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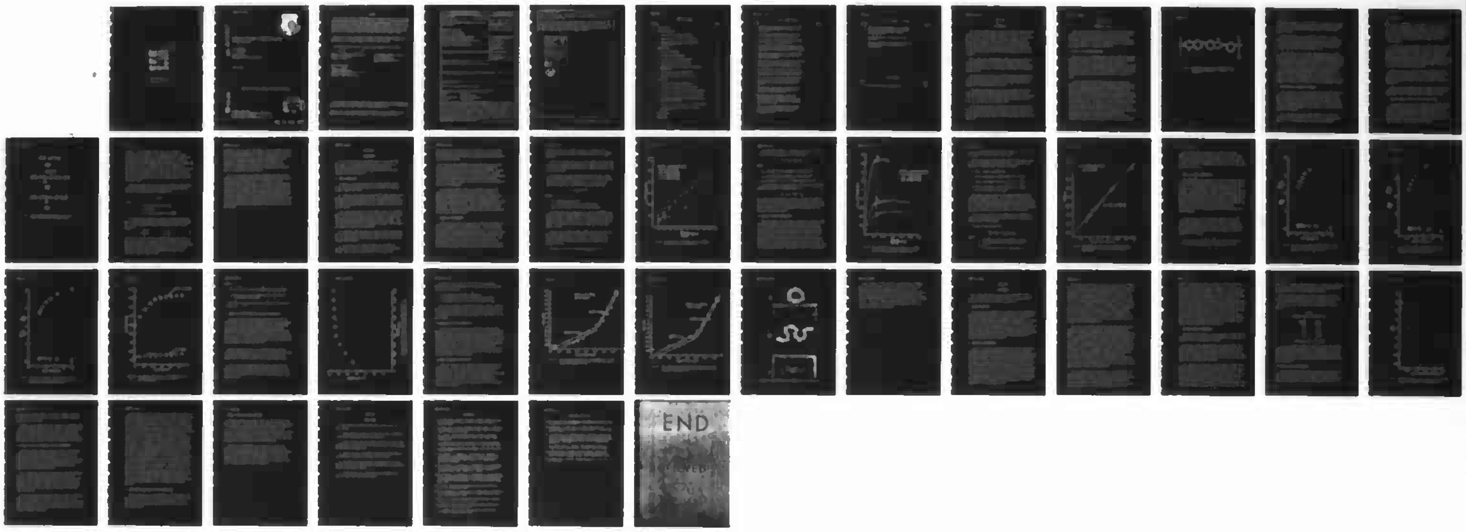

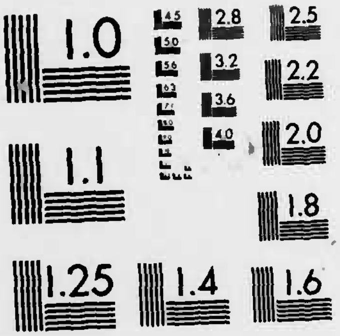

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BEHAVIOR OF AN AROMATIC HETEROCYCLIC POLYMER IN SALT SOLUTION

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Polymer Branch
Nonmetallic Materials Division

August 1983

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The addition of lithium chloride (LiCl) to solutions of poly(5,5'bibenzimidazole-2,2'diyl-1,3 phenylene) (PBI) and N,N dimethylacetamide (DMAC) resulted in the expansion of the PBI molecule in solution. This expansion was owing to the association of lithium and/or chloride ions in the region of the nitrogen atoms on the polymer chain. The presence of these ions expanded the polymer chain by means of electrostatic repulsion. This effect was reflected in the results of conductivity and viscosity studies. In general, LiCl can be used for both increased solubility and increased viscosity for this polymer-solvent system.

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20. Abstract (Continued)

A ratio of 0.125 gram of LiCl per gram of PBI was determined to be the optimum amount of LiCl to be added. This amount corresponds to one mole of LiCl for every mole of PBI repeat unit.

The PBI molecule was determined to have entanglements in concentrated solution at every 27 or 28 molecules along the polymer chain. This length between the entanglements is very low in comparison to other polymers, indicating a strongly interacting system. The chain length between entanglements was approximately the same for both PBI-DMAC and PBI-LiCl-DMAC solutions.

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SECTION I

INTRODUCTION

This research covered herein is part of the overall research attempt to obtain high-temperature aromatic heterocyclic polymers in a solid, oriented state. If this attempt is successful, fibers or films could be formed with the molecules oriented to afford the highest possible unidirectional strength. The use of poly (5,5' bibenzimidazole-2,2' diyl-1,3 phenylene) (PBI) in this study is based on PBI's desirable thermal, physical, and chemical properties in addition to its behavior in solution-- which lends itself to the specific approach used in this research.

PBI, as most other high-temperature aromatic heterocyclic polymers, will decompose before melting. Therefore, conventional methods of strength orientation, i.e., stretching at a temperature above the glass transition, cannot be used. This research is an attempt to circumvent the limitation.

The approach of this study is to expand the polymer molecules while in solution and retain this expansion while orienting these molecules during a spinning or extrusion process. This report deals with the expansion of the polymer while in solution.

The addition of lithium chloride (LiCl) to a solution of PBI and N,N'-dimethylacetamide (DMAC) has been determined to have a marked effect on the solubility of the polymer and the viscosity of the polymer in solution. Generally, the solutions increase in solubility and in viscosity with the addition of the LiCl salt.

This study was undertaken to determine the mechanism and effect of the LiCl on a PBI-DMAC solution and to conduct various analytical tests, such as conductivity, viscosity, and solubility studies, to determine the optimum solution concentrations for the maximum expansion of the PBI molecule.

SECTION II

LITERATURE REVIEW

This review covers the initial use of lithium chloride in solution to enhance the solubility and viscosity of polymers, the mechanism by which the LiCl affects the PBI polymer chain, and the properties expected of a PBI-LiCl-DMAC mixture. The molecular structure of poly (5,5' bibenzimidazole - 2,2' diyl-1,3 phenylene) (PBI) as presented by Vogel (Reference 19) is illustrated in Figure 1.

1. USE OF LiCl IN POLYMER SOLUTIONS

The use of LiCl in a PBI-DMAC system was first introduced by Denyes (Reference 6) working for Celanese under an AFWAL Materials Laboratory contract. The addition of LiCl was introduced to prevent the precipitation of PBI from a DMAC solution. Denyes (Reference 6 indicted that PBI would "phase out" of a PBI-DMAC solution if the solution were allowed to stand for 1 to 3 days. Upon the addition of 1 per cent LiCl, the solution stabilized and did not precipitate over a period of 30 days.

LiCl has been used in several polymer systems to enhance the solubility of polymer solution. Iwakura (Reference 12) indicated that solubility of polyphenylbenzimidazoles in DMSO, DMAC, NMP, and DMF was greatly increased by the addition of LiCl. Kwolek (Reference 13) reported that LiCl addition aided the solvation of a polyamide and was highly desirable for an amide-urea medium. Itoi (Reference 11) reported that polyvinyl alcohol (PVA), which is insoluble below 130 C in pure dimethylformamide (DMF), was dissolved at 80 C in DMF containing greater than 1.6 per cent LiCl. Ten grams of PVA in two grams of LiCl and ninety grams of DMF yielded a colorless solution with a viscosity of 29.5 poise at 30 C. The use of LiCl for solvation was again illustrated by Fedorov (Reference 7) in synthesizing poly(p-phenylene-terephthalamide) in DMAC. Fedorov indicated that the increased interaction between solvent and polymer due to LiCl addition promoted

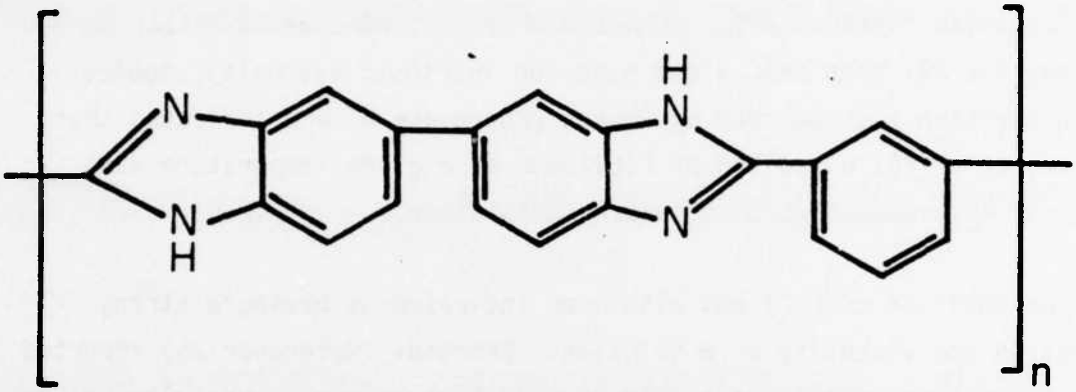


Figure 1. The Molecular Structure of the Repeat Unit of Poly (5,5' bibenzimidazole - 2,2' diyl - 1,3 phenylene)

higher molecular weights. Savinov (Reference 18) reported for the polycondensation of terephthaloyl chloride with p-phenylenediamine in DMAC, the presence of LiCl increased polyamide solubility and the polymer molecular weight.

Helminiak (Reference 10) reported that LiCl-DMAC was a better solvent for PBI than DMAC alone based on intrinsic viscosity studies. One dissention was recorded by Denyes (Reference 6) who indicated that the amount of PBI dissolved by LiCl-DMAC at a given temperature was slightly less than that dissolved by DMAC alone.

The addition of LiCl has also been indicated as having a strong effect on the viscosity of a solution. Nebrasov (Reference 16) reported that the characteristic viscosity of poly)m-phenylene isophthalamide) in N'N dimethylformamide (DMF) and DMAC in the absence of LICl are 1.55 and 1.75 respectively, and change in the presence of LiCl. The dependence of the viscosity on the concentration of LiCl is characterized by a curve with a maximum at low concentrations. These viscosities are doubled and tripled respectively. The results were explained by the absorption of LiCl by the polymer chains. Benner (Reference 3), Helminiak (Reference 10 and Denyes (Reference 6) have indicated a strong increase in viscosity with the addition of LiCl to a PBI-DMAC solution.

2. MECHANISM OF LiCl ADDITION TO POLYMERS

Bello (Reference 2) indicates that the mechanism for the addition of LiCl to a polymer chain can be attributed to the interaction of the polymer, LiCl, DMAC, and, in some instances, water. Lagowski (Reference 14) reported that DMAC and water have a strong affinity for each other, with water being present in small amounts in all DMAC solutions. Lagowski indicates that DMAC will tend to protonate the water hydrogens, thus forming a complex.

For a LiCl-DMAC-water system, Bello (Reference 1) claims that lithium ions would be complexed in either of two ways--between DMAC molecules or as a hydrated lithium ion which was held between

DMAC molecules. These situations can be seen as examples A and B in Figure 2. Bello (Reference 1) also reported that solutions of LiBr or LiCl in DMAC yield much higher viscosities than could be assumed by ideal mixing. Bello further indicated that the increased viscosity of proteins in strong LiBr solution may be due to extension of the polypeptide chain as a result of attaching hydrated lithium ions in close proximity.

In further work, Bello (Reference 2), basing his work on x-ray diffraction studies, reported that both Li^+ and Cl^- ions participate in the complexing of DMAC and water. Example C of Figure 2 illustrates this interaction. On the basis stated, the chlorine ion complexes the hydrogen molecules, hydrates, and then attaches a Li-DMAC complex. It was also reported that LiBr and LiCl are the only compounds that complex in this manner. For example, the same amount of NaBr increases the viscosity of NMA only half as much as LiBr.

Fedorov (Reference 8) reinforces the second approach of Bello. He indicates a direct interaction of Cl^- anions with the protons of the amide group in substituted benzanilides in the LiCl-DMAC system. Fedorov reported this interaction causes strong chemical shifts in the NMR spectra.

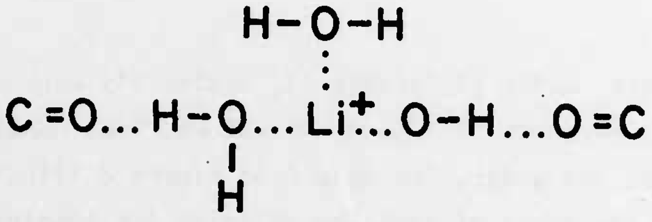
Several mechanisms therefore have been suggested in explanation of LiCl-DMAC interaction with polymer systems. Whichever mechanism is applicable, a basis for this interaction has been established.

3. EXPECTED CHARACTERISTICS FOR A PBI-LiCl-DMAC SYSTEM

One characteristic which might be exhibited by a PBI-DMAC system with the addition of LiCl would be an increase in solubility based on the fact that Iwakura (Reference 12), Kwolek (Reference 13), Itoi (Reference 11), Fedorov (Reference 7) and Savinov (Reference 18) have indicated that the addition of LiCl has increased solubility in several different polymer systems. Helminiak (Reference 10) has confirmed that LiCl does increase the solubility of PBI in DMAC.

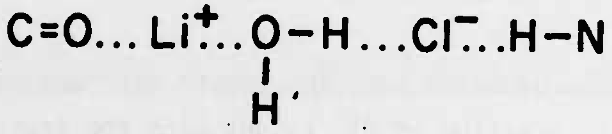
$\mathrm{C{=}O\cdots Li^{+}\cdots O{=}C}$

(A)



$$\mathrm{C{=}O\cdots H{-}\underset{\underset{H}{|}}{O}\cdots \overset{\overset{H-O-H}{\vdots}}{Li^{+}}\cdots O{-}H\cdots O{=}C}$$

(B)



$$\mathrm{C{=}O\cdots Li^{+}\cdots \underset{\underset{H}{|}}{O}{-}H\cdots Cl^{-}\cdots H{-}N}$$

(C)

Figure 2. Possible Complexing Mechanisms of LiCl with Water, Carbonyl Groups, and Amide Groups

The viscosity of a PBI-DMAC solution might also be markedly increased with the addition of LiCl. Nebrasov (Reference 16) has reported that the viscosity of a polyamide solution was substantially increased with LiCl addition while Benner (Reference 3), Helminiak (Reference 10) and Denyes (Reference 6) reported viscosity increases with the addition of LiCl to a PBI-DMAC system. Bello (Reference 1) explained the viscosity increase of proteins in a strong LiBr solution as being due to the extension of the polypeptide chain due to attaching lithium ions in close proximity. If this situation exists it could be used as an explanation for the viscosity increase observed in the PBI-LiCl-DMAC system.

From the experimental data taken on the viscosity of polymer melts and concentrated solutions, Bueche (Reference 5) indicates that the viscosity of a polymer system can be expressed by

$$\eta = KM^{3.5} \tag{1}$$

where:

η = the viscosity of the solution

K = a constant

M = the molecular weight of the polymer

This equation holds true for all values of molecular weight above M_b, the molecular weight between entanglements on the molecular polymer chain. Berry (Reference 4) refines the relation with the following equations:

$$\eta = KM^{3.4} \qquad M > M_b \tag{2}$$

$$\eta = KM^{1.0} \qquad M < M_b \tag{3}$$

A plot of this data for the PBI-LiCl-DMAC system would then yield the quantity M_b from which the number of chain atoms between entanglements could be calculated. This information would be useful in visualizing the physical situation existing in the polymer solution relative to the influence of chain extension on entanglements and comparing this situation to that for other polymers.

Entanglement data are usually translated in terms of the number of chain atoms between entanglements for the polymer. Although several terms are used to describe this quantity, Z, as used by Porter (Reference 17) will be used as the number of chain atoms between entanglements. Porter (Reference 17) and Markovitz (Reference 15) have presented the entanglement lengths for a large variety of polymers and polymer systems. The entanglement lengths nominally range from 100 to 800 for most of the polymer systems investigated.

As it is not possible to determine entanglement data using molten polymers for the system of materials being investigated, another method must be employed to obtain this data. Fox (Reference 9), Berry (Reference 4) and Porter (Reference 17) show tht the use of the product of volume fraction or weight fraction with the molecular weight may be substituted for the molecular weight. This allows the determination of entanglement lengths using just one polymer molecular weight by varying the polymer concentration. After the data have been determined, the molecular weight between the entanglements may be calculated by assuming a volume or weight fraction of one at the break point of the plot. The molecular weight between the entanglements is then used to calculate the chain length.

SECTION III

EXPERIMENTAL

This section presents the experimental work done on the PBI-LiCl-DMAC system. This includes PBI sample preparation, conductivity measurements, absolute and intrinsic viscosity measurements, concentrated solution studies, and a model estimation of the chain extension of the PBI molecules.

1. SAMPLE PREPARATION

To produce a more soluble sample with a higher surface area for easier solvation, the following process was performed on 50 grams of Celanese sample P-301-B PBI.

a. Solution - Past research revealed that PBI samples obtained from Celanese were not readily soluble in DMAC. This was because some of the sample was totally insoluble while the remainder of the sample had a low surface area which prevented the facile intermingling of the solute and the solvent.

Fifty grams (approximate) of PBI was heated to 160 C in 1 liter of DMAC. The heating was performed in an oil bath, with the sample purged with a steady flow of nitrogen to prevent oxidation. The sample was refluxed to prevent DMAC loss and stirred to prevent hot spots. This reflux heating was continued for approximately 36 hours. At this time the sample was cooled to room temperature.

b. Filtering - After the sample was cooled, it was filtered using coarse, medium, and fine-sintered glass filters to remove any insoluble PBI. The approximately 0.5 per cent of the PBI that was insoluble was removed from the sample.

c. Precipitation - The filtered solution was then added to approximately 15 liters of 2-butanone (MEK) and 3 liters of methanol (MeOH). This induced the precipitation of the dissolved PBI.

This induced the precipitation of the dissolved PBI. The precipitate was then collected in a Buckner funnel. Care was taken to insure that the precipitate was never allowed to dry during the filtration removal of the precipitating medium.

d. Washing - The precipitate was then washed with 500 milliliters of MEK. Washing with 100 milliliter mixtures of MEK and MeOH was accomplished proceeding at 20 per cent increases to pure MeOH. The wash was continued with 500 milliliters of MeOH, 500 milliliters of MeOH-diethyl ether mixtures, 500 milliliters of diethyl ether, 500 milliliters of diethyl ether-benzene mixtures, and 500 milliliters of benzene. Again care was taken to prevent drying of the precipitate and consequent exposure to the atmosphere.

e. Quasi-freeze drying - With the precipitate in benzene, the sample was frozen using dry ice and then dried in a vacuum until a pressure 2 microns was obtained and held for 2 hours. The sample was then heated in vacuum to 120 C and kept at this temperature until a pressure of 2 microns was held for 2 hours. This procedure yielded a dry sample with no exposure to oxygen. The resulting polymer was a light-brown powder. The particle size was small and the polymer particles were capable of clinging to the sample bottle owing to the electrostatic charges present on the particles.

2. CONDUCTIVITY MEASUREMENTS

Conductivity experiments were undertaken to determine the effect of PBI on the conductivity of a LiCl-DMAC solution. The basic hypothesis behind this study was that PBI molecules would attract Li^+ or Cl^- ions in the region of the nitrogen atoms on the PBI chain. The degree of this attraction could be determined by the reduction in conductivity of the LiCl-DMAC solution due to the loss of ions for electron transfer. The point of maximum reduction in conductivity would coincide with the maximum number of ions attracted to the chain of the polymer. With the ions on the polymer chain, the chain would expand owing to electrostatic repulsion by the ions. Therefore the point of greatest drop in conductivity would correspond to the maximum expansion of the polymer molecule.

Solutions of 1.58568 grams per deciliter PBI-DMAC and 4.99320 grams per deciliter PBI-DMAC were prepared using the sample produced earlier. A solution of 5.00612 grams per deciliter LiCl-DMAC was prepared for use as a titrating agent.

The resistance of a given solution was determined using a Thomas Serfass Conductivity Bridge, Model RCM 15B1, and a flat plate platinum conductivity cell with a cell constant of K = 1.0. The cell was replatinized before use. The conductance L_s was calculated by

$$L_s = \frac{K}{R_s D_s} \text{ (mho cm}^{-1}\text{)} \tag{4}$$

where

K = the cell constant (cm^{-1})
R_s = the resistance setting of the bridge (ohms)
D_s = the dial setting of the bridge (dimensionless)

The conductance versus concentration of LiCl was determined by the drop-wise titration of the PBI-DMAC or the DMAC sample with the 5.00612 grams per deciliter LiCl-DMAC solution. In each test 50 milliliters of sample was titrated until 500 drops of the LiCl-DMAC solution had been added. The sample was held at 20 C and stirred continuously with a magnetic stirrer.

Fifty milliliter samples of DMAC, 1.58568 grams per deciliter PBI-DMAC, 4.99320 grams per deciliter PBI-DMAC, and 0.95141 gram per deciliter PBI-DMAC were used in the testing. The 0.95141 gram per deciliter solution was prepared by diluting the 1.58568 grams per deciliter solution.

The results of the four titrations are found in Figure 3.

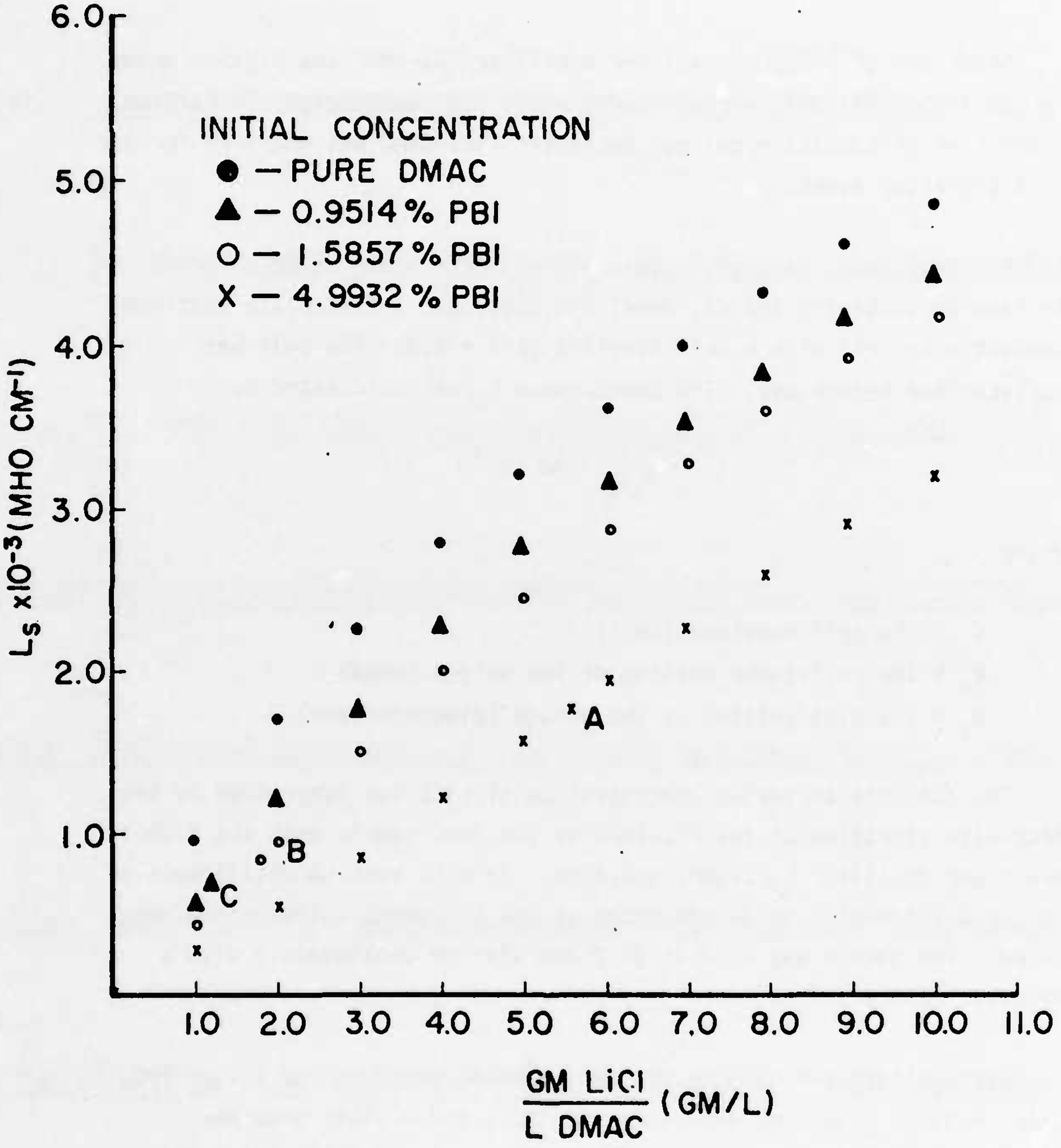


Figure 3. The Conductance of PBI-DMAC Solutions and DMAC as a Function of LiCl Concentration

To determine the reduction in conductance due to PBI attraction of the LiCl ions, the following term L_s was defined as

$$\Delta L_s = L_{sa} + L_{sb} - L_{sc} \qquad (5)$$

where

L_{sa} = the conductance of LiCl-DMAC solutions (mho cm^{-1})

L_{sb} = the conductance of PBI-DMAC solutions (mho cm^{-1})

L_{sc} = the conductance of PBI-LiCl-DMAC solutions (mho cm^{-1})

L_{sb} was determined to be approximately 0.001 for all concentrations studied, and therefore the equations reduce to

$$\Delta L_s = L_{sa} + 0.001 - L_{sc} \qquad (6)$$

The values of ΔL_s are plotted as a function of ratio of the grams of LiCl per gram of PBI shown in Figure 4. Note that the ΔL_s curve rose until a ratio of LiCl to PBI of approximately 0.125 was obtained. Here the curve flattens out. The significance of these results will be discussed later in this report.

3. INTRINSIC VISCOSITY MEASUREMENTS

These measurements were undertaken to reinforce the hypothesis that the addition of DMAC to a PBI-LiCl-DMAC solution with a LiCl to PBI ratio of approximately 0.125 or less would remove LiCl from the PBI molecule and result in the reduction of the viscosity of the polymer solution due to contraction of the polymer chain. Normally the plot used to determine the intrinsic viscosity of a solution would be straight-line plot and extrapolate to the intrinsic viscosity at zero concentration. If the expansion of the polymer molecules was changed during the dilutions, the plot would deviate from this straight-line plot and indicate this condition. The hypothesis tested by this experimental

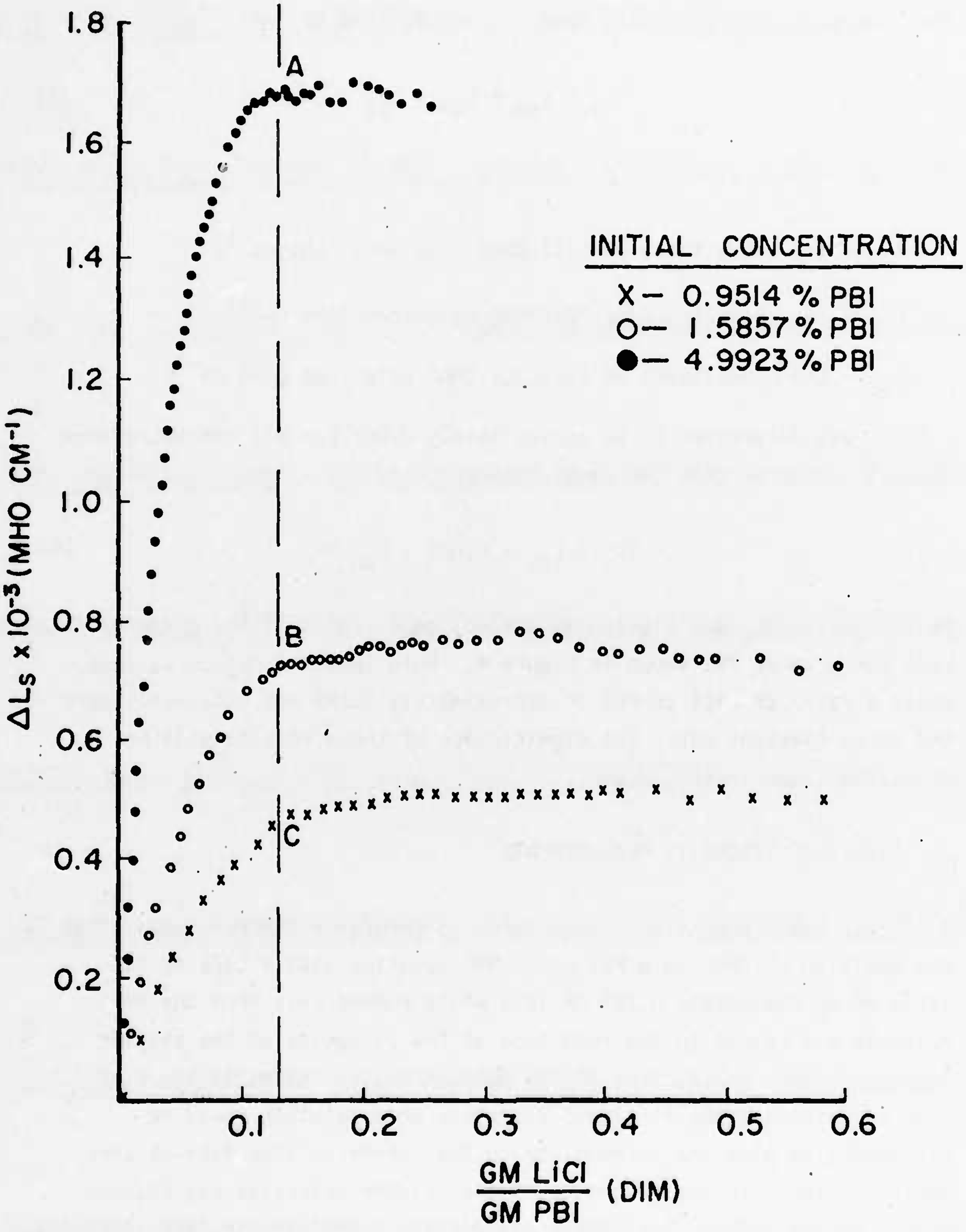


Figure 4. The Differences of Conductance Between a LiCl-DMAC Solution and Various PBI-LiCl-DMAC Solutions as a Function of the Weight Ratio of LiCl to PBI

work was formulated owing to the results of the conductivity testing. This subject is discussed later in this report.

Four solutions were prepared by the dilution of the 4.99320 grams per deciliter PBI-DMAC solution with DMAC and the 0.00612 gram per deciliter LiCl-DMAC solution. They were as follows:

1. %LiCl = 0.1330 (LiCl-DMAC only)
2. %LiCl = 0.1105 %PBI = 0.9766 LiCl/PBI ratio = 0.1132
3. %LiCl = 0.1231 %PBI = 0.9741 LiCl/PBI ratio = 0.1263
4. %LiCl = 0.1330 %PBI = 0.9721 LiCl/PBI ratio + 0.1369
   (% indicates grams per deciliter)

Measurements were performed in a #75 Cannon Ubbelohde dilution viscometer thermostated at 30 C. Five milliliters of solution and 5 milliliters of DMAC were added to the viscometer for the first reading. Five milliliter dilutions of DMAC were added and measured successively until a volume of 40 milliliters was reached. From four to six readings were taken and averaged to give the flow time for each dilution.

The calibration curve for the LiCl-DMAC sample is presented in Figure 5. The data indicated were used to calculate t_o for various concentrations in further tests.

Two plots of the data were made.

$$\frac{\ln \eta_r}{c} \text{ versus } c \text{ and } \frac{sp}{c} \text{ versus } c \qquad (7)$$

where:

η_r = flow time of the solution divided by the flow time for the corresponding LiCl-DMAC concentration

$\eta_{sp} = \eta_r - 1$

c = the concentration of PBI in DMAC (grams per deciliter)

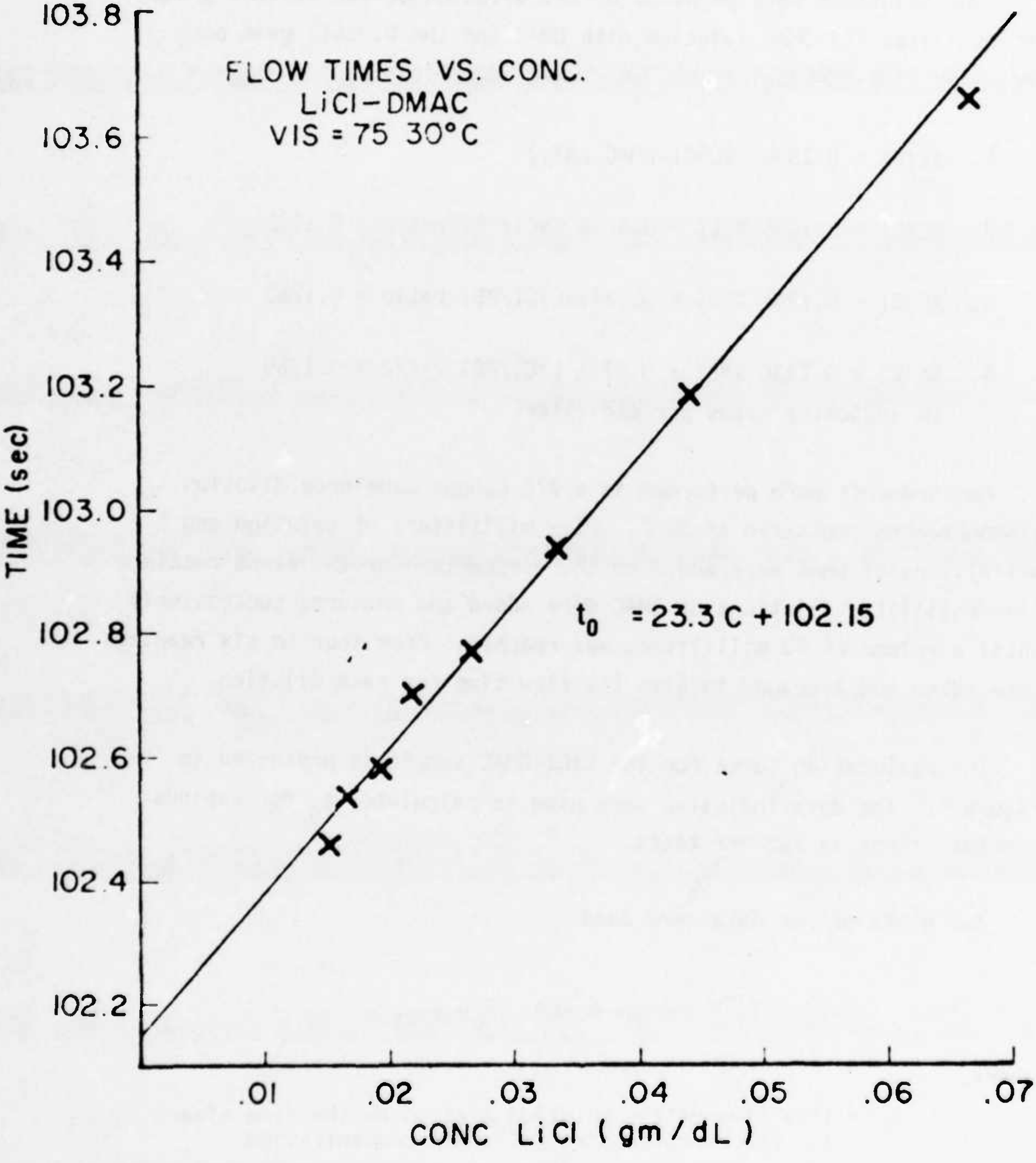


Figure 5. Flow Times as a Function of LiCl Concentration Used for the Calculation of t_o for Intrinsic Viscosity Measurements

The results of these measurements are graphed in Figures 6 through 8. By observation, the plots did not yield a straight-line extrapolation as expected in the determination of intrinsic viscosity. The results substantiate the hypothesis formulated in the discussion of the conductivity work. An explanation of these data will be presented in the discussion section.

4. ABSOLUTE VISCOSITY MEASUREMENTS

These measurements were undertaken to determine the optimum ratio of LiCl to PBI to provide the maximum viscosity for a given concentration of PBI. For this measurement a 0.21718 gram per deciliter solution of LiCl-DMAC and a 1.18332 grams per deciliter PBI-DMAC solution were prepared. Samples were prepared as follows: Ten milliliters of the PBI solution were diluted with the LiCl-DMAC solution and DMAC to produce a PBI-LiCl-DMAC solutionm of the desired concentration. Ten samples were prepared with the PBI concentration held constant at 0.47333 gram per deciliter and the ratio of LiCl to PBI varying from 0.00 to 0.225. Ten samples of LiCl-DMAC solutions were also prepared with the concentrations of the LiCl corresponding to the LiCl concentrations in the PBI samples.

The viscosities of the 20 samples were determined using a #50 Cannon-Fenske viscometer at 30 C. Ten milliliters of sample was filtered and delivered using a pipette. Four to six flow times were taken and averaged to determine the average flow time for the sample. The corresponding viscosities are plotted as a function of the LiCl concentration in Figure 9.

The viscosities of the PBI-LiCl-DMAC and the LiCl-DMAC solutions for equal LiCl concentrations were used to construct a ratio plot.

$$\eta_a = \eta_x/\eta_y \tag{8}$$

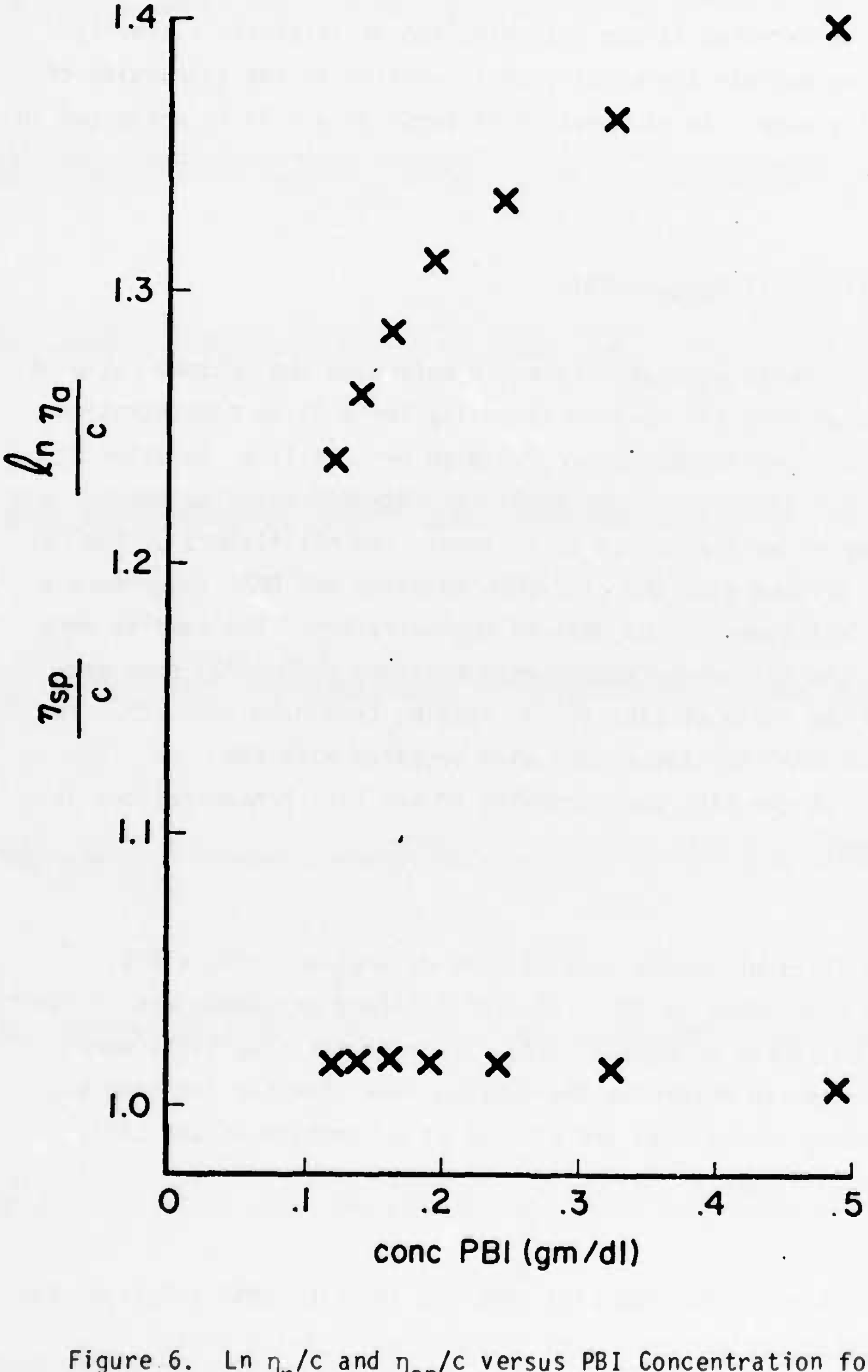


Figure 6. Ln η_r/c and η_{sp}/c versus PBI Concentration for the Dilution of a 0.9766 Gram per Deciliter PBI Solution Having a LiCl to PBI Ratio of 0.1132

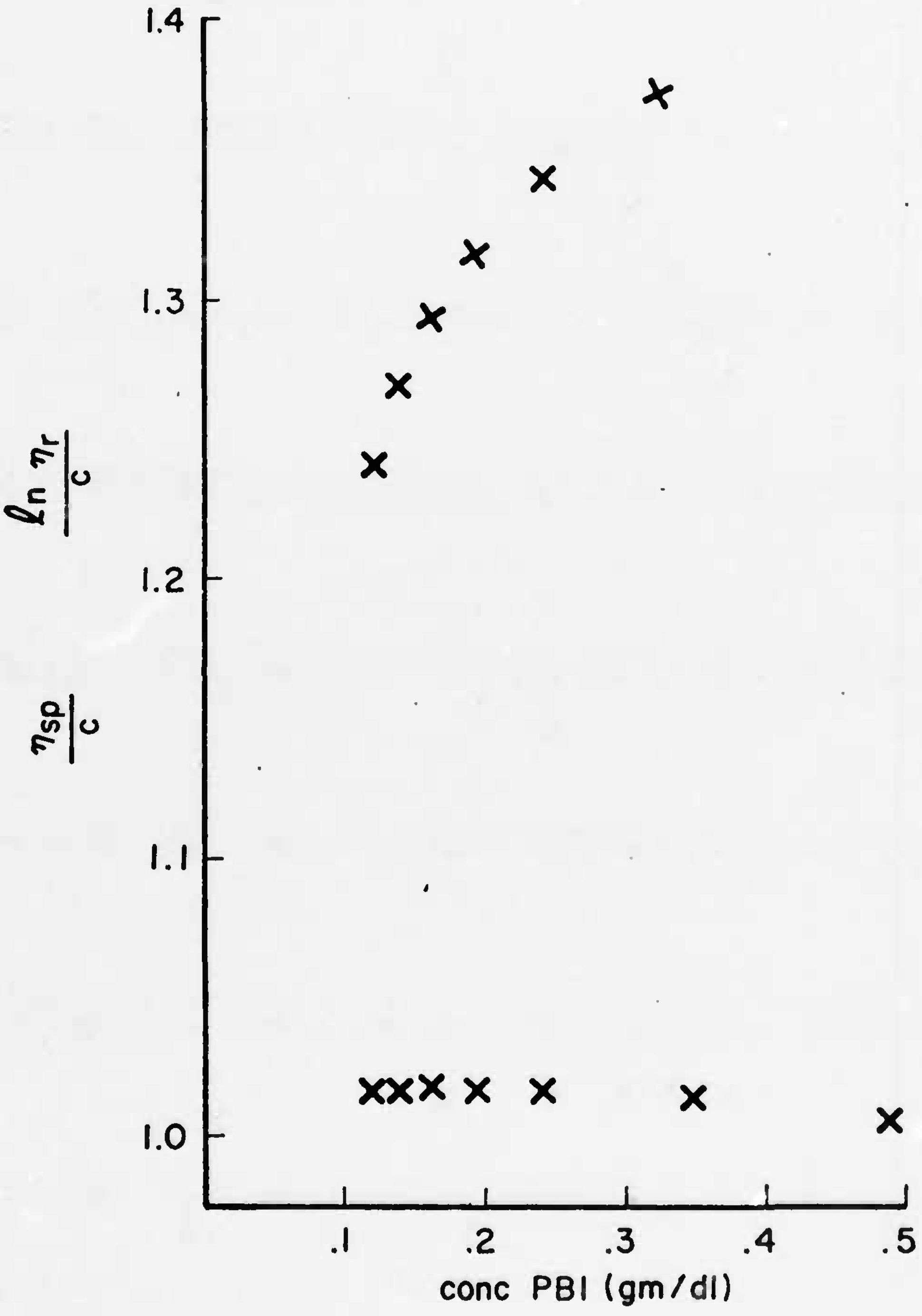


Figure 7. Ln η_r/c and η_{sp}/c versus PBI Concentration for the Dilution of a 0.9741 Gram per Deciliter PBI Solution Having a LiCl to PBI Ratio of 0.1263

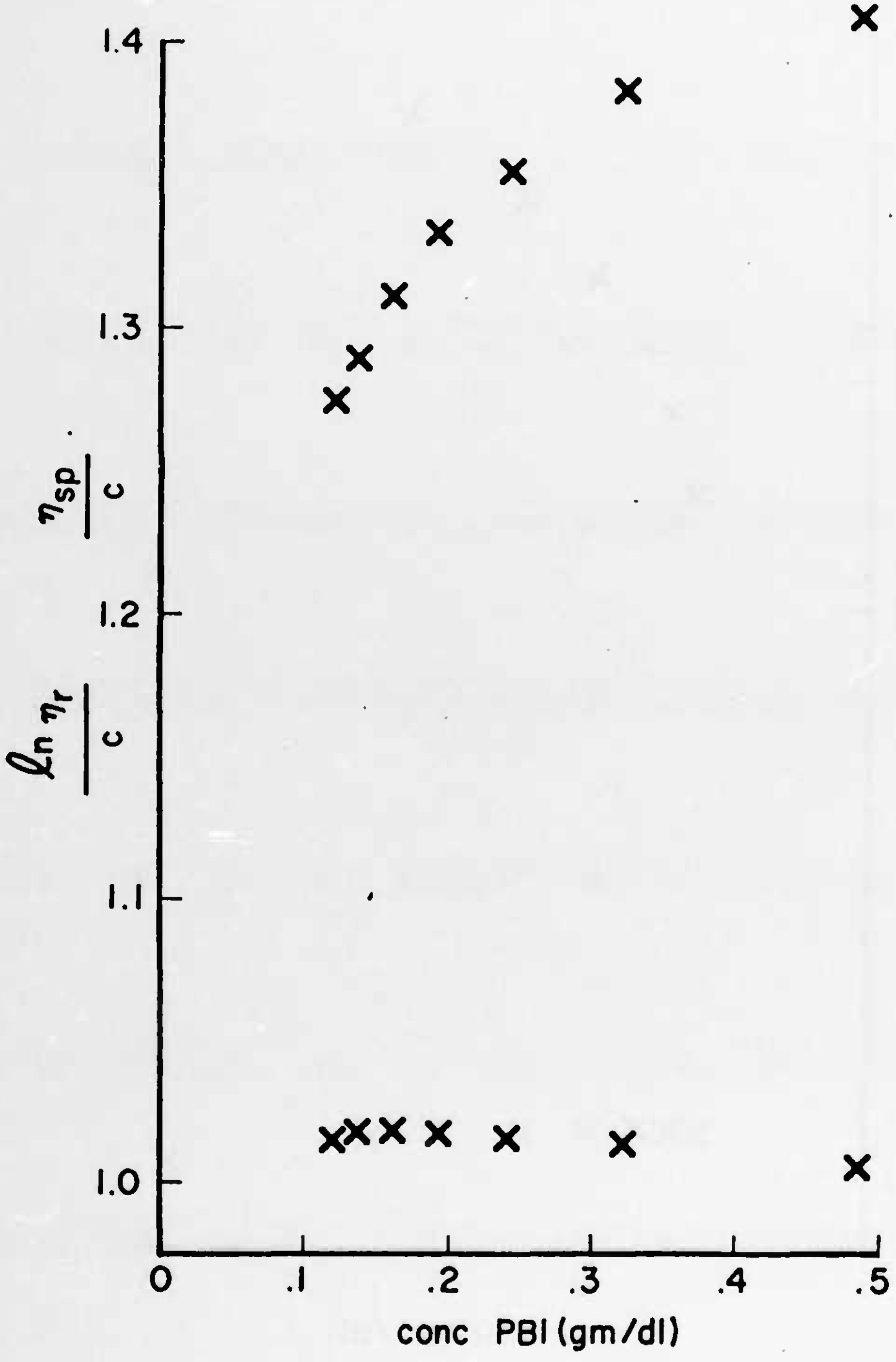


Figure 8. Ln η_r/c and η_{sp}/c versus PBI Concentration for the Dilution of a 0.9721 Gram per Deciliter PBI Solution Having a LiCl to PBI Ratio of 0.1369

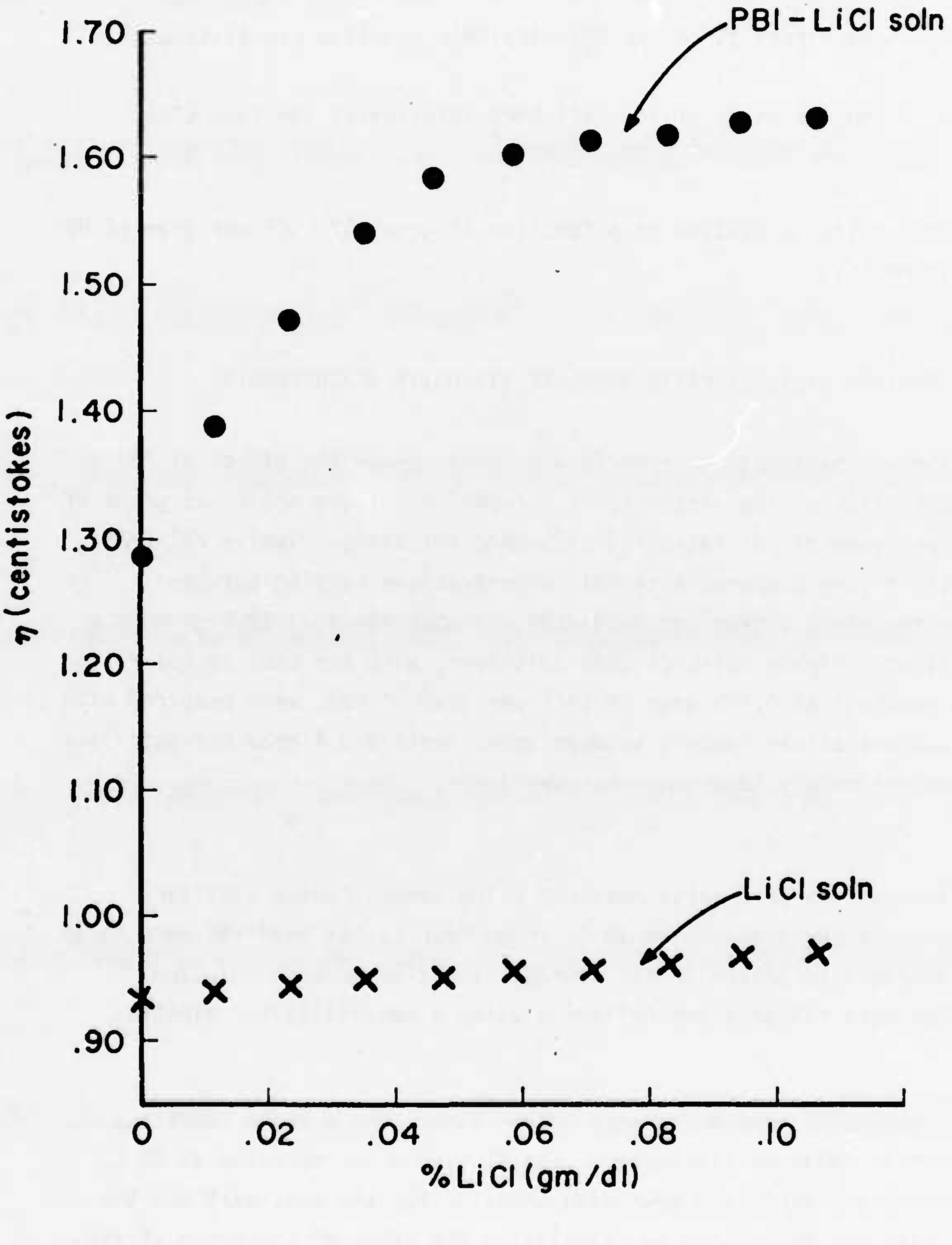


Figure 9. The Kinematic Viscosity of a 0.4733 Gram per Deciliter PBI-DMAC Solution and DMAC as a Function of LiCl Concentration

where

η_x = the viscosity of the PBI-LiCl-DMAC solution (centistokes)

η_y = the viscosity of the LiCl-DMAC solution at the same LiCl concentration (centistokes)

This ratio is plotted as a function of grams of LiCl per gram of PBI in Figure 10.

5. CONSTANT LiCl/PBI RATIO ABSOLUTE VISCOSITY MEASUREMENTS

These experiments were performed to determine the effect of PBI concentration on the viscosity of PBI-DMAC solutions and 0.125 grams of LiCl per gram of PBI ratio PBI-LiCl-DMAC solutions. Twelve PBI-DMAC solutions were prepared with PBI concentrations ranging between approximately 0.5 gram per deciliter and approximately 13.0 grams per deciliter. Eleven PBI-LiCl-DMAC solutions, with the LiCl to PBI ratio held constant at 0.125 gram of LiCl per gram of PBI, were prepared with PBI concentrations ranging between approximately 0.4 gram per deciliter and approximately 12.0 grams per deciliter.

Viscosities were first measured using Cannon-Fenske capillary viscometers thermostated at 30 C. From four to six readings were taken and averaged to determine the average flow time of each solution. Samples were filtered and delivered using a ten-milliliter pipette.

Viscosities were measured a second time using a Haake Rotovisco concentric cylinder viscometer. The NV system was operated at 30 C. The solutions exhibited Newtonian behavior for the most part and the viscosity was determined by calculating the slope of the shear stress-shear rate curve.

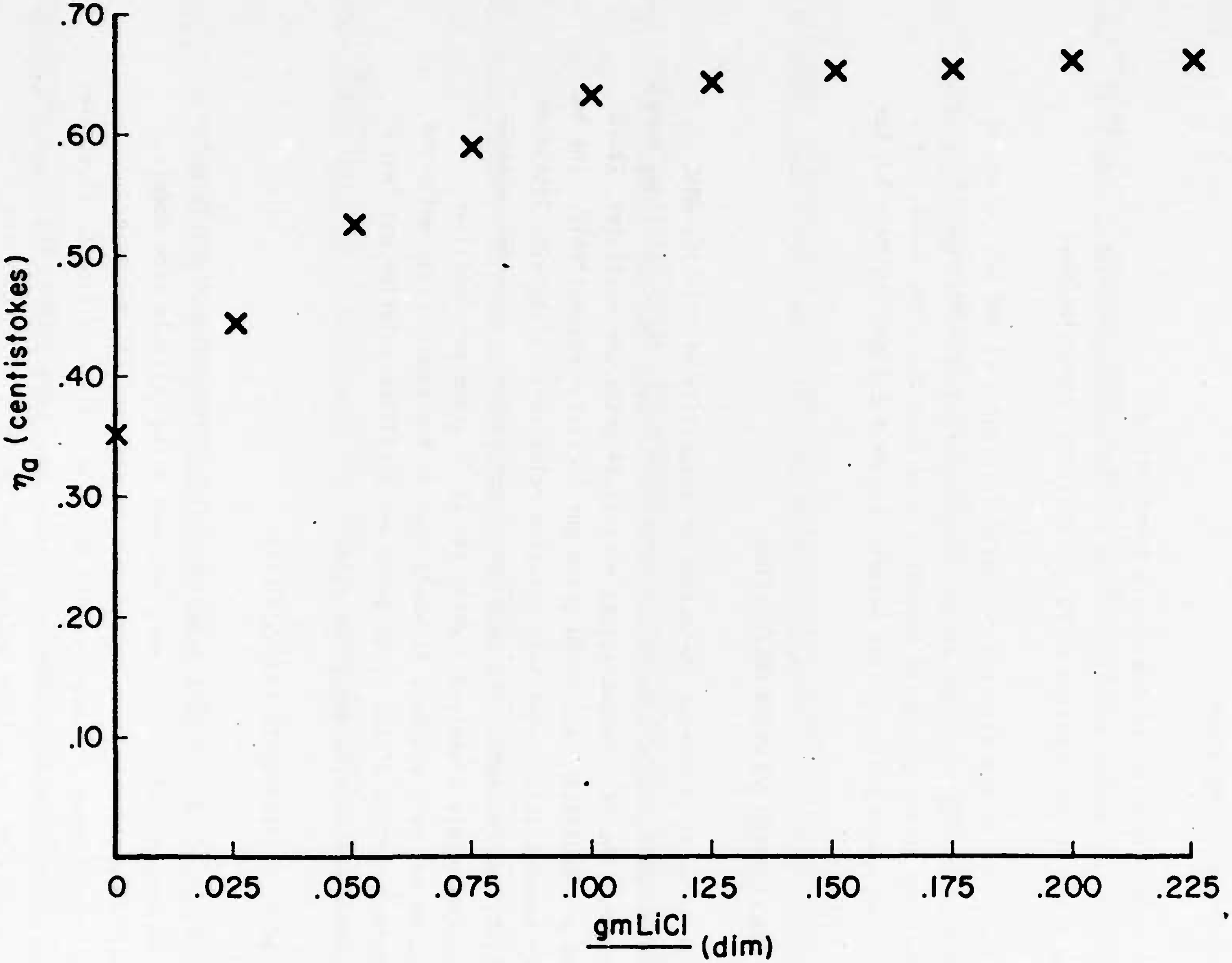


Figure 10. The Ratio of the Viscosity of a PBI-LiCl-DMAC Solution to a LiCl-DMAC Solution of Corresponding LiCl Concentration for Constant PBI Concentration as a Function of the Weight Ratio of LiCl to PBI

To determine if this data matched the predictions of Bueche (Reference 5) and Berry (Referene 4), the data were plotted in the form log η versus log MW where

η = the viscosity of the sample (centipoise)
M = the molecular weight of PBI = 16,000[3] (grams per mole)
W = the weight fraction of PBI in solution (dimensionless)

The plots of the data are presented in Figures 11 and 12. Lines of slope 1.0 and 3.5 are drawn in each figure to indicate the compatibility of the data to the predicted results. Note that the break point, i.e., the entanglement point, occurs between log MW = 2.8 and log MW = 3.0 for both figures.

6. CONCENTRATED SOLUTION PREPARATION

In order to determine the extent of solubility of PBI-LiCl-DMAC solutions with the LiCl to PBI ratio held at 0.125, three solutions were prepared. The PBI concentrations were 11.44 grams per deciliter, 21.70 grams per deciliter, and 36.00 grams per deciliter respectively. The two lower concentrations went into solution relatively easily with little or no agitation required. The 36.00 grams per deciliter solution, however, never completely dissolved. While the 21.70 grams per deciliter solution was very viscous, it would move in the sample flask while the dissolved portion of the 36.00 grams per deciliter solution was "hard" and would not move to any great extent.

7. MODEL ESTIMATION OF EXTENSIBILITY

Figure 13 illustrates three molecular configurations possible for PBI molecules. The models were prepared using Ley-bold atom models. Condition A shows a three repeat unit closed ring PBI molecule. Condition B shows a closely coiled molecule while Condition C illustrates a PBI molecule at full extension. From these photographs, the variability of the polymer molecule can be seen, supporting the assumption that chain extension is indeed possible due to the freedom of rotation in the molecule.

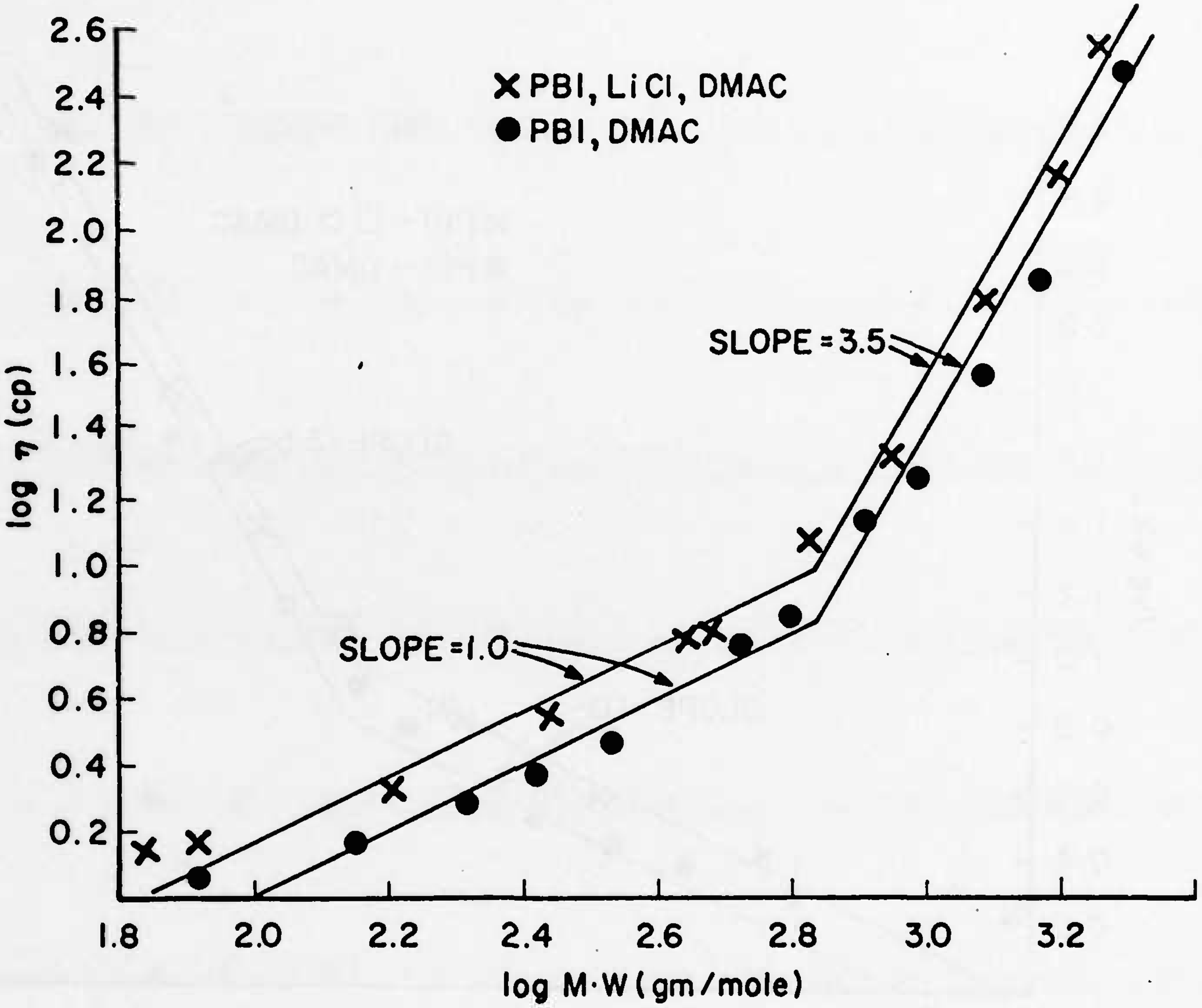


Figure 11. Log η Versus Log MW Determined for PBI-DMAC Solutions and PBI-LiCl-DMAC Solutions with a 0.125 LiCl/PBI Ratio Using a Capillary Viscometer at 30 C

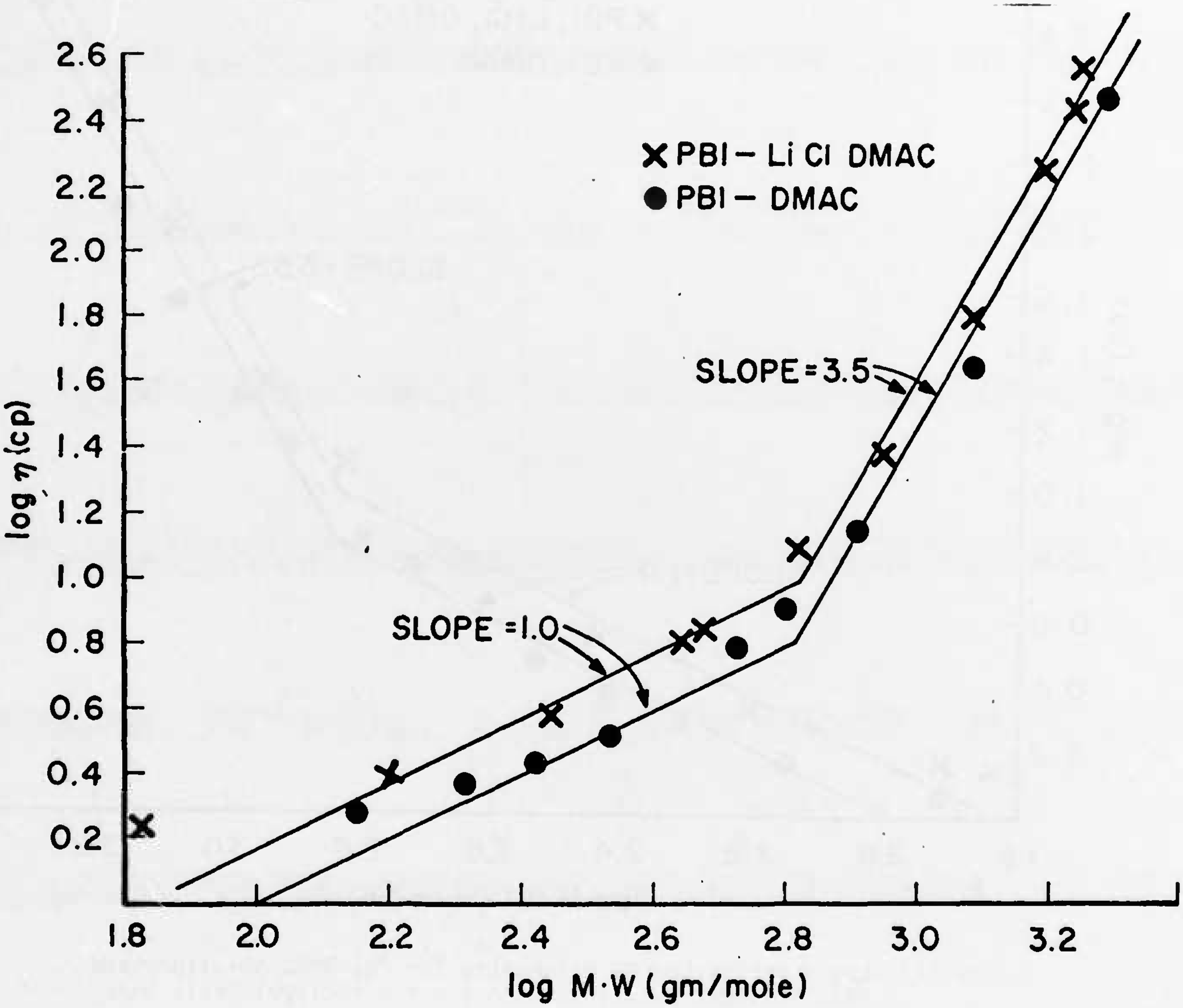


Figure 12. Log η Versus Log MW Determined for PBI-DMAC Solutions and PBI-LiCl-DMAC Solutions with a 0.125 LiCl/PBI Ratio Using a Cylinder Viscometer at 30 C

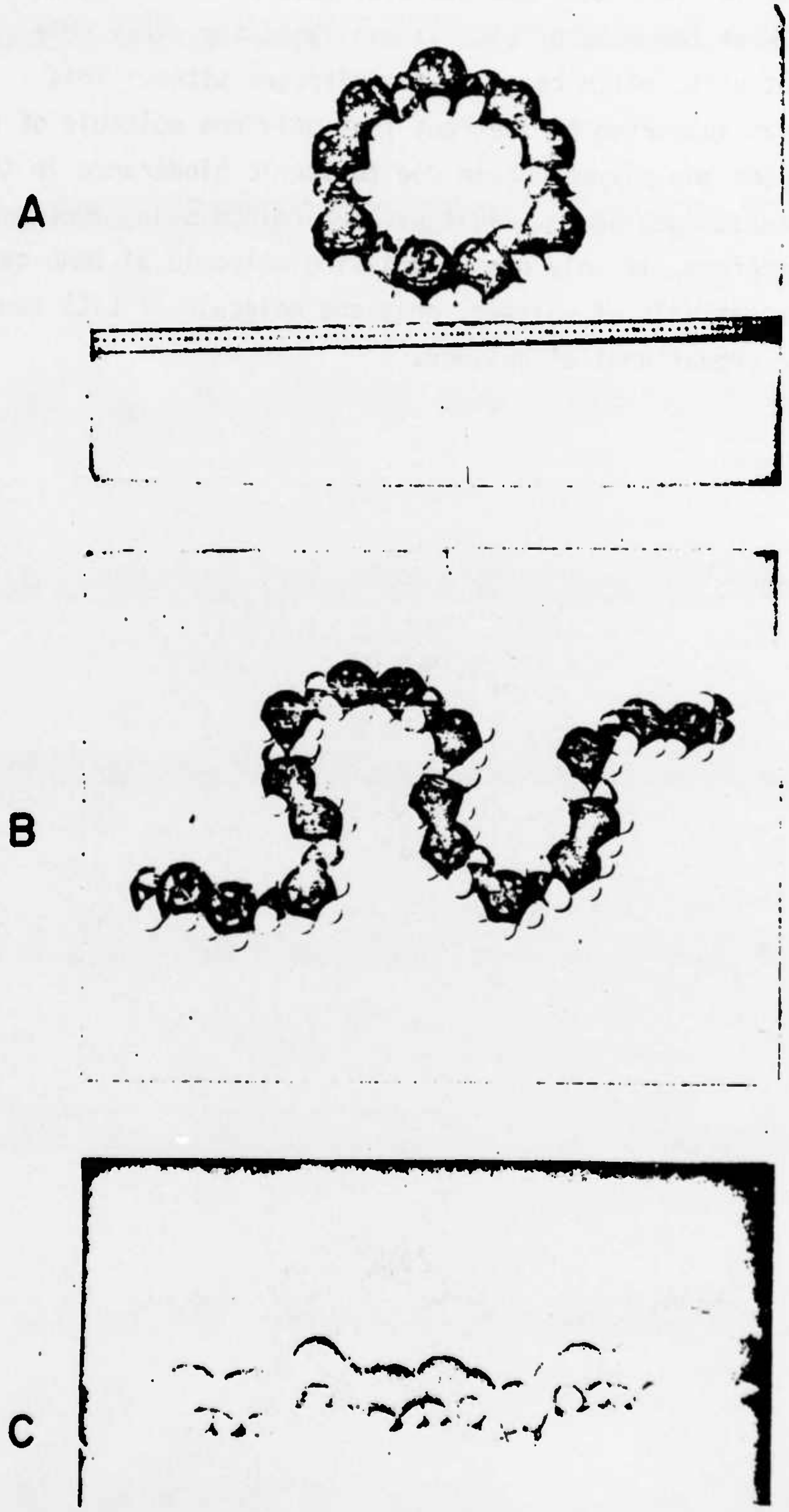


Figure 13. Possible Molecular Configurations for PBI Molecules

As was earlier reported, maximum LiCl absorption on the polymer chain occurs when one mole of LiCl is available for every mole of polymer repeat unit, which contains two nitrogen sites. This observation was supported by the fact that only one molecule of DMAC is able to approach the polymer chain due to steric hinderance in the region of the nitrogen bonds. This was determined using models of DMAC and PBI. Therefore, if only one associating molecule of DMAC can approach a repeat unit of polymer, only one molecule of LiCl could associate per repeat unit of polymer.

SECTION IV

DISCUSSION

This section discusses the results of the experimental testing covered in this report in an attempt to clarify and elaborate on all meaningful data obtained during the experimentation.

1. SAMPLE PREPARATION

The freeze-drying procedure used to produce a soluble, high-surface-area sample of PBI was successful. The PBI produced in this procedure has been completely soluble in all measurements and the speed of solubility is greatly enhanced when compared to untreated PBI. Little or no agitation is required to dissolve the PBI. The PBI particles do, however, tend to pick up an electrostatic charge. This can be avoided if care is taken to insure good packing in the benzene just before dry ice freezing. This packing tends to produce slightly larger particles which are still soluble but do not require the attention necessary for a lighter sample when preparing solutions.

2. CONDUCTIVITY MEASUREMENTS

A great deal of useful information can be derived from the conductivity work. The first point to be observed was the fact that the presence of PBI reduces the conductivity of the solution when compared to the LiCl-DMAC system. This reduction varies directly with the amount of PBI present. As shown in Figure 3, the higher the PBI concentration, the greater the reduction in conductivity. A related characteristic is that the PBI does not attract all the available LiCl, even at dilute LiCl concentrations. This means that the polymer and the solvent (DMAC) compete for the existing LiCl at all times, with neither strong enough to attract all of the LiCl. Therefore, this system could be viewed as a two-component system, a PBI-LiCl component and a LiCl-DMAC component. This concept will be used extensively in the explanation of various characteristics of the polymer solution.

The second characteristic of this system is illustrated in Figure 4. After the titration has reached the ratio of approximately 0.125 gram of LiCl per gram of PBI, any further addition of LiCl yields an increase in conductivity equal to that for the LiCl-DMAC system at the same LiCl concentration. Accordingly, the curves in Figure 4 flatten out as the difference in conductivity becomes a constant. This reveals that the PBI in the concentration range treated has an effect on LiCl up to the time the ratio of approximately 0.125 is achieved. After that, the PBI does not affect any additional LiCl. This indicates that the number of sites for LiCl addition to the polymer chain is limited, and when satisfied, the polymer sites have no effect on the surrounding LiCl. This ratio of 0.125 gram of LiCl per gram of PBI corresponds to 1 mole of LiCl per mole of PBI repeat unit, or 1 mole of LiCl per 2 moles of nitrogen sites on the polymer chain.

Also note is that the LiCl attached to the polymer chain does have an effect on the surrounding solution. LiCl does not completely dissociate in DMAC, as is evidenced by the curved conductivity line in Figure 3. Since the difference curve flattens out, one must assume that the surrounding DMAC is affected by the LiCl attached to the polymer or else it would dissociate more of the additional LiCl and increase the conductivity to a greater degree. To clarify, after the 0.125 ratio is reached, a solution of PBI-LiCl-DMAC will increase in conductivity with the addition of LiCl. This increase is equal to the increase in conductivity for the same concentration LiCl-DMAC solution with no PBI. This indicates that the LiCl attached to the PBI affects the dissociation of any additional LiCl in the same manner as unattached LiCl. Therefore, after the 0.125 ratio is reached, the increase in the conductivity for a PBI-LiCl-DMAC solution is the same as that of a LiCl-DMAC solution at the same LiCl concentration.

The last characteristic to be observed is a bit more obscure. By examining the points where the 0.125 ratio line crosses the curve in Figure 4 (labeled A, B, and C), we find three points with the same ratio of LiCl to PBI with only the amount of DMAC varying. Referring to Figure 3, the points A, B, and C have been marked. Visualizing a curve through these points, it is obvious that the conductivity of the

0.125 ratio solution line does not increase as rapidly as the LiCl-DMAC line does. This indicates that as the solution of the 0.125 ratio becomes more concentrated (less DMAC), a reduction in the LiCl available for conductivity purposes is observed. Conversely, a solution which contains the 0.125 ratio, when diluted, will lose LiCl that is attached to the polymer and the diluting DMAC will collect this freed LiCl. Physically, this means that the dilution of PBI-LiCl-DMAC solutions with DMAC will remove attached LiCl from the polymer and therefore change the characteristics of the polymer molecule. Therefore, the amount of LiCl which is attached to the PBI molecule for a given 0.125 ratio solution is a function of the DMAC concentration. Ideally, at very high concentrations, most of the LiCl is attached to the polymer molecule while at dilute concentrations practically no LiCl is attached to the polymer chain. To obtain the full extent of the LiCl addition, the solution should be as concentrated as possible.

3. INTRINSIC VISCOSITY MEASUREMENTS

The results of the intrinsic viscosity measurements strengthen the statements made in the discussion of the conductivity work concerning the behavior of the LiCl and the PBI in solution.

On the basis of the conductivity work, one would conclude that an addition of DMAC to a PBI-LiCl-DMAC system would remove attached LiCl from the polymer molecule, thus changing the characteristics of the polymer chain. Viewing Figures 6 through 8 one observes that the η_{sp}/c versus c curve indicates a steady decrease in viscosity, contrary to the straight-line plot expected of these data.

This is explained as the sample of PBI-LiCl-DMAC was diluted with DMAC, thus removing LiCl ions from the polymer chain. The polymer chain therefore would tend to collapse, changing the characteristic which affects viscosity, the polymer extension. Therefore, the state of the polymer chains is different after each dilution, yielding a curve of increasing slope and decreasing viscosity. Referring back to the conductivity discussion, it was determined that adding LiCl-DMAC solution to the PBI-LiCl-DMAC solution at the same concentration as the original solution does not affect the polymer molecule. If meaningful intrinsic viscosity tests were to be made, the diluting solution should have the same concentration of LiCl as the sample being tested.

Benner (Reference 3) produced this type of data by measuring the intrinsic viscosity of 0.8 gram per deciliter PBI-DMAC solutions. Both the original solution and the diluting solvent contained the same concentration of LiCl. The results of his measurements are shown in Table 1.

TABLE 1

INTRINSIC VISCOSITY VS PERCENT LiCl

% LiCl	[η]
0.0	0.79
0.1	1.50
0.5	1.21
1.0	1.16
2.5	1.07

(% indicates grams per deciliter)

The data, as plotted in Figure 14, indicate the intrinsic viscosity increases sharply initially then drops off. The maximum value of the intrinsic viscosity was obtained for a LiCl concentration of 0.1 for a PBI concentration of 0.8. This yields a ratio of approximately 0.125 gram of LiCl per gram of PBI and substantiates the preceding conclusions of the discussion.

4. ABSOLUTE VISCOSITY MEASUREMENTS

The results of the absolute viscosity measurements substantiate the conclusions drawn from the conductivity and the intrinsic viscosity work. From Figures 9 and 10, one can determine that additional LiCl has relatively no effect after a ratio of approximately 0.125 gram of LiCl

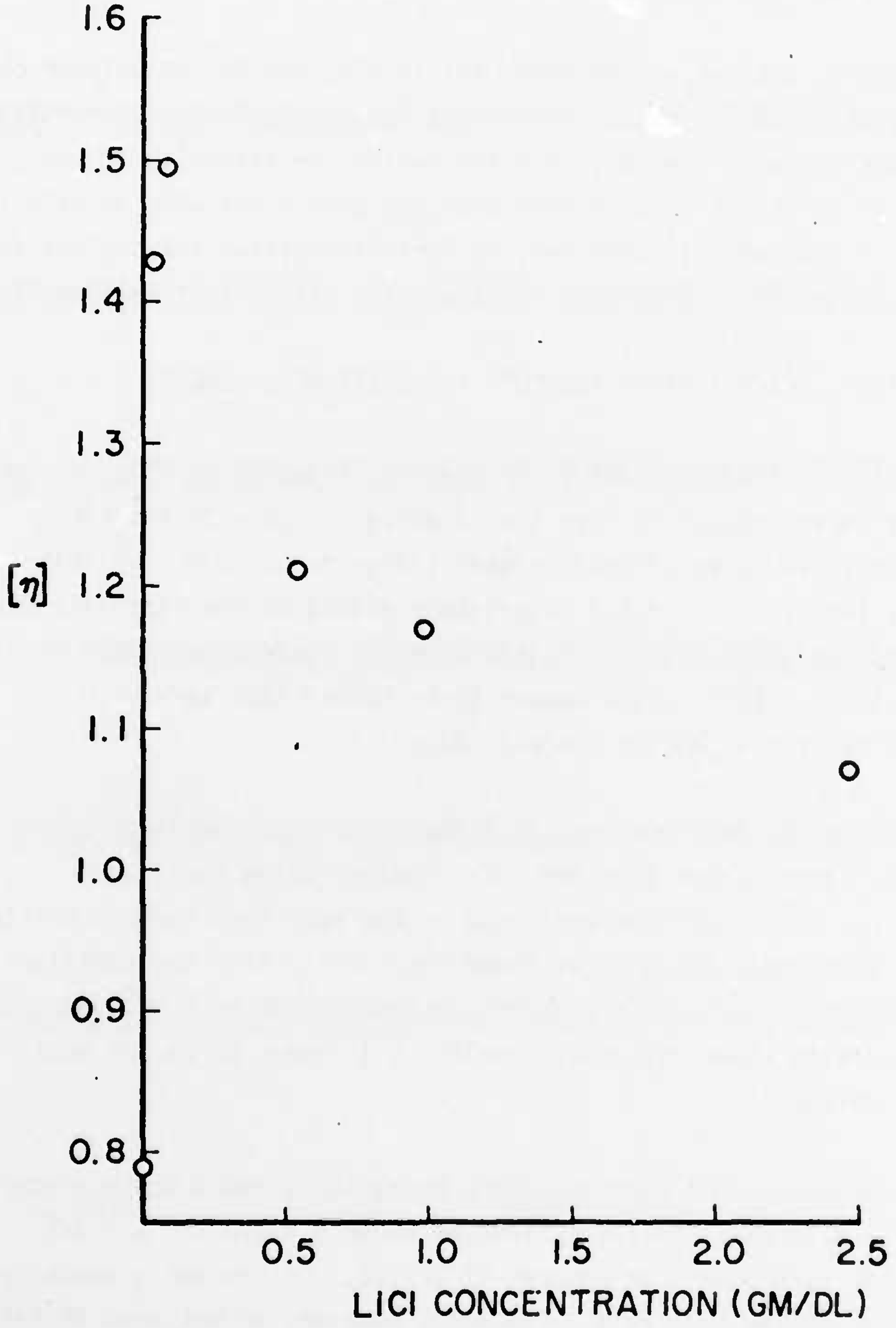


Figure 14. Intrinsic Viscosity of a 0.8 Gram per Deciliter PBI-DMAC Solution as a Function of LiCl Concentration

per gram of PBI has been reached. The viscosity increase of the PBI-LiCl-DMAC solution is the same as that for the LiCl-DMAC solution for points past the 0.125 ratio.

Therefore, one may assume that LiCl is attached to the polymer chain up to the point where the 0.125 ratio is achieved. During the addition, the polymer molecule expands, thus increasing the viscosity of the solution to an extent greater than that for just a PBI-DMAC solution. After the 0.125 ratio is achieved, no further addition takes place and the molecule remains relatively unchanged for the further LiCl addition.

5. CONSTANT LiCl/PBI RATIO ABSOLUTE VISCOSITY MEASUREMENTS

The first noticeable feature of Figures 11 and 12 is that the two viscosity curves appear to have the identical shape with the LiCl-containing curve being slightly higher ($\Delta\log\eta = 0.1$ to 0.2). This indicates that the LiCl has a logarithmic effect on the viscosity curve, increasing the viscosity by a fairly constant logarithmic ratio at all concentrations. Both curves appear to be headed into very high viscosity regions at higher concentration.

The viscosity data obtained from the concentric cyclinder apparatus was in all cases higher than the data obtained using capillary viscometers. This could be explained by the fact that the concentric cylinder viscometer operates at lower shear rates than the capillary viscometer, thus indicating a higher viscosity. As both systems were calibrated with known viscosity samples, this seems to be the most logical explanation.

The data show some correspondence to Bueche's and Berry's predicted behavior. By drawing best-fit lines of slope $a = 1.0$ and $a = 3.5$ through the data points on Figures 11 and 12, one can see a tendency for the data to follow this rule. The data, however, do not seem to fit the predicted behavior or both high and low PBI concentrations. This could be due to equipment limitations.

In both Figures 11 and 12 for both viscosity systems, the best-fit slopes meet between values of Log MW equal to 2.800 and 2.825. Assuming that the pure polymer was tested for each point, varying the molecular weight, the weight fraction W can be set equal to 1.00. Therefore, Log M, the log of the molecular weight of the polymer at the critical point, would then equal between 2.800 and 2.825. Taking the antilogs, it was determined that the molecular weight between entanglements ranged between 631 and 668 grams per mole. Dividing by the molecular weight of a repeat unit of PBI, approximately 308, it is determined that there are between 2.04 and 2.17 repeat units between entanglements. As there are 13 chain atoms per repeat unit, Z, the number of chain atoms between entanglements, is calculated to be between 26 and 28 atoms. Comparing this number for those reported by Porter (Reference 17), one finds that this length is very low when compared to other polymer systems. Only copolymers of methyl methacrylate and n-butyl methacrylate (Z = 53 to 91) and poly (ethylene-propylene (Z = 31 to 89) approach this low value for the many systems reported in this review. Most systems exhibt a value of Z between 100 and 1000. This bit of data indicates that the polymer has a strong matrix of entanglements. However, another factor could have contributed to this low result. The polymer chains could require a sizable amount of energy when pulled past one another. This combined with the high entanglements could combine to make the value of Z so low. Note that both the PBI-DMAC and the PBI-LiCl-DMAC system indicate the same approximate value of entanglement length, even though one knows that the system containing LiCl contains more extended molecules.

6. DISCUSSION-OF-CONCENTRATED SOLUTION PREPARATION

The only valid point to be discussed here is that 36 grams of PBI per deciliter of DMAC with a 0.125 LiCl to PBI ratio is an upper limit to the solubility of this system. Further investigation will be necessary in order to determine the absolute limit of solubility for this polymer system.

7. MODEL ESTIMATION OF CHAIN EXTENSION

The models prepared gave a physical grasp of the extensibility of the PBI molecules. From these models, the assumption of chain extension, LiCl attachment, and electrostatic repulsion can be seen as feasible, if not likely. The C-C bonds on the polymer chain backbone provide excellent rotational sites, which help to fortify the assumption of chain extension, as evidenced by the viscosity changes. The models show that the PBI molecules have the ability to form nearly linear rods, ideal for preparation of a unidirectional, high-strength material.

The fact that a DMAC molecule is large enough to prevent the association with an adjoining nitrogen site for a given repeat unit fortifies the observed situation that 1 mole of LiCl per mole of repeat unit is the concentration of maximum association of the LiCl to the polymer chain. The fact that the DMAC molecule is so large does not eliminate the association of both nitrogen sites in a repeat unit, but makes it unlikely, owing to stearic hinderance.

SECTION V

CONCLUSIONS

The following conclusions were drawn from the experimental work done in this paper.

1. Approximately 0.125 gram of LiCl per gram of PBI is the maximum ratio at which LiCl affects the PBI chain molecules.

2. Dilution of any given PBI-LiCl-DMAC solution of the ratio 0.125 (approximate) or lower will remove LiCl from the polymer chain and change the PBI molecular configuration.

3. Addition of LiCl to the molecule increases the polymer extension and consequently increases the viscosity of the solution.

4. The number of chain atoms between entanglements for both the PBI-DMAC and the PBI-LiCl-DMAC systems is between 26 and 28, indicating a highly matrixed polymer solution.

5. The addition of LiC to a PBI solution has no effect on the number of chain atoms between entanglements.

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