

AN ABSTRACT OF THE THESIS OF

Turgay Seckin for the degree of Master of Science in Chemistry
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TITLE : Polybenzimidazole Synthesis From Compounds with Sulfonate
Ester Linkages

Redacted for privacy

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Dr. R.W. THIES

This investigation of polybenzimidazole synthesis involved the two-stage low temperature solution polymerization of dialdehydes, One-step polycondensation of dialdehydes, two-stage melt polycondensation of diesters, and one-step solution polycondensation of diesters with 3,3'-diaminobenzidine. Dialdehyde or diester monomers were prepared which contained aromatic units which were hooked together with sulfonate linkages. Polymerization of these monomers with 3,3'-diaminobenzidine resulted in moderate viscosities of 0.4-0.8 dl/g in DMSO at 19°C. The polybenzimidazoles obtained appear to be linear; most of them when tested immediately after preparation, were largely soluble in certain acidic or dipolar aprotic solvents. Films, obtained by dissolving the polymer in dipolar aprotic solvents such as N,N-dimethylacetamide or N,N-dimethyl formamide, were flexible, clear, yellow to brown in color, and foldable depending upon which monomers and which polymerization methods were used.

*Polybenzimidazole Synthesis From Compounds with
Sulfonate Ester Linkages*

by

Turgay Seckin

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To my family

for their never failing love and support

NE MUTLU TURKUM DIYENE

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POLYBENZIMIDAZOLE SYNTHESIS FROM COMPOUNDS WITH SULFONATE ESTER

LINKAGES

I. INTRODUCTION

I.I. GENERAL BACKGROUND

I.1.a. Polymers in General

Polymer, a high molecular weight substance, is built by linking large numbers of smaller molecules known as monomers.

Polymerization could be defined as a reaction in which monomer molecules react each other to form giant molecules.



Polyethylene $n= 100, \dots 10000, \dots \text{etc.}$

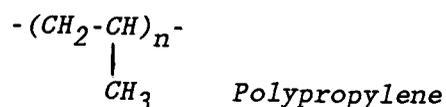
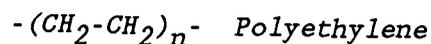
I.1.b. PROPERTIES OF POLYMER¹

Properties of polymer vary depending on which polymerization methods, conditions, and monomers are used. The combinations of properties possessed by a particular polymer determines the application of the polymer as fiber or a plastic. With this idea in mind polymer properties could be classified in four different groups.²

- A. Chemical structure
- B. Molecular weight
- C. Molecular shape
- D. Physical state

A. CHEMICAL STRUCTURE

a. Non-polar polymer



- b. Polar polymer
 - $(\text{CO}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_6\text{NH})_n$ Polyamides
- c. Streamlined polymer chain (Non-bulky)
 - $(\text{CH}_2-\text{CH}_2)_n$ Polyethylene
- d. Bulky chain (Bulky side groups)
 - Polystyrene

B. MOLECULAR WEIGHT OF A POLYMER²

A knowledge of the molecular weight of a polymer is necessary to understand the relationship between structure, properties, and its synthesis and applications. The molecular weight of a polymer is quite different from the molecular weight of small-sized compounds. Since polymers invariably contain different species of different chain lengths, molecular weight studies always yield average values³. Polymers are polydisperse and heterogeneous in molecular weight, because polymerization is a random process. The statistical variations present in the polymerization process give rise to the polydispersity of polymers. When one discusses the molecular weight of a polymer one is actually involved with its average molecular weight. Both the average molecular weight and the exact distribution of different molecular weights in a polymer are required in order to fully characterize it. The control of molecular weight (MW), and molecular weight distribution (MWD) is often used to obtain and improve certain desired physical properties in a polymer sample. There are numerous methods to determine the molecular weight of a polymer⁴.

B.1. EXPERIMENTAL MEASUREMENT OF MOLECULAR WEIGHT OF A POLYMER

A. The number average molecular weight (M_n), is determined by the measurement of colligative properties such as freezing point depression (crosscut), boiling point elevation (ebulliometry), osmotic pressure, and vapor pressure lowering.

M_n is defined as the total weight w of all the molecules in a polymer sample divided by the total numbers of moles present

$$M_n = w / \sum N_x = \sum N_x M_x / \sum N_x$$

$$x=1 \text{ to } x=\infty$$

N_x - the numbers of moles whose weight = M_x

B. The weight-average molecular weight (M_w), is obtained from the light scattering measurements and is defined as,

$$M_w = \sum w_x M_x$$

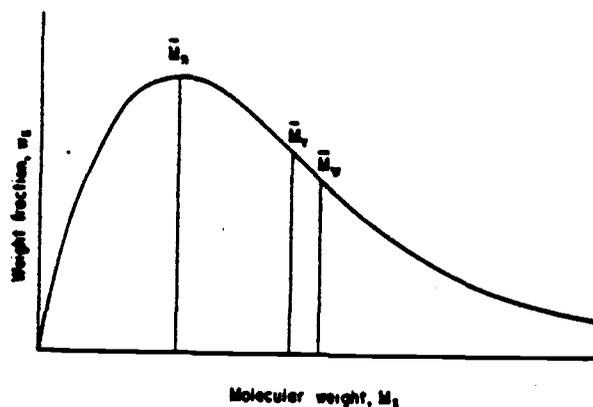
w_x = weight fraction of molecules whose molecular weight is M_x .

C. The viscosity average molecular weight (M_v) is obtained from viscosity measurements and is defined by

$$M_v = (\sum w_x M_x^a)^{1/a} = (\sum N_x M_x^{a+1} / \sum N_x M_x)^{1/a}$$

where a is a constant

FIGURE-1- Distribution of M.W. in a typical polymer sample⁴

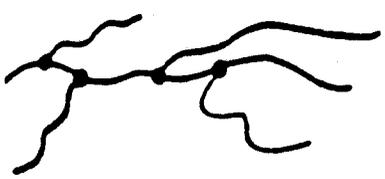


C. MOLECULAR SHAPE OF POLYMERS

Linear



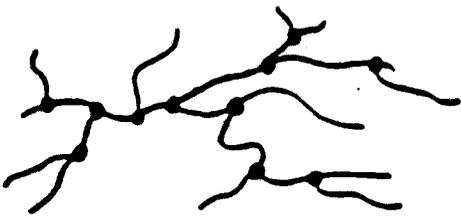
Branched-long branches



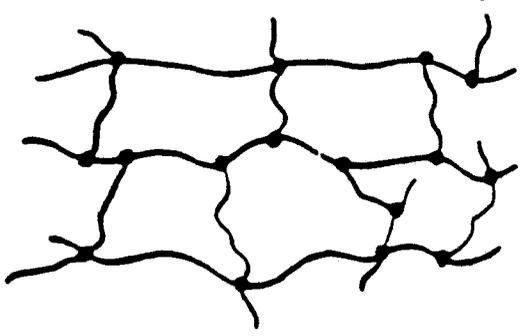
Branched-short branches



Branched-branches protruding from branches give a dendritic structures.



Cross-linked



D. PHYSICAL STATE OF POLYMERS

1. Thermal transitions:

Polymeric materials are characterized by two major types of transition temperatures.

T_m : Crystalline melting temperature

T_g : Glass transition temperature

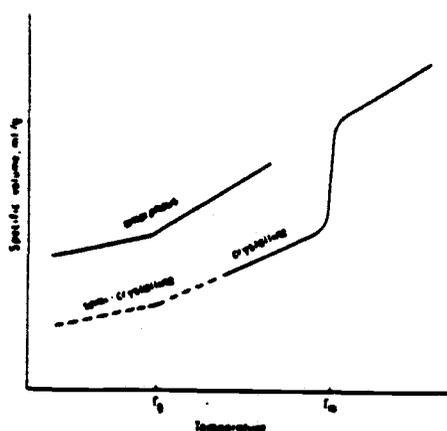
"Crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample"¹.

"The glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state-brittleness, stiffness, and rigidity"¹.

The difference between two thermal transitions can be understood more clearly by considering changes which take place in a polymer as it is cooled. "The translational, rotational, and vibrational energies of the polymer molecules go down on cooling. When the total energies of the polymer molecules have fallen to the point where the translational and rotational energies are zero, crystallization is possible. If certain symmetry requirements are met, the molecules are able to pack into an ordered lattice arrangement and crystallization takes place. The temperature at which this takes place is T_m . However not all polymers possess the essential symmetry requirements for crystallization. If crystallization requirements aren't met crystallization is not possible, but the energies of molecules continue to decrease as the temperature decreases. A temperature is finally reached the T_g , at which the motions of the polymer chains stop due to the lack of bond rotation"¹.

Determination of glass transition and crystalline melting temperatures by changes in specific volume is plotted in Figure-2- A polymer may possess just a T_g if it is amorphous only or just a T_m if it is crystalline only.

FIGURE-2-Glass transition and crystalline melting temperature

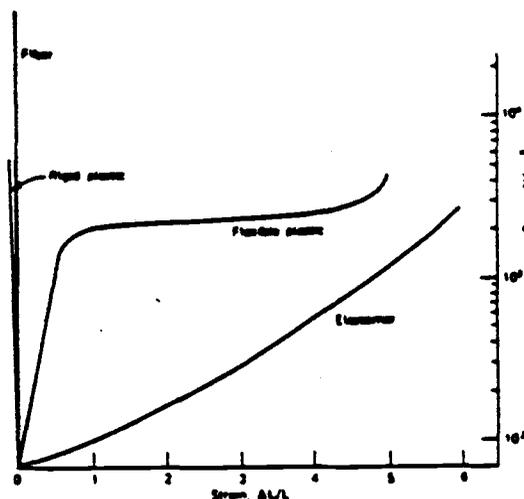


Crystalline polymers possess high molecular forces, compact molecular structure, and highly regular structure. Polymers with low crystallinity possess bulky or rigid side chains.

I.1.c. APPLICATION OF POLYMERS

Many polymer properties such as solvent and chemical resistance, and electrical resistance determine the general utility of a polymer. Mechanical strength (Figure-3-) is the property that is generally considered most important. In this regard different polymers are synthesized to yield various mechanical

FIGURE-3-Mechanical strength of polymers



behaviors by using the appropriate combinations of crystallinity, crosslinking, T_g , and T_m depending on whether the polymer will be used as fiber, flexible plastic, rigid plastic or elastomer(rubber).

Some important terms are defined below.

Strength is the resistance of the polymer to mechanical stress.

Extensibility is the ability to undergo elongation without breaking.

- a. High strength, low extensibility
 1. High crystallinity
 2. Extensive crosslinking
 3. Rigid polymer chain
- b. Low strength and high extensibility
 1. Low crystallinity
 2. Low crosslinking
 3. Absence of rigid chain

RUBBERS: Low strength, undergo large reversible elongations.

Amorphous polymers with low intermolecular forces and some crosslinking are needed for reversible extensibility.

Polyethylene

Polybutadiene

Polysiloxane

FIBERS: Very high strength, low extensibility. Highly crystalline polymer with high intermolecular forces.

Polyamides

Polyesters

Polybenzimidazoles

FLEXIBLE PLASTICS: Moderate-to-high strength and extensibilities.

Moderate crystallinity, low or no crosslinking, absence of rigid chains.

Polyethylene

Polyesters

Polyacrylonitrile

RIGID PLASTICS: Very high strength, almost zero extensibility.

Amorphous polymers with very rigid chains or extensive crosslinking

Polystyrene

Phenol-Formaldehyde

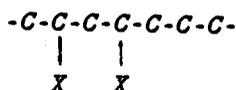
I.2. CLASSIFICATION OF POLYMERS

Polymers can be classified into many categories. Various aspects of molecular structure can be used to determine these classification, but polymers can also be classified according to the chemical reactions that can produce the polymer, e.g.,

- A. Addition polymers
- B. Condensation polymers
- C. Natural polymers

For addition polymers the following applies¹;

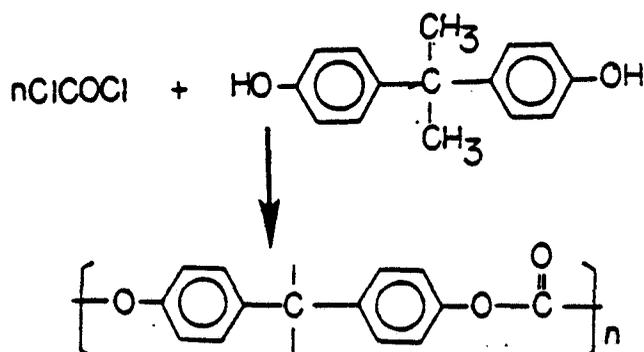
1. The repeat unit in the polymer and the monomer have the same composition, although, the bonding is different in each.
2. The mechanism of these reactions places addition polymerizations in the kinetic category of chain reactions, with either free radicals or ionic groups responsible for propagating the chain reaction.
3. The product molecules usually have a carbon chain backbone, with pendant substituent groups.



In condensation polymers, the following applies:

1. The polymer repeat unit often arises by reacting together two different functional groups which usually originate on different monomers. In this case the repeat unit is different from either of the monomers. In addition, small molecules are eliminated during the condensation reaction.

SCHEME-1-



(Poly(4,4'-isopropylidenediphenylene carbonate)

(Dexan)

2. The mechanism is summarized by saying that reaction occurs in steps.
3. The product molecules have the functional groups formed by the condensation reactions dispersed regularly along the backbone of the polymer molecule.

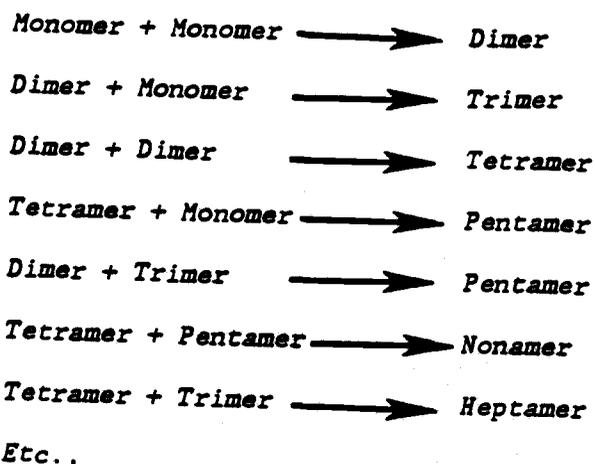


Natural polymers are ones such as carbohydrates and polypeptides and are found in the nature.

In recent years emphasis has been given to what reaction mechanism is involved for forming a polymer.² The most common mechanisms are outlined below.

A-STEP POLYMERIZATION

A step reaction takes place in a stepwise manner in which the chain growth occurs by a slow process which could be depicted as shown below.



which can be expressed as the general reaction



- a. High molecular weight is achieved only at very high conversion
- b. Molecular weight increases with conversion
- c. Any two molecular species can react
- d. Monomer concentration decreases rapidly in early stages of reaction
- e. The reaction mixture contains a range of different sized species

Condensation reactions and some noncondensation reactions, such as Diels-Alder additions, fall into this category.

B-CHAIN POLYMERIZATION

- a. High molecular weight is obtained initially and continuously
- b. Molecular weight is generally unaffected by conversion
- c. Monomer can react only with reactive species
- d. Monomer concentration decreases continuously throughout the reaction
- e. The reaction mixture contains high polymer, monomer, and reactive species.

I.3. KINETICS AND DEGREE OF POLYMERIZATION

Degree of polymerization (DP) can be expressed in terms of repeating unit in a polymer chain.



$$-dX/dt = k(X)(Y) \quad (1.)$$

when $(X) = (Y) = M$

$$-dM/dt = kM^2 \quad (2.)$$

Integration of equation 2. between time 0 and time t and between M values of M_0 and M yields

$$1/M - 1/M_0 = kt \quad (3.)$$

$$M = M_0 - M_0p = M_0(1-p) \quad (4.)$$

p = fraction of X group which has reacted

Combination of 3. and 4. yields

$$1/(1-p) = M_0kt + 1$$

where $DP = M_0/M$

$$DP = 1/(1-p) \text{ or}$$

$$DP = M_0kt + 1$$

I.4. VISCOSITY MEASUREMENT OF POLYMERS⁴

In dilute polymer solutions, the following viscosity related quantities can be found

1. The viscosity ratio (The relative viscosity η_{rel}), Which is given by the ratio of the outflow time for which solution (τ) to the outflow time for the pure solvent (τ_0).

$$\eta_{rel} = \tau/\tau_0$$

2. Specific viscosity (η_{sp}), which is the relative increment in viscosity of the solution over the viscosity of the solvent

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_{rel} - 1$$

3. Inherent viscosity (η_{inh}), is defined as

$$\eta_{inh} = (\ln \eta_{rel})/c$$

where c is the concentration of polymer in grams per deciliter (cgd)

A number of methods are available for the determination of the viscosity of a liquid³. The most useful methods are based on a measurement of flow rate of the liquid through a capillary tube. In practice the capillary tube is the part of a viscometer.

I.5. THE VISCOSITY AVERAGE MOLECULAR WEIGHT

For polydisperse linear polymers the viscosity average molecular weight (M_v) is given by the Mark-Houwink-Sakatura equation⁴.

$$\eta_{inh} = K * M_v^a$$

K and a are constants for a given polymer

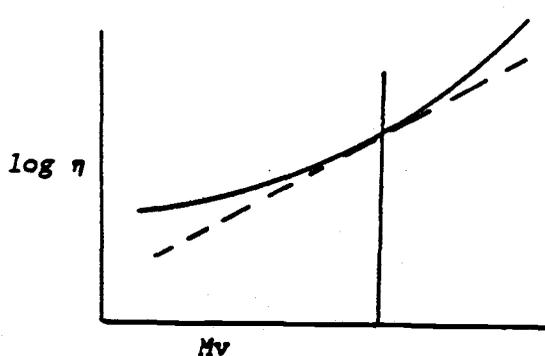
$$M_v = (\sum N_i M_i^{1+a} / \sum N_i M_i)^{1/a}$$

where N_i is the number of moles whose weight is M_i

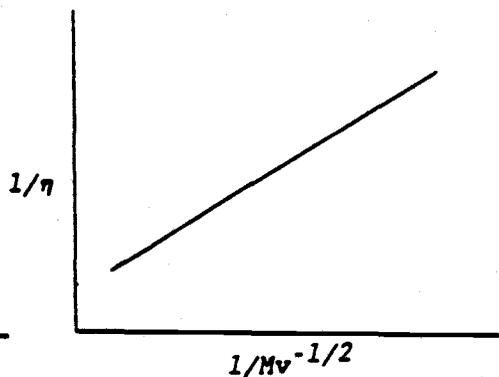
The viscosity average molecular weight is not available from experiments other than viscosity measurements. A typical plot of $\log \eta$ versus $\log M_v$ for a given polymer at a given temperature in a given solvent should be as it is shown below.

FIGURE-4

Molecular weight

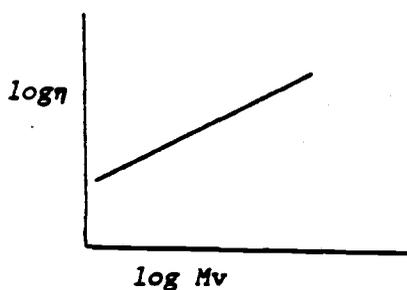
FIGURE-5

Mark-Houwink-Sakatura relation



The constant a usually varies within the range $0.5 < a < 0.8$, but higher values are obtained for stiff or short molecules.

The constant a is related to the solvent power and the expansion factor α that depends on the thermodynamic interactions between polymer segments and solvent molecules. The constant K and a are determined by plotting $\log \eta$ versus $\log M_n$ or $\log M_v$ or $\log M_w$.

FIGURE-6-Determination of (a) value of a polymer sample

$$\log \eta = \log K + a \log M_v$$

$$\text{Slope} = a$$

I.6. THERMALLY STABLE POLYMERS

One face of materials science which has been the subject of intensive research over the last decade is the development of new thermally stable polymers. The main stimulus has come from the need to meet the demands of modern technological advances and, in particular, the increasingly environmental requirements of the space program⁵. Much effort has been expended on the synthesis and evaluation of the thermal stability of new organic polymers. The goal has been to reach the useful upper temperature limits at which polymer maintains their desirable properties to at least 300°C, with an ultimate objective of 500°C or above.

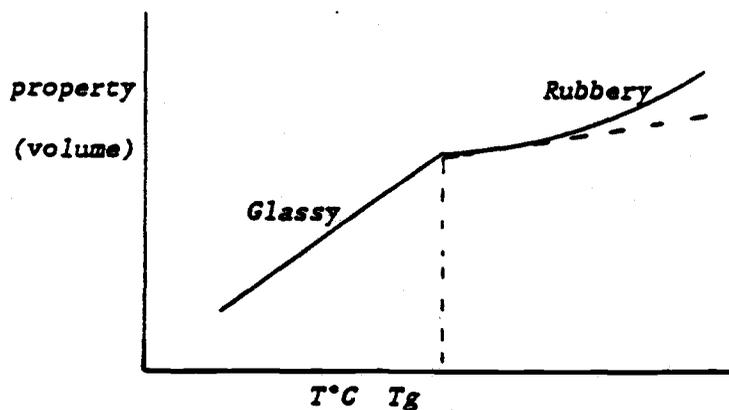
The protection of space craft and missiles against the intense heat encountered on "reentry" has focused attention on strong properties of plastics, and many studies have been devoted to the protective mechanism and performance of various materials, most importantly reinforced plastics.⁶ Thermally stable polymers have been recognized as specialty areas in polymer science. The goal of the thermally stable polymer or high temperature polymer chemist is to achieve a polymer that can resist heat up to 500°C. The only way to get data on thermal stability is to use thermogravimetric analysis (TGA).⁷

Thermal analytic data can determine the following.

1. Tg.... Glass transition temperature
2. Tm.... Crystalline temperature
3. PMT... Polymer melt temperature or melting point, temperature of adhesion when a slight force is exerted on a polymer which is resting on a hot surface

4. Softening point ... Qualitative observation of the temperature at which polymer softens.
5. HDT ... Heat deflection temperature test for rigidity versus temperature stress applied.

FIGURE-7 : The relationship of properties to temperature through the glass transition region.



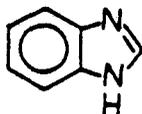
Some examples of high temperature polymers are,

- a. Polythiazoles
- b. Polytriazoles
- c. Polypyrrazoles
- d. Polybenzoxazoles
- e. Polybenzimidazoles

I.7. POLYBENZIMIDAZOLES

I.7.a. INTRODUCTION

Polybenzimidazoles are a class of thermally stable polymers incorporating the benzimidazole ring system in the polymer backbone.



These polymers are notable for their high resistance to high temperatures, retaining their oxidative stability to temperatures about 200°C above that of most common polymers. They also have high molecular weights and excellent resistance to hydrolytic attack in acidic or basic media. These properties make polybenzimidazoles especially suitable for uses such as those in the aerospace field.

Study of the synthesis, development and application of polybenzimidazoles has had several significant effects, since these were the first organic polymers to provide a major advance in thermal and oxidative stability in many years without the usual penalties of low molecular weight and thermal stability⁸. Adhesives and laminating resins, made with polybenzimidazoles can have high strength at elevated temperatures without the need of crosslinking. Polybenzimidazoles are truly thermoplastics because of their linear chains, and the disadvantages of crosslinking are avoided. Since polybenzimidazoles have Tg values of over 400°C, only their outstanding thermal and oxidative stability permit reaching temperatures where the detection of thermoplastic behavior becomes possible. The absence of crosslinking contributes to toughness, or ability to resist brittle failures by crack propagation.

I.7.b. HISTORY OF POLYBENZIMIDAZOLES

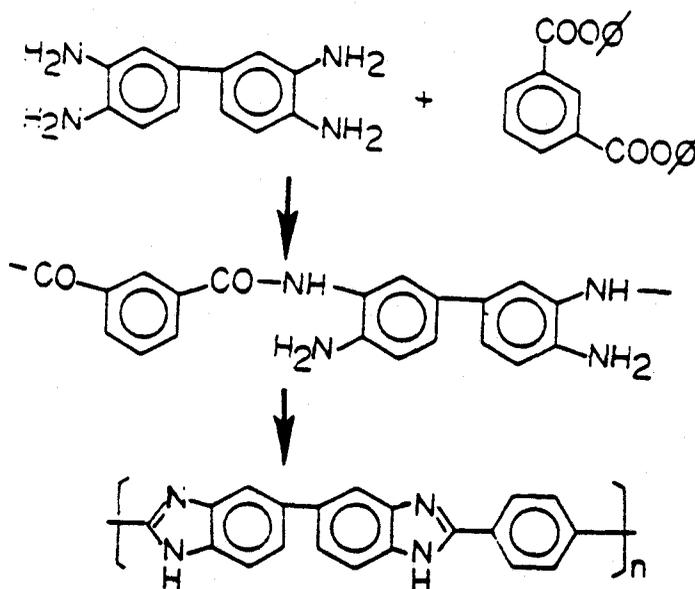
The technical development and applications history of polybenzimidazoles are remarkable from several points of view. This polymer system was not developed on the basis of economic considerations, to compete with existing textile fibers. In the case of polybenzimidazole, highly specialized technical demands that could

not possibly be met by conventional fibers were the motivation of this development.

Polybenzimidazoles first appeared around 1960, because the U.S. Air Force needed materials suitable for drouge chutes which could tolerate short-time exposure to extreme temperature while retaining a large portions of their mechanical strength. From the point of view of the necessary energy absorption characteristics, the stress strain curves of textile-type filaments were attractive. However, the thermal resistance of all known filaments was completely inadequate. Originally, the search for suitable materials concentrated on aromatic condensation polymers. Fully aromatic nylons or, as they have recently been named, aramids were well known. Unfortunately, the amide linkage proved to be the weak link determining the maximal thermal stability of the polymer. For that reason the following requirements were formulated⁹.

- A. Iso- or - heterocyclic aromatic moieties in the backbone provided the only chance to meet thermal stability.
- B. The linear concatenation of such building blocks could only be expected via condensation polymerization.
- C. A means had to be found to stabilize the weak links in the case of condensation polymers, the amide or ester linkages.
- D. Lastly, the resulting polymer had to be sufficiently soluble to permit the forming into filaments.

The solution, eventually provided by Marvel and Vogel¹⁰, was elegant and deceptively simple. One of the classical polybenzimidazole syntheses was used for the preparation of the polymer.

SCHEME-2-

Here, the spontaneous cyclization of the amino-amide intermediate to an imidazole provide desirable stabilization of the amide linkages (Scheme 2). The initial Polybenzimidazole (PBI) program was nearing completion when a disastrous fire on board an Apollo spacecraft brought about an abrupt change in objective. Both AFML and NASA initiated a search for nonflammable fibers for personal protection. PBI was essentially rediscovered at that time as a nonflammable fiber and emphasis was placed on development of a stable product.¹¹

I.7.c. CHEMISTRY OF POLYBENZIMIDAZOLES

Polybenzimidazoles first prepared by Marvel and Vogel¹⁰ opened a new field in high temperature polymers which included studies of the thermal stability of aromatic polybenzimidazoles.

Polybenzimidazoles are synthesized from aromatic tetramines (bis-o-diamines) and dicarboxylates (acids, esters or amides), and from amides and dialdehydes.

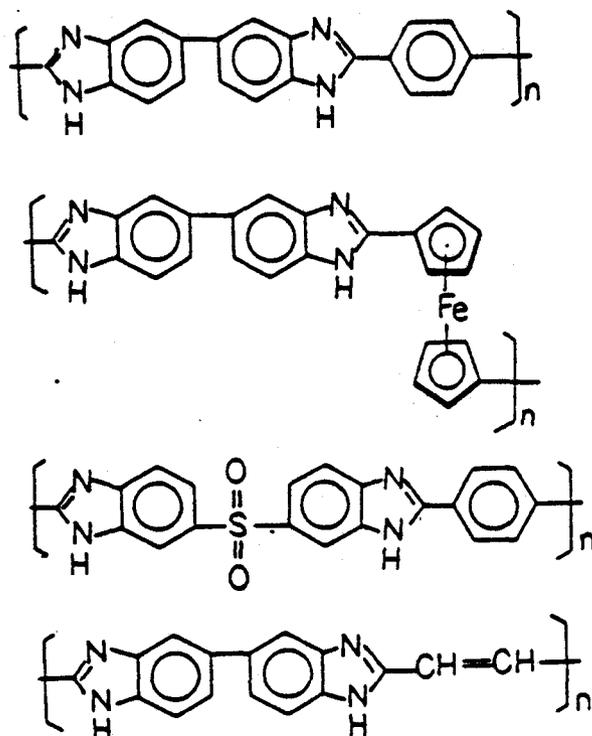
I.7.d. SYNTHESES OF POLYBENZIMIDAZOLES

TWO-STAGE MELT POLYCONDENSATION OF DIESTERS

" The year 1961 marks the beginning of one of the most remarkable periods of polymer research in the science of advanced materials. In this year Carl S. Marvel, one of the forerunner researchers in the field of heterocyclic polymer chemistry, reported the first synthesis of all-aromatic, high-molecular-mass polybenzimidazoles."^{10,12}

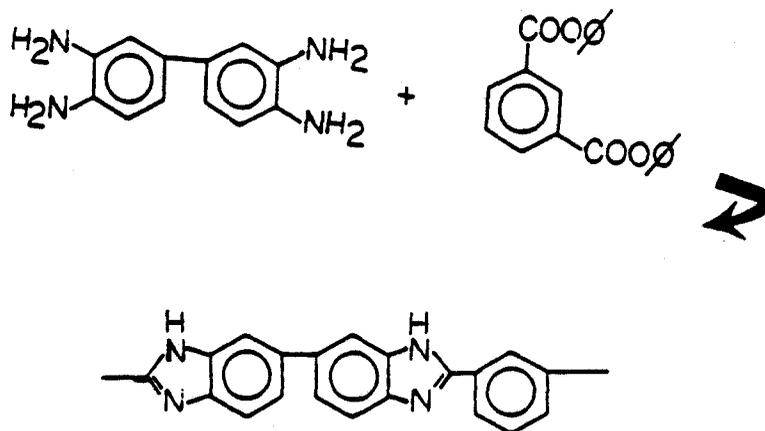
Marvel's pioneering approach involved a polycondensation that was carried out in two steps. One is the prepolymer stage where the polymer mixture was heated to 200-300°C, and the final stage where mixture was pulverized, and was heated to 400°C. Some representative polybenzimidazoles prepared by these methods are listed below.

SCHEME-3



An example of a typical melt polycondensation of 3,3'-diamino-benzidine with the diphenyl esters of a large number of carboxylic acids is shown in Scheme 4.

SCHEME-4-



In this method equimolar quantities of tetraamine and diphenyl esters were heated at temperatures 200 to 280°C. After pulverizing the initially formed prepolymer, heating was continued under high vacuum at temperatures 380 to 400°C. The final fully aromatized polybenzimidazole and its structure were reported by Marvel¹³. This procedure was extended with minor modification^{14,15}.

Many other polymer chemists have attempted to improve the methods of preparing polybenzimidazoles and they have used different monomers¹⁶. Many different polymers and monomer pair combinations have been used in this principal approach which has been used for laboratory synthesis, specialty preparations of adhesives, foam, and fiber applications

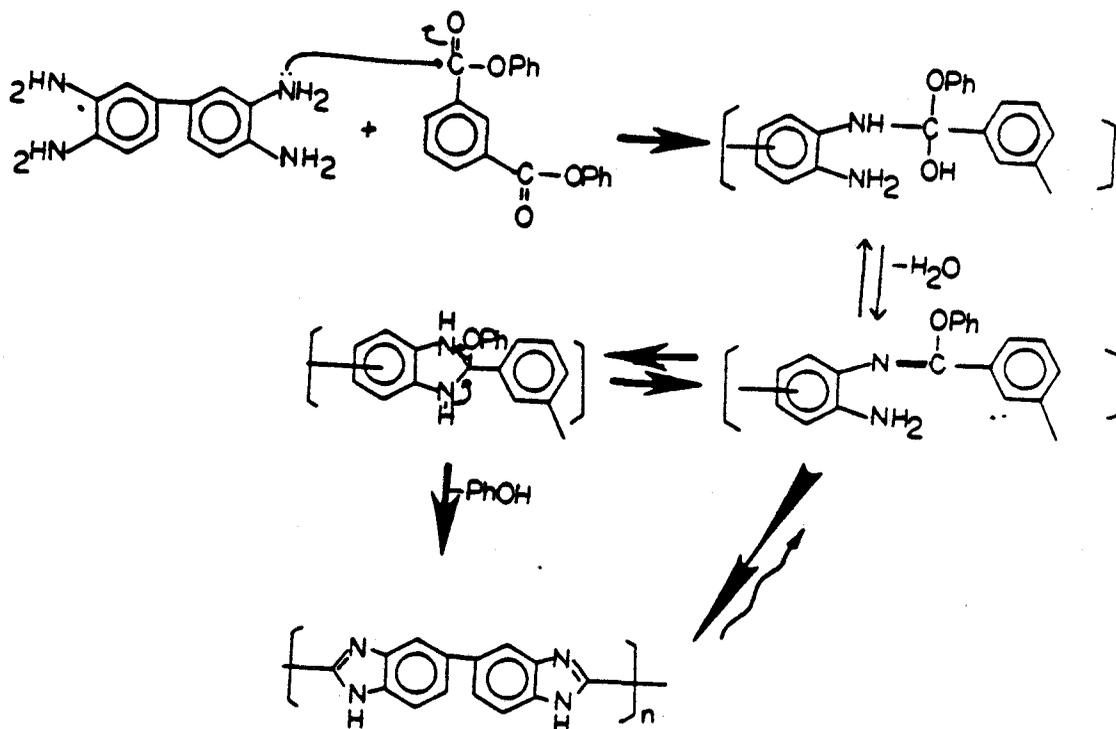
There has been a continued search for new high molecular weight materials with superior properties such as stability, retention or stiffness, toughness at elevated temperatures. This method of polybenzimidazole synthesis has several disadvantages:

1. High temperature control is necessary.
2. Crosslinking is easier with no solvent
3. Absolute absence of wetness and oxygen are necessary.

MECHANISMS OF POLYBENZIMIDAZOLES FORMED FROM DIESTERS

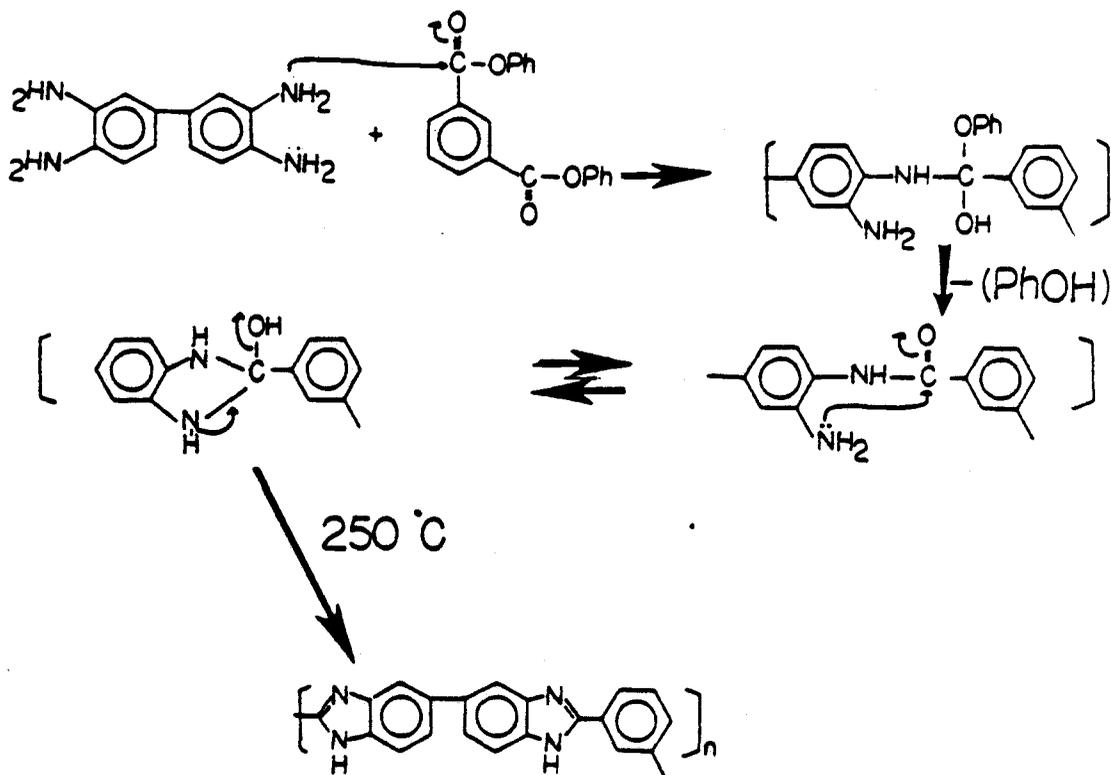
A number of reports dealing with the mechanism of polybenzimidazole formation have been published.^{17,18} This mechanism below was postulated by Izyneev and his co-workers¹⁸. The data, obtained in a sealed capillary tube indicates that water evolution occurs first to give a Schiff-base intermediate, and this is followed by loss of phenol to give the final polymer.

SCHEME-5-



The alternative mechanism has been proposed¹⁸ (Scheme 6)

SCHEME-6-

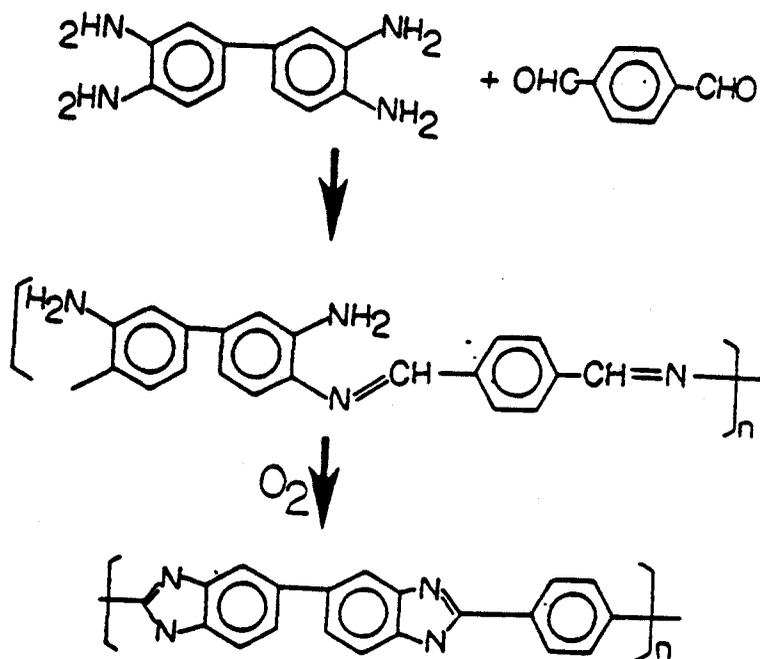


LOW TEMPERATURE SOLUTION POLYCONDENSATION OF DIALDEHYDES

As reported by D'Alelio²¹, a low temperature solution polycondensation of dialdehydes can be used to prepare polybenzimidazoles for cases where the monomers are subjected to being decomposed by heat from the reaction conditions. The first sub-zero low temperature solution polycondensation was reported by Neuse²². In this technique, an isolatable intermediate stage was found to be

useful as a more soluble form of the polymer. If the conditions are sub zero temperatures, strict absence of oxygen, and a dipolar aprotic solvent, then polybenzimidazoline intermediates can be isolated. The initial polycondensation reaction, performed in dipolar aprotic solvents, gives rise to an intermediate poly(azo)methine, which has been identified from the IR and UV spectra. This intermediate can be converted to the corresponding polybenzimidazoles by dehydrogenation under mild experimental conditions³². It has been reported that in the final dehydrogenation step oxygen was necessary to form an imidazole ring¹⁴.

SCHEME-7-



In order to prevent branching during the two-stage polymerization, reactions were carried out under rigorously controlled conditions such that highly diluted dialdehyde solution was added to the amine solution and temperatures were kept at the lowest possible level (-15 to 20 °C). Oxygen was carefully precluded in an effort to suppress cycloaromatization during this primary polycondensation stage. Polyazomethines were yellow-brown in color changing to orange-red with increasing extent of conjugation. Inherent viscosities determined in DMSO at 5% at 19 were in the range of 0.2 to 0.9 dl/g.

The poly(azomethines) and polybenzimidazoles could be differentiated from the spectral data shown below.

INFRARED BANDS OF AZOMETHINES^{22,33}

- a. 1600 cm^{-1} -C=N- stretching of the azomethine
- b. 1590-1600 cm^{-1}Adjacent benzene aromatic ring
- c. 3450-3360 cm^{-1}Bonded or nonbonded -N-H-
stretching
- d. 1280(s)-1250(m) cm^{-1} ...-C-N- of -C-N=C- and the -C-NH-
groupings
- e. 1485 cm^{-1} Aromatic ring vibration

NMR spectra generally were of limited diagnostic value because of strong broadening. Multiplets at 6.6 δ and 8.5 δ representing the aromatic protons, and two signals due to the -CH=N- and NH_2 protons at 8.9 δ and 5.5 δ respectively were of some value.

INFRARED BANDS OF POLYBENZIMIDAZOLES^{22,34}

- a. 3600-2800 cm^{-1} -N-H- (broad) band replaced by the two
bands at 3450-3360 cm^{-1} of the amino group.

- b. In the vicinity of 1600 cm^{-1} , where -C=C- and -C=N- ring absorption of the benzimidazoles
- c. $1600\text{-}1625\text{ cm}^{-1}$ in plane of -C=N- stretching band to the low frequency side.
- d. $1500\text{-}1400\text{ cm}^{-1}$ region in which a strong band group, likely due to aromatic -C-H- in plane bending modes appeared at $1450\text{-}1400\text{ cm}^{-1}$ whereas 1485 cm^{-1} band of polyazomethines spectra vanished entirely.
- e. The -C-NH- stretching band near 1250 cm^{-1} disappeared.

Neuse and co-workers have emphasized several important aspects of two-stage low temperature polymerization reaction.

1. Although the prepolymer (polyazomethine) was shown by a single structural formula in Scheme 7, the actual structure of it presumably consists of isomeric repeat units such as tetraamine moieties variously disubstituted at the 3,3- and 3,4'- and 4,4'-amino groups¹⁶.

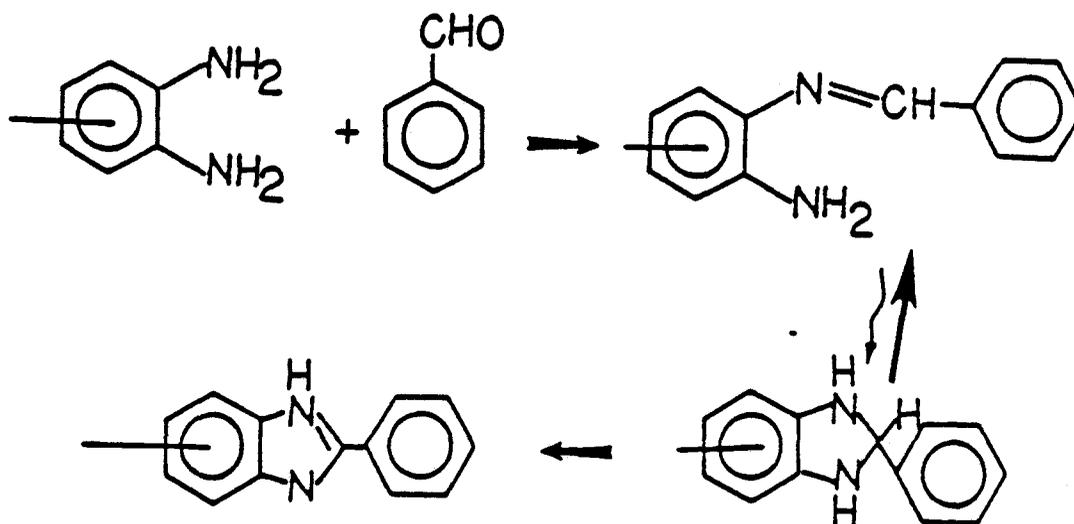
" While MO calculations indicate a slightly higher basicity for the amino substituents at position 3(3') than those at 4(4') in the monomer, the calculated electronic charge difference is too small⁴¹, to warrant the prediction of exclusive or even prevalent -C=N- bond formation at 3(3') as indicated in the structural representation of Scheme 7."

2. Added heating periods of 4-8h. at $50\text{-}100^\circ\text{C}$, again in the absence of oxygen, did not result in a significant viscosity increase. On the other hand, the color of the mixture changes brown to orange indicating some cyclohydrogenation in the course of such treatment.

3. Aromatic azomethines in which an ortho position of the anil ring system is occupied by an amino group are capable of rearranging to the corresponding closed-ring imidazole tautomer.³⁵

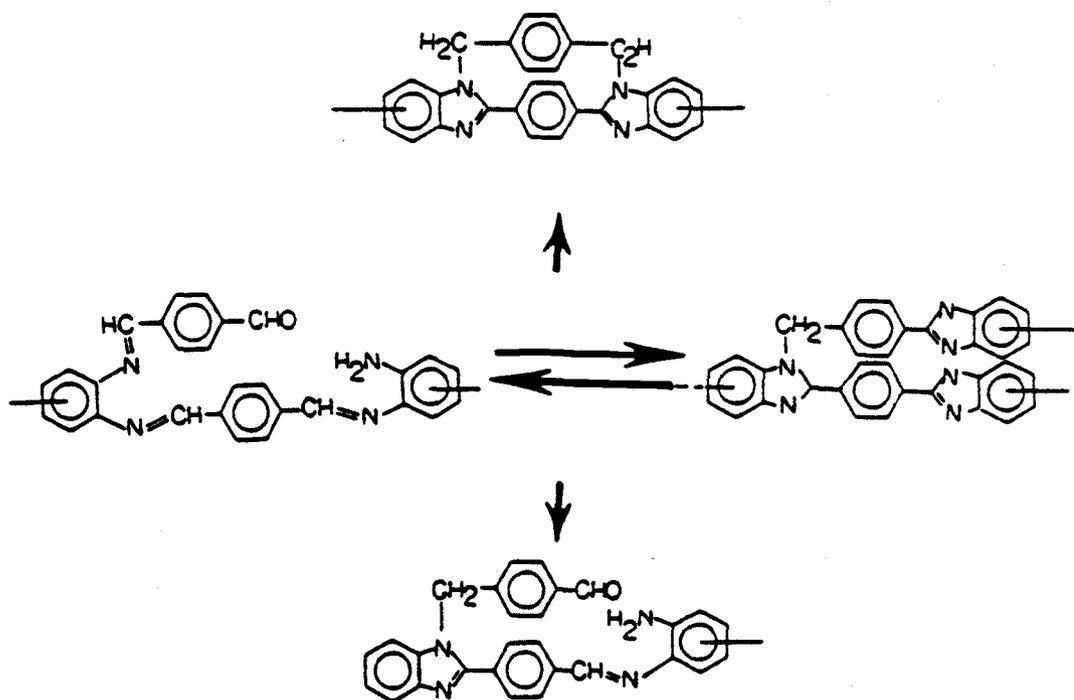
For the amino group case shown in Scheme 8, the open-chain Schiff-base form is not predominant.³⁶ Contrasting with this situation, the more acidic -SH group in the place of -NH₂ enters into cyclization readily, i.e., the corresponding thiazoline tautomers are generally favored over their Schiff-base counterparts.

SCHEME-8-



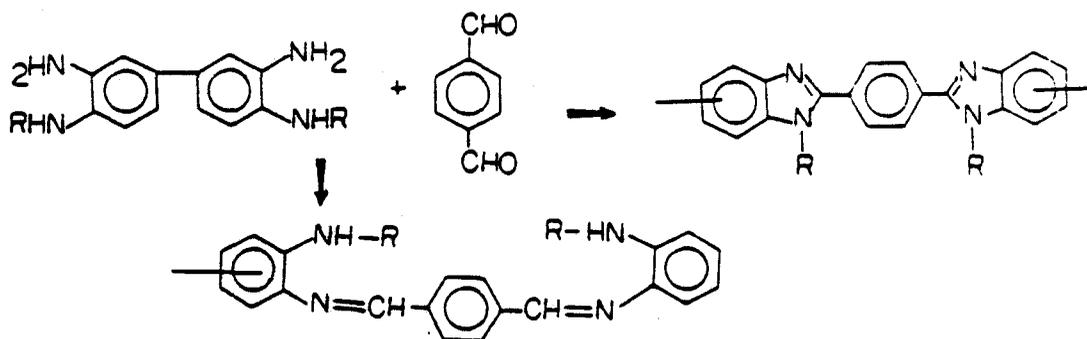
4. In this two-stage, low-temperature solution polycondensation, it is necessary to carry out an oxidative dehydrogenation step in order to obtain the closed-ring imidazole moieties.

5. Oxidation took place in air or more efficiently in the presence of FeCl₃, but in the absence of moisture. Some unwanted species can be formed during this process³⁶ are shown below.

SCHEME-9-

ONE STEP SOLUTION POLYCONDENSATION OF DIALDEHYDES

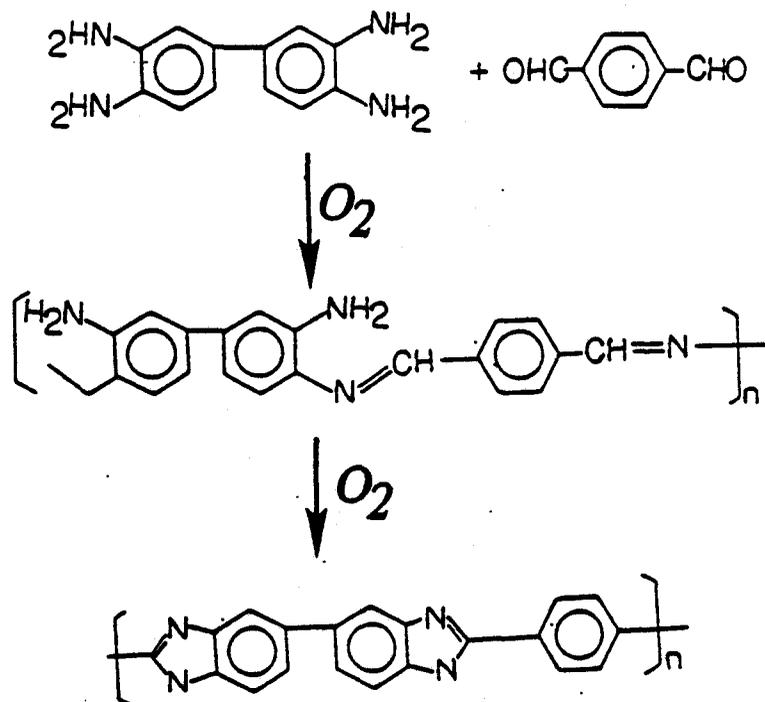
This process²⁰ is another way to prepare polybenzimidazoles with monomers that would be sensitive to the high temperature used in diester methods.



In this method, the dialdehyde is reacted with an aromatic tetraamino compound, in which the -NH₂ groups are ortho to each other, by adding the dialdehyde to the amine solution while simultaneously passing oxygen or oxygen-containing gases through the solution. The condensation polymerization of an aromatic tetraamino compound with an aromatic dialdehyde was found to be useful as evidenced by viscosities in the range of 0.6 to 0.8 dl/g and good polymer films. Any aromatic-type tetraamino compound having two pairs of ortho -NH₂ group, are suitable for the preparation of the polymer.

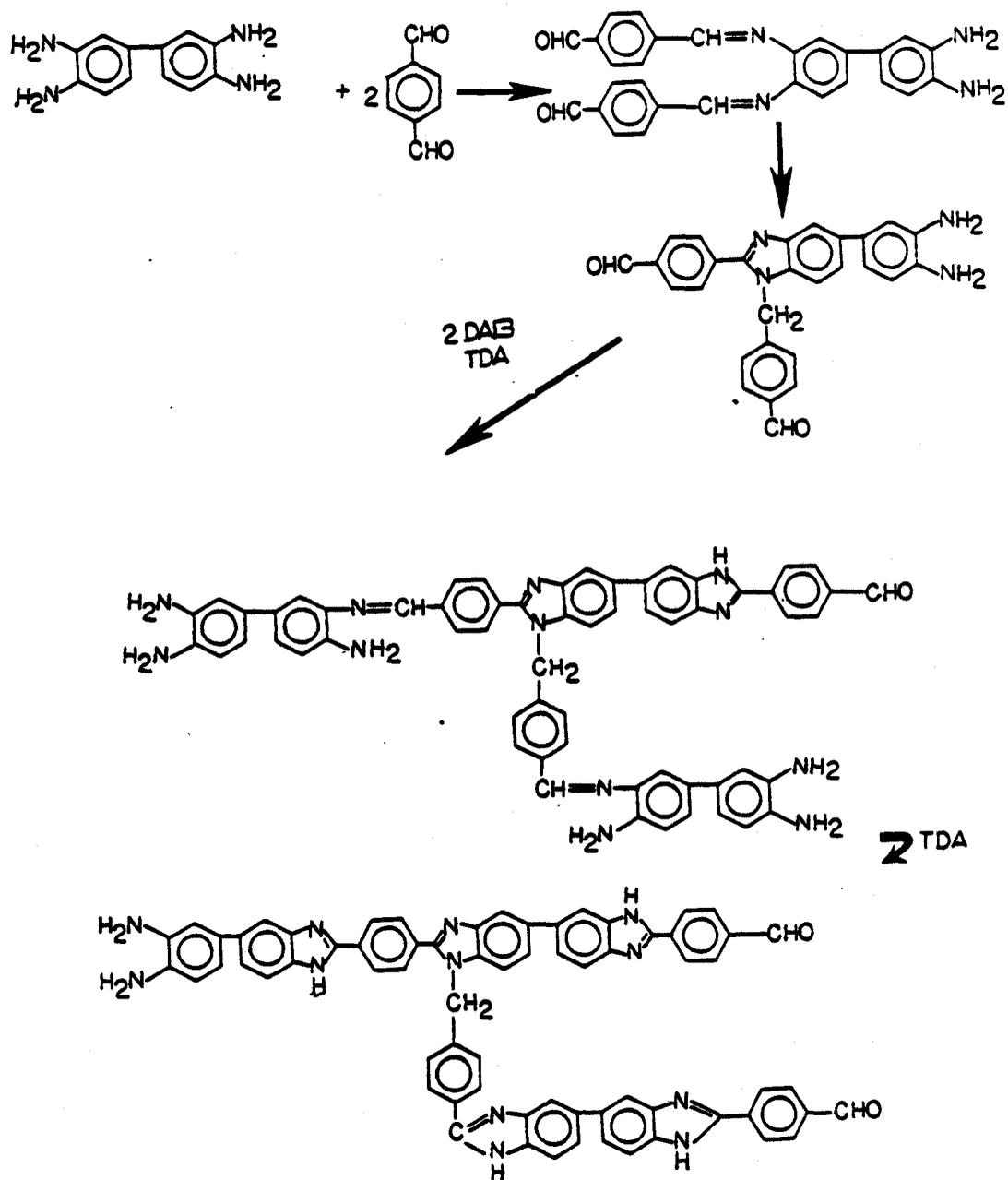
The mechanism for the imidazole formation was postulated to be a multistep reaction involving formation of a Schiff-base, a ring closure, and oxidation by O₂. The oxidation appears to facilitate the ring closure; an poly(azomethine) is the probable intermediate as it is shown in Scheme 10.

SCHEME-10-



The final product is a polybenzimidazole. In this polymerization process, the dialdehyde is added slowly to the tetraamine, so that at any particular moment, there exists no large amount of dialdehyde in the reaction mixture. If a substantial portion of the Schiff-base moieties are oxidatively cyclized, crosslinking is avoided and polymer remains in solution. Some branches can form by a non-oxidative process as shown in Scheme 11.

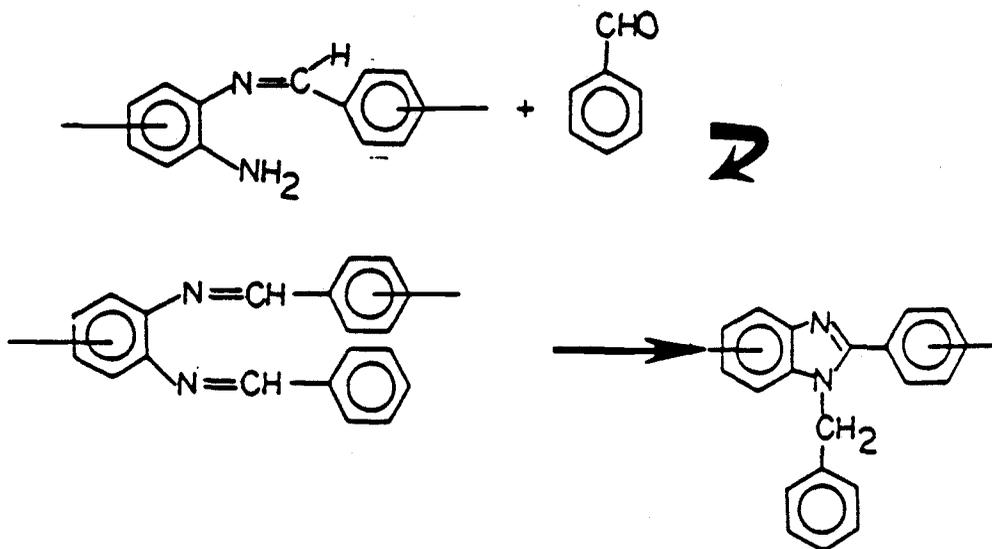
SCHEME-11



These molecules are soluble in the reaction media as crosslinkable polymers. Thus slightly crosslinked or highly crosslinked polybenzimidazoles can be prepared by this process.

It has also been shown that, a monoaldehyde, such as benzaldehyde used to modify the reaction between the tetraamine and the dialdehyde. Benzaldehyde is also capable of yielding *N*-substituted benzimidazoles by reaction with an amine function of an amino Schiff-base²⁰ followed by subsequent rearrangement of the di-Schiff base, as shown in Scheme 12. The introduction of such *N*-Substituted benzimidazole structures into the polymer eliminates the interchain hydrogen bonding which is present in the non-*N*-substituted benzimidazoles. It also reduces the possibility of crosslinking by the dialdehyde. This enhances the solubility of the polymers as does the introduction of *N*-substitution in the polymer.

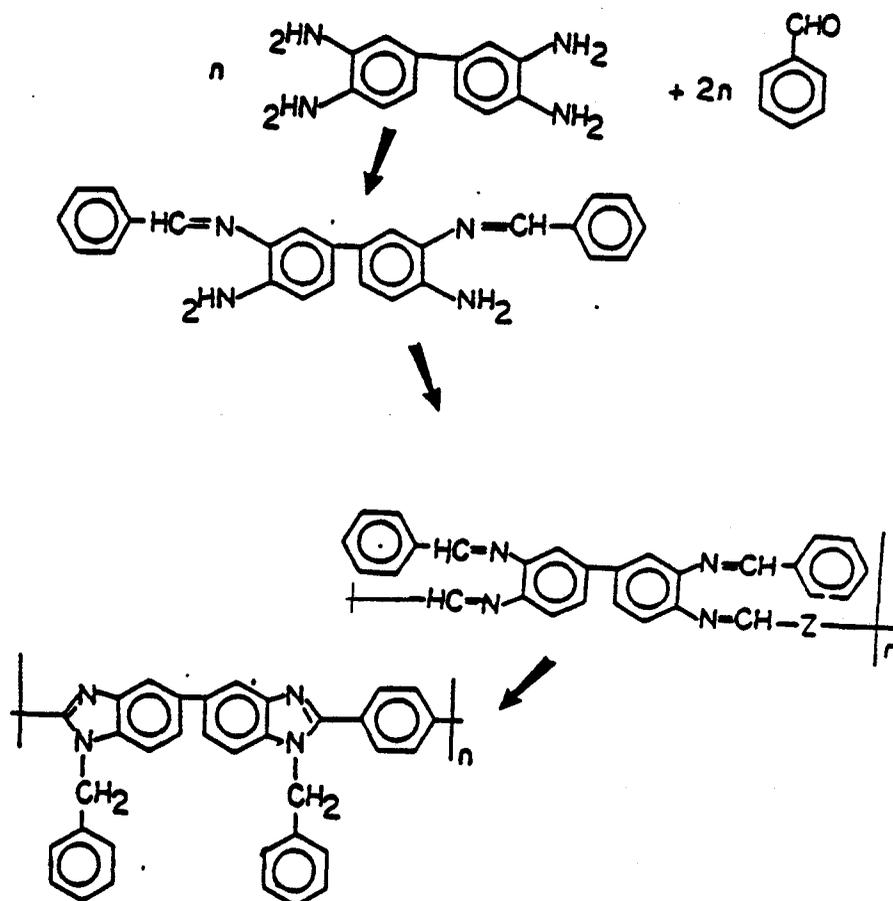
SCHEME-12



Maximum *N*-substituted benzimidazole structures could be obtained when each mole of tetraamino compound is reacted with two moles of

monoaldehyde and one mole of dialdehyde. In such case side reactions could be avoided by first forming the Schiff-base of the tetraamino compound by reaction with monoaldehyde and thereafter reacting the bis-Schiff-base with the dialdehyde as shown in Scheme 13. The main reason of modifying polybenzimidazoles through the reaction is to prepare polymers that are soluble and non crosslinked. There is a danger that molecular weight would be decreased by adding the monoaldehyde since it can cap a chain. This would be evidenced by a decrease in viscosity and poor properties of the polymer films that are cast from the reaction mixture.

SCHEME-13



SINGLE STEP DIESTER OR BISORTHOESTER POLYMERIZATION IN SOLUTION

Some of the advantages of solution polymerization of diesters over the other methods are,

- a. One-step versus two steps
- b. No attention to temperature control is necessary
- c. Less chance of crosslinking when solvent is used.
- d. Constant mixing is possible throughout the course of the reaction

A. AROMATIC DIESTERS IN PHENYLSULFONE AND SULFOLANE

Aromatic polybenzimidazoles have been prepared by the reaction of the tetraamine and diester in refluxing sulfolane and phenyl sulfone³⁷. The ease of using these solvents together with observed moderate viscosities and absence of crosslinking made this method an attractive new way to prepare polybenzimidazoles. Reasonably high viscosities were obtained by this procedure (0.69-0.93 dl/g), and the polymers were soluble in *N,N*-dimethylacetamide (DMAc), indicating absence of crosslinking. Although the polymerization was found to be less convenient to run in phenyl sulfone due to its high melting point (125°C), the polymerization can still be begun as a solution in the presence of low-boiling inert solvents such as toluene or xylene that was removed during the reaction³⁷.

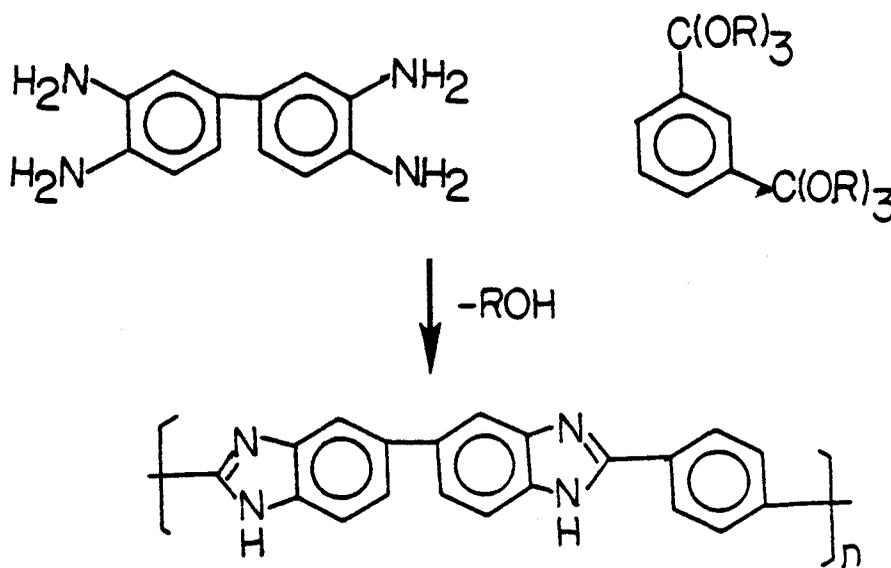
B. AROMATIC BISORTHOESTERS IN DIMETHYLSULFOXIDE

Aromatic bisorthoesters were found to be good polymer intermediates and could be polymerized by condensation with aromatic tetraamines under mild conditions in DMSO at 100°C³⁸. The hexa-propyl orthoesters of terephthalic and isophthalic acid were reported to be the preferred orthoesters because they were easily purified.

The polybenzimidazoles obtained by this method gave 0.1 to 0.8 dl/g inherent viscosities with varying molecular weight which in some cases were in the fiber forming range³⁸.

Even though polybenzimidazole synthesis by this process cannot provide the polymer intermediate (polyazomethine), the mild polymerization conditions suggest that heat sensitive reactants can be polymerized by this method¹⁴. Synthesis of one polybenzimidazole from a bisorthoester and tetraamine is shown in Scheme 14.

SCHEME-14-



I.7.e. PROPERTIES OF POLYBENZIMIDAZOLES

SOLUBILITY

The vast majority of available data on properties on PBI's deals with completely aromatic systems because of their potential aerospace and military applications. Solubility of aromatic polymers is definitely poorer than other corresponding thermally stable polymers, however solubility can be improved in many solvents. Although high molecular weight polymers are difficult or incompletely soluble in DMF, or DMSO, improved solubility results when about 1-5% of lithium chloride is dissolved in the solvent²³. Nevertheless, several qualitative trends in structure solubility relationships can be defined. Thus,

- a. Oxygen, sulfur or sulfolane bridges between aromatic units enhance chain flexibility.
- b. C-C or C-O single bond "hinges" enhance chain flexibility therefore solubility.
- c. N-alkylation improves the properties of the polymer.
- d. PBI's prepared by low temperature polymerization show better solubility than others.

VISCOSITY STUDIES OF POLYBENZIMIDAZOLES

The viscosities obtained on a given polymer sample may show considerable variation when measured in different solvents. Formic acid, for example, has been reported to give appreciably higher η_{inh} values than DMSO and sulfuric acid, because of the

polyelectrolyte effect of formic acid is larger than DMSO and sulfuric acid^{20,24,12}.

Some values have been observed, and corroborated by Fuoss-Strouss plots with formic acid as the solvent⁴³.

The Fuoss-Strouss equation is,

$$\eta_{sp}/c = A/(1+Bc^{1/2})$$

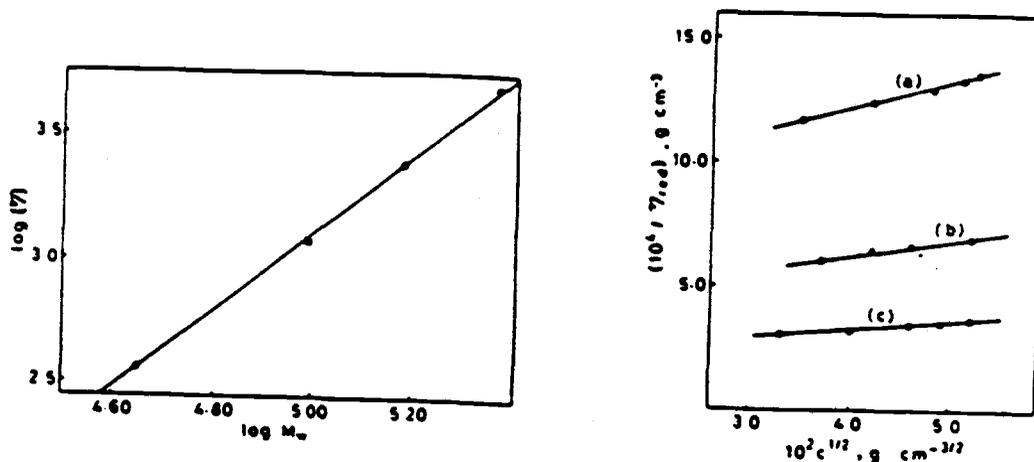
This equation has been generally used to find out the intrinsic viscosity of the polyanion by extrapolation of the data for reduced viscosity to zero concentration²⁶. Fuoss constants for polybenzimidazoles are listed in Table-1. B is assumed to be a measure of the electrostatic forces, between the polyions, and A value is the hydrodynamic ratio. Values tend to become larger with molecular weight.

TABLE-1: FUOSS CONSTANTS OF POLYBENZIMIDAZOLES

| PBI | MW | A/cm ³ g ⁻¹ | B/cm ^{3/2} g ^{-1/2} |
|-----|----------------------|-----------------------------------|---------------------------------------|
| | 4.5x10 ⁴ | 0.36x10 ³ | 10.2 |
| | 9.7x10 ⁴ | 1.21x10 ³ | 11.8 |
| | 15.0x10 ⁴ | 2.44x10 ³ | 13.3 |

The approximate intrinsic viscosity (η_{inh}) of PBI is plotted as a function of weight-average molecular weight. The value obtained for a PBI ($a = 1.58$) is larger than the value 1.41 obtained for polyamides and indicates a considerable long stiff repeating units within the main chain of PBI.

FIGURE-8 The approximate η_{inh} of PBI as function of MW



I.8. APPLICATION OF POLYBENZIMIDAZOLES

I.8.a. Structural application of PBI

With respect to synthesized polymers, aromatic polybenzimidazoles range among the most heat resistant polymers. They are synthesized by a multistep process that may yield different polymers with varying inherent viscosities. Polybenzimidazoles having inherent viscosities between 0.03 and 0.10 were reported to be fusible and capable of becoming infusible when heated in industrial applications³⁹. Structural application of thermally stable polymers such as polybenzoxazole, polybenzthiazole, and polybenzimidazole have found their place in today's world, mainly in the field of aerospace application. Among them only polybenzimidazole can maintain their desired properties at higher temperatures up to 700°C⁴⁰. The structural application of polybenzimidazoles have yet to be discovered. Inherent viscosity versus melting points and applications of a typical polybenzimidazole are shown in Table 2.

TABLE-2 : INHERENT VISCOSITY VERSUS APPLICATION FOR A PBI

| INHERENT VISCOSITY ^a | T _m (°C) | APPLICATION |
|---------------------------------|---------------------|--|
| 0.030 | 175 | MELTS-FLOWS, |
| 0.032 | 120 | POLYMERIZES IN PLACE |
| 0.038 | 95 | " |
| 0.042 | 85 | " |
| 0.050 | 105 | " |
| 0.062 | 200 | COMPOSITES, ADHESIVES |
| 0.075 | 240 | & FOAMS |
| 0.100 | 320 | " |
| 0.150 | 460 | " |
| 0.200 | >500 | INJECTION MOLD |
| 0.800 | NON-MELTING | FIBER MANUFACTURING |
| | | COMPRESSION MOLDABLE, FORMABLE FROM SOLUTION |
| | | SHEETS, SHAPES, SIZING, COATINGS, FILM |
| | | FIBRID, PAPER, MICROPOROUS RESIN |

a. Inherent viscosities were measured at 0.5% in DMSO

1.8.b. PBI applications as fiber

End-uses for PBI are primarily in two areas;

- 1) Those applications where extreme flame resistance is critical.
- 2) Those applications where low smoke emission and/or nontoxic offgases are critical.

High-flame-resistance includes:

- a. Safety apparel for firemen
- b. Work clothing for,
 1. Fuel handlers
 2. Race car drivers
 3. Welders
 4. Foundry workers
- c. Military clothing
 1. Flight suits
 2. Survival gear
- d. Hospital operating
 1. Room drapes
 2. Gowns

Low smoke emission/low offgas toxicity applications are,

- a. Commercial aircraft interior material
 1. Upholstery
 2. Curtains and drapes
 3. Carpets
- b. Interior materials in submarines

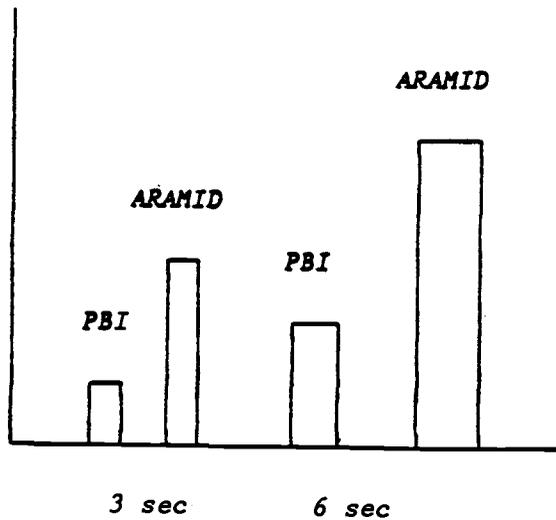
Considerable thought has gone into detailing the possible markets where PBI fiber, with its unique prior performance characteristics, might compete.

I.8.c. Flame resistance

The ASTM D-2863 limiting oxygen index (LOI) is the standard basis for comparing the relative flammability of materials. This index, which corresponds to the highest concentration of oxygen that fabric samples can withstand before ignition, gives values of 38% for PBI

versus 24% for Kynol, 20% for Nomex (poly-m-phenylene isophthalamide), and 2% for cotton. The high performance of PBI was demonstrated during the extensive fuel-fire-pit tests conducted by Air Force Material Laboratory⁴¹.

FIGURE-9 : Limiting oxygen index (LOI)



I.8.d. Smoke generation

Flammability is of primary importance for many applications. There are however, numerous applications where smoke generation and offgas toxicity are equally important. Experience to date indicates that PBI generates little or no smoke when heated or exposed to a flame source.

I.8.e. Light stability

PBI might be used in fabrics that are designed for outdoor uses and, hence, must resist deterioration in sunlight³⁰.

I.8.f. Offgases

Unlike some other high-temperature fibers, the offgases of natural PBI up to 560°C are not toxic. Aramids (polyamides), on the other hand release toxic offgases at temperatures well below that for PBI.

PBI's emission of only harmless offgases up to 560°C is one reason for its being considered as a primary material for use in many areas such as aircraft interior.

I.8.g. Thermal stability

Associated with its high degradation temperature, PBI has excellent thermal stability. Thermal degradation of PBI in an inert atmosphere has a maximum evolution of by-products, the polymer structure degrades at;

590°C for the natural, untreated material, and
680°C for thermally-stabilized materials.

I.8.h. Dimensional stability

Untreated PBI fabric exhibits good dimensional stability when heated. There is less than 1% shrinkage between room temperature and 275°C and a total of 10% shrinkage at about 540°C. The high-temperature dimensional stability of PBI can be improved further by a post-extrusion treatment of the filament, using various acids. The dimensional stability of fabric is particularly important for protective clothing, for example, where excessive shrinkage could severely restrict the movement of individual and, eventually, lead to rupture of the fabric and exposure of the wearer to the high temperature environment. Good dimensional stability may be equally important for applications such as fire-resistant aircraft seat fabrics.

I.8.i. Textile properties

One primary emphasis of PBI research has been to maximize the comfort for Air Force flight suits. PBI can be easily spun into yarn at commercially acceptable levels of efficiency.

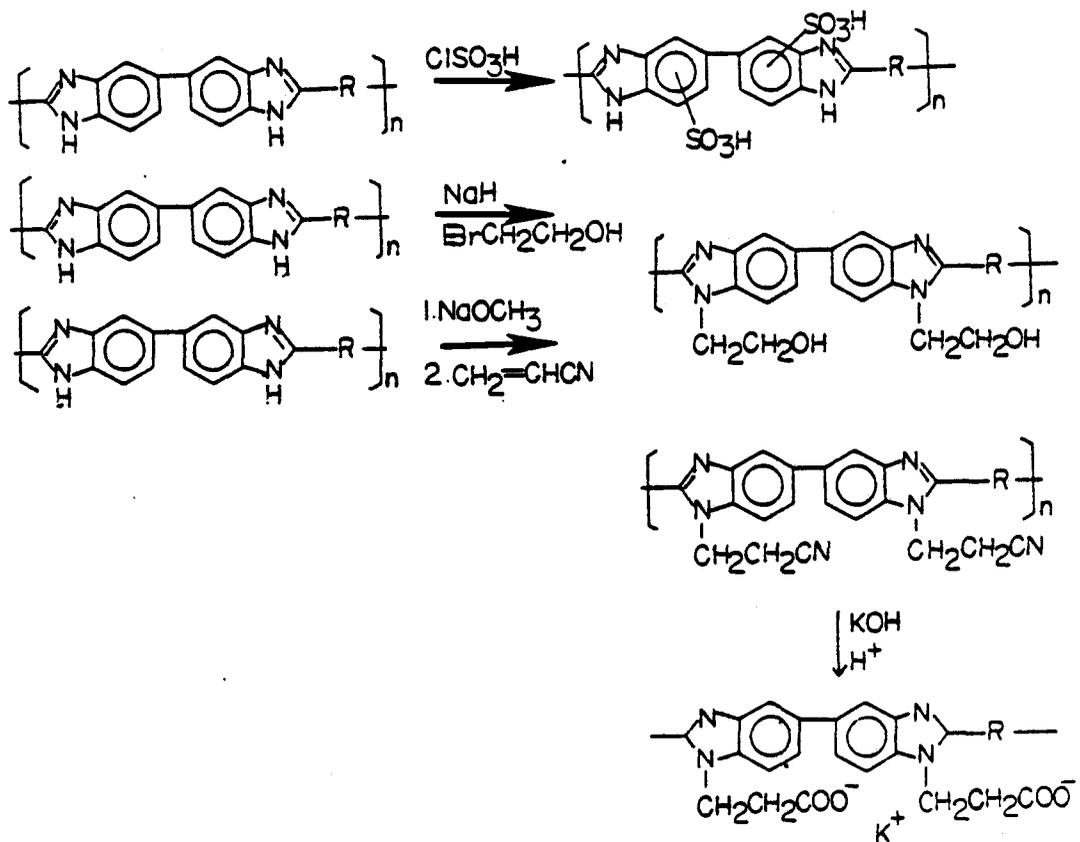
PBI filament and spun yarns have been fabricated successfully into a wide variety of structures and fabrics; including woven goods (for shirting, parachute, packs, and canopies), flight suits, ribbon, and some knit goods.

I.8.j. Moisture regain

Properly designed fabrics of PBI are exceptionally comfortable. One reason may be its outstanding moisture regain of greater than 18%. Corresponding figures are 10% for cotton, and 5% for aramid. This high moisture regain of PBI has significance beyond comfort. It has been proposed that one reason flight suits of PBI provide better thermal protection than those of other high-temperature fibers is that the heat required to dissipate the great moisture contents of the PBI fabrics is not available to cause burns.

I.8.k. PBI application as battery membrane separator

In certain specialty batteries, polybenzimidazoles have shown definite potential as a material for the battery separator and battery case⁴¹. Films made from the polymer were found to be unaffected by exposure to the electrolyte, which was a 40% solution of aqueous KOH saturated with silver oxide, which exhibited high resistivity. The reason for this apparently is that the polymer is not wetted with an electrolyte. For the film to function as a separator, it has to have the ability to permit movement of metallic ions and hydroxyl ions. Therefore it was necessary to modify the high molecular weight polymers so as to permit wetting and migration of electrolyte. Some modified polymers are shown in Scheme 15.

SCHEME - 15

II. OBJECTIVES OF THIS STUDY

The exceptional properties of polybenzimidazoles have made them one of the most desirable, thermally stable polymers.

Most of the applications utilize PBI's thermal flame protection properties and its comfort when it is made into fabric.^{30,31}

The unusual properties of polybenzimidazoles also suits many different applications which utilize PBI's thermal and chemical resistance as well as its high strength. Very little has been done to explore its use as a membrane for separations. It has been examined for use in batteries²⁹ and for removal of the salt from water³⁰.

The main focus of this thesis is to examine the current synthetic methods to see which ones can best be used to make good films for gas separations and then make some new types of films that would have high strength and selective gas permeability properties. High temperature properties are not important for this use, so different structures from the current PBI's can be used. In the long term it would be desirable to find cheaper ways to produce PBI since cost is a major reason it is not more widely used.

III. RESULTS AND DISCUSSION

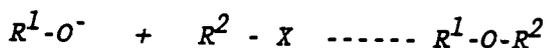
III.1. MONOMER SYNTHESIS

III.1.a. Synthesis of Bisorthoesters

Ortho esters, are very reactive intermediates and can be used for many applications where a carboxylic acid derivative is needed⁴². They are more reactive than regular carboxylic acid esters, but usually less reactive than corresponding acid chlorides. Orthoesters can be used to form five-or-six membered heterocyclic compounds⁴³. This makes them most interesting for generating polybenzimidazole intermediates.

The most general method for preparing orthoesters is the Pinner synthesis⁴⁴. In this method, a nitrile is converted with an alcohol and anhydrous HCl into the iminoether hydrochloride, which is then allowed to react with excess alcohol in a separate step to the orthoester. The Pinner synthesis is most suitable for preparing aliphatic, orthoesters, and orthoformates.

The Williamson synthesis³⁹ is the method of choice for the synthesis of orthoesters which don't have an α -hydrogen atom on one side. The Williamson syntheses for any ether with two different alkyl groups proceeds best if R^2 is favorable for SN_2 reaction.

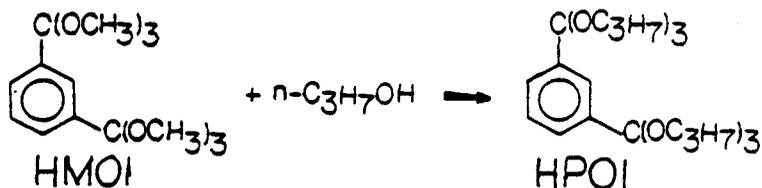


Interestingly, α,α,α -trihalo compounds such chloroform or α,α,α -trichloro-toluene, are suitable for this triple SN_2 displacement reaction as shown.



The orthoesters generated in this way can be transesterified with other alcohols without catalyst.

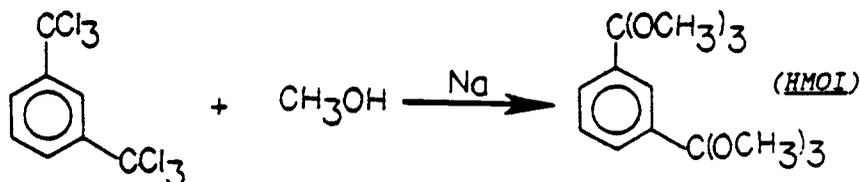
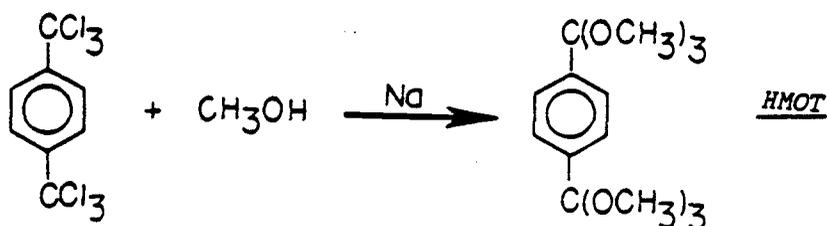
For example, HMOI was converted to the propyl orthoester, HPOI, as shown below.



Very few bisorthoesters have been reported. Aliphatic bisorthoesters have been studied by McElvain²⁸ who made orthosuccinate, and also the orthomalonates. A very few aromatic orthoesters are also known⁴¹. Hexamethyl-orthoisophthalate and hexamethyl-terephthalate were prepared in moderate yield from $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*m*-xylene or a $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*para*-xylene with sodium methoxide in methanol³⁸.

One objective of this work was to synthesize and purify orthoesters of isophthalic acid, and terephthalic acid, and to test them as polymer intermediates for polycondensation reactions.

REACTIONS



For the preparation of hexamethylorthoterephthalate (HMOT), and hexamethylorthoisoophthalate (HMOI), the reaction of hexachloro-para-xylene (HCPX), and hexachloro-meta-xylene (HCMX) with sodium methoxide in refluxing methanol gave moderate yields of HMOT, HMOI. The NMR and IR spectra of these compounds were consistent with their structures.

For the HMOT case, a singlet at 8.05 δ which is caused by the four equivalent aromatic protons of HCPX decreased, and a singlet at 7.58 δ which is caused by for aromatic protons of HMOT increased. HMOT was also identified by inspection of the IR spectra. The absence of any carbonyl stretching band in the 1700 cm^{-1} region was noted.

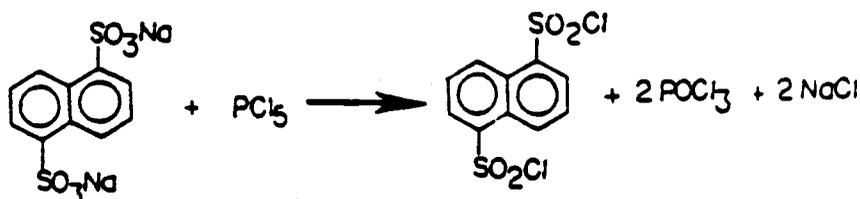
For the HMOI case, the IR spectrum showed a strong band at 1100 cm^{-1} (C-O-stretch) and the absence of a band in the 1730-1700 cm^{-1} region (C=O stretch). The NMR spectrum showed a multiplet at 7.2 δ (4H aromatic protons), and a singlet 3.14 δ (18 H). The IR showed for HPOI a strong band at 1120 cm^{-1} region (-C-O-stretch), and as the reaction proceeds the band in the 1750-1700 cm^{-1} region diminished. The NMR spectrum showed a singlet at 7.65 δ (4H aromatic), a triplet at 3.50 δ (12H, O- CH_2 - CH_2 - CH_3), a multiplet at 1.65 δ (12H, O- CH_2 - CH_2 - CH_3), and a triplet at 0.98 δ (18H, O- CH_2 - CH_2 - CH_3).

All of the bisorthoesters were crystallized many times from petroleum ether and dried over CaCl_2 in vacuo until they exhibited a sharp melting point. The purity was then considered high enough to carry out polymerization using these bisorthoesters.

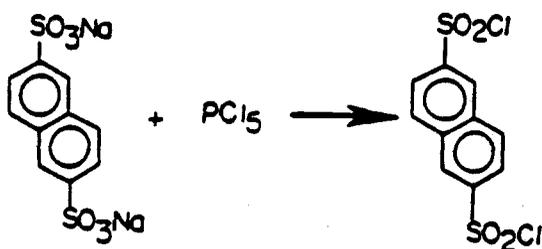
1.b. SYNTHESIS OF DIALDEHYDES AS MONOMERS

These monomers were prepared in straightforward manner as shown below. All of them were recrystallized before used.

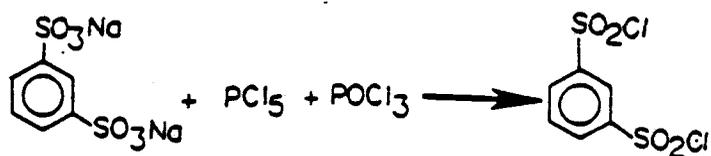
1. Synthesis of Napthalene-1,5-disulfonyl chloride³¹



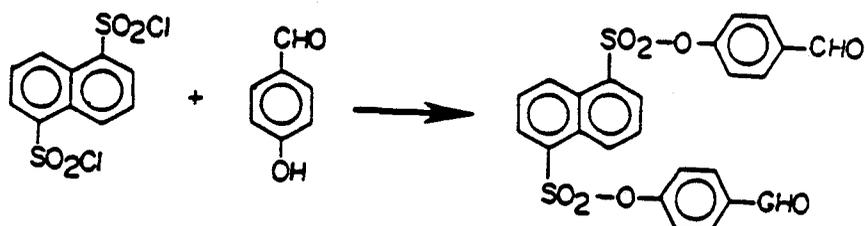
2. Synthesis of Napthalene-2,6-disulfonyl chloride



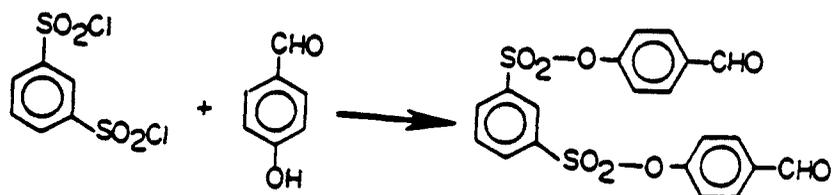
3. Synthesis of Benzene 1,3-disulfonyl chloride



5.a. Napthalene-1,5-bis-(4'-formyl-phenyl-(1)-sulfonic acid ester)



5.c. Benzene-1,3-bis-(4' formyl-phenyl-(1)-sulfonic acid ester)



5.b. Naphthalene-2,6-bis-(4' formyl-phenyl-(1)-sulfonic acid ester)

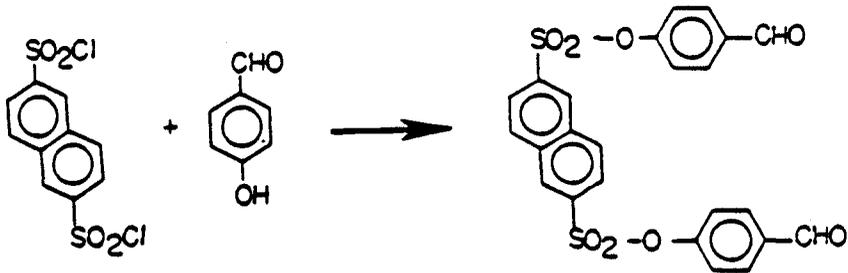
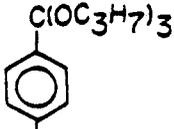
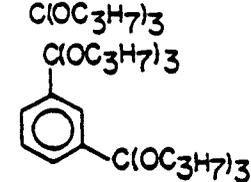
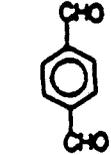
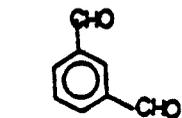
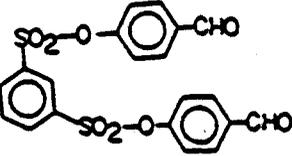
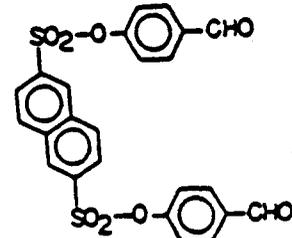
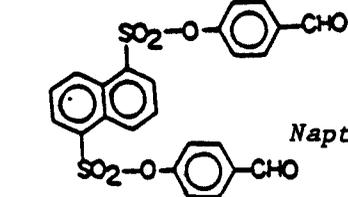


TABLE-3-MONOMERS USED FOR PREPARATION OF POLYBENZIMIDAZOLES

| <u>MONOMERS</u> | <u>NAME</u> | <u>SYMBOL</u> |
|-----------------|---------------------------------|---------------|
| | 3,3'-diaminobenzidine | (DAB) |
| | Diphenylisophthalate | (ISO) |
| | Diphenylterephthalate | (TERE) |
| | Hexamethyl-orthoterephthalate | (HMOT) |
| | Hexamethyl-orthoisoisophthalate | (HMOI) |

TABLE-3-CONTINUED

| MONOMERS | NAME | SYMBOL |
|---|---------------------------------------|-----------|
|  | Hexa-n-propylterephthalate | (HPOT) |
|  | Hexa-n-propylisophthalate | (HPOI) |
|  | Isophthalaldehyde | (ISO) |
|  | Terephthalaldehyde | (TERE) |
|  | Benzene-1,3-disulfonic acid ester | (BDS-1,3) |
|  | Naphthalene-2,6-disulfonic acid ester | (NDS-2,6) |
|  | Naphthalene-1,5-disulfonic acid ester | (NDS-1,5) |

III.2. POLYMERIZATION REACTION

Before polymers were made from the new monomers, it was necessary to determine the best way of preparing polybenzimidazoles. Many polymerization methods and experimental conditions were first tested with readily available monomers. Viscosity measurements and polymer films obtained from samples removed during the polymerization process, indicated that polymerization reactions had to be repeated many times to determine the optimum conditions for attaining a maximum viscosity. A viscosity with $\eta_{inh} > 0.8$ seemed to be needed to produce film with reasonable properties. The properties of the polymer films varied depending on which polymerization method and which monomers were used. Flexible and tough films could be obtained that were reasonably strong; flexible but not elastic. A strong pull didn't break the films unless they were damaged. Many of them were flexible, yellow to brown in color, and clear, but folding them cause them to break.

Four basic methods including two-stage melt polycondensation, high temperature polycondensation, one-step solution polycondensation, and low temperature solution polycondensation were tested. The low temperature dialdehyde method and one step solution polycondensation of dialdehydes seemed to produce the best films so they were used with new monomers. In many polymerization method it was found that reaction had to be repeated many times by changing experimental conditions such as heat, dialdehyde addition time, and solvent.

III.2.a. TWO STAGE MELT POLYCONDENSATION OF DIESTERS

Studies were carried out to determine the best way of making new polybenzimidazoles. Equimolar amounts of tetraamine and diphenyl-esters of tere- and iso- phthalic acid were heated at temperatures gradually rising from 200 to 300°C. When the initially liquid melt had solidified, heating was continued for a short time under reduced pressure, in the presence of nitrogen.

TABLE-4-MELT POLYCONDENSATION (METHOD IV.2b)

| COMPOUND | REACTION CONDITIONS | | η_{inh} dl/g | SOLUBILITY | | |
|------------|---------------------|------------------|----------------------|------------|-------|--------------------------------|
| | TIME | °C | | DMSO | HCOOH | H ₂ SO ₄ |
| DAB + TERE | 20 min. | 240 | - | - | - | - |
| DAB + ISO | 30 min. | 260 | 0.09 | ++ | ++ | ++ |
| DAB + TERE | 5h | 400 | 0.74 | + | + | + |
| DAB + ISO | 10h | 400 | 0.37 | + | + | + |
| DAB + TERE | 5h | 400 ^a | 0.62 | ++ | ++ | ++ |
| DAB + ISO | 10h | 400 ^a | 0.59 | ++ | ++ | ++ |
| DAB + TERE | 1h | 400 ^b | 0.83 | +++ | +++ | +++ |
| DAB + ISO | 4h | 400 | 0.77 | +++ | +++ | +++ |

a. Initial temperature is 400 °C

b. Reaction temperature increased gradually

c. Inherent viscosities were measured in DMSO at 5% at 19 °C

d. For limited solubility case η_{inh} was not corrected.

The pulverized polymeric solid intermediate, when post heated for several hours at 350 to 400°C under high vacuum, did undergo a nearly quantitative conversion to fully aromatized structure as evidenced by increased viscosity. In this method absolute absence of wetness and oxygen were found to be necessary. In the presence of wetness and oxygen the final polymer product was dark and insoluble in any media indicating high degree of crosslinking. η_{inh} shown below were not corrected for partially soluble PBI.

TABLE-5- TWO-STAGE MELT POLYCONDENSATION (METHOD IV.2b)

| COMPOUND | η_{inh} dl/g | SOLUBILITY | | | |
|-------------------------|----------------------|-------------------------|-------|------|--------------------------------|
| | | HCHO ₂ /LiCl | HCOOH | DMSO | H ₂ SO ₄ |
| DAB + TERE | 0.53/DMSO | - | - | + | + |
| DAB + ISO | 0.09/Formic | + | - | - | - |
| DAB + ISO | 0.428/DMSO | + | - | + | + |
| DAB + TERE | 0.61/DMSO | + | + | + | + |
| DAB + TERE | 0.59/Formic | ++ | ++ | ++ | ++ |
| DAB + TERE ^a | 0.60/Formic | +++ | +++ | +++ | +++ |
| DAB + TERE ^b | 0.80/ " | ++ | ++ | ++ | ++ |
| DAB + ISO ^a | 0.83/ " | +++ | +++ | +++ | +++ |
| DAB + ISO ^b | 0.79/ " | ++ | ++ | ++ | ++ |
| DAB + ISO ^b | 0.84/ " | +++ | +++ | +++ | +++ |

a. First stage at 240-260 °C

b. Second stage at up to 400 °C

c. For limited solubility cases η_{inh} was not corrected

III.2.b. TWO-STAGE LOW TEMPERATURE SOLUTION POLYCONDENSATION

Although polybenzimidazoles prepared by the melt polycondensation had moderate viscosities, they had limited solubilities in some cases. Since the preparative procedure didn't provide good polymer films because of limited solubilities of PBI's, The seemingly obvious answer to this problem was thought to be the low-temperature solution polycondensation of a tetraamine with aromatic dialdehydes. Polybenzimidazoles prepared by this method showed excellent properties evidenced by tough flexible films, and higher viscosities. In this method the first step of the polymerization reaction, carried out in dipolar aprotic solvents (NMP, DMF, DMAc, DMSO), gave rise to a polymer intermediate poly(azomethine) which was converted to the corresponding polybenzimidazole by oxidation in the presence of air and $FeCl_3$. Crosslinking was prevented by adding highly diluted dialdehyde solution to the tetraamine solution at $-15^{\circ}C$ to $-20^{\circ}C$. Satisfactory results have been obtained in our laboratories. Films cast from the reaction mixture were yellow to brown in color, flexible, and foldable. While NMR spectra generally were of limited diagnostic value because of strong line broadening, the UV and IR spectra were useful.

With this low-temperature solution polycondensation reaction, many polymerization reactions were carried out using the original procedure. With some minor modifications, this method gave excellent results as evidenced by the increased viscosities near 0.80 dl/g and the flexibility and toughness of the polymer films.

TABLE-6- TWO-STAGE LOW TEMPERATURE SOLUTION POLYCONDENSATION
(METHOD IV.2d)

| COMPOUND | SOLVENT | REACTION CONDITIONS ^a | | | η_{inh}^b dl/g |
|-----------|------------------|----------------------------------|-------------------|-----------|------------------------|
| | | Time ^r | Time ^d | °C | |
| DAB + TDA | DMF | 24h | 6h | -15 to 20 | 0.87 |
| DAB + IDA | NMP ^a | 24h | 6h | -15 to 20 | 0.84 |
| DAB + TDA | NMP | 24h | 6h | -15 to 20 | 0.92 |
| DAB + IDA | DMSO | 24h | 2h | -15 to 20 | 0.79 |

a. N,N-methyl-2-pyrrolidone as solvent

b. Inherent viscosities were measured in DMSO at 19 °C

r. Reaction time

d. Adding time of dialdehydes to the tetraamine solution.

TABLE-7-PBI SYNTHESIS WITH TWO DIALDEHYDES, AND DAB

METHOD: IV.2d

| COMPOUND & RATIO | | | η_{inh} dl/g | FILM | | |
|------------------|-----|-----|----------------------|--------|----------|----------|
| DAB | TDA | IDA | | Color | Flexible | Foldable |
| 1.1 | 1 | | 0.72 | Yellow | + | + |
| 1 | 1.1 | | 0.55 | Red | + | - |
| 1 | 1.1 | | 0.99 | Yellow | + | + |
| 1 | - | 1.1 | 0.82 | Yellow | + | + |

Added heating periods didn't give significant viscosity increase in the second stage of polymerization reaction. Films cast from the reaction mixture were reddish to yellow in color indicating a high degree of conversion of poly(azomethines) to polybenzimidazoles. Films, cast during the first stage of the polymerization reaction, were heated in vacuo at 280 to 300°C and resulted in flexible films.

TABLE-8- PBI SYNTHESIS WITH DIFFERENT RATIOS OF MONOMERS

METHOD: IV.2d

| DAB | MONOMERS | | | | η_{inh}^b dl/g | FILM ^a | | |
|-----|----------|----------------|---------|---------|------------------------|-------------------|-------|-------|
| | IDA | NDS-2,6 | NDS-1,5 | BDS-1,3 | | Color | Flex. | Fold. |
| 1 | : 0.78 | : - | - | : 0.28 | 0.78 | Red | + | - |
| 1 | : 0.5 | : 0.5 | - | - | 0.74 | Brown | + | - |
| 1 | : 0.5 | (:0.5 of TDA) | - | - | 0.92 | Yellow | + | + |
| 1 | : 0.75 | : 0.25 | - | - | 0.77 | Yellow | + | - |
| 1 | : 0.7 | : 0.4 | - | - | 0.72 | Brown | + | - |
| 3 | : 2.0 | : 1.0 | - | - | 0.82 | Yellow | + | + |

a. All films were obtained as flexible,

b. Inherent viscosities were measured in DMSO at 19 °C.

c. Dialdehydes were added separately to the tetraamine solution.

In some instances the stoichiometric amounts of tetraamine and dialdehyde were changed to test whether a stoichiometric imbalance (r) of monomers might give an improved result. The resulting polymer had moderate to high viscosities. Films were flexible, tough, and didn't break unless damaged.

TABLE-2- PBI SYNTHESIS WITH DIFFERENT RATIOS OF DIALDEHYDESMETHOD: IV.2d

| MONOMERS | | | | η_{inh} dl/g | FILM | | |
|----------|--------|------|---------|----------------------|--------|----------|----------|
| DAB | IDA | TDA | NDS-2,6 | | Color | Flexible | Foldable |
| 4 | : 3 | : - | : 1 | 0.87 | Yellow | + | - |
| 1.8 | : 1 | : 1 | : - | 0.97 | Yellow | + | + |
| 2 | : 1.1: | 1.1: | - | 0.96 | Yellow | + | + |

a. Dialdehydes were added separately to the tetraamine solution.

III.2.c. ONE-STEP SOLUTION POLYCONDENSATION OF DIALDEHYDES

Although polybenzimidazoles prepared by the above method gave satisfactory results, in some cases a one-step process can give satisfactory results as well. With this idea in mind, all polymerization reactions of dialdehydes with 3,3'-diaminobenzidine were performed by using one-step solution polycondensation method in the presence of dipolar aprotic solvents (NMP, DMF, DMSO, etc.), with air passing through the reaction mixture.

The rate of reaction depends on a number of factors, such as reactivity of the specific dialdehydes, the reactivity of tetraamine toward dialdehydes, whether 100% oxygen or diluted oxygen as when air is used, the nature of the solvent and the temperature at which each polymerization was conducted. The temperature ranged from about 0°C to the boiling point of the solvent or the melting point of

dialdehydes and diesters. At lower temperatures, the rates of the condensation reaction and oxidative ring closure should be slower than at higher temperatures, so that longer dialdehyde addition time should be better. The different experimental conditions used to carry out polymerization reactions at various temperatures were designed to take this into account.

TABLE-10-ONE STEP DIALDEHYDE POLYCONDENSATION

| COMPOUND | SOLVENT | METHOD | REACTION CONDITIONS | | | η_{inh} dl/g | FILM |
|-----------|-------------------|--------------------|---------------------|---------|-------------|----------------------|------|
| | | | T_1^a | T_2^b | $^{\circ}C$ | | |
| DAB + TDA | DMac ^c | IV.2f ₀ | 70 min | 2h | 110 | 0.42 | + |
| DAB + TDA | DMac | IV.2f ₀ | 90 min | 2h | 120 | 0.35 | + |
| DAB + IDA | DMac | IV.2f ₀ | 60 min | 2h | 135 | 0.10 ^f | - |
| DAB + IDA | DMac | IV.2f ₀ | 60 min | 2h | 135 | 0.47 | + |
| DAB + TDA | DMAC | IV.2f ₁ | 30 min | 5h | 50 | 0.10 ^f | - |
| DAB + IDA | DMac | IV.2f ₁ | 30 min | 5h | 50 | 0.54 | + |
| DAB + TDA | DMac | IV.2f ₂ | 30 min | 12h | 50 | 0.55 ^e | + |
| DAB + TDA | DMF | IV.2f ₁ | 30 min | 2h | 110 | 0.62 | + |

a. Dialdehyde adding time to the tetraamine solution

b. Reaction time

c. N,N-Dimethyl acetamide

d. + indicates films were obtained

e. Benzaldehyde is (%1 of dialdehyde) used.

f. Viscosities not corrected for partially soluble PBI's.

TABLE-11-PBI SYNTHESIS WITH BDS-1,3, AND DABMETHOD: IV.2d, and IV.2f₁ and IV.2f₀

| COMPOUND | SOLVENT | REACTION CONDITIONS | | | η_{inh}^a dl/g |
|---------------|---------|---------------------|-------------------|-----|------------------------|
| | | Time ^r | Time ^d | °C | |
| DAB + BDS-1,3 | DMSO | 24h | 6h | -15 | 0.47 |
| " | DMF | 24h | 6h | -15 | 0.58 |
| " | NMP | 5h | 2h | 50 | 0.64 |
| " | DMSO | 3h | 2h | 110 | 0.40 |
| " | DMSO | 20h | 2h | 120 | 0.62 |
| " | DMSO | 12h | 2h | 50 | 0.48 |

a. Inherent viscosities were measured in DMSO 5% at 19 °C

TABLE-12-PBI SYNTHESIS WITH BDS-1,3 AND DABMETHOD: One stage solution polycondensation (IV.2f₁)

| COMPOUND | SOLVENT | REACTION CONDITIONS | | | η_{inh} dl/g | FILM |
|---------------|---------|---------------------|-------------------|-----|----------------------|------|
| | | Time ^r | Time ^d | °C | | |
| DAB + BDS-1,3 | DMAc | 4h | 1h | 140 | 0.4 | - |
| " | NMP | 5h | 1h | 50 | 0.25 | - |
| " | NMP | 5h | 1h | 50 | 0.59 | - |
| " | NMP | 12h | 1h | 50 | 0.48 | - |

r : Reaction time; d : Adding time for dialdehyde

a : Inherent viscosities were measured in DMSO 5% at 19°C.

Many of the polymer reactions carried out were used to obtain polymer films. The solutions were cast on glass plates which were heated, the films peeled off if possible, and some of their properties such as flexibility, brittleness, color, etc., were noted.

It was the purpose of this experiment to obtain moderately flexible, tough polymer films indicating higher molecular weight. However all experiments carried out by varying temperature, polymerization method, time of addition, only yielded moderate viscosities.

TABLE-13-PBI SYNTHESIS WITH NDS-2,6 AND DAB

Method: IV.2f₀, 2f₁

| COMPOUND ^a | SOLVENT | REACTION CONDITIONS | | | $\eta_{inh}^{c,e}$ dl/g |
|-----------------------|-----------------------|---------------------|-------------------|-----|----------------------------|
| | | Time ^r | Time ^d | °C | |
| DAB + NDS-2,6 | DMSO | 8h | 2h | 120 | 0.69 |
| " | NMP ^b | 8h | 2h | 180 | 0.52 |
| " | NMP | 5h | 2h | 50 | 0.51 |
| " | DMF | 12h | 2h | 50 | 0.42 |
| " | NMP | 12h | 2h | 50 | 0.63 |
| " | DMSO | 2h | 1h | 160 | 0.51 |
| " | DMF/FeCl ₃ | 2h | 2h | 170 | 0.20 |

a. Starting compounds were purified twice

b. N,N-methyl-pyrrolidone

c. Inherent viscosities were measured in DMSO at 19°C.

d. Adding time ; r. Reaction time

e. Films were brittle

TABLE-14-PBI SYNTHESIS WITH NDS-1,5 ,NDS-2,6 , AND DAB

METHOD: One or Two step dialdehyde solution polycondensation

| COMPOUND | METHOD | SOLVENT | REACTION CONDITIONS | | | η_{inh} dl/g | FILM ^{a,b} |
|----------|--------------------|---------|---------------------|-------------------|-----|----------------------|---------------------|
| | | | Time ^c | Time ^d | °C | | |
| NDS-1,5 | IV.2f ₀ | DMF | 2h | 2h | 110 | 0.50 | - |
| " | IV.2d | DMAc | 24h | 6h | -15 | 0.69 | - |
| " | IV.2f ₀ | NMP | 4h | 2h | 110 | 0.57 | - |
| " | IV.2f ₁ | NMP | 5h | 2h | 50 | 0.45 | - |
| NDS-2,6 | IV.2f ₀ | DMF | 2h | 2h | 140 | 0.47 | - |
| " | IV.2d | DMAc | 24h | 6h | -15 | 0.60 | - |
| " | IV.2f ₀ | NMP | 4h | 2h | 125 | 0.35 | - |
| " | IV.2f ₁ | NMP | 5h | 2h | 50 | 0.25 | - |
| " | IV.2f ₁ | NMP | 5h | 2h | 50 | 0.52 | - |
| " | IV.2f ₀ | NMP | 4h | 2h | 110 | 0.59 | - |

a. Brittle films were obtained.

b. Varying experimental conditions did not help to obtain good film

c. DAB is used as tetraamine

d. Adding time of dialdehyde

e. Reaction time

In some cases precipitation from solution took place when an excess amount of dialdehyde was used. The precipitated polymer was insoluble in any media.

TABLE-15-PBI SYNTHESIES WITH NDS-1,5, AND DABMETHOD: IV.2f₀, IV.2f₁

| COMPOUND | METHOD | SOLVENT | REACTION CONDITIONS ^e | | | η_{inh}^b | FILM ^{a,b} |
|----------|--------------------|---------|----------------------------------|-------------------|-----|----------------|---------------------|
| | | | Time ^r | Time ^d | °C | | |
| NDS-1,5 | IV.2f ₀ | NMP | 20h | 2h | 170 | 0.42 | - |
| " | " | DMSO | 20h | 2h | 110 | 0.59 | - |
| " | IV.2f ₁ | DMF | 20h | 2h | 50 | 0.49 | - |
| " | IV.2f ₀ | DMSO | 10h | 2h | 110 | 0.58 | - |
| " | " | NMP | 10h | 2h | 170 | 0.62 | - |
| " | IV.2f ₁ | DMF | 10h | 2h | 50 | 0.42 | - |
| " | IV.2f ₀ | DMSO | 16h | 2h | 110 | 0.39 | - |
| " | " | DMF | 16h | 2h | 110 | 0.47 | - |
| " | " | NMP | 16h | 2h | 110 | 0.62 | - |
| " | IV.2f ₁ | DMSO | 5h | 2h | 50 | 0.52 | - |
| " | " | DMF | 5h | 2h | 50 | 0.58 | - |
| " | " | NMP | 5h | 2h | 50 | 0.42 | - |
| " | " | DMSO | 12h | 2h | 50 | 0.58 | - |
| " | " | DMF | 12h | 2h | 50 | 0.40 | - |
| " | " | NMP | 12h | 2h | 50 | 0.37 | - |

a. Films were yellow in color but brittle

b. Inherent viscosities were measured in DMSO 5 % at 19 °C

c. Soluble polymers were obtained

e. Extra care was taken to exclude wetness from reaction environment.

d. Adding time; r. Reaction time

III.2.d. SINGLE STEP DIESTER POLYMERIZATION IN SOLUTION

A. High Temperature

Recognizing the shortcomings of the melt polycondensation approach, many research groups have directed their attention to the task of finding prepolymer generating procedures. Numerous communications describe the use of high-temperature solution polymerization techniques. Poly(phosphoric acid), (PPA), was introduced in 1964 into PBI chemistry by Iwakura¹¹. Many syntheses employing the poly(phosphoric acid) solution technique have been reported from various sources¹². PPA was always used with diacids to prepare PBI's. Other solvents used in high temperature solution polymerization, which use the same monomers as those employed in the melt polycondensation process, include;

a. N,N-dimethyl acetamide

b. N,N-dimethyl sulfoxide

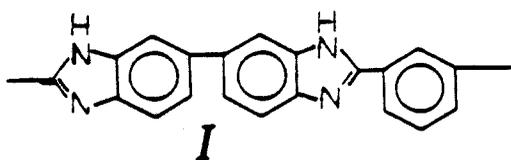
c. Sulfolane

d. Diphenyl sulfone

e. N,N-dimethyl aniline

f. N,N-methyl pyrrolidone

Aromatic polybenzimidazoles have been prepared by reaction of the corresponding tetraamine and diester in refluxing diphenyl sulfone or sulfolane. These solvents are reported to give moderate viscosities and an absence of crosslinking which make this an attractive method for preparing polybenzimidazoles³⁷. The preparation of poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) (1)¹⁴ by the reaction of 3,3'-diaminobenzidine (DAB), diphenylisophthalate (ISO) and



and diphenylterephthalate (TERE) in sulfolane with varying periods of time has been reported to give yields up to moderate level and moderate viscosities ($\eta_{inh}=0.69$ dl/g). In our laboratory, it gave $\eta_{inh} = 0.62$ dl/g for ISO case. The extent of reaction appeared to be time-dependent; but more runs are necessary to determine the optimum time for obtaining a maximum viscosity.

Attempts to extend this procedure to the reaction between DAB and TERE yielded polymerization, but the resulting polymer poly(2,2'--(p-phenylene)-5,5'-bibenzimidazole) came out of solution as a sticky gel which stuck to the walls of the reaction flask resulting in insoluble polymer.

TABLE-16- ONE-STEP POLYBENZIMIDAZOLE SYNTHESIS IN SULFOLANE

| MONOMERS | METHOD | TIME (h) | TEMP. (°C) | η_{INH} (dl/g) |
|------------|--------|----------|------------|---------------------|
| DAB + ISO | IV.2a | 72 | 270 | 0.62 ^a |
| DAB + TERE | IV.2a | 72 | 270 | .b |
| DAB + ISO | IV.2a | 48 | 270 | 0.24 ^a |
| DAB + TERE | IV.2a | 48 | 270 | .b |

a. Inherent viscosities were measured at 5 DMSO at 19 °C

b. Insoluble polymer

Another solvent seemed to offer better promise for the synthesis of poly(2,2'-(p-phenylene)-5,5'-bibenzimidazole). In fact diphenylsulfone was found to be more efficient than the sulfolane. The reaction between DAB and TERE by refluxing in phenyl sulfone gave a yellow solid which was completely soluble in sulfuric acid and N,N-methyl acetamide (DMAc), and had an inherent viscosity of 0.88 dl/g. The result is probably due to the high temperature (370°C) reaction conditions and better solubilizing ability of diphenyl sulfone over sulfolane.

TABLE-17- ONE-STEP SOLUTION POLYCONDENSATION OF DIESTERS (METHOD IV.2)

| COMPOUND | SOLVENT | REACTION CONDITIONS | | η_{inh} dl/g | FILM ^a |
|------------|----------------|---------------------|-----|----------------------|-------------------|
| | | Time | °C | | |
| DAB + TERE | Sulfolane | 72h | 270 | 0.62 ^b | - |
| DAB + TERE | Phenyl sulfone | 5h | 370 | 0.88 | - |
| DAB + ISO | Phenyl sulfone | 5h | 370 | 0.61 | - |
| DAB + TERE | Phenyl sulfone | 6h | 380 | 0.80 | - |
| DAB + ISO | Phenylsulfone | 6h | 400 | - | - |
| DAB + ISO | Phenylsulfone | 5h | 280 | 0.80 | - |

a. Films were cast by solving the resulting polymer if soluble (0.5%)

b. Inherent viscosities were measured in DMSO at 19 °C

B. PBI SYNTHESIS WITH BISORTHOESTERS

Polybenzimidazoles prepared by using aromatic bisorthoesters and 3,3'-diaminobenzidine gave viscosities near 0.70 dl/g in DMSO at 19°C. Films obtained were flexible, but not foldable.

TABLE-18- PBI SYNTHESIS WITH BISORTHOESTERS , AND DAB

METHOD: IV.2e.

| COMPOUND | SOLVENT | REACTION CONDITIONS | | η_{inh} dl/g | FILM ^{a,b} |
|------------|---------------|---------------------|-----|----------------------|---------------------|
| | | Time | °C | | |
| DAB + HMOT | DMSO/Pyridine | 5min | 100 | 0.50 | + |
| DAB + HMOI | DMSO/Pyridine | 5min | 100 | 0.61 | + |
| DAB + HMOI | " | 10h | 110 | 0.65 | + |
| DAB + HMOT | " | 10h | 110 | 0.70 | + |
| DAB + HMOI | " | 10h | 110 | 0.60 | + |
| DAB + HPOT | " | 10h | 110 | 0.40 | - |
| DAB + HPOI | " | 10h | 110 | 0.04 | - |

a. + indicates film was obtained flexible, but not foldable

b. Color of films were yellow-brown (5% solution)

IV. EXPERIMENTALIV.1.a. SYNTHESES OF MONOMERSMATERIALS:

Benzene was allowed to stand overnight with CaCl_2 . It was decanted, fractionally distilled from freshly cut, clean dry sodium, and stored over activated 3A° molecular sieves.

Methanol was placed over CaH_2 , as needed, the alcohol was distilled (bp 65°C) directly into the flask where it was to be used.

Molecular sieves were newly activated by heating to 300°C under a stream of dry nitrogen for 6h. Once used they were reactivated by heating at 300°C/0.01 mm Hg for 12h.

n-propanol was dried with anhydrous K_2CO_3 , filtered and distilled from CaH_2 (bp 97 °C).

$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro-m-xylene (HCMX) (Tokyo Kasei Inc.) was recrystallized from methanol and dried in a dessiccator over CaCl_2 in vacuo (mp 39-40 °C).

$\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro-p-xylene (HCPX) (Aldrich) was recrystallized from methanol and dried in a dessiccator over CaCl_2 . (mp 109-110 °C)

Preparation of Hexamethyl-o-terephthalate (HMOT)³⁸

To a dry 3-L three-necked flask equipped with a reflux condenser protected by a CaCl_2 drying tube, was added dry methanol (1200 mL) and freshly cut, clean, dry sodium (15g, 0.65 mol). The solution was chilled to 5 °C in an ice bath and HCPX (31.3g, 0.10 mol) was added. The solution was allowed to reflux for 7 days, cooled, filtered in order to remove NaCl. The solvent was removed with a rotary evaporator at 15 mm Hg leaving a white solid which was mixed with water (400 mL)

and the HMOT was extracted with chloroform (5X50 mL). The combined extracts were washed with saturated NaHCO_3 solution (100 mL), and dried over anhydrous K_2CO_3 . Evaporation of the solvent gave 22.7 g of crude HMOT. This HMOT was recrystallized from petroleum ether (bp 60-70 °C), dried in vacuo over CaCl_2 , which yielded pure HMOT as white crystals, mp 123-125°C (lit.³⁰ mp 124.5-126°C) in an overall yield of 54%. The IR and NMR spectra were consistent with the compound; ^1H NMR (CDCl_3) δ 7.58 (4H, s), 2.96 (18H, s); IR (KBr), (no 1700-1750 band), 1100 cm^{-1} .

Preparation of Hexamethyl-ortho isophthalate (HMOI)

To a dry 2L three-necked flask was fitted with a reflux condenser protected by a CaCl_2 drying tube was, added dry methanol (1200 mL) distilled directly into the flask and freshly cut, dry clean sodium (15g 0.65 mol). The flask was then cooled in an ice bath to 5°C and HCMX (31.3g, 0.1 mol) added. The solution was allowed to reflux for 7 days; it was then cooled, and filtered to remove NaCl. The solvent was removed on a rotary evaporator leaving a white solid which was then mixed with water (400 mL); the HMOI was extracted with chloroform (5X50 mL). The combined chloroform extracts were washed with NaHCO_3 and the solution was dried over anhydrous K_2CO_3 . The solvent was removed. The crude sample was recrystallized from petroleum ether and dried which gave 16.5 g of pure HMOI, mp 98-100 °C. (lit. mp 95.4-96.6°C); IR (KBr), 1100 cm^{-1} (sharp), (no 1700--1750 cm^{-1} band); ^1H NMR (CDCl_3) δ 7.2 (4H, s), 3.14 (18H, s).

Preparation of Hexa-n-propyl-orthoterephthalate

To a dry 1L three-necked flask fitted with a nitrogen inlet and

reflux condenser connected to a paraffin oil bubbler, was added dry benzene (400 mL), dry n-propanol (230 mL), activated 3A° molecular sieves (210 g), and HMOT (28.6 g). The suspension was allowed to reflux under nitrogen for a day; the suspension was cooled to room temperature, filtered to remove solid. The solvent was removed on a rotary evaporator, leaving a very viscous liquid which was then fractionally distilled through a 45 cm spinning band column to give 16 g (52 %) of pure HPOT, bp 121-123°C (lit 124-126°C).

^1H NMR (CDCl_3) δ 7.65 (4H, s), 3.23 (12H, t), 1.65 (12H, m), 0.92 (18H, t). IR (KBr), (no 1750-1700 band) 1050 cm^{-1} .

Preparation of Hexa-n-propyl-ortho-isophthalate

Above procedures was repeated for HMOI. The yield was 10 g (20 %) bp 119-121 °C.(lit. bp 118-120°C); ^1H NMR δ 7.5 (4H, m), 3,30 (12H, t), 1.60 (12H, m), 1.0 (18H, t). IR (KBr), no 1750-1700 band, 1080 cm^{-1} .

IV.1.b. SYNTHESES OF DISULFONYL CHLORIDES

Preparation of Napthalene-1,5-disulfonyl chloride(NDS-1,5 SC)³⁶

In a 1L three-necked round bottomed flask was placed a mixture of 204.3g (1 mol) of disodium salt of the napthalene-1,5-disulfonic acid di sodium salt (Aldrich) which has been dried at 140°C for 56h prior to use. The flask was provided with an air condenser which has fitted at the top with a CaCl_2 drying tube. It was then placed in an oil bath at 110°C, the mixture was kept at that temperature for 2h; the condenser was removed for brief intervals during the heating period, because an appreciable pressure develops in the flask care must be taken in removing the stopper. At the end of the heating period, the product was a thick paste. The flask and contents were

hooked up to a vacuum pump protected with two traps, and was heated heated under nitrogen to remove unreacted phosphorus pentachloride, and phosphorus oxychloride. The dry cake was pulverized in a mortar and transferred into 4L beaker. To this was added 750 mL of distilled water and 2L chloroform. The mixture was placed in a bath, heated to boiling, and stirred vigorously until nearly all solid dissolved. The layers separated hot by means of a separatory funnel. The chloroform solution was again heated to boiling and filtered. The solution was cooled in an ice bath and the crystallized product was collected on a filter, and then dried in vacuo; This gave 80g of NDS-1,5-SC; mp 178-180°C; ^1H NMR (DMSO/ d_6) δ 9.25 (2H, d), 8.40 (2H, d), 7.6 (2H, d); IR (KBr) 3250, 2700, 1150, 800, 600 cm^{-1} ;

Synthesis of 2,6-naphthalene disulfonyl chloride (NDS-2,6 SC)

The method described previously was applied for this synthesis. Two layers were formed during the reaction which were separated; mp 217-220°C; ^1H NMR (DMSO/ d_6) 7.95-6.80 (6H, m); IR (KBr), 3275, 2750, 1150 cm^{-1} ;

Synthesis of Benzene-1,3-disulfonyl chloride³⁶

In a three-necked round bottomed flask was placed 1 mol of 1,3-benzene disulfonic acid disodium salt, 0.3 mol of phosphorus oxychloride, and 0.7 mol of phosphorus pentachloride. The apparatus was equipped with a mechanical stirrer, air condenser fitted with a CaCl_2 drying tube at the top, and a bubbler. The mixture was heated to 110°C and was allowed to react overnight at 110°C in an oil bath. Unreacted PCl_5 and POCl_3 were removed from the mixture by using a vacuum pump equipped with two traps.

The residual solid was dissolved in benzene, washed with 5% sodium bicarbonate solution, dried over $MgSO_4$ and drierite; precipitated in hexane; mp 55-58°C; 1H NMR (DMSO/ d_6) δ 8.60 (1H, d), 8.35 (1H, q), 7.90 (1H, d);

Preparation of sulfonic acid ester-dialdehydes⁴⁵

Synthesis of Napthalene-1,5-bis-(4-formyl-phenyl-(1)-sulfonic acid ester. (NDS-1,5-DA)

In a 100 mL round bottomed flask was placed 3.25g of napthalene 1,5-disulfonyl chloride, and 2.42g of 4-hydroxy benzaldehyde. The flask was fitted with a thermometer and nitrogen inlet. The mixture was kept at 0°C for 3h. The mixture was then transferred into sulfuric acid (5N at -5°C), and precipitate was collected, filtered, and dried in vacuo at 50°C which gave 4.2g of NDS-1,5-DA, mp 132-134°C.

The reaction described above was repeated in 50 ml pyridine which gave 4.4g of NDS-1,5-DA. mp 133-135°C; IR (KBr), 3300, 1690, 1600, 1500, 1390, 1200, 1150, 880, 600 cm^{-1} ; 1H NMR (DMSO/ d_6) δ 10.0 (2H, s), 8.60 (2H, s), 8.25 (2H, d), 7.90 (4H, q), 6.90 (4H, d); Anal. Calcd for $C_{24}H_{16}S_2O_8$: C, 58.06; H, 3.25. Found: C, 57.96; H, 3.39.

Synthesis of napthalene-2,6-bis-(4-formyl-phenyl-(1)-sulfonic acid ester) (NDS-2,6-DA)

In a round bottomed flask was placed 3.25g of Napthalene 2,6-disulfonyl chloride, 2.42g 4-hydroxy benzaldehyde, and 100 mL distilled water. The mixture was heated in a water bath for 3h; during the course of the reaction Na_2CO_3 was added at a rate of 0.01 mol every 30 min. The reaction mixture was filtered hot,

washed with water and benzene, and dried over CaCl_2 in a desiccator. Removal of solvent gave 6.3 g of product. mp 180-182°C. The crude sample was recrystallized from methanol mp 157-159°C; The crude sample was also crystalized from dioxane-hexane; mp 159-161°C.

IR (KBr), 3300, 1700, 1600, 1500, 1390, 1220, 1180, 900 cm^{-1} ; ^1H NMR δ 13.5 (2H, s), 8.25 (6H, s), 7.90 (6H, q); ^{13}C NMR δ = 191, 152, 146, 135, 134, 132, 130, 127, 124, 122; Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{S}_2\text{O}_8$: C, 58.06; H, 3.25. Found: C, 52.08; H, 3.39.

Synthesis of Benzene-1,3-bis-(4-formyl-phenyl-(1)-sulfonic acid ester) (BDS-1,3-DA)

A 2.75g portion of BDS-1,3-Sc, and 2.42g of 4-hydroxy benzaldehyde, and 80 mL of distilled water were mixed in a one neck flask equipped with a Claisen head and a condenser. During the reaction, 0.01 mol portions of Na_2CO_3 was added every 30 min. The reaction was very fast and white precipitate formed immediately. The solid was collected by filtration, washed with hot water, and Na_2CO_3 solution, and then, dried in vacuo which gave 3.8 g of BDS-1,3-DA; mp 125-127°C; IR (KBr) 3300, 2950, 2850, 1700, 1590, 1490, 1420, 1390, 1300, 1200, 1020, 875 cm^{-1} ; ^1H NMR (DMSO/ d_6) δ 10.0 (2H, s), 8.50 (1H, q), 8.40 (1H, d), 8.25 (2H, d), 7.95 (4H, d), 7.25 (4H, d); Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{S}_2\text{O}_8$: C, 53.81; H, 3.16. Found: C, 53.18; H, 3.25.

IV.2. POLYMERIZATION REACTIONS

IV.2.a. One-stage solution polymerization of diesters^{37,46}

Reaction of ISO with DAB in sulfolane

In a three-necked round bottom flask equipped with a Dean-Stark condenser, was placed 79.30 mL of sulfolane, 2.67 g of ISO, 3.97 g of DAB, and 25 ml of toluene. The mixture was deaerated with nitrogen for 30 min; and then refluxed under nitrogen for 72 h. Toluene was driven out from the reaction as well as phenol and water formed during the reaction. The reaction mixture was allowed to cool to room temperature, and was poured, with stirring, into a mixture of methanol (500 mL), and acetone (250 mL). The precipitate was stirred overnight, filtered, washed with acetone, and dried for 24 h, in vacuo at 150 °C to give the yellow polymer. A 0.2% solution in sulfuric acid at 19 °C gave η_{inh} of 0.62 dl/g.

The same reaction was repeated, with a reaction time of 48h. which gave a 0.24 inherent viscosity in sulfuric acid at 19°C.

Reaction of TERE with DAB in sulfolane

A mixture of sulfolane (100 mL), TERE (0.02 mol), and DAB (0.02 mol) was deaerated with nitrogen for 20 min; then stirred and refluxed under nitrogen for 72 h. The reaction mixture changed from a suspension to an orange solution. At the end of the reaction insoluble dark-brown polymer was obtained which was insoluble in concentrated sulfuric acid and formic acid.

Reaction of TERE with DAB in phenyl sulfone

A mixture of phenyl sulfone (100g), TERE (0.0125 mol), DAB (0.0125 mol), and 50 mL of toluene was mixed in a three-necked flask

equipped with a Dean-Stark trap, and nitrogen inlet. The mixture was deaerated with nitrogen and stirred mechanically with heating. The reaction mixture was heated to 270 °C and the temperature was gradually raised to 370 °C. Toluene was distilled off at 170°C. The mixture was allowed to react overnight, cooled and poured into methanol/acetone solution, the yellow precipitate was collected on a filter paper. The crude polymer was extracted continuously for 24h with ethanol, and for 24h with benzene. Drying in vacuo at 125 °C gave a polymer with 0.81 inherent viscosity in concentrated sulfuric acid at 19 °C. The polymer was insoluble in other solvents such as DMSO, NMP, and DMF.

Reaction of ISO with DAB in phenyl sulfone

A mixture of ISO (0.025 mol), DAB (0.025 mol), phenyl sulfone (75g), and 75 mL toluene was stirred and deaerated with nitrogen for 20-30 min. It was heated by increasing the temperature gradually to 370 °C . During this time phenol, water, and toluene were distilled off; and a tan suspension formed. The reaction mixture was cooled to room temperature and poured into 500 mL acetone, The yellow precipitate was collected and, dried in vacuo. The crude polymer was extracted as explained previously. The resulting polymer had an inherent viscosity in sulfuric acid at 19 °C of 0.67 dl/g. The resulting polymer was soluble only in sulfuric acid therefore no film was obtained.

IV.2.b. MELT POLYCONDENSATION OF DIESTERS^{10,13,47}

DAB : was recrystallized from methanol and dried over CaCl₂.

ISO : was recrystallized from methanol and dried over CaCl₂.

TERE : was recrystallized from methanol and dried over CaCl_2 .

GENERAL PROCEDURE^{33,48}

Equimolar amounts of the monomer components were placed in a round bottom flask having a capacity of about ten times the volume of the reactants. The flask was connected with tubing to a cooled receiver. The apparatus was purged with pure nitrogen by repeated evacuation and refilling. The flask was then placed in a sand bath preheated to 280 °C. When heated the reaction mixture formed a melt which was then heated to temperature necessary for the reaction.

The evolution of phenol and water indicated that the reaction had commenced. After 20 to 40 min when the melt had changed to a more or less solid mass, the flask was carefully put under high vacuum with two traps, and heating was continued for 30 min at the particular temperature. In many cases a sort of glassy foam was produced during this treatment. The apparatus was then filled with nitrogen and cooled. The materials were pulverized in a glove bag under N_2 and reheated for several hours under high vacuum at temperatures gradually rising to 400 °C.

Preparation of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

A mixture of 4.28 g (0.02 mol) of DAB, and 0.02 mole of ISO⁴⁷ was melted at 220 °C and heating was continued for 30 min. Evacuation to 0.6 mm Hg pressure produced a glassy foam and removed most of the liberated phenol and water. After 30 min the material was pulverized under nitrogen and placed in a round bottomed dry flask, reheated under high vacuum for 9 h while the temperature was raised from 280 to 400°C. (Results are shown in Table 4 and 5).

IV.2.c. TWO-STAGE LOW TEMPERATURE SOLUTION POLYMERIZATION OF

DIALDEHYDESMaterials:

DMAC (N,N-dimethylacetamide), used as it is obtained

DAB was recrystallized from boiling methanol dried over CaCl₂.

Nitrogen was deoxygenated by passing it through a column (silica gel/ sode lime/ P₂O₅) at 150 °C.

IDA was recrystallized from ethanol (mp 91-92°C)

TDA was recrystallized from ethanol (mp 117-118 °C)

NDS-2,6 was crystalized from DMSO

NDS-1,5 " "

BDS-1,3 " "

BDC-1,4 " "

NDC-2,6 " "

GENERAL POLYMERIZATION REACTION^{22,49,50}

FIRST STEP : A dry, three-necked flask equipped with a dropping funnel and nitrogen inlet, was purged with nitrogen for an hour. A solution of 2.5 mmol of DAB in 5 mL of nitrogen saturated DMAC or other aprotic solvents(DMF, DMSO or NMP) was added. To the magnetically stirred solution was added over a 6h period in a steady stream of nitrogen (gas inlet reaching below surface of the liquid) a nitrogen saturated solution of 2.5mmol of dialdehyde in 25 mL DMAC. Throughout the addition, the temperature of the reaction mixture was kept at -15°C to -20°C. Stirring under nitrogen was continued for an additional 15h (this time varies see tables), as the temperature was allowed to to rise to room temperature. The product was precipitated by adding 50 mL of methanol, filtered, and washed with methanol/water many times. The solid was dried in vacuum oven at 100°C for 5h.

The same basic procedures was applied for all dialdehydes listed. Depending upon the addition time and other less predictable factors, the polymerization process gave different viscosities.

STEP-2- A three-necked flask equipped with a gas inlet, reaching nearly to the bottom of the vessel, was charged with a solution or suspension of poly(azomethines) (1.5 mmol, based on polymer repeat unit), and 10 mL dry DMAc containing anhydrous Iron(III)-chloride (0.015 mmol). Dry air (10L/h) was bubbled into the liquid for 8 to 88h¹⁴, while the temperature of the reaction was maintained at 60 °C. The solution was poured into water with vigorous shaking. The precipitated polybenzimidazole collected by filtration, was washed with water/methanol(50:50), and dried in vacuo at 180 °C.

this second step mainly gave dark, insoluble polymers.

IV.2.d. Modified two-stage solution polycondensation

FIRST STEP : A dry, three-necked flask equipped with a dropping funnel and nitrogen inlet, was purged with nitrogen for an hour. A solution of 2.5 mmol of DAB in 5 mL of nitrogen saturated DMAc or other aprotic solvents(DMF, DMSO or NMP) was added. To the magnetically stirred solution was added over a 6h period in a steady stream of nitrogen (gas inlet reaching below surface of the liquid) a nitrogen saturated solution of 2.5mmol of dialdehyde in 25 mL DMAc. Throughout the addition, the temperature of the reaction mixture was kept at -15°C to -20°C. Stirring under nitrogen was continued for an additional 15h (this time varies see tables), as the temperature was allowed to to rise to room temperature.

SECOND STEP: Instead of going through the tedious isolation procedure of step 1 of 2c above, anhydrous FeCl_3 was added to the original solution; 10 of mL solution containing 20 mg FeCl_3 was added to the solution after dialdehyde addition was completed. Then the reaction was carried out for 16h (time varies see tables) using the procedure described as a first step. The reaction temperature was raised to 50 to 60 °C and kept there at least 4h. The resulting polymer had higher viscosities than the viscosities of the original procedure.

IV.2.e. POLYMER SYNTHESIS WITH BISORTHOESTERS AND DAB³⁸

HMOT, HMOI, HPOT, HPOI were prepared and purified according to the procedures described previously.

DMSO (Dimethyl sulfoxide) was fractionally distilled from CaH_2 at reduced pressure, and collected over activated 3A° molecular sieves. DMAC (N,N-dimethyl acetamide) was used as it is obtained (gold label) DMF (N,N dimethyl formamide) was dried over MgSO_4 , filtered, fractionally distilled at reduced pressure and stored over 4A° molecular sieves.

PYRIDINE was distilled from BaO and stored over BaO.

DAB was recrystallized from methanol before use

SPECIAL DRYING PROCEDURES

Because of the ease of the hydrolysis of orthoesters to normal esters, special precautions have to be taken to remove any possible sources of moisture. Several methods were used to dry glassware, including flaming under a stream of nitrogen, but it was found to be most convenient to dry all glassware for at least four hours at 150°C, assemble hot, and allow to cool filled with purified nitrogen.

Solvents, used for polymerizations were transferred from their storage containers under nitrogen via syringe. When nitrogen tanks were changed, the line was purged with nitrogen from the tank before use.

PBI synthesis with DAB and HMOT³⁸

To a dry 50 ml three-necked flask was added HMOT (0.67g 2.37 mmole), DAB (0.5g 2.26 mmol), dry DMSO (30 mL), and dry pyridine (3ml). The flask was equipped with a mechanical stirrer, nitrogen capillary inlet tube, and exit tube connected to a paraffin bubbler. The solution was stirred under a slow stream of nitrogen for 15 min, then placed in an oil bath at 100°C, and heated with stirring under nitrogen for 12h. The solution was dark-brown in color. The polymer was precipitated by adding acetone with stirring, collected by filtration, and extracted for 12h with acetone in a Soxhlet, dried over P₂O₅ at 100°C. Films were cast from the reaction mixture and gave golden brown flexible films. η_{inh} was 0.62-0.7 dl/d in DMSO at 19 °C.

PBI synthesis with DAB and HPOT

To a 6 in. test tube was added DAB (0.06g 0.28 mmol), HPOT (0.28 mmole), and dry DMSO (3.5 mL). The tube was tightly stoppered with a rubber stopper and placed in an oil bath at 100°C. In 5 min the contents of the tube had completely solidified. The tube was then cooled to room temperature, polymer was collected by filtration washed with acetone and extracted with acetone for 12h in a Soxhlet apparatus. The η_{inh} was 0.25 dl/g in DMSO at 19°C.

PBI synthesis with DAB and HMOI

To a dry 50 ml three-necked flask was added HMOI (1.65 mmol), DAB (0.35g 1.65 mmol), dry DMSO (25 mL), and dry pyridine (2.5 mL). The

flask fitted with a mechanical stirrer, nitrogen capillary inlet tube, and nitrogen exit connected to an oil bubbler. The solution was stirred under nitrogen for 15 min, then placed in an oil bath preheated to 100°C, and heated with stirring under nitrogen for 12h. The solution was cooled to room temperature and the polymer was precipitated by adding the solution dropwise with stirring to acetone. After extraction the η_{inh} was 0.4-0.6 dl/g in DMSO at 19°C.

PBI synthesis with DAB and HPOT

HPOT (0.75g 1.65 mmole), DAB (0.35g 1.65 mmole), dry DMSO, (25 ml), and dry pyridine (2.5 mL) were mixed and heated to 100°C for 12h, and worked up before the η_{inh} was 0.40 dl/g in DMSO at 19°C.

PBI synthesis with DAB and HPOI

HPOI (0.75g 1.65 mmole), DAB (0.35g 1.65 mmole), dry DMSO (25 ml), and dry pyridine (2.5 ml) were mixed and heated to 100°C for 12h, and the worked up before the η_{inh} was 0.04 dl/g in DMSO at 19°C.

IV.2.f. ONE STEP POLYCONDENSATION OF DIALDEHYDES²¹

2.f₀. High temperature

In a 100-mL three-necked flask equipped with a dropping funnel, thermometer, water condenser, and capillary inlet was placed DAB (9.875 mmol) and 50 mL DMAc. The amine solution was heated to 105-110 °C or higher depending on monomers and solvent used, and a rapid stream of air passed through the amine solution while 9.875 mmol of dialdehyde dissolved in 10 ml DMAc was added slowly dropwise over 2-4h to the amine solution. The reaction mixture was heated at

105-110°C for 2 to 4 h after addition was completed, yielding a viscous yellow-brown solution. Films cast from this solution was flexible, and clear. The η_{inh} ranged 0.4-0.7 in DMSO at 19°C.

A sample of the solution was cast as a film at 135 °C.

2.f₁. Low-temperature

Into a 50-mL three-necked flask equipped with a dropping funnel and air capillary inlet were placed DAB (4.991 mmole), and 11 mL DMAc. The amine solution was warmed to 50 °C, and a rapid stream of air passed through the solution while dialdehyde (4.991 mmole) in 7 mL DMAc was added dropwise to the amine solution (2-4h). Within 30 min the mixture formed a red-brown homogeneous solution which become increasingly viscous as the reaction proceeds for a period of five hours. As the reaction proceeds, the color of the films cast from the reaction solution vary from red to brownish yellow; the shade of the color indicates the extent of the reaction. A red color indicates low degree of cyclization whereas yellow color indicate high degree of cyclization.^{21,22} Films cast from the reaction solution was clear, yellowish to brown in color and η_{inh} ranged from 0.3 to 0.6 dl/g in DMSO at 19 °C.

2.f₂. Modification of the polymer with benzaldehyde²¹

Into a 50-mL three-necked flask equipped with a dropping funnel and a air capillary inlet were placed 4.170 mmol of DAB in 9 mL DMAc. The solution is heated to 50 °C, and a mixture of dialdehyde 3.962 mmol and benzaldehyde 0.42 mmol in 7 mL DMAc was added to the amine solution dropwise in a period of 2-4h. Films cast from this solution was flexible, clear, and the solution had η_{inh} of 0.35 to .45 dl/g in DMSO at 19°C.

IV.3. POLYMER FILMS

Polymer films were cast either from the reaction mixture or by dissolving the prepared polymer in a proper solvent (5% to 10%). As soon as polymer films cast (5% or 10%) on clean glass plates, plates were placed in an oven and heated to 30-40°C for 30-40 min, then heated gradually by raising the temperature to 120-130 °C in a vacuum oven under high vacuum. Plates were allowed to stay in an oven for an hour or so. Finally the films were taken out and placed in boiling water which allowed the films to peel off. Peeled films were washed with acetone/water and dried in a vacuum oven at 120-130 °C for 2h under high vacuum.

In some cases films were cast at the first stage of the reaction, therefore it was found that heating these films at 280-300°C helps to improve the quality of film evidenced by flexibility and the color (changing red to yellow-brown) of films.

IV.4. VISCOSITY MEASUREMENTS

Procedure:

1. Clean the viscometer using acetone/ CH_2Cl_2 as solvents and dry by passing clean dry filtered air through the instrument to remove the final traces of solvents. Periodically, traces of organic deposits should be removed with chromic acid.
2. If there is a possibility of lint, dust, or other solid material in the liquid sample, filter the sample through a fritted glass filter or fine mesh screen.

3. Charge the viscometer into the holder, and insert it into the constant temperature bath. Vertically align the viscometer in the bath if a self aligning holder has not been used.
4. Allow approximately 20 minutes for the sample to come to bath temperature.
5. Measure the efflux time between two lines. (t/t_0)
6. Calculate the viscosity of the sample by multiplying the efflux time by the viscometer constant.
7. Without recharging the viscometer, make check determination by repeating steps 5 to 8.
8. Calibration factor for 2B Ubbelohde viscometer is 0.5615.

V. VISCOSITY MOLECULAR WEIGHT CALCULATION

The number average molecular weight, M_v , where $a = 1.58$; $K = 10^{-6}$

$$\eta = K(M_v)^a \text{ (Mark-Houwink equation)}^{25,5}$$

is related to the weight average molecular weight, M_w , by

$$M_v/M_w = 0.93 \text{ for most probable distribution}^{51}.$$

TABLE-19-VISCOSITY AND MOLECULAR WEIGHT²⁰

| POLYMER NO | η_{inh} | $M_w \times 10^{-4}$ | $M_v \times 10^{-4}$ |
|------------|--------------|----------------------|----------------------|
| 1 | 3.2 | 22.7 | 21.1 |
| 2 | 2.8 | 20.8 | 19.3 |
| 3 | 2.0 | 16.8 | 15.6 |
| 4 | 1.1 | 11.5 | 10.6 |
| 5 | 0.9 | 10.1 | 9.4 |
| 6 | 0.7 | 8.6 | 8.0 |

Determination of a molecular weight of a polymer is necessary in order to fully understand the polymerization process. Both the weight average molecular weight and the viscosity average molecular weight can be calculated using above equations. These values always yield average values because determination of a and K values for each polymer in a given solvent are necessary. For a typical polybenzimidazole case corrected values should be in the range of 10%, due to the stiffness of a PBI prepared from all aromatic monomers.

DP, degree of polymerization, and p , extent of reaction, were calculated using below equations. ($r = 1$)

$$DP = 1/(1-p) \text{ or } DP = (1+r)/(1+r-2rp) \text{ if } r \neq 1$$

$$DP = M_v \text{ of a polymer} / (MW \text{ of incorporated monomeric unit}/2)$$

FIGURE-10 Dependence of DP on r and p ²

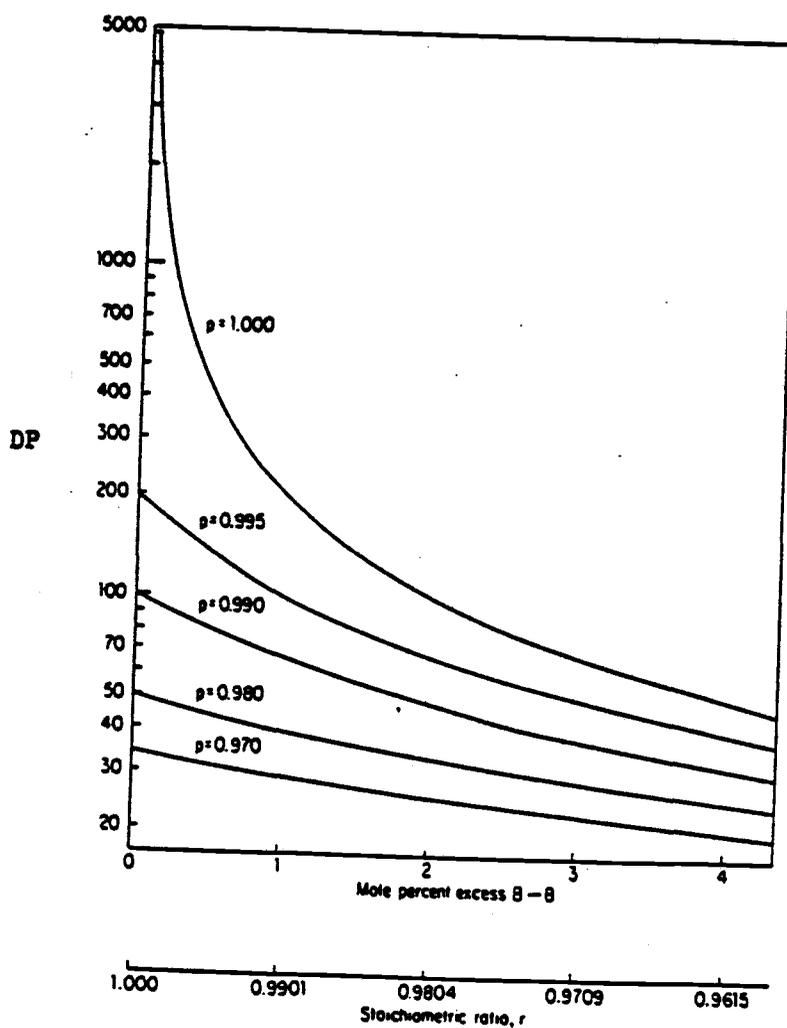


TABLE-20- CALCULATED DP, p, VALUES FOR POLYBENZIMIDAZOLES

| POLYMER | $\eta_{inh}(dl/g)$ | $\bar{M}_v \times 10^{-4}$ | DP | p |
|---------------|--------------------|----------------------------|-----|-------|
| DAB + ISO | 0.62 | 4.29 | 279 | 0.996 |
| DAB + TERE | 0.88 | 5.56 | 361 | 0.997 |
| DAB + TERE | 0.74 | 4.68 | 304 | 0.996 |
| DAB + TDA | 0.35 | 3.75 | 244 | 0.995 |
| DAB + IDA | 0.54 | 4.19 | 272 | 0.996 |
| DAB + NDS-2,6 | 0.69 | 4.36 | 283 | 0.996 |
| DAB + NDS-1,5 | 0.52 | 4.15 | 269 | 0.996 |
| DAB + BDS-1,3 | 0.64 | 4.32 | 281 | 0.996 |

For the synthesis of many polymers by step polymerization, p should be at least 0.98 to obtain DP value of 50.

VI. CONCLUSION

Polybenzimidazole synthesis with DAB and all aromatic sulfonic acid esters offers a potential advantage over conventional polybenzimidazoles formed by direct linking of aromatic rings, in that many monomers of this type can be readily prepared. They will probably not have as much high temperature stability, but they could have improved polymer properties such as solubility and fusibility. Different monomeric units will influence the properties of the PBI polymer. Therefore a series of new polybenzimidazoles with different monomeric units was planned to determine their properties.

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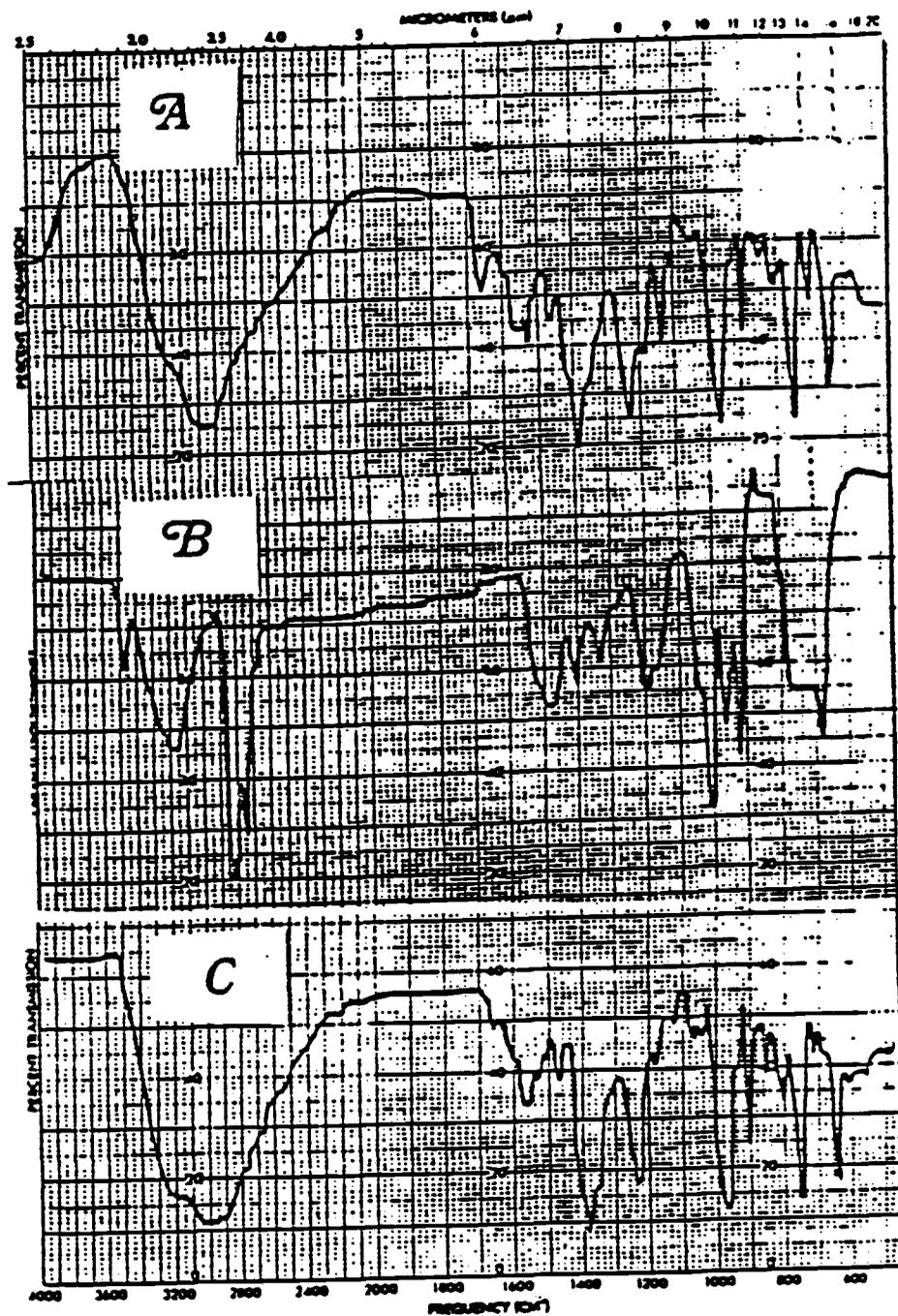
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APPENDIX

APPENDIX

INFRARED PATTERNS OF BENZIMIDAZOLE POLYMERS



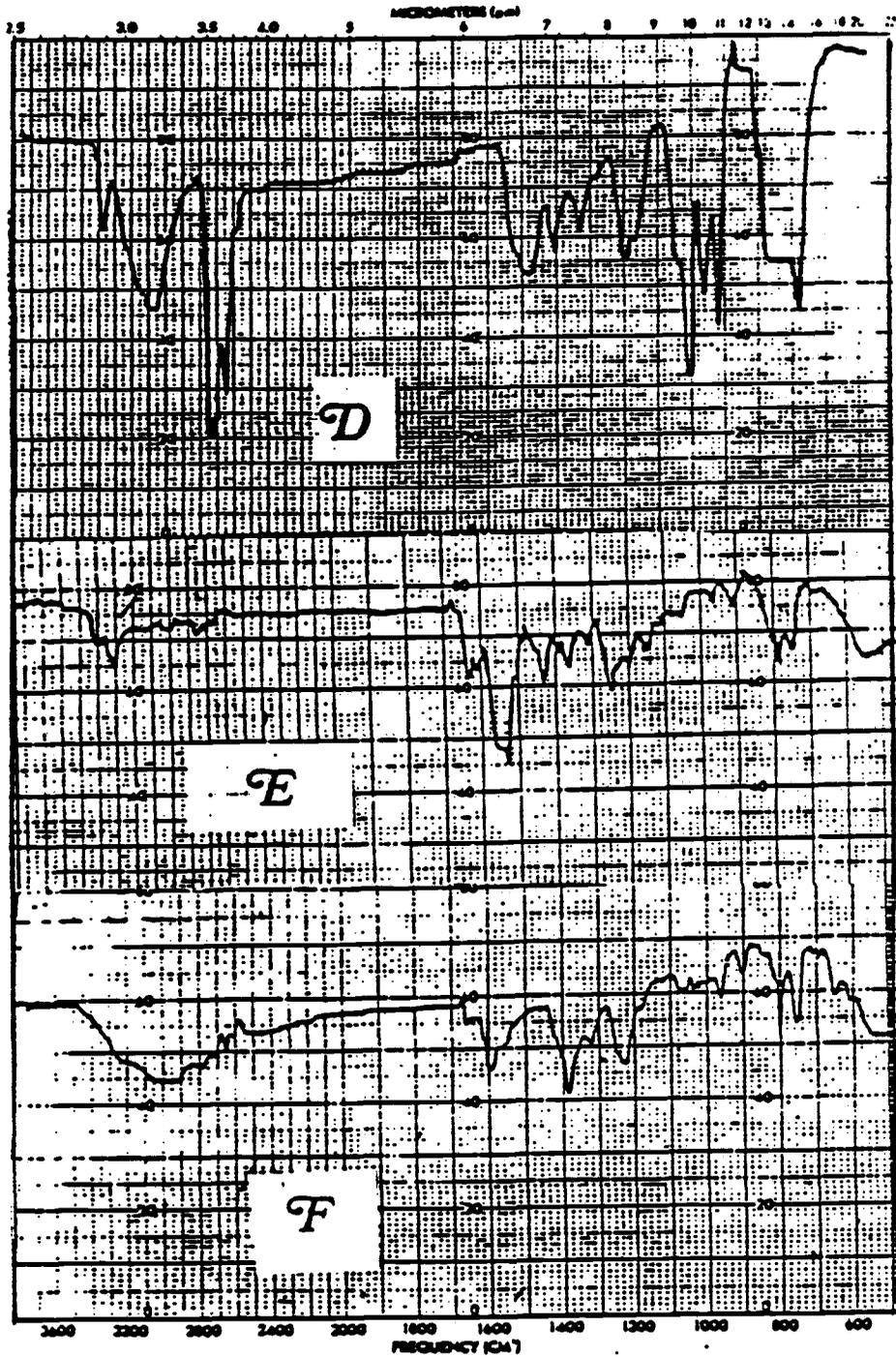


FIGURE-A : IR spectra of a film of poly-2,2'-(p-phenylene)-5,5'--bibenzimidazole heated under nitrogen for 2h at 280°C.

FIGURE-B : IR spectra of a film of poly-2,2'-(m-phenylene)-5,5'--bibenzimidazole heated under nitrogen for 4h at 280°C.

FIGURE-C : IR spectra of a film of poly-2,2'-(p-phenylene)-5,5'--bibenzimidazole heated under nitrogen for 24h at 280°C under vacuum.

FIGURE-D : IR spectra of a film of a poly-2,2'-(m-phenylene)-5,5'--bibenzimidazole heated under nitrogen for 24h at 280°C under vacuum.

FIGURE-D : IR spectra of a KBr disc of a PBI (meta)

FIGURE-E : IR spectra of a KBr disc of a PBI (para).