

AFML-TR-73-134

AD0769342

OFFICIAL FILE COPY

**PROTON MAGNETIC SPECTRA OF
POLY(M-PHENYLENE BIBENZIMIDAZOLE)-LITHIUM
CHLORIDE SOLUTIONS IN DIMETHYLACETAMIDE**

M. T. RYAN

T. E. HELMINIAK

TECHNICAL REPORT AFML-TR-73-134

SEPTEMBER 1973

Approved for public release; distribution unlimited

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

20040303244

BEST AVAILABLE COPY

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AFML-TR-73-134

**PROTON MAGNETIC SPECTRA OF
POLY(M-PHENYLENE BIBENZIMIDAZOLE)-LITHIUM
CHLORIDE SOLUTIONS IN DIMETHYLACETAMIDE**

M.T. RYAN
T.E. HELMINIAK

Approved for public release; distribution unlimited

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The reported work was initiated under Project 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. T. E. Helminiak as Project Scientist.

The report covers the work conducted from September 1972 to April 1973. This manuscript was released by the authors in May 1973 for publication as a technical report.

The authors wish to thank Mr. William Crawford and Mr. Charles Benner of the University of Dayton Research Institute, for their helpful discussions concerning this problem and the research data.

This technical report has been reviewed and is approved.



R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The solubility of high temperature polymers is an extremely important property governing, in many cases, the extent to which a polymer can be utilized. For poly(meta-phenylene bibenzimidazole), PBI, N,N-dimethyl acetamide (DMAC) has been a useful solvent; however, the solubility of the polymer is enhanced by the addition of lithium chloride and this procedure is used in the preparation of fiber spinning dopes for PBI. Lithium chloride also influences physical properties such as the dilute and concentrated solution viscosities of PBI as well as conductivities. In order to obtain a better understanding of these molecular interactions, the proton magnetic resonance spectra of PBI solutions has been investigated.

The proton magnetic resonance spectra of poly(meta-phenylene bibenzimidazole) and model compound, 2,2'-diphenyl-5,5'-bibenzimidazole, in N,N'-dimethylacetamide have revealed a large downfield shift of the benz proton singlet in the polymer as compared to the model compound. Lithium chloride has been shown to have a concentration dependent effect on this chemical shift, increasing the shift through a maximum and then decreasing at higher concentrations of lithium chloride. Similar effects have been found for lithium bromide. These chemical shift changes are attributed to conformational changes in the polymer and can provide a measure of the degree of expansion of the macromolecule.

This information indicates that the conformation of PBI in solution can be altered by manipulation of lithium chloride concentration, and

AFML-TR-73-134

thus provides a potential route to the preparation of anisotropic films and fibers having enhanced physical properties.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	EXPERIMENTAL	1
III	RESULTS AND DISCUSSION	2
IV	CONCLUSIONS	5
V	REFERENCES	8

LIST OF FIGURES

FIGURE		PAGE
1	Poly(Meta-Phenylene Bibenzimidazole) 2,2'-Diphenyl-5,5'-Bibenzimidazole	9
2	PBI in DMAC	10
3	2,2'-Diphenyl-5,5'Bibenzimidazole in DMAC	11
4	LiCl/PBI Gram Ratio of .125 in DMAC	12
5	Chemical Shift Difference of Benz Protons vs. Lithium Halide/PBI Ratio	13

I. INTRODUCTION

The polymer (meta-phenylene bibenzimidazole)⁽¹⁾, PBI, (See Figure 1), is soluble in N,N-dimethylacetamide (DMAC)⁽²⁾ and solution properties in this solvent have been reported^(3,4). Although DMAC is a good solvent for PBI, the addition of lithium chloride to PBI-DMAC solutions increases the solubility of PBI⁽²⁾ and prevents its precipitation from concentrated solutions⁽⁵⁾. Intrinsic viscosity measurements have shown that the addition of LiCl to DMAC solutions of PBI markedly influences their viscosity behavior^(3,4) and recent conductivity studies of PBI-DMAC-LiCl solutions have demonstrated interactions between PBI and LiCl which are concentration dependent to a limit⁽⁶⁾. When the ratio of LiCl to PBI is increased beyond a value of 0.13 gm LiCl/gm PBI, no additional changes in conductivity are observed.

In order to obtain a better understanding of the interactions between PBI, DMAC, and LiCl, proton magnetic resonance spectra of polymer solutions and several model compounds were investigated. The effect of LiCl, LiBr, LiF, ZnCl₂, and NH₄Cl on the spectra of solutions was studied.

II. EXPERIMENTAL

The proton magnetic resonance spectra were obtained using a Varian A56/60 Nuclear Magnetic Resonance Spectrometer. When necessary, spectral intensities were enhanced by multi-scan averaging using a Varian 620/i computer interfaced with the spectrometer.

The crude polymer was purified as described previously⁽⁴⁾ except that the final washing was with benzene and the polymer was freeze dried from a benzene slurry. The PBI-LiCl solutions were prepared by mixing a 9% wt/vol polymer solution in DMAC with varying quantities of a 1Molar solution of LiCl in DMAC. The solutions were diluted with DMAC maintaining constant polymer concentration while varying the LiCl concentration.

III. RESULTS AND DISCUSSION

The proton magnetic resonance spectrum of PBI in DMAC shows the solvent absorption, a multiplicity of peaks in the region from 7.5 to 9.3 ppm, and a broad NH peak at about 13.5 ppm downfield from tetramethylsilane (TMS). In the region between 7.5 and 9.3 ppm, the multiplet centered around 7.8 ppm appears to be due to the protons of the phenyl group. A doublet at 8.4 ppm and singlet at 9.3 ppm are due to the benz protons of the benzimidazole group. Figure 2 shows the spectrum in the region from 7.5 to 15 ppm from TMS.

The spectrum from 7 to 9 ppm of the model compound, 2,2'diphenyl, 5,5'bibenzimidazole is shown in Figure 3. The multiplet for the phenyl protons occurs around 7.6 ppm, the benz protons are a singlet at 7.9 ppm and a multiplet at about 8.3 ppm. The multiplicity of the absorption at 8.3 ppm indicates this absorption is due to the protons adjacent to each other in the benz portion of the compound. The small meta and para coupling is not resolved giving the absorption at 7.9 ppm the appearance of a singlet. The singlet for the benz protons is shifted downfield by more than 1 ppm in the polymer as compared to the model compound, the other absorptions being only slightly changed.

Upon addition of PBI, the C-methyl absorption of DMAC is shifted downfield by about 0.025 ppm and the separation between the N-methyl peaks is slightly decreased, indicating interaction between the polymer and the carbonyl group of the solvent. A solution of approximately 1Molar concentration of LiCl in DMAC shows that the C-methyl absorption is shifted downfield by about 0.05 ppm compared to pure DMAC. There is a slightly larger separation between the N-methyl peaks than in DMAC.

Figure 4 is a spectrum of 11% PBI in DMAC with a LiCl/PBI ratio of 0.125. When LiCl is added to a DMAC solution of the polymer, the 9.3 ppm peak appears further downfield until the ratio of LiCl/PBI approaches 0.15. Upon further addition of LiCl this peak is then shifted upfield. The doublet absorption is shifted downfield continuously at all concentrations of LiCl that were studied. Figure 5 shows a plot of the chemical shift difference between the benz protons singlet and doublet absorptions of the polymer as a function of the ratio of LiCl/PBI. As the ratio increases the chemical shift difference becomes larger until a ratio of about 0.15 is reached, after which the difference levels off and eventually decreases. Figure 5 also shows a similar effect obtained with LiBr. The chemical shift difference is smaller with LiBr and the curve begins to level off at a LiBr/PBI ratio of about 0.30.

The effect of DMAC-LiCl on a series of substituted benzanilides was reported by Federov, et al.⁽⁷⁾. They show a downfield shift of the NH proton in DMAC-LiCl as compared to the shift in DMAC. They attribute the shift to interaction between the chloride anion and the NH proton of benzanilide.

LiCl and LiBr have been shown to affect appreciably the spectrum of pyridine⁽⁸⁾, both for the pure compound and for aqueous pyridine solutions. Larsen explains the results as being due to interactions between the nitrogen non-bonding pair of electrons and LiCl (or LiBr) which affects the quadruple coupling between nitrogen and the alpha protons of pyridine.

The addition of LiCl to DMAC solutions of benzimidazole causes an upfield shift and decrease in line width of the imidazole CH and an upfield shift of the beta phenyl protons. These results are consistent with formation of a complex between nitrogen and LiCl which would decrease the electron density at the alpha carbon and affect N-H coupling. However, the coupling between the CH and the benz protons which is evident in the spectrum of benzimidazole in CDCl₃ is absent in the spectrum of this compound in DMAC. Exchange effects with the solvent or interaction with the chloride anion will have to be studied further.

When LiCl is added to solutions of 2,2'diphenyl-5,5'bibenzimidazole (See Figure 1), the separation between the benz proton singlet at 7.9 ppm and multiplet around 8.3 ppm is observed to increase. The multiplet shifts downfield. These results are similar to those observed for the polymer, except that no reversal in the chemical shift difference between the benz protons is observed; even at molar ratios of LiCl to model compound of 3 to 1.

Of the other salts used in this study, only NH_4Cl appeared to have an effect on the benz protons chemical shifts. Its solubility in DMAC is too low to determine concentration effects but an increase in the chemical shift difference of the benz protons of the polymer was noted when a saturated solution of NH_4Cl in DMAC was added to a polymer solution. LiF is only sparingly soluble in DMAC and no change in the benz protons was observed with a saturated solution. ZnCl_2 in DMAC also produced no change. This compound and DMAC are known to form a complex $\text{ZnCl}_2 \cdot 2 \text{DMAC}^{(9)}$.

IV. CONCLUSIONS

The large downfield shift, observed in DMAC solutions, of the benz proton singlet in the polymer as compared to the model compound (9.3 ppm and 7.9 ppm respectively) is indicative of interactions with neighboring groups in the coiled macromolecule which cause this proton to be deshielded relative to a proton in a similar electronic environment in the low molecular weight model compound. The chemical shift of this proton in the polymer should, therefore, be sensitive to changes in conformation of the coiled macromolecule. The effect of LiCl on this chemical shift, and, in particular, the reversal from a downfield shift to an upfield shift with increasing quantities of LiCl indicate that LiCl is causing an expansion of the macromolecule reaching a maximum. The reversal in chemical shift with increasing quantities of LiCl occurs at a LiCl/PBI gram ratio of about 0.15, which is consistent with reported viscosity data⁽⁴⁾, showing a decrease in viscosity at high LiCl/PBI ratios, and

AFML-TR-73-134

with conductivity studies for the same system⁽⁶⁾. This reversal in chemical shift is occurring at approximately 1 mole of LiCl per repeat unit of the PBI.

The mechanism for the interaction between LiCl and PBI in DMAC has not been definitely established. The changes in chemical shift of the DMAC absorptions upon addition of PBI show that there are interactions between the solvent and polymer. The spectra indicate that PBI interacts with DMAC, probably through hydrogen bonding. LiCl also interacts with DMAC causing changes in the solvent absorptions. The changes are similar to those observed for DMAC metal salt complexes⁽¹⁰⁾ in which coordination of the metal through the carbonyl oxygen occurs. Although no crystalline complex of DMAC and LiCl (or LiBr) is known, a crystalline complex of water, N-methyl acetamide and LiBr has been isolated⁽¹¹⁾. Coordination between Li and the carbonyl group is indicated in this compound. LiCl and LiBr are known to act as denaturants in aqueous protein solutions⁽¹¹⁾ and apparently affect hydrogen bonding in the peptide chains of these molecules. Since the spectra show that PBI interacts with DMAC, probably through hydrogen bonding, the effect of LiCl on this hydrogen bonding may account for the observed results in the PBI shifts. The crude polymer is known to have bound water, and the effect of LiCl on residual water in the polymer could be responsible in part for the observed changes. The possibility also exists for direct nitrogen-lithium interactions.

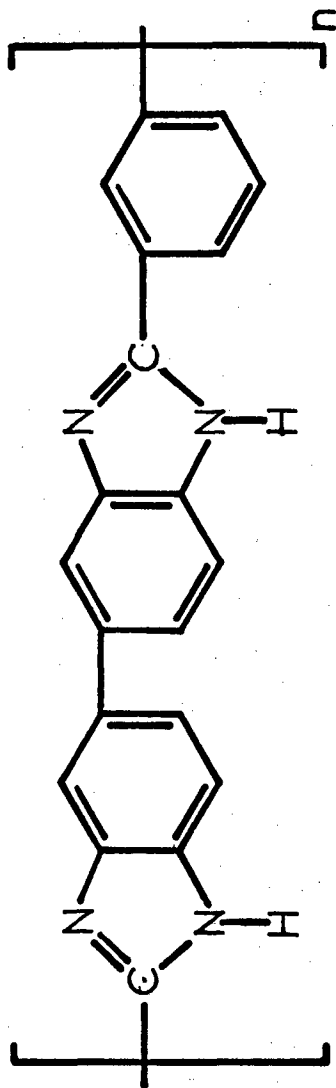
AFML-TR-73-134

These results demonstrate that lithium chloride can influence the conformation of PBI in DMAC solutions. This knowledge provides insight to an approach for the orientation of highly extended macromolecules in solution leading to the preparation of anisotropic films and fibers having enhanced physical properties.

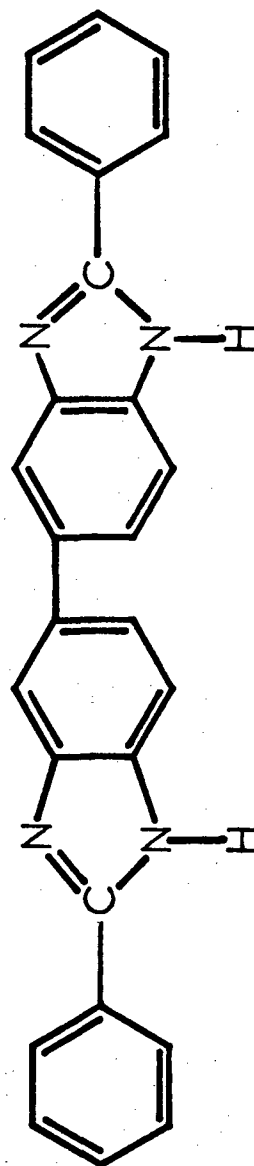
V. REFERENCES

1. Vogel, H.; and Marvel, C. S., Journal of Polymer Science, 50, 511 (1961).
2. Iwakura, Y.; Uno, K.; and Imai, Y., Journal of Polymer Science, Part A, 2, 2605 (1964).
3. Benner, C. L., AFML-TR-70-7, WPAFB, Ohio (1970).
4. Helminiak, T. E.; Benner, C. L.; and Gibbs, W. E., Polymer Preprints, 11, 291 (1970).
5. Denyes, R. O.; Bokrer, T. C.; Conciatori, A. B.; Chenevey, E. C.; Prince, A. E.; Santangelo, J. G.; and Zellner, C. N., AFML-TR-66-167, Vol. I, WPAFB, Ohio (1966).
6. Hanley, T. R.; Benner, C. L.; and Helminiak, T. E., AFML-Technical Report - (1973) in press.
7. Federov, A. A.; Sokolov, L. B.; Zlatogorskii, M. L.; Grechishkin, V. S.; and Proshchutinskii, V. I.; Journal of Structural Chemistry, 12, 848 (1971).
8. Larsen, D. W., Journal of Physical Chemistry, 76, 53 (1972).
9. Bull, W. E.; Madan, S. K.; and Willis, J. E., Inorganic Chemistry, 2, 303 (1963).
10. Carty, A. J., Canadian Journal of Chemistry, 44, 1881 (1966).
11. Bello, J.; and Bello, H. R., Nature, 190, #4829, 681 (1962).

FIGURE 1



POLY (META-PHENYLENE BIBENZIMIDAZOLE)



2,2'-DIPHENYL-5,5'-BIBENZIMIDAZOLE

FIGURE 2

PBI IN DMAC

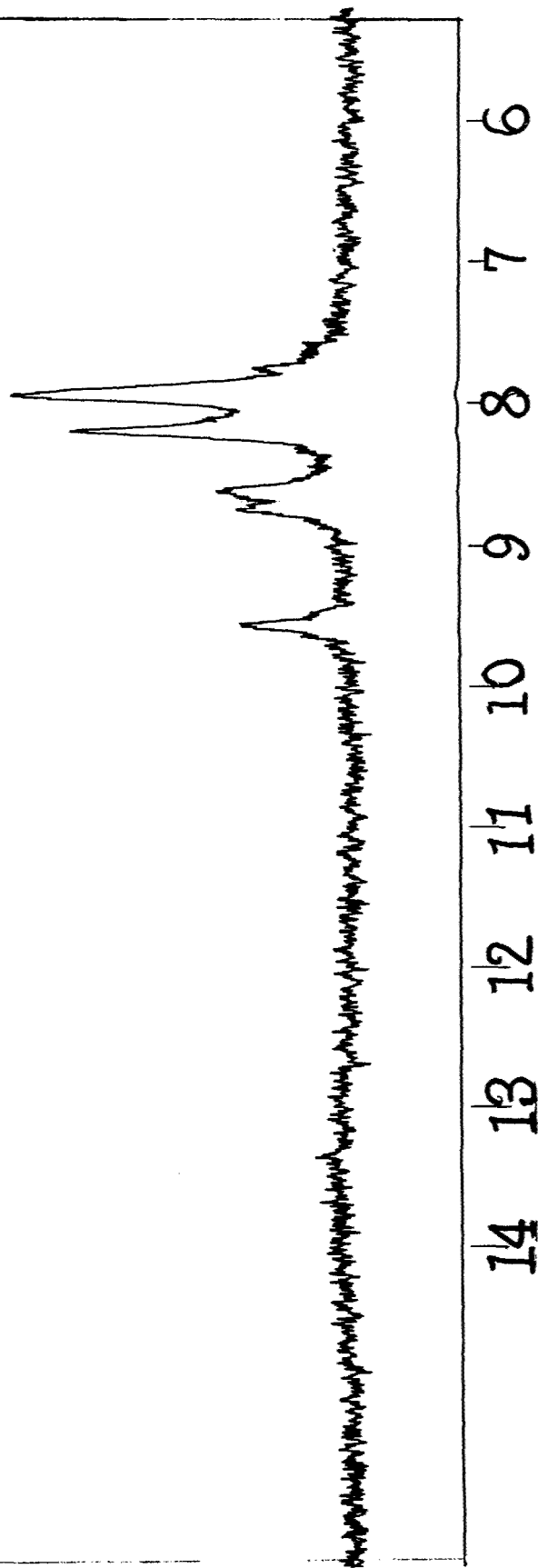


FIGURE 3

2,2' DIPHENYL - 5,5' BIBENZIMIDAZOLE
IN DNAC

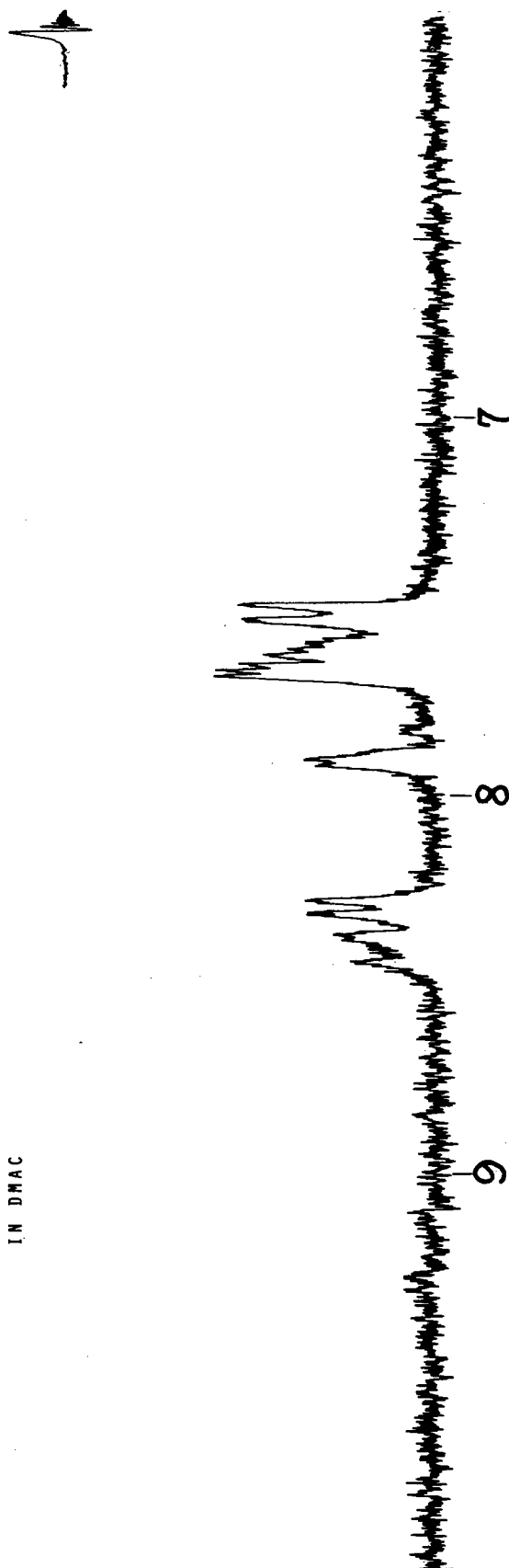


Figure 4

LICL/PBI GRAM RATIO OF 0.125
IN DMAC

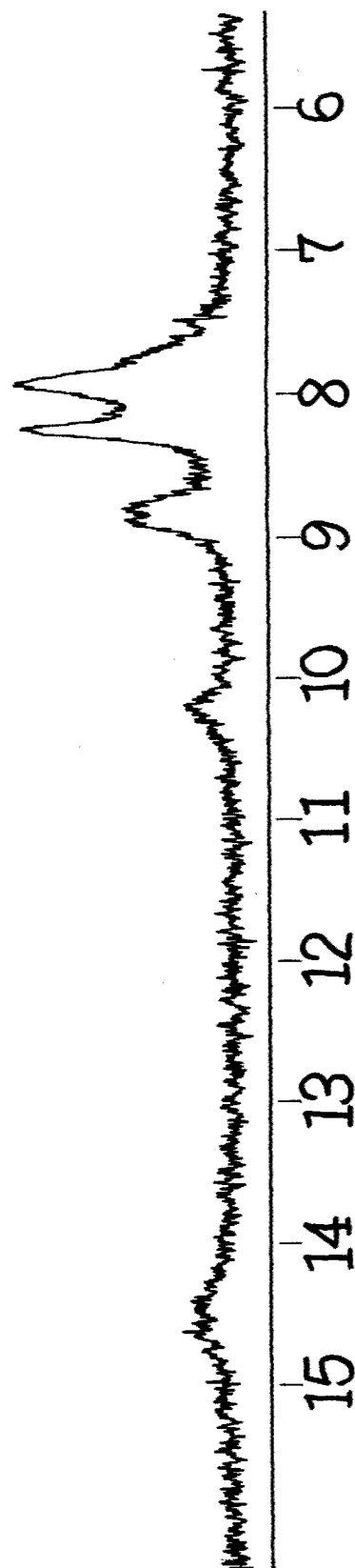
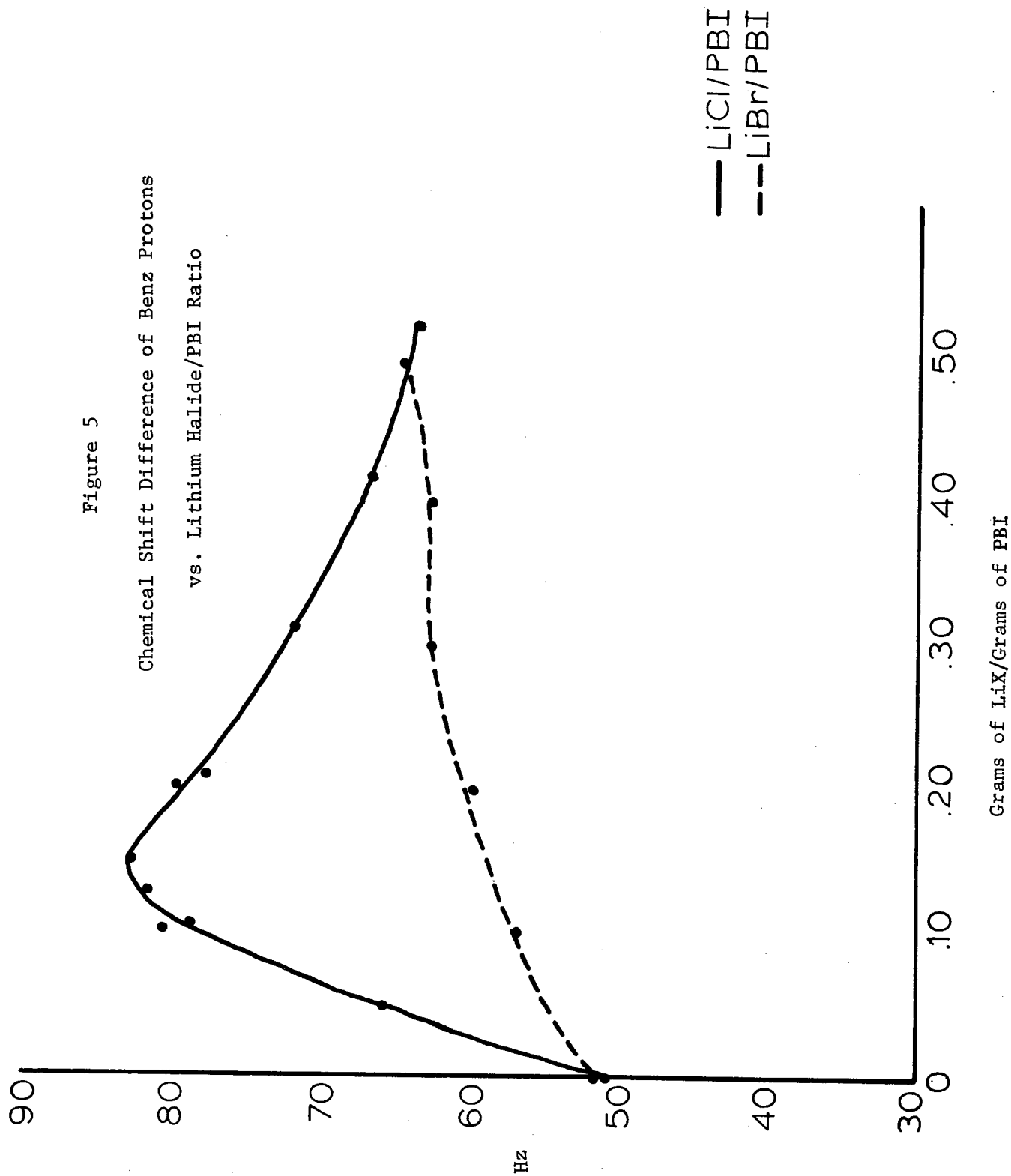


Figure 5
Chemical Shift Difference of Benz Protons
vs. Lithium Halide/PBI Ratio



UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Polymer Branch (AFML/MBP) Wright-Patterson AFB, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE Proton Magnetic Spectra of Poly(Meta-Phenylene Bibenzimidazole)-Lithium Chloride Solutions in Dimethyl Acetamide			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report September 1972 to April 1973			
5. AUTHOR(S) (First name, middle initial, last name) Ryan, M. T. Helminiak, T. E.			
6. REPORT DATE September 1973		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-73- 134	
b. PROJECT NO. 7340			
c. Task 734004		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for publication release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT The solubility of high temperature polymers is an extremely important property governing, in many cases, the extent to which a polymer can be utilized. For poly (meta-phenylene bibenzimidazole), PBI, N,N-dimethyl acetamide (DMAC) has been a useful solvent; however, the solubility of the polymer is enhanced by the addition of lithium chloride and this procedure is used in the preparation of fiber spinning dopes for PBI. Lithium chloride also influences physical properties such as the dilute and concentrated solution viscosities of PBI as well as conductivities. In order to obtain a better understanding of these molecular interactions, the proton magnetic resonance of PBI solutions have been investigated. The proton magnetic resonance spectra of poly(meta-phenylene bibenzimidazole) and model compound, 2,2'-diphenyl-5,5'bibenzimidazole, in N,N'-dimethylacetamide have revealed a large downfield shift of the benz proton singlet in the polymer as compared to the model compound. Lithium chloride has been shown to have a concentration dependent effect on this chemical shift, increasing the shift through a maximum and then decreasing at higher concentrations of lithium chloride. Similar effects have been found for lithium bromide. These chemical shift changes are attributed to conformational changes in the polymer and can provide a measure of the degree of expansion of the macromolecule. This information indicates that the conformation of PBI in solution can be altered by manipulation of lithium chloride concentration, and thus provides a potential route to the preparation of anisotropic films and fibers having enhanced physical properties.			

