

# Expansion of Aromatic Heterocyclic Polymers in Salt Solution

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## Synopsis

The addition of lithium chloride to solutions of poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene) (PBI) and N,N-dimethylacetamide (DMAC) resulted in the elongation of the PBI molecule in solution. This elongation is due 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 expands the polymer chain by means of electrostatic repulsion. This effect was reflected in the results of the conductivity and viscosity studies. In general, LiCl can be used for both increased solubility and increased viscosity for this system. A ratio of 0.125 g LiCl/gram PBI was determined to be the optimum amount of LiCl to be added. This amount corresponds to 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 matrixed system. The chain length between entanglements was approximately the same for both PBI-DMAC and PBI-LiCl solutions.

## INTRODUCTION

The purpose of this research is 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 desirable thermal, physical, and chemical properties of PBI, in addition to its behavior in solution, which lends itself to the approaches 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. The objective of the overall study is to expand the polymer molecules while in solution and retain this expansion and orient these molecules during a spinning or extrusion process. This paper deals with the first objective, the expansion of the polymer while in solution.

It has been determined that the addition of lithium chloride to a solution of PBI and N,N-dimethylacetamide (DMAC) has 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.

The purpose of this paper is to determine the mechanism and effect of the LiCl on PBI-DMAC solution and to conduct various analytical tests, such as con-

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ductivity, viscosity, and solubility studies, to determine the optimum solution concentrations for the maximum expansion of the PBI molecule.

### LITERATURE REVIEW

This review includes the initial use of lithium chloride in solution as a solubility and viscosity enhancer, the mechanism by which the LiCl affects the PBI polymer chain, and the qualities expected of a PBI–LiCl–DMAC systems. The molecular structure of poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene) (PBI), as presented by Vogel,<sup>1</sup> is illustrated in Figure 1.

#### Use of LiCl in Polymer Solutions

The use of LiCl in a PBI–DMAC system was first introduced by Denyes.<sup>2</sup> The addition of LiCl was introduced to prevent the precipitation of PBI from a DMAC solution. Denyes<sup>2</sup> indicated that PBI would “phase out” of a PBI–DMAC solution if the solution were allowed to stand for one to three days. Upon the addition of 1% LiCl, the solution stabilized and did not precipitate over a period of 30 days.

The use of LiCl to enhance the solubility of a polymer solution has been used in several polymer systems. Iwakura<sup>3</sup> indicated that solubility of poly(phenylbenzimidazoles) in DMSO, DMAC, NMP, and DMF were greatly increased by the addition of LiCl. Kwolek<sup>4</sup> reported that LiCl addition aided the solvation of a polyamide and was highly desirable for an amide–urea medium. Itoi<sup>5</sup> reported that poly(vinyl alcohol) (PVA), which is insoluble below 130°C in pure dimethylformamide (DMF), was dissolved at 80°C in DMF containing more than 1.6% LiCl. Ten grams PVA in 2 g LiCl and 90 g DMF yielded a colorless solution with a viscosity of 29.5 poises at 30°C. The use of LiCl for solvation was again illustrated by Fedorov<sup>6</sup> in synthesizing poly(*p*-phenyleneterephthalamide) in DMAC. Fedorov indicated that the increased interaction between solvent and polymer due to LiCl addition promoted higher molecular weights. Savinov<sup>7</sup> reported that for the polycondensation of terephthaloyl chloride with *p*-phenylenediamine in DMAC the presence of LiCl increased polyamide solubility and the polymer molecular weight.

Helminiak<sup>8</sup> reported that LiCl–DMAC was a better solvent for PBI than DMAC alone based on intrinsic viscosity studies. One dissention was recorded by Denyes<sup>2</sup> 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<sup>9</sup> reported that the characteristic viscosity of poly(*m*-phenyleneisophthalamide) in HCONMe<sub>2</sub> and DMAC in the absence of LiCl is 1.55 and 1.75, respectively, and that it changes in the presence of LiCl.

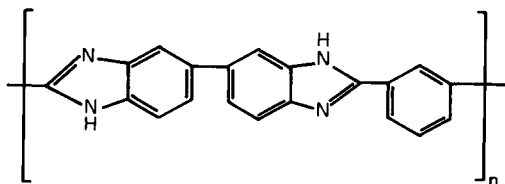


Fig. 1. Molecular structure of the repeat unit of poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene) (PBI).

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,<sup>10</sup> Helminiak,<sup>8</sup> and Denyes<sup>2</sup> have indicated a strong increase in viscosity with the addition of LiCl to a PBI-DMAC solution.

### Mechanism of LiCl Addition to Polymers

Bello<sup>11</sup> indicates that the mechanism for the addition of LiCl to a polymer chain can be attributed to the interactions of the polymer, LiCl, DMAC, and, in some instances, water. Lagowski<sup>12</sup> 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<sup>13</sup> indicated that the 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. Bello<sup>13</sup> 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,<sup>11</sup> basing his work on x-ray diffraction studies, reported that both Li<sup>+</sup> and Cl<sup>-</sup> ions participate in the complexing of DMAC and water. 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<sup>14</sup> reinforces the second approach of Bello. He indicates a direct interaction of Cl<sup>-</sup> 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 systems 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.

### Expected Qualities for a PBI-LiCl-DMAC System

One quality which should be exhibited by a PBI-DMAC system with the addition of LiCl would be an increase in solubility. Iwakura,<sup>3</sup> Kwolek,<sup>4</sup> Ito,<sup>5</sup> Fedorov,<sup>6</sup> and Savinov<sup>7</sup> have indicated that the addition of LiCl has increased solubility in several polymer systems, while Helminiak<sup>8</sup> has indicated that LiCl would increase the solubility of PBI in DMAC.

The viscosity of a PBI-DMAC solution should also be markedly increased with the addition of LiCl. Nebrasov<sup>9</sup> has reported that the viscosity of a polyamide solution was substantially increased with LiCl addition, while Benner,<sup>1</sup> Helminiak,<sup>8</sup> and Denyes<sup>2</sup> reported viscosity increases with the addition of LiCl to a PBI-DMAC system.

Perhaps the most important quality to be expected was introduced by Bello<sup>13</sup> when he indicated that the viscosity increase of proteins in strong LiBr solution

could be due to the extension of 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 in the PBI-LiCl-DMAC system.

From the experimental data taken on the viscosity of polymer melts and concentrated solutions, Bueche<sup>15</sup> indicates that the viscosity of a polymer system can be expressed by

$$\eta = KM^{3.5} \quad (1)$$

where  $\eta$  = the viscosity of the solution,  $K$  = a constant, and  $M$  = 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<sup>6</sup> refines the relation with the following equations:

$$\eta = KM^{3.4} \quad M > M_b \quad (2)$$

$$\eta = KM^{1.0} \quad M < M_b \quad (3)$$

A plot of these 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 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,<sup>17</sup> will be used as the number of chain atoms between entanglements. Porter<sup>17</sup> and Markovitz<sup>18</sup> 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 uncover these data. Fox,<sup>19</sup> Berry,<sup>16</sup> and Porter<sup>17</sup> have shown that 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 1 at the break point of the plot. The molecular weight between the entanglements is then used to calculate the chain length.

## EXPERIMENTAL

The purpose of this section is to present the experimental work done on the PBI-LiCl-DMAC system. This includes conductivity measurements and absolute intrinsic viscosity testing.

### Conductivity Measurements

The purpose of this section of experiments was 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  $\text{Li}^+$  or  $\text{Cl}^-$  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 due to electrostatic repulsion by the ions. Therefore, the point of greatest drop in conductivity would correspond to the maximum extension of the polymer molecule.

Solutions of 1.58568 g PBI/dl DMAC and 4.99320 g PBI/dl DMAC were prepared. A solution of 5.00612 g LiCl/dl DMAC was prepared for use as a titrating agent.

The conductance versus concentration of LiCl was determined by the dropwise titration of the PBI-DMAC or the DMAC sample with the 5.00612 g LiCl/dl DMAC solution. In each test, a 50-ml sample was titrated until 500 drops of the LiCl-DMAC solution had been added. The sample was held at 20°C and stirred continuously.

Fifty-milliliter samples of DMAC and 1.58568, 4.99320, and 0.95141 g PBI/dl DMAC solutions were used in the testing. The 0.95141 g/dl solution was prepared by diluting the 1.58568 g/dl solution. The results of the four titrations are found in Figure 2.

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

$$\Delta L_s = L_{sa} + L_{sb} - L_{sc} \quad (4)$$

where  $L_{sa}$  = conductance of LiCl-DMAC solutions (mho/cm),  $L_{sb}$  = conductance of PBI-DMAC solutions (mho/cm), and  $L_{sc}$  = conductance of PBI-LiCl-DMAC solutions (mho/cm).

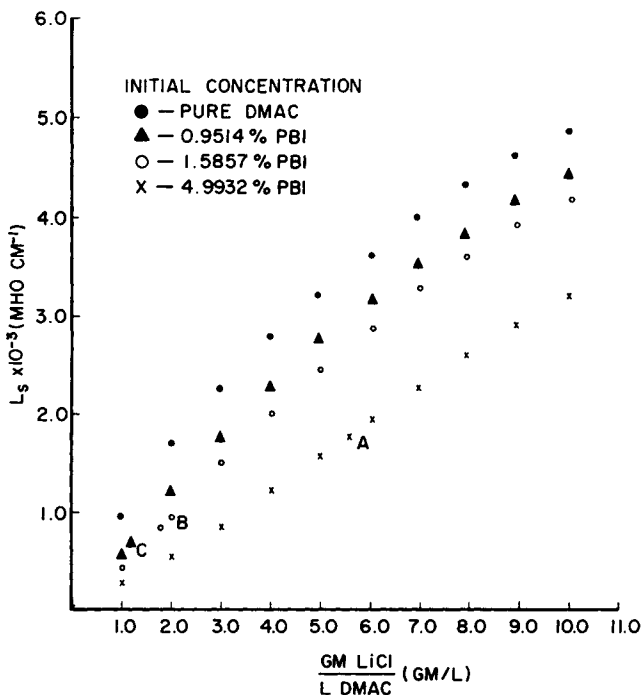


Fig. 2. Conductances of PBI-DMAC solutions and DMAC as function of LiCl concentration. Initial concentration: (●) pure DMAC; (▲) 0.9514% PBI; (○) 1.5857% PBI; (×) 4.9932% PBI.

$L_{sb}$  was determined to be approximately 0.001 for all concentrations studied and therefore the equation reduced to

$$\Delta L_s = L_{sa} + 0.001 - L_{sc} \quad (5)$$

The values of  $\Delta_s$  are plotted as a function of the g LiCl/g PBI ratio in Figure 3.

### Intrinsic Viscosity Measurements

The purpose of this testing was to reinforce the hypothesis that the addition of DMAC to a PBI-LiCl-DMAC solution 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 a straight-line plot and extrapolate to the intrinsic viscosity at zero concentration. If the polymer molecule were changed during the dilutions, the plot would deviate from this straight-line plot and indicate this condition.

Four solutions were prepared by the dilution of the 4.99320 g/dl PBI-DMAC solution with DMAC and the 5.00612 g/dl 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 g/dl).

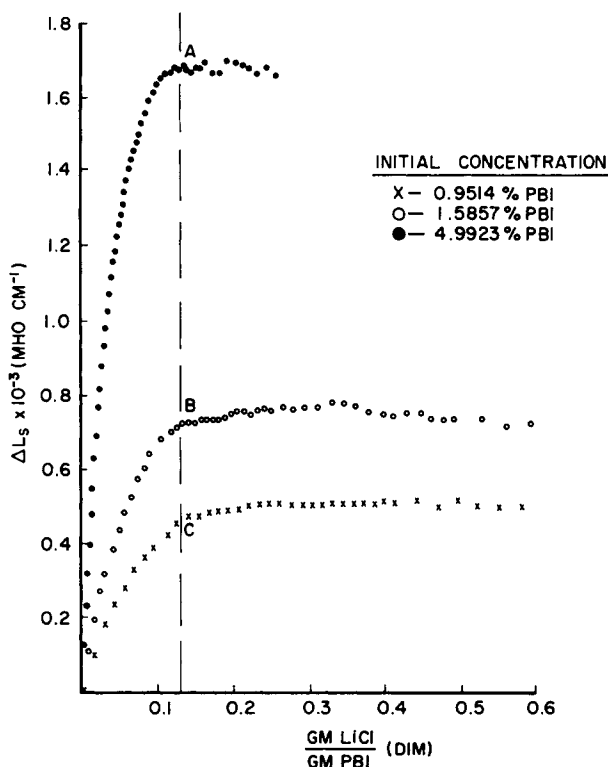


Fig. 3. Differences of conductance between a LiCl-DMAC solution and various PBI-LiCl-DMAC solutions as function of the weight ratio of LiCl to PBI. Initial concentration: (x) 0.9514% PBI; (o) 1.5857% PBI; (●) 4.9923% PBI.

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

A typical result of this testing is shown in Figure 4. By observation, the plot does 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.

#### Absolute Viscosity Measurements

The purpose of this section was to determine the optimum ratio of LiCl to PBI to provide the maximum viscosity for a given concentration of PBI. For this testing, a 0.21718 g/dl solution of LiCl-DMAC and a 1.18332 g/dl PBI-DMAC solution were prepared. Samples were prepared as follows: 10 ml of the PBI solution was diluted with the LiCl-DMAC solution and DMAC to produce a PBI-LiCl-DMAC solution of the desired concentration. Ten samples were prepared with the PBI concentration held constant at 0.47333 g/dl and the ratio of LiCl to PBI varying from 0.00 to 0.225. Ten samples of LiCl-DMAC 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 pipet. Four to six flow times were taken and averaged to determine the final

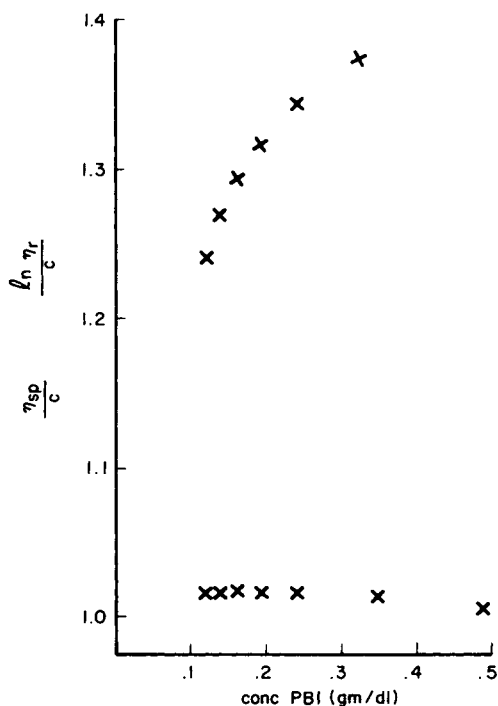


Fig. 4. Plot of  $\ln \eta_R/c$  and  $\eta_{sp}/c$  vs PBI concentration for the dilution of a 0.9766 g PBI per deciliter solution having a LiCl to PBI ratio of 0.1263.

flow time for the sample. The corresponding viscosities are plotted as a function of the LiCl concentration in Figure 5.

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

$$\eta_a = \eta_x / \eta_y \quad (6)$$

where  $\eta_x$  = the viscosity of the PBI-LiCl-DMAC solution (centistokes), and  $\eta_y$  = the viscosity of the LiCl-DMAC solution at the same LiCl concentration (centistokes). This ratio is plotted as a function of g LiCl/PBI in Figure 6.

### 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 g LiCl/g PBI ratio PBI-LiCl-DMAC solutions. Twelve PBI-DMAC solutions were prepared with PBI concentrations ranging between approximately 0.5 and 13.0 g/dl. Eleven PBI-LiCl-DMAC solutions, with the LiCl/PBI ratio held constant at 0.125 g LiCl/g PBI, were prepared with PBI concentrations ranging between approximately 0.04 and 12.0 g/dl.

Viscosities were measured using Cannon-Fenske capillary viscometers at 30°C. From four to six readings were taken and averaged to determine the final value of each solution. Samples were filtered and delivered using a 10-ml pipet.

In order to determine if these data matched the predictions of Bueche<sup>15</sup> and Berry,<sup>16</sup> the data were plotted in the form  $\log \eta$  versus  $\log MW$ , where  $\eta$  = the

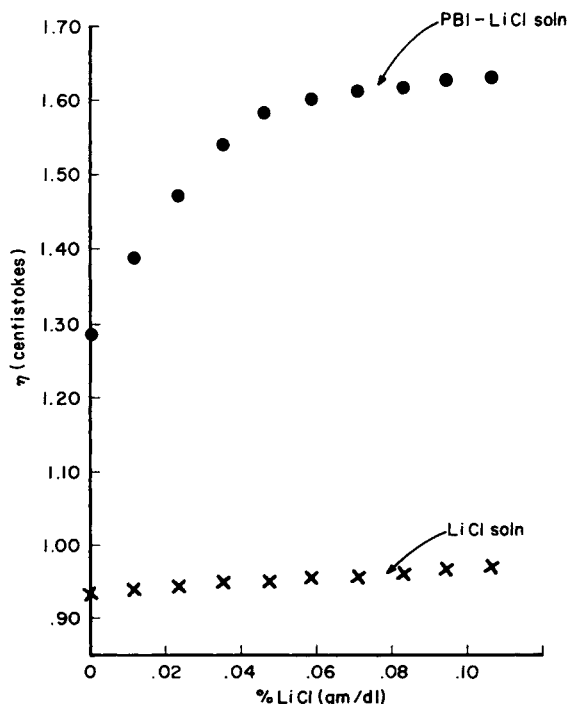


Fig. 5. Kinematic viscosity of a 0.4733 g/dl PBI-DMAC solution and DMAC as function of LiCl concentration.



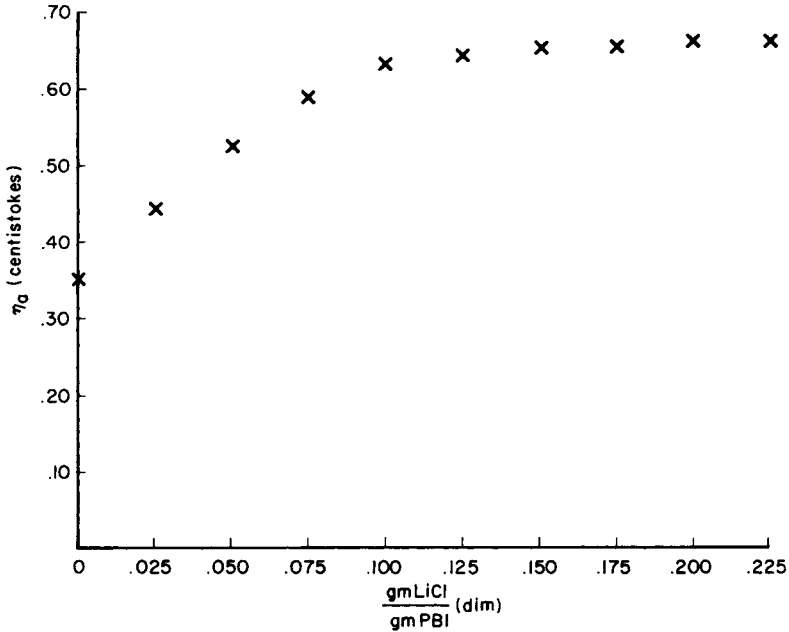


Fig. 6. Ratio of viscosity of a PBI-LiCl-DMAC solution to a LiCl-DMAC solution of corresponding LiCl concentration for constant PBI concentration as function of weight ratio of LiCl to PBI.

viscosity of the sample (centipoises),  $M$  = the molecular weight of PBI = 16,000 (g/mole),<sup>3</sup> and  $W$  = the weight fraction of PBI in solution (dimensionless). The plot of the data is presented in Figure 7. Lines of slope 1.0 and 3.5 are drawn in the figure to indicate the compatibility of the data to the predicted results.

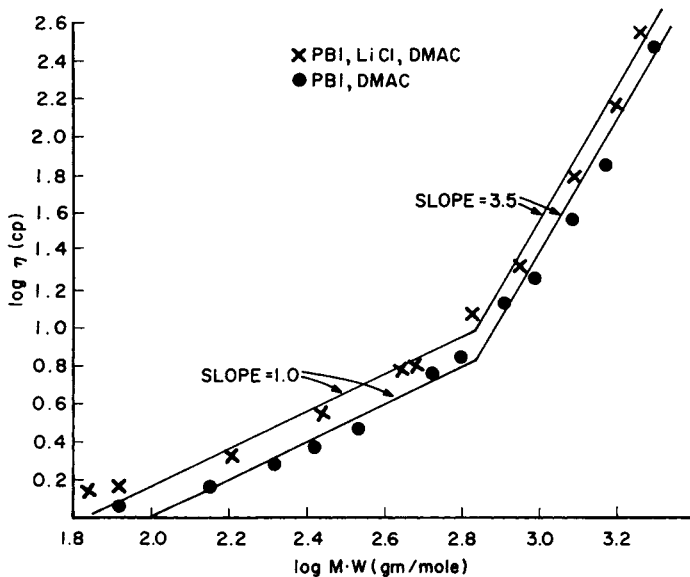


Fig. 7. Plot of  $\log \eta$  vs  $\log MW$  determined for PBI-DMAC solutions and PBI-LiCl-DMAC solutions with a 0.125 LiCl/PBI ratio using a capillary viscometer at 30°C: (x) PBI-LiCl-DMCA; (●) PBI-DMCA.

Note that the break point, i.e., the entanglement point, occurs between  $\log MW = 2.8$  and  $\log MW = 3.0$ .

## DISCUSSION

The purpose of this section is to discuss the results of the experimental testing in this paper. This section will attempt to clarify and elaborate on all meaningful data obtained during the experimentation.

### Discussion of 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. The reduction varies directly with the amount of PBI present. As can be seen in Figure 2, the higher the PBI concentration, the greater the reduction in conductivity. A related characteristic is that the PBI does not affect all of the LiCl. That is, the polymer does not attach to 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 the LiCl. Therefore, this system could be viewed as two systems, a PBI-LiCl system and a LiCl-DMAC system. 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 3. After the titration has reached the ratio of approximately 0.125 g LiCl/g 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 3 flatten out as the difference in conductivity becomes 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 g LiCl/g PBI corresponds to 1 mole of LiCl per 1 mole of PBI repeat unit, or 1 mole of LiCl per 2 moles of nitrogen sites on the polymer chain.

Another point to be noted 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 2. Since the difference curve flattens out, it must be assumed 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 does 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 3 (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 2, 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 does the LiCl-DMAC line. 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. In order to obtain the full extent of the LiCl addition, the solution should be as concentrated as possible.

### Discussion of Intrinsic Viscosity Measurements

The results of the intrinsic viscosity testing 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, it was concluded 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. By viewing Figure 4, it is observed that the  $\eta_{sp}/c$ -versus- $c$  curve indicates a steady decrease in viscosity, contrary to the straight-line plot expected of these data.

This is explained by the fact that 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<sup>10</sup> produced this type of data by measuring the intrinsic viscosity of 0.8 g/dl PBI-DMAC solutions. Both the original solution and the diluting solution contained the same concentration of LiCl. The results of his testing are shown in Figure 8.

The data indicate that 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 g LiCl/g PBI and substantiates the preceding conclusions of the discussion thus far.

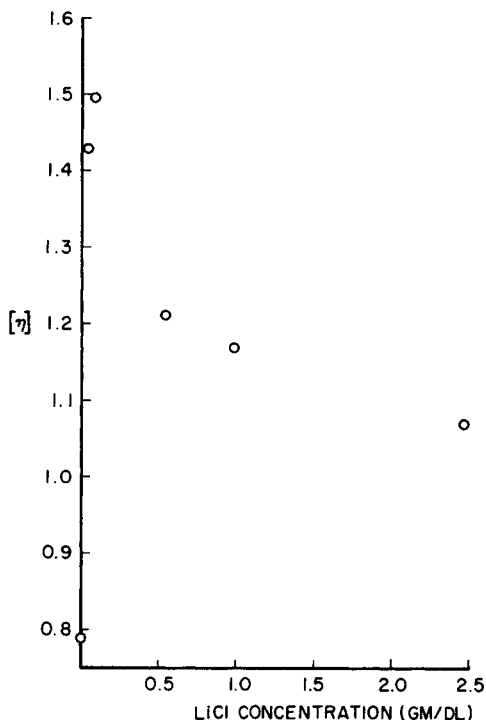


Fig. 8. Intrinsic viscosity of a 0.8 g/dl PBI-DMAC solution as function of LiCl concentration.

### Discussion of Absolute Viscosity Measurements

The results of the absolute viscosity testing substantiate the conclusions drawn from the conductivity and the intrinsic viscosity work. From Figures 5 and 6, it can be determined that additional LiCl has relatively no effect after a ratio of approximately 0.125 g LiCl/g 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, it can be assumed 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.

### Discussion of Constant LiCl/PBI Ratio Absolute Viscosity Measurements

The first noticeable quality of Figure 7 is that the two viscosity curves appear to have an 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 entering very high viscosity regions at higher concentration.

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 Figure 7, one can see a tendency for the data to follow this rule. The data, however, do not seem to fit the predicted behavior at both high and low PBI concentrations. This could be due to equipment limitations.

In Figure 7 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 friction  $W$  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 2.800 and 2.825, respectively. Taking the antilogs, it was determined that the molecular weight between entanglements ranged between 631 and 668 g 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,<sup>17</sup> it is seen 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 polyethylene-propylene ( $Z = 31$  to 89) approach this low value for the many systems reported in this review. Most systems exhibit a  $Z$  value 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 make the value of  $Z$  so low. It should be noted that both the PBI-DMAC and the PBI-LiCl-DMAC systems indicate the same approximate value of entanglement length, even though it is known that the system containing LiCl contains more extended molecules.

## CONCLUSIONS

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

1. Approximately 0.125 g LiCl/g 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. 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.

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