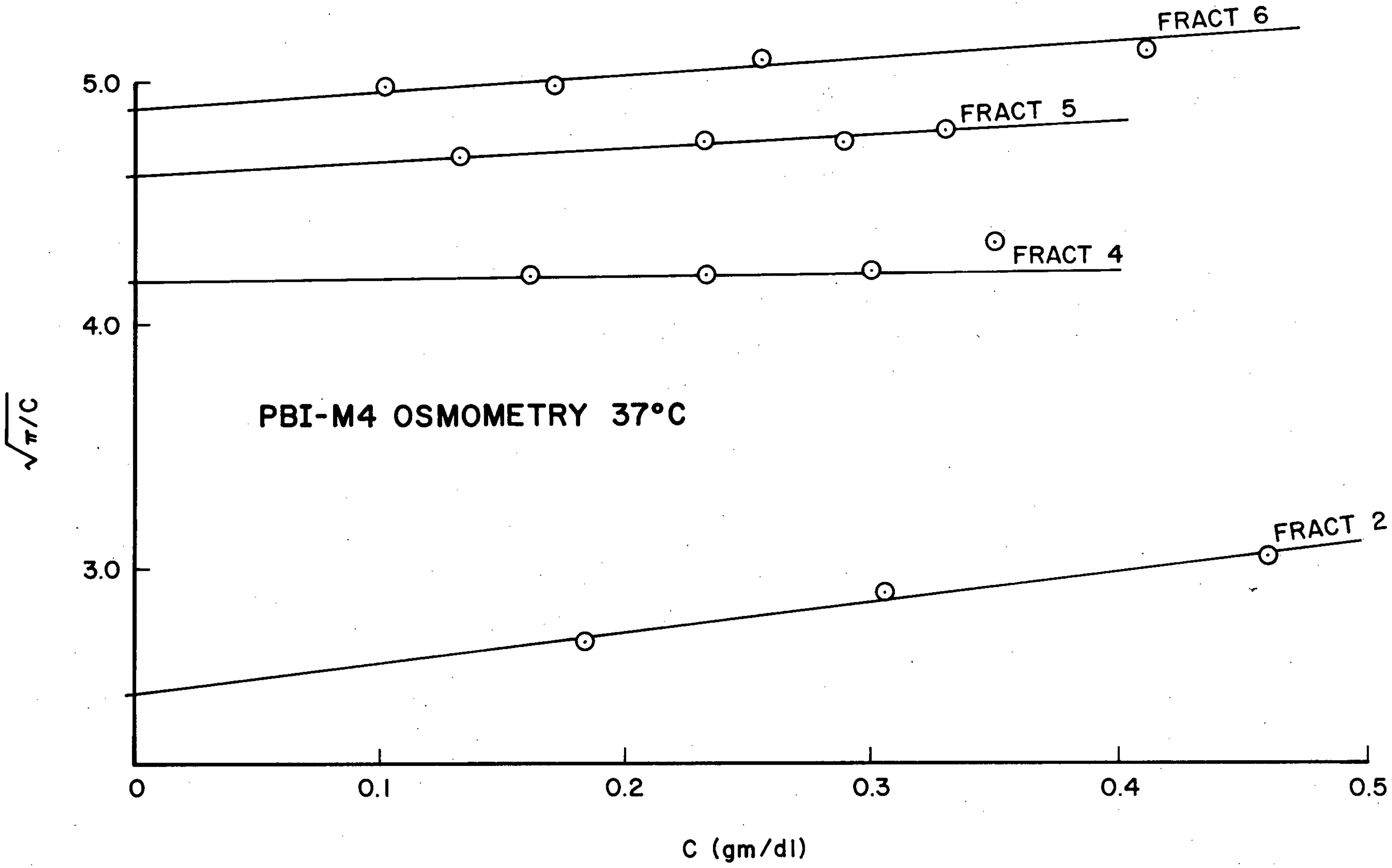

Figure 4. Osmotic pressure, PBI-M4 fractions in DMAC at 37°C $\sqrt{\pi/C}$ versus concentration.

Fraction 5 of PBI-M5 had a small amount of insoluble material which became readily soluble upon being precipitated in MEOH. The insoluble portion is thought to have hexane trapped in it which is removed upon precipitation and drying. This fraction was redissolved and handled in the same manner as the rest of the fractions.

TABLE XI

Intrinsic Viscosity for PBI-M5 and M6

Fraction	wt (gms)	[η] (dl/gm)
PBI-M5-F1	11.25	1.026
F2	9.05	0.894
F3	4.00	0.808
F4	5.70	0.654
F5	9.05	0.471
F6	9.00	0.321
PBI-M6-F1	16.76	1.294
F2	11.67	1.006
F3	10.72	0.780
F4	10.48	0.571
F5	5.40	0.412
F6	6.91	0.251

Using the technique previously described, intrinsic viscosities were run on each of the fractions and those with similar viscosities were combined to be fractionated. The fraction size and viscosity of each fraction is shown in Table XI.

It had been noted that fraction size can be predicted by plotting grams sample ppct divided by excess solvent added versus concentration of sample before addition of excess non-solvent [11]. (See Figure 5 and 6).

PBI-M8 FRACTIONATION AND VISCOSITIES

The sample designated as PBI-M8 was obtained by combining fractions of PBI-M5 and PBI-M6 that were of similar molecular weight as determined by viscosity measurements. The precipitation and purification procedure for PBI-M8 was similar to that for M5 and M6 except the starting samples were combined fractions rather than whole sample. Once the fractions were obtained, viscosity measurements were run on them in order to determine the efficiency of the fractionation. In cases where two or more fractions had very similar viscosities they were combined into one fraction and refraction-

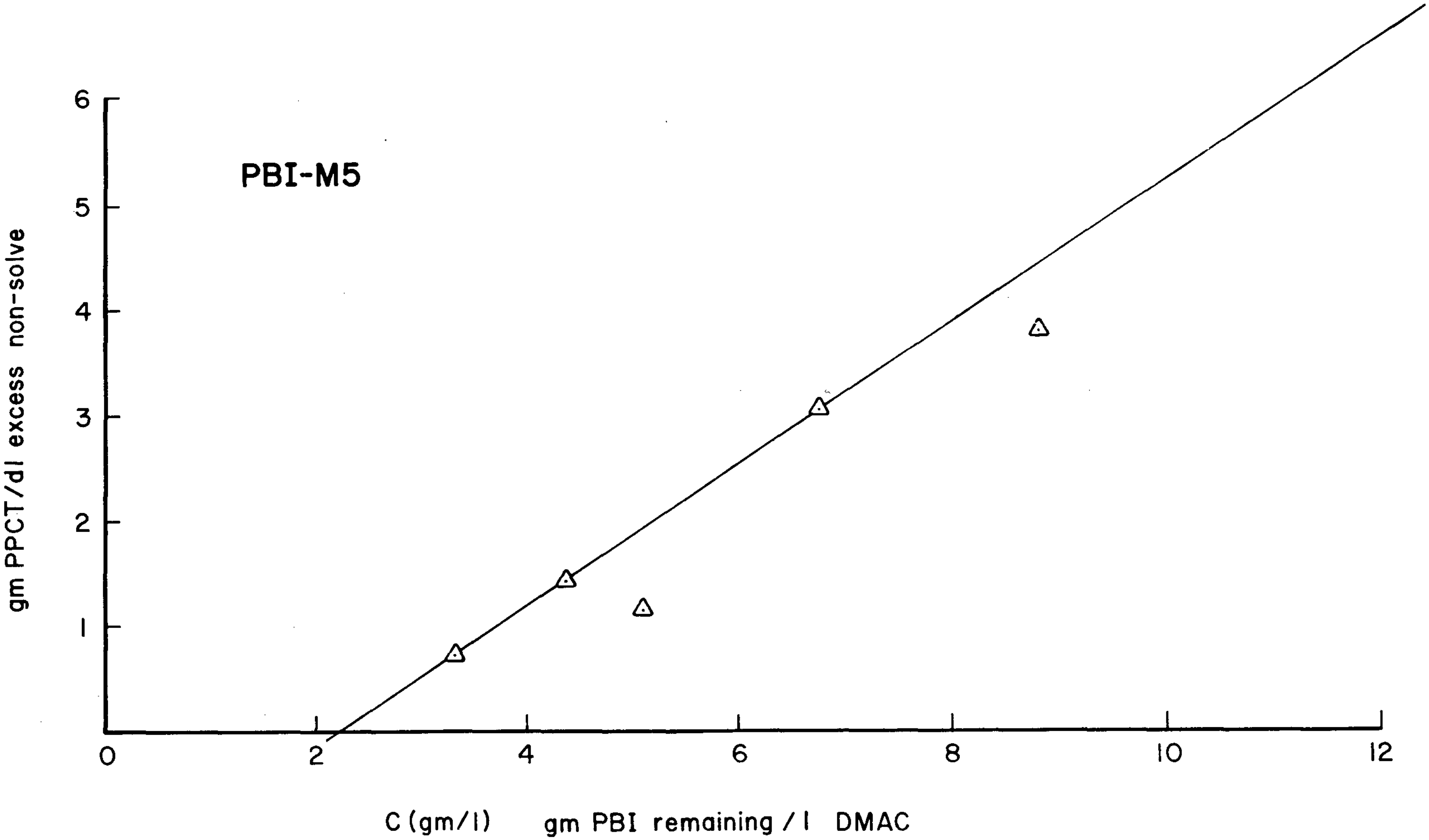

Figure 5. Fractionation of PBI-M5, grams of sample precipitated per deciliter excess non-solvent versus concentration of PBI solution.

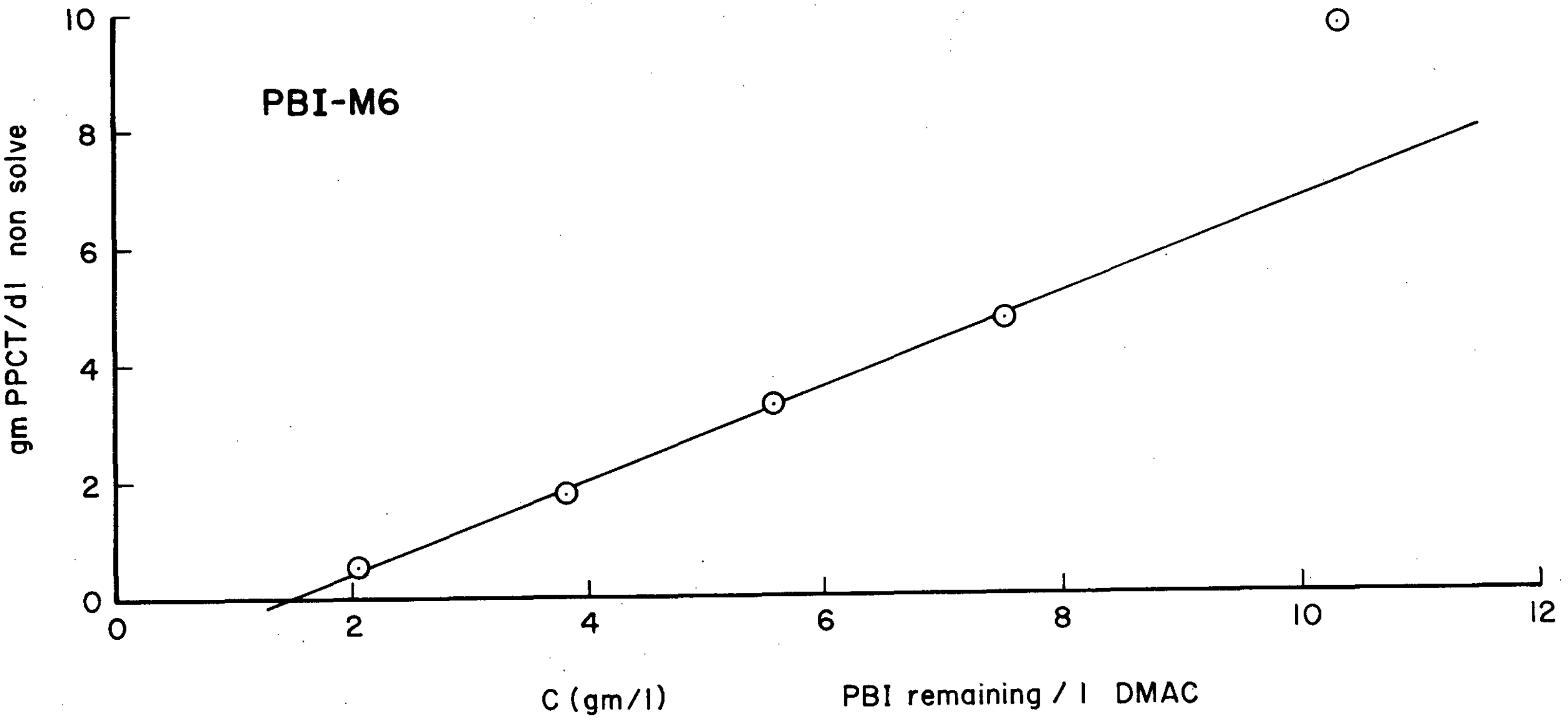

Figure 6. Fractionation of PBI-M6, grams of sample precipitated per deciliter excess non-solvent versus concentration of PBI solution.

ated if the sample size was large. As was the case with PBI-M6 the DMAC was dried over molecular sieves and the hexane was dried over calcium chloride prior to being used.

An attempt to run viscosity measurements in DMAC was abandoned after not being able to obtain reasonable data. The fractions were readily soluble in DMSO, so it was chosen as the solvent for the viscosity measurements.

The data were calculated and plotted as $\ln \eta r/C$ (Figure 7). Table XII shows fractions of PBI-M5 and PBI-M6 that were combined and the resultant fractions of PBI-M8 with their viscosities.

TABLE XII

PBI-M8 Fractionation

Samples Combined	wt. (gm)	[η] *	Resultant Samples	wt. (gm)	[η] **
M-5-F1	11.25	1.026	M-8-F1	12.0	1.485
M-6-F1	15.0	1.294	M-8-F2	16.0	0.728
M-6-F2	11.67	1.006	M-8-F3	12.0	0.621
	37.92			40.0	
M-5-F2	9.05	0.894	M-8-F4	2.1	1.204
M-5-F3	4.00	0.808	M-8-F5	10.6	0.754
M-6-F3	10.72	0.780	M-8-F6	16.1	0.564
	23.77			28.8	
M-5-F4	5.70	0.654	M-8-F7	2.8	0.668
M-6-F4	10.48	0.571	M-8-F8	11.0	0.463
	16.18		M-8-F9	4.6	0.373
				18.4	
M-5-F5	9.05	0.471	M-8-F10	1.9	0.535
M-6-F5	5.40	0.412	M-8-F11	8.9	0.399
	14.45		M-8-F12	4.5	0.289
				15.3	
M-5-F6	9.00	0.321	M-8-F13	5.0	0.340
M-6-F6	6.91	0.251	M-8-F14	10.8	0.187
	15.91			15.8	

* DMAC, 30°C

** DMSO, 30°C

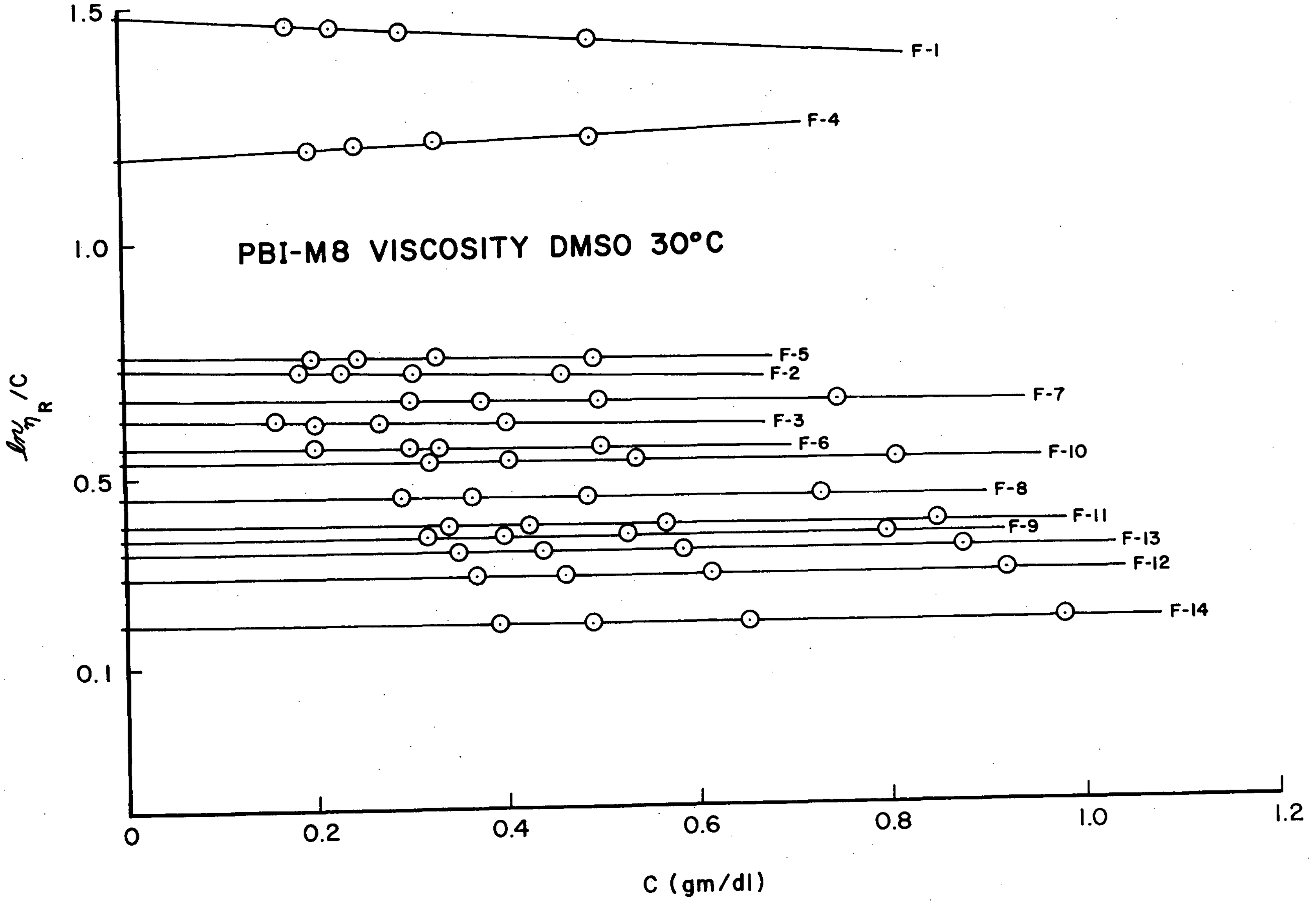

Figure 7. Intrinsic viscosity, PBI-M8 fractions in DMSO at 30°C. $\ln \eta_r / C$ versus concentration.

VISCOSITY AND OSMOMETRY MEASUREMENTS OF PBI-M-2-F3

Intrinsic viscosity and osmometry measurements were made on a sample of poly(5, 5' bibenzenedazole, 2, 2' diyl, 1, 3 phenylene) designated PBI-M-2-F3[12]. After it had been purified, the sample was precipitated in MEOH and dried overnight when precipitation could not be accomplished with MEK. It was then redissolved in DMAC and precipitated in MEK with no further problem. A one percent solution was made up for the intrinsic viscosity measurement which was run in a Cannon-Ubblodhe dilution viscometer. The data which consisted of an original concentration plus three dilutions were calculated and plotted as $\eta sp/c$ vs C. The make up concentration was used in the calculations. The temperature was 35°C ± 0.01°C. The intrinsic viscosity is 1.07. Four solutions ranging from 0.15% to 0.30% were made up for the osmometry measurements. The samples were run in a Mechrolab Model 502 high speed membrane osmometer thermostated at 37°C. The data were obtained on the third portion of each aliquots of the solution. The data were reduced and plotted at π/c vs C and the molecular weight calculated. The molecular weight for this sample is 26,650. The results are shown in Figure 8 and Figure 9.

PBI-M5 and PBI-M6 SPECTRA

When viscosity solutions were made up, it was noted that the solutions were slightly different in color. The PBI-M5 fractions were the normal yellowish color, while the PBI-M6 fractions appeared to have a slight reddish tint. To determine whether the color difference was due to absorption at different wavelengths or just a matter of intensity, the spectra from two samples of each series were run on a Beckman model DK-2A ratio recording Spectrophotometer. In order to insure that the difference was not due to differences in molecular weight, samples having similar molecular weights were used for the measurements. The samples were scanned from 750 mμ-325 mμ. Both showed the PBI absorption peak at 347 mμ, but the reddish solutions (PBI-M6) also had a shoulder on the absorption curve at 550 mμ. (See Figure 10).

There appeared to also be a difference in the degree of absorbance since PBI-M5-F5 and PBI-M6-F5 were approximately the same concentration, but PBI-M6-F5 showed a higher absorbance. (See Figure 11). Solutions of PBI-M6-F4 and PBI-M5-F4 were carefully made up to the same concentration and run on the Beckman model DK-2A Spectrophotometer. The absorbance of PBI-M6-F4 appears to be approximately twice that of PBI-M5-F4.

PBI-M6-F1 PRECIPITATION

In an attempt to remove the red coloration in the PBI-M6 fractions, PBI-M6 fraction 1 was dissolved in DMAC, which had been dried over molecular sieves, and precipitated in MEK.

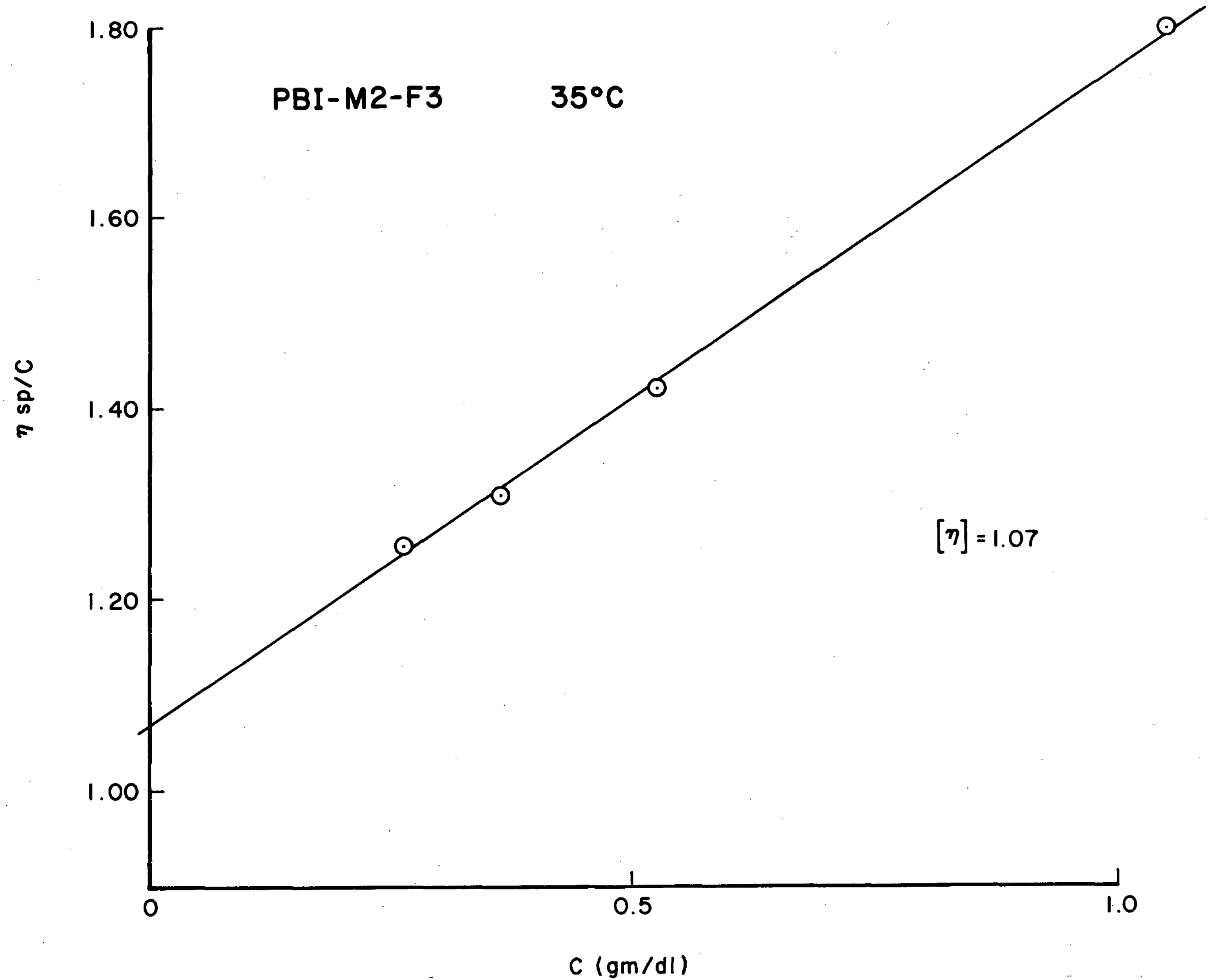

Figure 8. Intrinsic viscosity, PBI-M2-F3 in DMAC at 37°C. η_{sp}/C versus concentration.

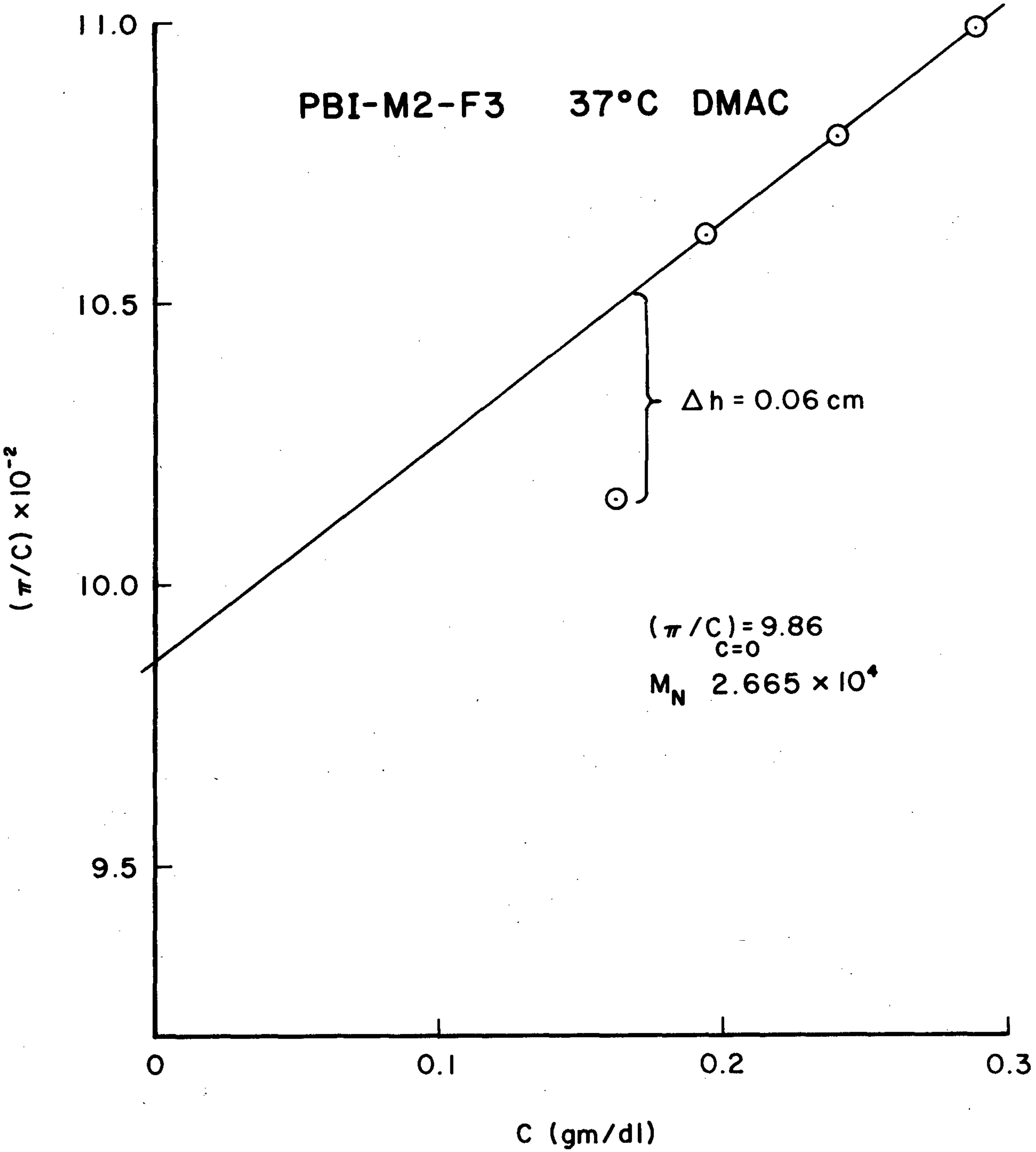

Figure 9. Osmotic pressure, PBI-M2-F3 in DMAC at 37°C. π/C versus concentration

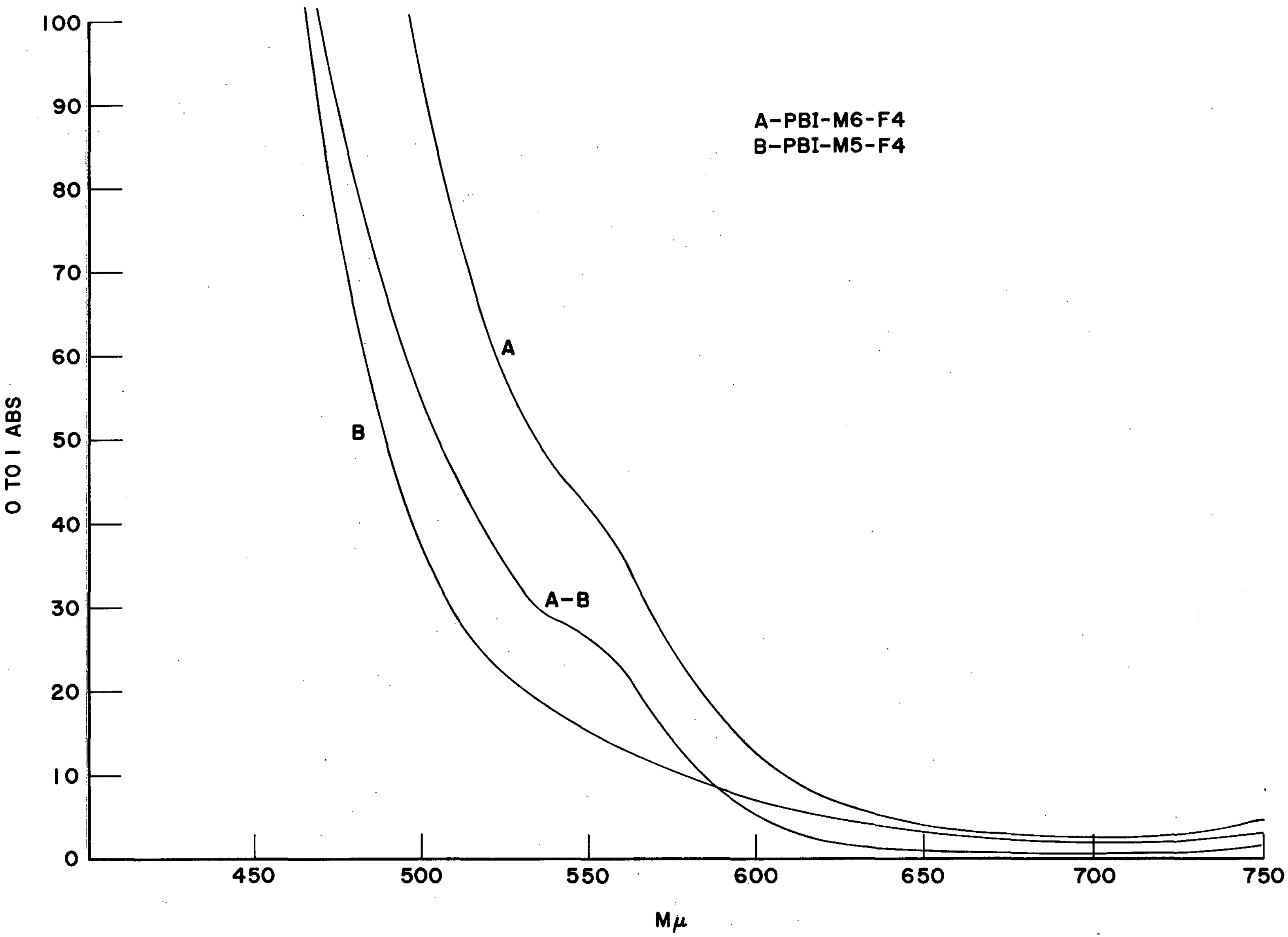

Figure 10. Absorption versus wavelength. Curve A-PBI-M6-F4 with DMAC in solvent cell. Curve B-PBI-M5-F4 with DMAC in solvent cell. Curve A-B-PBI-M6-F4 with PBI-M5-F4 in solvent cell

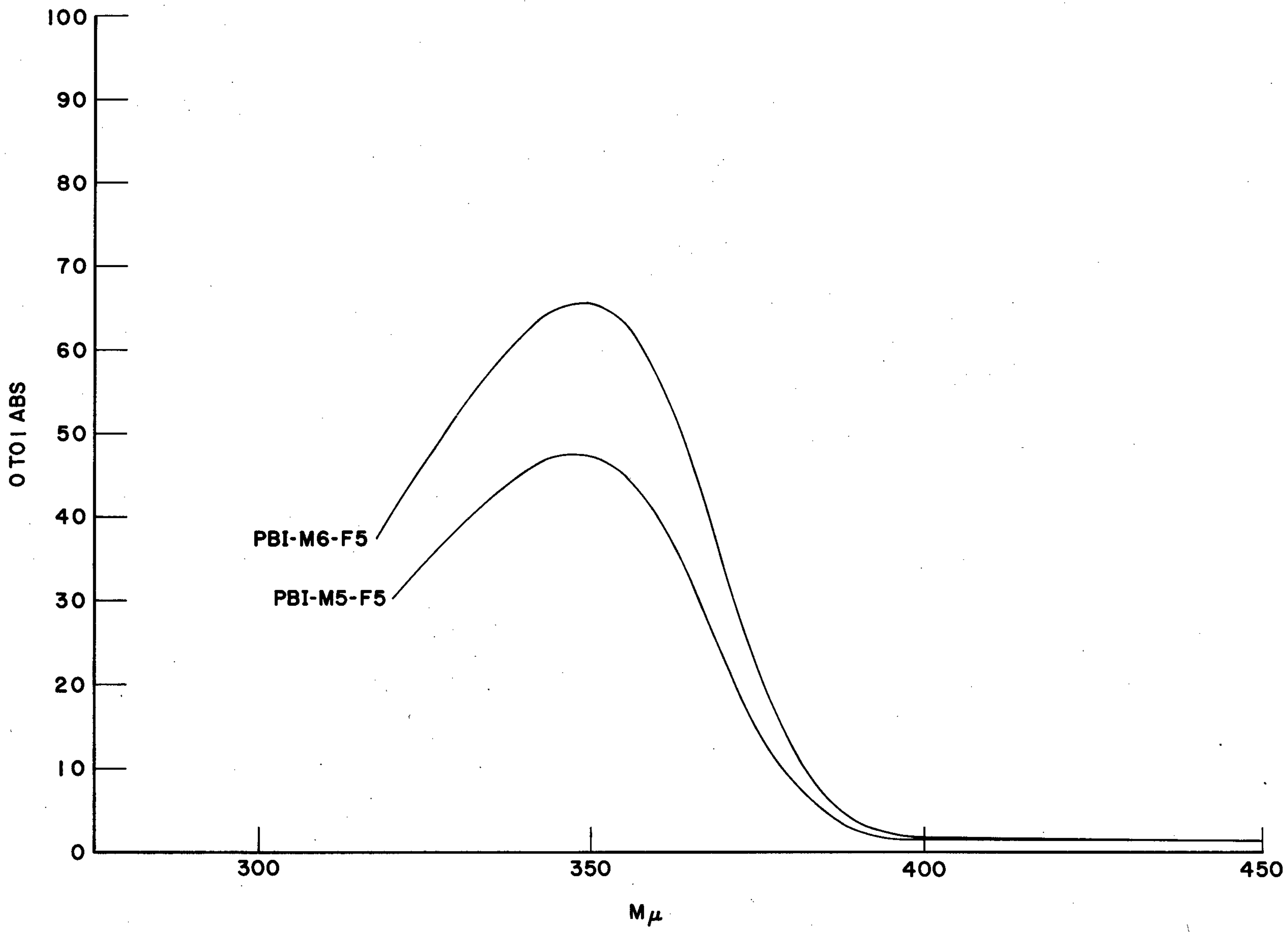

Figure 11. Absorption difference for solutions of approximately the same concentration. Absorption versus wavelength.

Approximately 15 grams of PBI-M6-F1 was dissolved in 800 cc of dried DMAC. The solution was made up in a 1 liter flask which was not large enough to accomodate the 40% (335 cc) MEK necessary to cause turbidity; therefore, 300 cc was poured off into a graduate cylinder and redistilled MEK was added to the flask, but no turbidity occurred even with addition of approximately 550 cc MEK. Next, 600 cc of this mixture was added to 2500 cc MEK. The remaining 300 cc was brought to turbidity and approximately 100 cc was added to the second beaker. The remainder was added to a third beaker containing 2500 cc. A small amount of the polymer in the third beaker did precipitate and was filterable, but beakers one and two remained crystal clear. Beaker one was heated to approximately 70°C and beaker two was cooled to approximately -60°C with no change occurring. After the first beaker had cooled to room temperature, 600 cc of ether was added with no success in causing precipitation. Next, 70 cc MEOH, 85 cc water and 190 cc benzene was added. The solution remained clear for a short time and then a precipitate started forming. The solution was stirred about one and one-half hours and allowed to stand over the weekend. The beaker to which the H_2O, benzene, ether and methanol had been added precipitated but did not settle out until it was stirred for a short time after having stood over the weekend. The non-solvents were stripped off the solution and the PBI-DMAC solution was precipitated with MEOH. After drying in a vacuum oven the PBI was dissolved in dry DMAC and precipitated in MEK, washed with MEK, MEOH, and ether and vacuum oven dried. The red coloration still remained.

VISIBLE AND UV SPECTRA OF PBI-M

It was thought that the color difference which had been observed in various samples of PBI-M might be due to water somehow attaching to the PBI molecule. A set of experiments were designed to determine whether or not this might be the case. A sample of PBI-M was dissolved in sulfuric acid to dehydrate the molecule. A portion of the sample was precipitated in acetone, filtered, washed with acetone, washed with methanol, washed with ether, and then dried in a vacuum oven. A second portion was precipitated in water, filtered, washed with water and freeze-dried in water. A third portion was precipitated in acetone after acetone was added to the sulfuric acid solution to get a more finely divided precipitate. It was washed with acetone, methanol, benzene, and then freeze-dried in benzene. Spectra were run on the samples to determine if there were any differences. Neither sample showed any absorption peaks in the region from 700 mμ to 400 mμ when run with DMAC as the reference, but when the acetone precipitated sample was run with the water precipitated sample in the reference side of the spectraphotometer, there was a peak at 403 mμ (See Figure 12). When the acetone precipitated sample was run against the water precipitated which had CaH_2 added to it, the 403 peak disappears and there are two peaks; one at 422 which is small and broad and one at 397 which is large and sharp (See Figure 13). A sample of the water precipitated PBI-M was treated with CaH_2 to determine if a drying agent would affect the absorption peaks. The sample was run three times: once after being heated at 90°C for approximately one hour; after allowing the solution to stand overnight; and again after heating it overnight at 90°C. As may be noted from the spectra in Figure 14, there was a decrease in the peak characteristic of PBI at 347 mμ. Upon heating the soltuion overnight at 90°C, this peak decreased further and a new one appeared at 290 mμ.

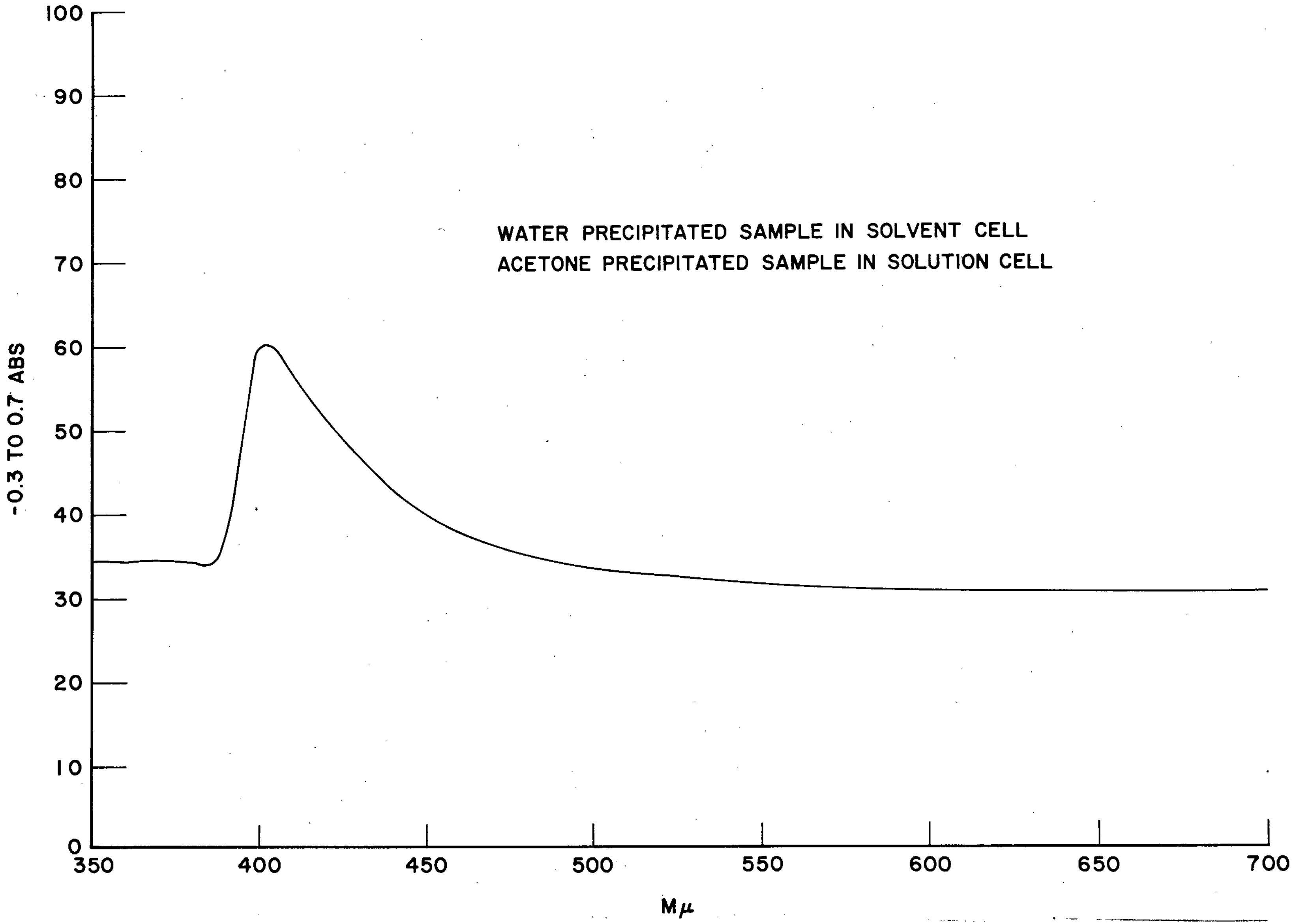

Figure 12. Absorption curve for PBI-M acetone precipitated solution with PBI-M water precipitated solution in the solvent cell. Absorption *versus* wavelength.

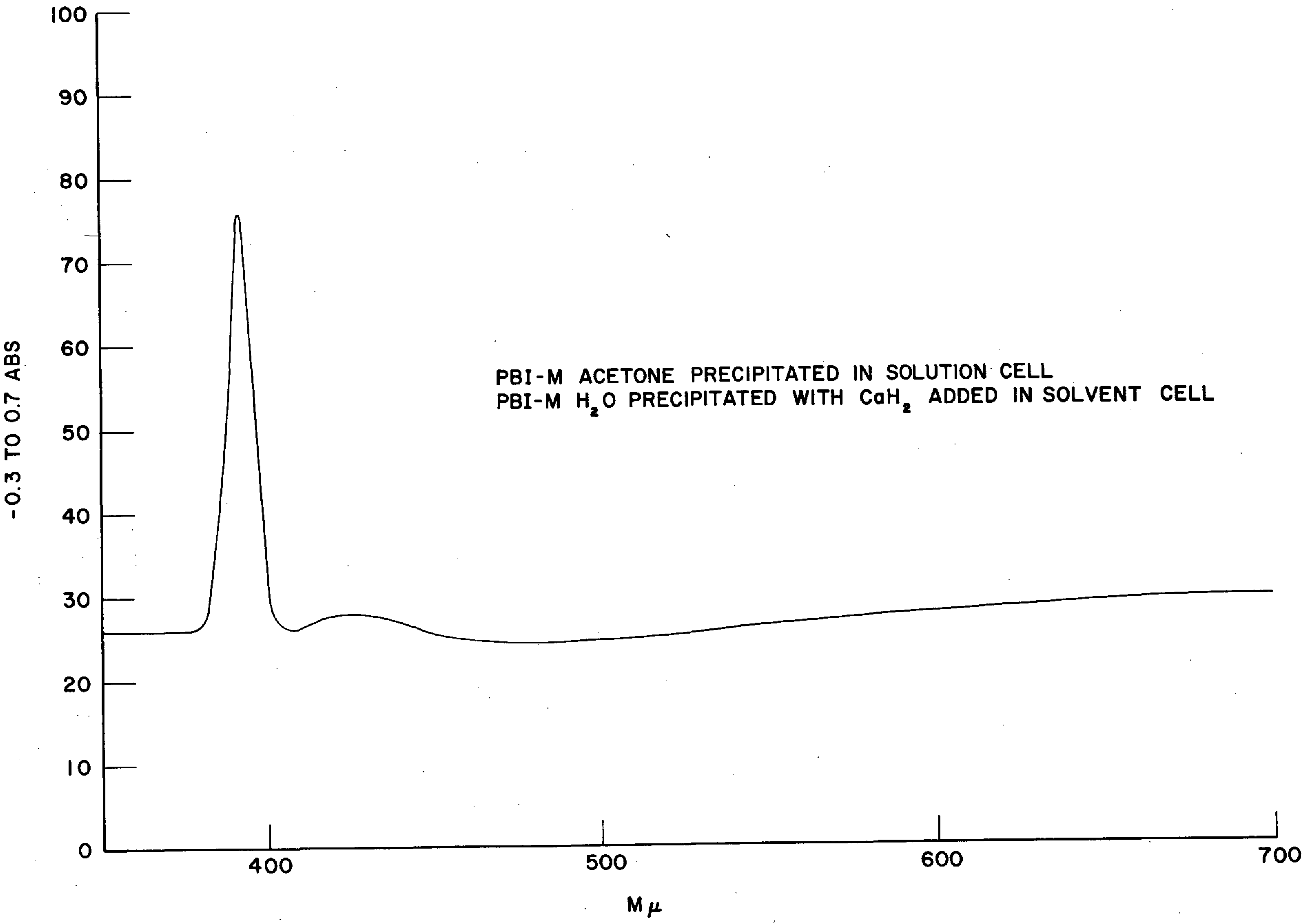

Figure 13. Absorption curves for PBI-M acetone precipitated solution with water precipitated solution which had been treated with CaH_2 in the solvent cell. Absorption versus wavelength.

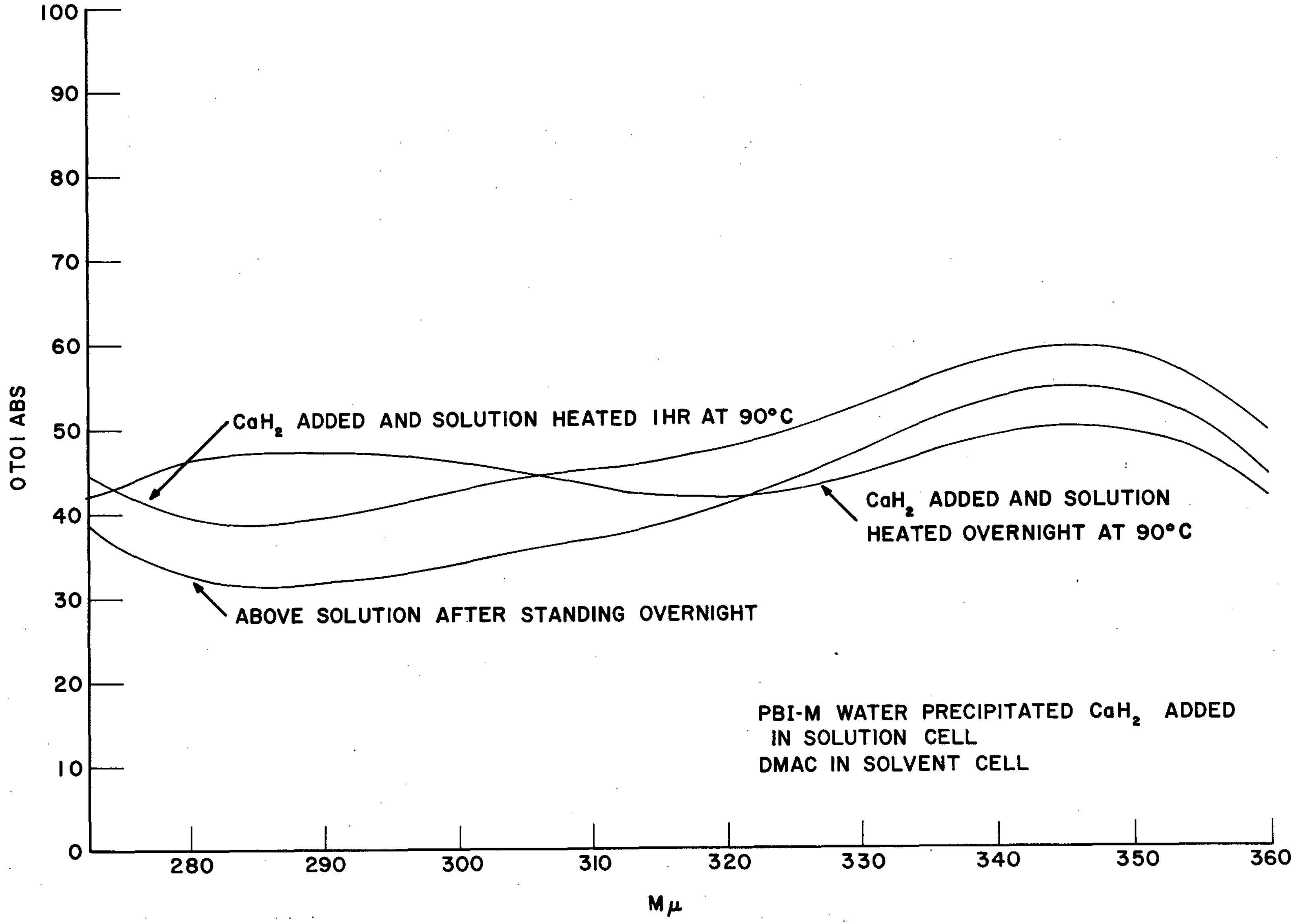

Figure 14. Absorption curves for PBI-M water precipitated solution after treatment with CaH_2. DMAC was used in the solvent cell. Absorption versus wavelength.

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12. Sample was obtained from T. E. Helminiak, WPAFB

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13. ABSTRACT

Some solution property measurements have been made on two samples of Poly(5, 5'bibenzimidazole, 2, 2'-diyl, 1-3-phenylene). Fractions were obtained from these samples by using a solvent-nonsolvent system (DMAC-hexane).

Intrinsic viscosities were determined for both whole samples and fractions in DMAC at 37°C. Several problems concerning sample solubility, concentration determination, and coloration of the solutions have been encountered.

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