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The synthesis and characterization of polycarbonates based on 1,1'-dihydroxyethyl-2,2'-biimidazole

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THE SYNTHESIS AND CHARACTERIZATION

OF POLYCARBONATES BASED ON

1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE

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ABSTRACT

The synthesis of polycarbonates formed by the reaction of 1,1'-dihydroxyethyl-2,2'- biimidazole and diphenyl or diethyl carbonates was investigated and the products formed were characterized. The molecular weights of the polymers were dependent on catalyst, ratio of starting materials, nature of carbonate (aromatic or aliphatic) and method of polymerization. Isolated polymers exhibit a linear structure. They have no well-defined melting points (melting pt. range of 280- 330°C) indicating low degree of crystallization, and undergo less than 9% decomposition below 200°C.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

The search for polymers with superior thermal stability
has led to the synthesis of many new polymeric substances
for use as fibers, films, rubbers, adhesives, plastics and
electronic applications. The main stimulus has come from the
need to meet the demands of modern technological advances
and, in particular, the increasingly stringent requirements
for applications in outer space. Thermal stability, in the
most practical sense, means the ability of a material to
maintain the required mechanical properties such as
strength, toughness, or elasticity at a given temperature
[1].

Some of the outstanding achievements in the development
of thermally stable polymers have stemmed from research
directed toward the incorporation of heterocyclic ring
systems into a polymer chain [2]. The discovery of the
unique thermal and oxidative stability of the polyimides,
poly(1,3,4-oxadiazoles), and polybenzimidazoles allied with
the ability to fabricate them into useful forms served to
focus attention on the potential of heterocyclic polymers as
a class.

This work focused on the preparation and
characterization of polycarbonates based on 1,1'-
dihydroxyethyl-2,2'-biimidazole. Commercial aromatic poly-
carbonates are produced predominantly on the basis of
bisphenol A [3]. Bisphenol A is preferable to other

aromatic dihydroxy compounds because of the relative ease with which it is produced from widely available and economical raw materials. A search for new aromatic polycarbonates with properties different and superior to bisphenol A is under way [4]. Also, routes to polycarbonates without phosgene are currently the subject of extensive research.

The two main goals of this work were first to establish the experimental parameters for generation of polycarbonates incorporating 2,2'-biimidazole in the polymeric chain and second to characterize techniques for understanding how variations in properties of polymers are manifested. It was anticipated that by incorporating 2,2'-biimidazole in the polymeric chain, with its aromatic-heterocyclic properties [5], polymers with enhanced thermal properties comparable to poly[2,2-propane-bis(4-phenyl carbonate)] could be prepared.

There are three major steps in the synthesis of the 2,2'-biimidazole-containing polymer. First, 2,2'-biimidazole is synthesized from glyoxal and ammonium hydroxide. Second, 1,1'-dihydroxyethyl-2,2'-biimidazole is synthesized by using ethylene carbonate [6,7] or 2-chloroethanol [8] as hydroxyethylating agents. In the last, aromatic-heterocyclic polycarbonates are synthesized by reacting 1,1'-dihydroxyethyl-2,2'-biimidazole with diethyl carbonate or diphenyl carbonate using: (1) a non-catalyzed reaction to test the self-catalyzing ability of 1,1'-dihydroxyethyl-2,2'biimidazole; (2) a reaction

catalyzed by the base sodium methoxide; (3) a reaction catalyzed by the acid, titanium tetrachloride. All the above reactions are carried out under non-solvent and solvent conditions. These polycarbonates are characterized by using the fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC).

Present research projects in this laboratory involve the syntheses of other 2,2"-biimidazole containing polymers. These include the preparation of polyurethanes, polyepoxides and vinyl polymers. In addition, the transition metal-ion binding ability of 2,2'-biimidazole [9-13] has prompted investigations of metal binding stabilities, polymer complex structure, and the contributions bound metals make to polymer properties. The combination of these properties will make the polymers suitable for many applications. Typical areas of use include electrical applications, adhesives, polymeric chelation, coatings and engineering applications.

II. REVIEW OF LITERATURE

A. STRUCTURE AND PROPERTIES OF 2,2'-BIIMIDAZOLE

Although biimidazole ($C_6H_6N_4$) has been known for many years, its synthesis has never been the object of an extensive investigation. The synthesis used by Debus (shown in equation 1) has been known to give very low yields [5]. The low yield obtained can be explained based on the numerous side products being formed by competing reactions [14]. Although Debus established the correct composition of biimidazole, he did not propose a structural formula. It was Bamberger who furnished the most convincing evidence for the structure of biimidazole [15].

$$3(C_2H_2O_2) + 4NH_3 \rightarrow C_6H_6N_4 + 6H_2O \qquad (1)$$
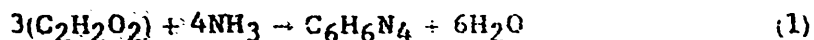
Studies of transition metal complexes of biimidazole have presented a clear picture of the structure of 2,2'-biimidazole (see Figure 1) [9-13]. The term 2,2'-biimidazole implies two five-membered heterocyclic imidazole ring systems bonded together at the carbons numbered 2; each ring consists of a tertiary nitrogen and an imino group. The imino nitrogen, also called "azole" [16] or "pyrrole" [12] possesses two electrons in the unhybridized 'p' orbital which are contributed to the II cloud. While the
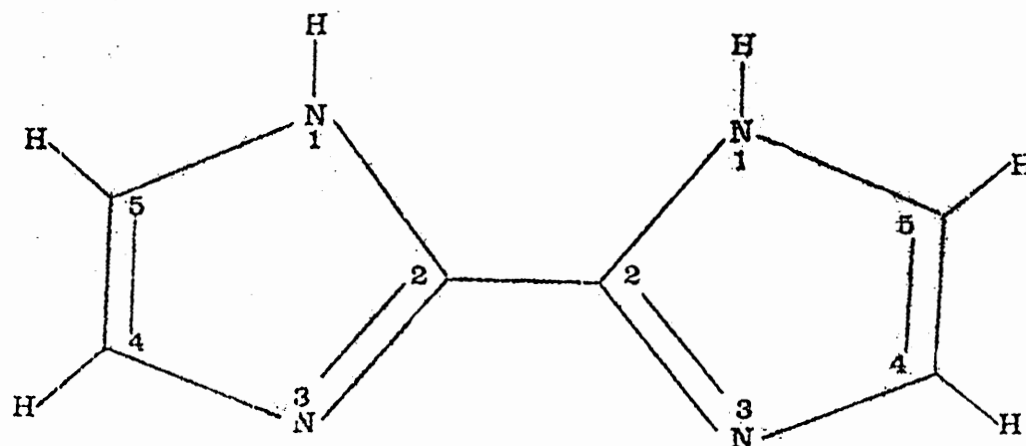
Figure 1. The 2,2'-Biimidazole Molecule

tertiary nitrogen ("pyridine" nitrogen), which is designated with position 3, contains a lone pair of electrons in a hybrid orbital and a single electron in the 'p' orbital which is donated to the Π cloud. Each of the three carbon atoms contribute a $1p_z$ electron to the molecular orbital [13]. An aromatic sextet [17], (4n + 2) $\Pi = 6\Pi$ is then available for each imidazole ring.

Biimidazole has high solubility in very polar solvents and low solubility in non-polar solvents [18]. Hydrochloric acid solubilizes the biimidazole by salt formation. Biimidazole is only slightly soluble in boiling water. The presence of the acidic pyrrole and basic nitrogens in the biimidazole structure (pKa = 4.57) accounts for its amphoteric behavior.

B.   SYNTHESIS OF 1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE

Two methods for the synthesis of 1,1'-dihydroxyethyl-2,2'-biimidazole were investigated by a joint effort between the author and others [19]. One was prepared as reported by Melloni et. al [8] usiŋg 2-chloroethanol as the hydroxyethylating agent (Figure 2). The other method, involving ethylene carbonate [6,7], is a general method for hydroxyethylation of secondary amines (Figure 3).
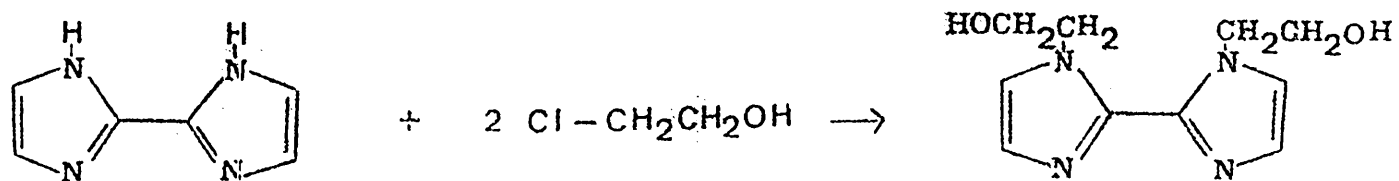
Figure 2.   Synthesis of 1,1'-Dihydroxyethyl-2,2'-Biimidazole
using 2-Chloroethanol
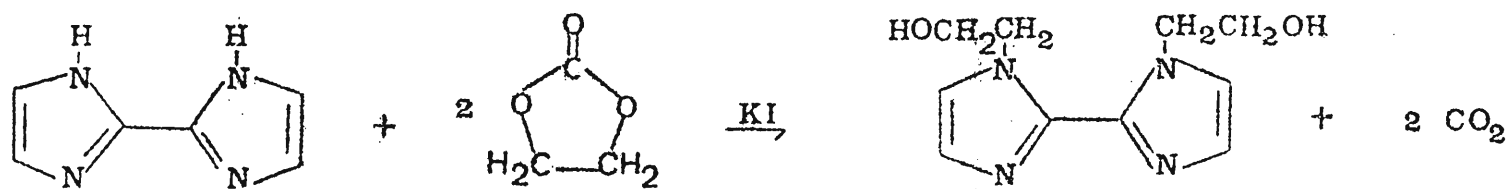
Figure 3.   Synthesis of 1,1'-Dihydroxyethyl-2,2'-Biimidazole
using Ethylene Carbonate

Ethylene carbonate is highly effective as a reagent for introducing the hydroxyethyl groups into many types of organic compounds [20]. The high dielectric constant of ethylene carbonate, plus its ease of handling, low toxicity, and low corrosivity, make it especially suitable as a solvent for specialized applications. Yoshino reported that a strong nucleophilic or basic catalyst is required to accomplish the hydroxyethylation with the carbonate [6]. The catalyst employed in this work was potassium iodide (KI) based on Yoshino's observations. According to Yoshino the reaction of KI with the heterocyclic compound with acidic imino hydrogens is initiated by nucleophilic attack on the ethylene carbonate methylene carbon by the halide anion (I^-). The halide anion is then displaced by the biimidazole anion to yield the β-hydroxyethyl compound. Ethylene carbonate undergoes protonation on the carbonyl oxygen atom. Once the hydroxyethylation is accomplished, the active hydroxyl group can undergo further reactions typical of alcohols, and gives rise to the synthetic methods employed in this study.

C. STRUCTURE AND SYNTHESIS OF POLYCARBONATES

1. Structure.

Polycarbonates are a special class of thermoplastic polyesters formed from the reaction of carbonic acid derivatives with aliphatic, aliphatic-aromatic, or aromatic

dihydroxy compounds [21]. They may be represented by a general structure as shown.

$$H-[-ORO-\overset{\overset{\textstyle O}{\textstyle \|}}{C}-]_n-OROH$$
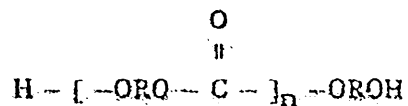
The first systematic investigation of the preparation of high-molecular-weight polycarbonates was carried out by Carothers and co-workers [22]. They were able to prepare relatively high molecular- weight polycarbonates from aliphatic and cycloaliphatic diols by transesterification with diethyl carbonate. The preparation of aromatic polycarbonates from bisphenol by various procedures was carried out by Schnell and co-workers of Farbenfabriken Bayer [23]. These polycarbonates were the first high-melting polycarbonates developed with potential applications in areas demanding high temperature stability. Depending on the nature of R, in the above formula the polycarbonates can be subdivided into aliphatic, aliphatic-aromatic, or aromatic polycarbonates

2. Methods of Preparation.

Aliphatic polycarbonates may be synthesized by a variety of procedures [3] including : reaction of dihydroxy compounds with phosgene or with bischloroformates of aliphatic dihydroxy compounds; transesterification; and polymerization of cyclic carbonates. The most suitable method for the preparation of aliphatic polycarbonates is

the transesterification of diesters of carbonic acid with equimolar amounts of aliphatic dihydroxy compounds as shown in equation (2). Phosgenation of dihydroxy compounds in pyridine is less favorable due to the difficulty associated in carrying out the reaction in gaseous phase and high toxicity of pyridine. It is difficult to prepare bis-chlorocarbonic acid esters of aliphatic dihydroxy compounds in a sufficiently high purity for the preparation of high molecular weight polycarbonates bacause of their thermal instability. Therefore the preparation by this route is of interest only when different dihydroxy compounds are to be used to form a regular copolymer with alternating monomer units.

$$nHO - R - OH + nR'O - \overset{\overset{\textstyle O}{\textstyle \|}}{C} - OR' \rightarrow H - [ORO - \overset{\overset{\textstyle O}{\textstyle \|}}{C}]_n -OR' + (2n-1)R'-OH \quad (2)$$
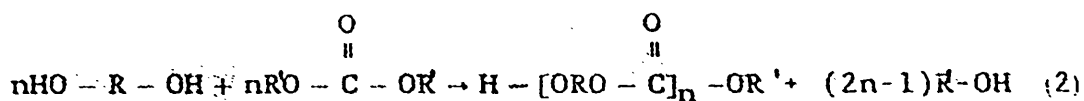
Peterson reported that high molecular-weight aliphatic polycarbonates with fiber- and film-forming properties are obtained by transesterification of aliphatic carbonate diesters such as diethyl or dibutyl carbonate only in the presence of a strongly alkaline catalyst [24]. Piepenbrink [25] reported that aliphatic dihydroxy compounds can be transesterified with diphenyl carbonate without catalyst and at relatively low temperatures.

Aliphatic-aromatic polycarbonates were prepared [26] by polycondensation of the bisalkyl or bisaryl carbonates of aliphatic-aromatic dihydroxy compounds by splitting off

dialkyl or diaryl carbonates in the presence of titanium catalysts such as tetrabutyl titanate, titanium tetrachloride or titanium tetrabromide as shown in equation (3).

$$x R'-O-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-O-R' \rightarrow$$

$$R'-O-\overset{\overset{O}{\|}}{C}-[-O-R-O-\overset{\overset{O}{\|}}{C}-]_x-O-R'+(x+1)R-O-\overset{\overset{O}{\|}}{C}-O-R' \qquad (3)$$
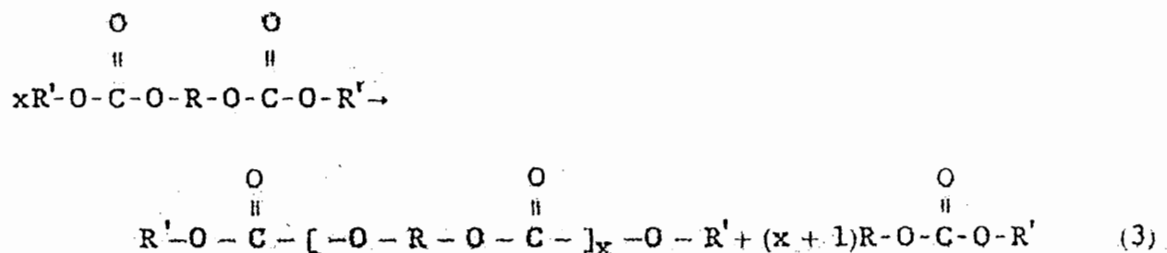
where R = aliphatic-aromatic group from dihydroxy compound

R' = alkyl or aryl group from carbonate compound

The bisalkyl or bisaryl carbonates of aliphatic-aromatic dihydroxy compounds used as the raw material for this condensation can be made by reaction of the aliphatic-aromatic dihydroxy compounds with alkyl or aryl chlorocarbonic acid esters in pyridine.

Aromatic polycarbonates refer to polyesters of carbonic acid which are derived from dihydroxyl compounds in which the hydroxyl groups are directly attached to an aromatic ring [3]. High molecular weight polymers of aromatic polycarbonates may be prepared by: phosgenation of aromatic

dihydroxy compounds in the presence of pyridine (Figure 4), the interfacial polycondensation of aqueous solutions of the alkali salts of aromatic dihydroxy compounds with a phosgene solution, and the transesterification of aromatic dihydroxy compounds with diaryl carbonates (Figure 5).

3. Mechanism of Transesterification.

The transesterification reaction proceeds in a way such that the ester link of the ester component of the reactant interacts with an alcohol forming a new ester link and eliminating the corresponding alcohol as shown in equation (4).

$$RCOOR' + R''OH \xrightleftharpoons{H^+ \text{ or } ^-OR} RCOOR'' + R'OH \tag{4}$$
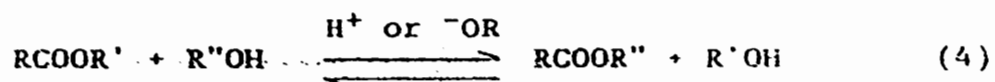
Transesterification may be catalyzed by acid or base. The mechanisms for the two reactions are presented in Figures 6 and 7 respectively [17,27]. Theoretically, the transesterification requires practically equivalent amounts of starting materials. Since the polycondensation is an equilibrium reaction, the monohydroxy compounds must be quantitatively removed from the reaction melt to shift the equilibrium to the right.
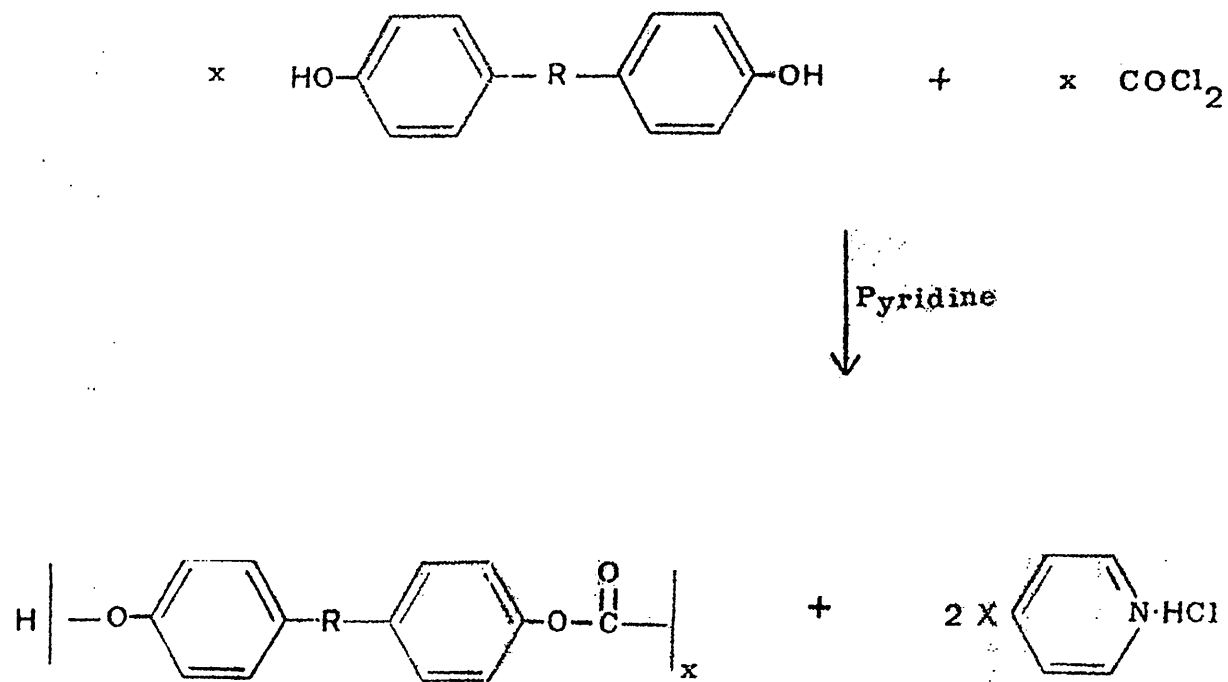
Figure 4. The Phosgenation of Aromatic Dihydroxy Compound in Pyridine
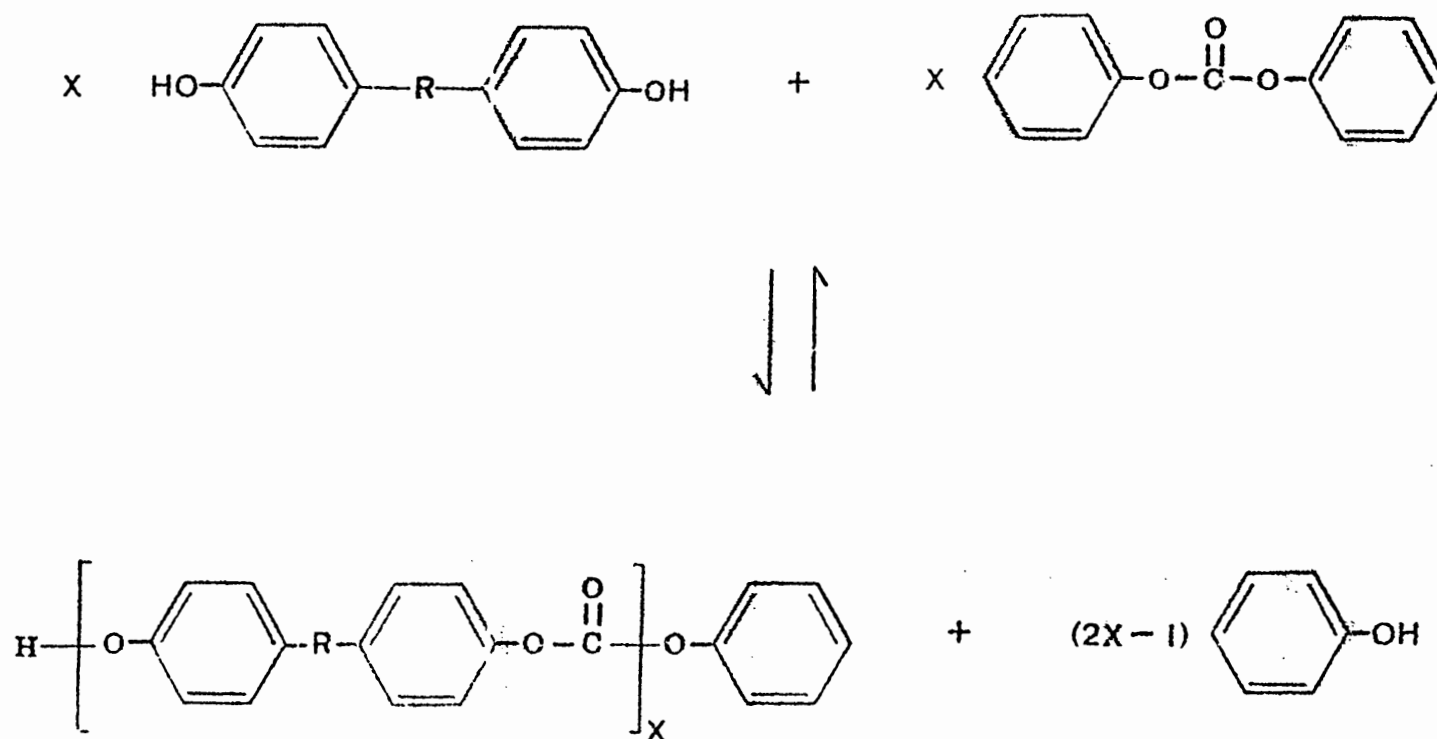
Figure 5. Transesterification of Aromatic Dihydroxy Compound with Diphenyl Carbonate
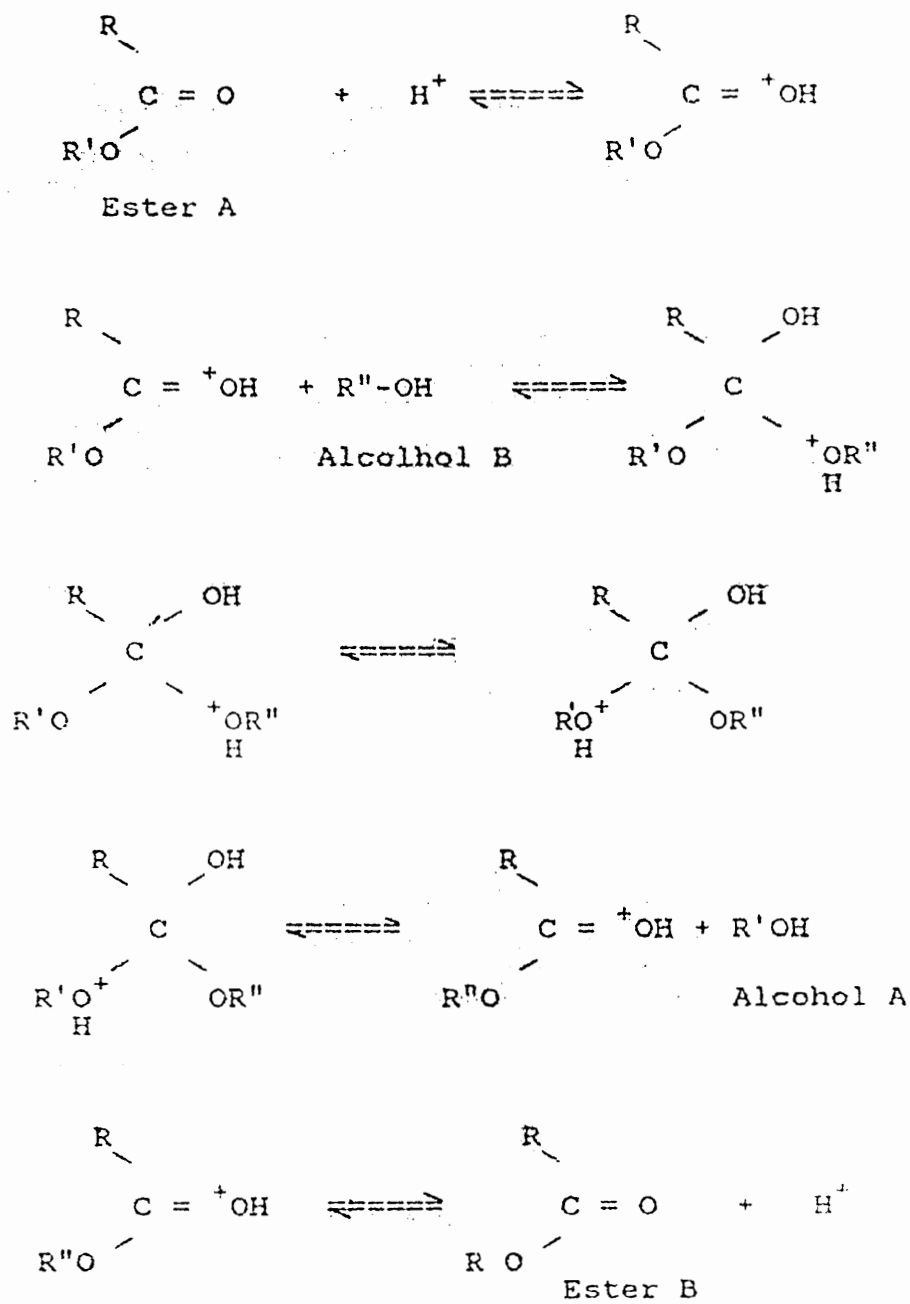
Figure 6. Mechanism for Acid-Catalyzed Transesterification
Reaction

$$\underset{R'O}{\overset{R}{>}}C = O \quad + \quad :OR'' \rightleftharpoons \underset{R'O}{\overset{R}{>}}C\underset{OR''}{\overset{O^-}{<}}$$

Ester A   Alkoxide B

$$\underset{R'O}{\overset{R}{>}}C\underset{OR''}{\overset{O^-}{<}} \longrightarrow \underset{R''O}{\overset{R}{>}}C = O \quad + \quad :OR'$$

Ester B   Alkoxide A

$$\underset{R''O}{\overset{R}{>}}C=O \quad + \quad R'''-OH \rightleftharpoons \underset{R''O}{\overset{R}{>}}C\underset{OR'''}{\overset{OH}{<}}$$

$$\underset{R''O}{\overset{R}{>}}C\underset{OR'''}{\overset{OH}{<}} \rightleftharpoons \underset{R'''O}{\overset{R}{>}}C=O \quad + \quad :OR'' \quad + \quad H^+$$
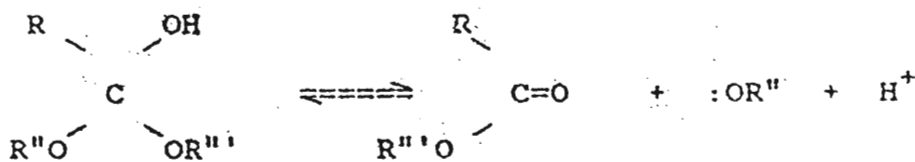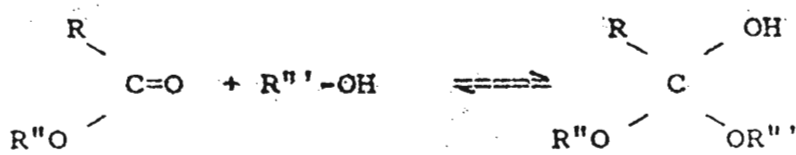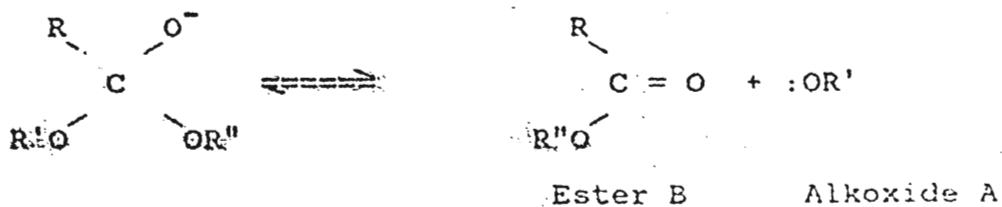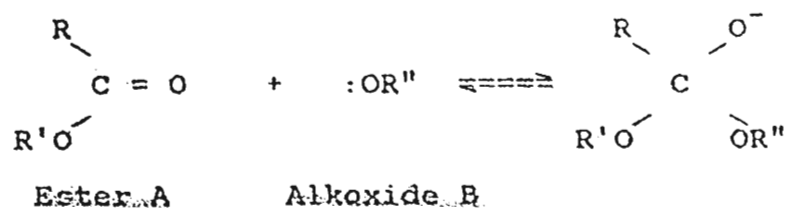
Figure 7. Mechanism for Base-Catalyzed
Transesterification Reaction

4. Effect of Catalysts.

A large number of catalysts have been described for the transesterification of aromatic dihydroxy compounds with diphenyl carbonate. Basic compounds are particularly effective. These include the alkali and alkaline earth metal oxides, hydroxides, and amides [21]. Acetates of calcium, magnesium, and zinc, as well as antimony compounds [28] and soluble manganese compounds [29] are not very effective. Acidic catalysts, such as phosphoric acid and its acidic salts, increase the rate of transesterification [30]. High molecular weight aromatic-aliphatic poly-carbonates were obtained from bisalkyl or bisaryl carbonates with p-xylylene glycol when special catalysts such as titanium tetrabutoxide or titanium tetrachloride were used [31].

D. PROPERTIES OF POLYCARBONATES

Relatively little is known about the properties of aliphatic, cycloaliphatic, and aromatic-aliphatic poly-carbonates. The most extensively studied polycarbonates are the aromatic type, particularly those derived from bisphenol A.

1. Crosslinking.

The commercially used aromatic polycarbonates are high melting point thermoplastics soluble in common solvents. In

some applications it is advantageous to reduce the solubility and swelling in organic solvents and to raise the heat distortion point. Both results can be achieved by primary crosslinking of the linear macromolecules. Such crosslinking can be obtained in polycarbonates to a limited degree by ionizing radiation, by treatment with oxygen and formaldehyde, substances which form formaldehyde [32], or polyepoxides at higher temperature, as well as by heating those polycarbonates with functional groups with tendencies to undergo crosslinking reactions.

Aliphatic polycarbonates have not found any commercial significance as intermediates for the preparation of crosslinked molded articles or in the area of films, fibers, or thermoplastics. This result is due primarily to their low melting points, their high solubility, their hydrophylic nature, and their often times low thermal stability.

2. Crystallinity.

The tendency of an aromatic polycarbonate to crystallize depends or its constitution, molecular weight, and to some extent, its molecular-weight distribution [21]. The general rule in the polycarbonate series is that the tendency of the polymers to crystallize decreases as the substituting groups on the central carbon atom of the dihydric phenol becomes less symmetrical and more branched [33].

Many of the aliphatic aromatic polycarbonates investigated showed a great tendency to crystallize [3]. They usually solidify from the molten state to an opaque and, in many cases, brittle microcrystalline mass. Fibers which can be oriented by stretching can be pulled from their respective melts. The orientation is fixed by the high degree of crystallinity.

3. Thermal Stability.

Aromatic polycarbonates possess a high degree of thermal stability and undergo little decomposition below 250°C [34]. The processing of polycarbonates at higher temperature can, however, lead to thermal and thermo-oxidative breakdown with consequent deterioration in mechanical properties.

Aliphatic polycarbonates are stable in a molten state at temperatures above 200°C if alkaline or acidic impurities are not present [3]. However, extremely small amounts of impurities, especially of alkaline reaction, cause degradation and decomposition of the aliphatic poly-carbonates at temperatures above 150°C.

4. Transition Temperatures.

Aromatic polycarbonates with low crystallinity do not have a definite melting range [3]. Above the glass-transition temperature they soften and undergo plastic

deformation under the influence of mechanical stress. On the other hand, aromatic crystalline polycarbonates exhibit an exact melting point measurable by common methods, such as optical measurement of birefringence, determination of specific heat or heat of phase change by differential thermal analysis, thermal mechanical behavior by torsional modulus, and others. A noncrystalline polycarbonate from bisphenol A softens significantly above 200°C whereas crystalline polycarbonate of the same constitution melts between 255-265°C [3].

The glass transition temperature (Tg) at 149°C for bisphenol A polycarbonate is unusually high compared to that of polystyrene (100°C), poly-ethylene terephthalate (69°C), nylon 6,6 (45°C) and polyethylene (-45°C). At the Tg, an important determinant of many physical-mechanical properties, there is a significant onset of molecular mobility (rotation). A high Tg indicates excellent dimensional stability and resistance to creep under load, both properties of bisphenol A polycarbonate. The Tg essentially sets the upper temperature limit for maintenance of mechanical and electrical properties.

The aliphatic-aromatic polycarbonates, which have the same degree of crystallinity as the corresponding aromatic polycarbonates, melt at considerable lower temperatures [3]. This lowering of melting temperature (Tm) is caused primarily by the increased mobility of the macromolecules due to the aliphatic groups.

Because of the low polarity of the carbonic acid ester group, aliphatic polycarbonates are, at room temperature, generally viscous liquids or microcrystalline, low-melting masses with a relatively narrow melting range [3].

5. Related Work.

Except for the polyimidazoles and polybenzimidazoles, the thermal and thermoxidative stabilities of the imidazole-containing polymers have not been studied extensively. The synthesis of polyimidazoyl esters by polycondensation of acid chlorides of imidazoyl dicarboxylic acids with glycols has been reported [35]. Linear polyesters were found that exhibit good thermal stability, high solubility in strong acids, and partial solubility in dimethylformamide (DMF), hot pyridine, and N-methyl pyrrolidone.

III. EXPERIMENTAL

A. THE PREPARATION OF 2,2'-BIIMIDAZOLE

Equal volumes of 29% solution of ammonium hydroxide and 40% solution of glyoxal were combined with stirring. The reaction proceeded rapidly and the precipitate formed was immediately suction filtered and washed repeatedly with distilled water until the filtrate was clear. The crude precipitate was placed in 3000-4000 ml of distilled water. The mixture was brought to boiling with stirring and then filtered by suction while hot. Light-brown crystals of biimidazole were obtained upon cooling and isolated by suction filtration. The recrystallized biimidazole was dried at 100°C for a period of 24 hours. The recrystallization process was repeated with the insoluble portions collected in the suction funnels until all the biimidazole was extracted by the boiling water. The melting point of biimidazole was determined with a Fisher Johns melting point apparatus. Infrared spectrum of sample suspended in KBr pellet was recorded on a Perkin-Elmer Model 1750 Fourier transform infrared spectrophotometer. Elemental analysis was done by Galbraith Laboratory (located at 2323 Sycamore Drive, Knoxville, Tennessee).

B. THE PREPARATION OF 1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE

1. Ethylene Carbonate Preparation Method.

The hydroxyethylation of 2,2'-biimidazole using ethylene carbonate as the hydroxyethylating agent was extensively studied. Many syntheses were performed varying the temperature, time, catalyst and amounts of reactants until optimum conditions and reactants quantities were found. Reaction temperatures were controlled by an autotransformer and the optimum temperature was found to be at 99°C. The optimum reaction time, determined by observing the rate of evolution of CO_2 through a water bubbler was found to be approximately 2.5-3.0 hours. A general procedure is described:

A 1.650 g quantity (0.0187 mole) of ethylene carbonate (reagent grade from Fischer Scientific) was weighed into a 50 ml round bottomed flask. Because ethylene carbonate was used as the solvent, it was important to allow it to melt (m.p. 35- 37°C) at the beginning of the reaction in order to maximize blending of reactants. Then 1.250 g (0.0093 mole) of recrystallized 2,2'-biimidazole along with 0.0041 g KI and a stirring bar were added to the flask. The catalyst, KI was added at 0.1% based on moles of ethylene carbonate. The reaction was conducted at 99°C for about 2.5-3.0 hours, or until no CO_2 evolution was detected using a bubble gas trap. Product isolation was accomplished by first washing the reaction mixture with acetone to precipitate unreacted

biimidazole which was then removed by gravity filtration. The acetone was removed from the filtrate by rotary evaporation. A dark brown, highly viscous crude hydroxy-ethylated 2,2'-biimidazole (60-70% yield) was collected.

Due to the formation of monosubstituted hydroxy-ethylation products and other side-products formed from reaction of ethylene carbonate and KI, separation of 1,1'-dihydroxyethyl-2,2'-biimidazole from the reaction mixture was difficult to achieve. Purification of 1,1'-dihydroxyethyl- 2,2'-biimidazole was carried out by first treating the crude product with decolorizing carbon using acetone (Reagent grade), stored over molecular sieves (Type 3A grade 564) as solvent until a light yellow product was obtained. The desired product isolation was obtained by eluting the reaction mixture through a chromatograph column of 28-500 mesh silica gel (Grade 12 from Aldrich) dessicant with dry acetone. The reaction mixture was eluded with acetone until the effluent was colorless. The fraction containing the purified product was then eluded with MeOH/ H_2O (55:45) solvent. The solvent was removed by rotary evaporation. The purity of the final product was determined by thin layer chromatography (TLC) on 20x5 cm Whatman KC_{18} plates. The sample, dissolved in methanol-water (67.5:32.5) was applied to the plate with a micropipet to form a 2-5 mm spot. The product was stored in dessicator over calcium chloride at room temperature. An elemental analysis of this product was performed by Galbraith Laboratory. The

structure was confirmed by FTIR (Perkin-Elmer 1750) on NaCl disks; and Proton and Carbon-13 NMR (JEOL FX 100) by using methyl sulfoxide-d_6 as solvent. The preparation and recrystallization procedures were repeated to generate significant quantities of 1,1'-dihydroxyethyl-2,2'-biimidazole. The elemental analysis and spectral data are given in section IV.

2. 2-Chloroethanol Preparation Method.

A suspension of 4.02 g (0.03 mole) of 2,2'-biimidazole in 150 ml of ethanol and 19.65 ml 20% NaOH (0.1 mole) was heated at 60°C to effect solution. 7.249 g (0.09 mole) of 2-chloroethanol were slowly dropped into the solution over 1 hour. The mixture was kept at 60°C for 24 hours. After cooling to room temperature, excess biimidazole was filtered off and separately washed with water. The washings were added to the reaction mother liquors. The solution was evaporated to dryness, the residue dissolved in 75.0 ml of water, neutralized with 8% HCl, and the solution extracted with 1 L chloroform. The dark oil obtained after removal of solvent in vacuo was dried in a vacuum oven at 60°C for 24 hours. The structure was confirmed by proton NMR (using D_2O as solvent) and carbon-13 NMR (using DMSO-d_6 as solvent).

C. THE PREPARATION OF POLYCARBONATES

The polycarbonates were synthesized by two methods: by transesterification reaction in the melt (without solvent) and in solution.   Generally, in carrying out polyesterification in the melt, reaction is performed in two stages [36]. First the reaction mixture is heated in a current of inert gas followed by heating in vacuo to eliminate the low molecular weight reaction by-products. The heating in a current of inert gas satisfies several criteria: operating the process in the absence of atmospheric oxygen, which may cause the degradation of the high molecular weight polymer formed; stirring the reaction mass, if the current of inert gas is passed through it; and facilitating the elimination of low molecular weight reaction products (phenol or ethanol) from the reaction medium.   The   preparation   of   polycarbonates   by polycondensation in solution was carried out at the boiling point of the solvents DMSO and DMF. During the reaction the solvent was distilled off, carrying with it the low molecular weight reaction products and thereby shifting the equilibrium in the direction of the formation of the polymeric molecules.

1. Synthesis of Polycarbonates 1-6.

Table I-II summarizes the conditions used in the preparation of polycarbonates.   PC-1 through PC-6 were synthesized by transesterification in the melt using the

TABLE I

SUMMARY OF THE CONDITIONS IN THE SYNTHESIS OF

POLYCARBONATES AT 1:1 DIOL/CARBONATE RATIO

Name	Carbonate	Wt. Diol (g)	Wt. Carb. (g)	Solvent	Catalyst
PC-1	DEC	0.500	0.266	none	NaOMe
PC-2	DEC	0.500	0.266	none	none
PC-3	DPC	0.500	0.482	none	none
PC-4	DEC	0.500	0.266	none	TTC
PC-5	DPC	0.500	0.482	none	NaOMe
PC-6	DPC	0.500	0.482	none	TTC
PC-I	DPC	2.1127	2.0386	DMSO	none
PC-II	DPC	1.9913	1.9174	DMSO	NaOMe
PC-III	DPC	1.8529	1.7841	DMSO	TTC
PC-IV	DEC	2.1580	1.1470	DMF	none
PC-V	DEC	2.2497	1.1958	DMF	NaOMe
PC-VI	DEC	1.9051	1.0126	DMF	TTC
PC-XVI	DPC	0.7240	0.698	DMSO	none
PC-XVII	DPC	1.0450	1.0072	DMSO	NaOMe
PC-XVIII	DPC	0.9460	0.911	DMSO	TTC

DPC = Diphenyl Carbonate; DEC = Diethyl Carbonate

TTC = Titanium Tetrachloride; PC (1-6) and PC (I-VI) prepared

via ethylene carbonate route; PC (XVI-XVIII) = prepared via

2-chloroethanol route

TABLE II

SUMMARY OF THE CONDITIONS IN THE SYNTHESIS OF POLY

CARBONATES AT 2:1 AND 1:2 DIOL/CARBONATE RATIO

Name	Carbonate	Wt. Diol (g)	Wt. Carb. (g)	Solvent	Catalyst
2:1 (DIOL/CARBONATE) Ratio					
PC-VII	DPC	1.6030	0.7718	DMSO	none
PC-VIII	DPC	1.6721	0.8050	DMSO	NaOMe
PC-IX	DPC	1.9363	0.9322	DMSO	TTC
PC-X	DEC	1.8236	0.4846	DMF	none
PC-XI	DEC	1.1831	0.3144	DMF	NaOMe
PC-XII	DEC	1.8514	0.4929	DMF	TTC
1:2 (DIOL/CARBONATE) Ratio					
PC-XIII	DPC	1.8846	3.6293	DMSO	none
PC-XIV	DPC	2.0278	3.9051	DMSO	NaOMe
PC-XV	DPC	2.1712	4.1812	DMSO	TTC

DPC = Diphenyl Carbonate; DEC = Diethyl Carbonate;

TTC = Titanium Tetrachloride; PC (VII-XV) = prepared

via ethylene carbonate route

general procedure as follows: Equimolar ratio of 1,1'-dihydroxyethyl- 2,2'-biimidazole (prepared via ethylene carbonate route) and diphenyl or diethyl carbonate were weighed into a condensation test tube plus catalyst at levels of 0.1 to 0.2% based on weight of 1,1'-dihydroxyethyl -2,2'-biimidazole. The condensation test tube was fitted with a thermometer and a glass tube for the passage of argon. The side arm of the tube was connected to a receiver for the low molecular weight raction products. The system was swept free of air by passage of a current of argon. The condensation test tube with the reaction mixture was heated at constant temperature in a paraffin oil bath at 90°C for 12 hours with care taken to maintain temperature below 105°C to prevent decomposition of initial materials. In the second stage of the reaction the side arm of the tube was connected through an intermediate flask to a vacuum apparatus to permit heating under vacuum (5.0 mm Hg) with the temperature of the bath gradually increased to 185°C. Phenol or ethanol distilled over rapidly during the first hour at 180- 185°C and then slowly during the next two hours at the same temperature. The terperature of the mixture was maintained at this level until there was no distillate and the syrupy mass solidified into dark brown solid mass upon cooling to room temperature.

2.   Synthesis of Polycarbonates I-XVIII.

Polymerization reactions were carried out in a three-neck 0.1 L round bottom flask fitted with a reflux condenser, mechanical stirrer, an argon inlet tube, thermometer and a heating mantel to control the reaction temperature. Table I-II summarizes the conditions of synthesis of polycarbonates I-XVIII. Polycarbonates I-XV were prepared from monomer synthesized via ethylene carbonate route. While polycarbonates XVI-XVIII were prepared from monomer synthesized via 2-chloroethanol route. DMSO (b.p. 189°C) and DMF (b.p. 153°C) were chosen as solvents because they have a higher boiling point than the low molecular weight reaction products evolved in the polyesterification process (phenol: 182°C ; ethanol: 78°C). Catalyst was added at levels of 0.1 to 0.2% based on weight of 1,1'-dihydroxyethyl-2,2'-biimidazole. The system was gassed with argon before beginning the reaction. The reaction mixture was heated with continuous passage of argon at 100°C for 12 hours with a reflux condenser. Then the condenser was turned into the position for direct distillation and the temperature was gradually raised to 210°C, while the phenol/ethanol formed was distilled off with the solvent. Further heating was carried out at 210 C for about 12 hours. The polymer was isolated either by precipitation with water or removal of solvent under 5.0 mm Hg vacuum (see Table VII). The polymer was dried in a vacuum oven at 225 mm Hg and 60°C for 1 week.

D. CHARACTERIZATION OF POLYCARBONATES

1. Solubility.

The solubility of the polycarbonates was evaluated by weighing about 0.1 g of polymer material into small vials, and adding 1.0 ml of different solvents to each at room temperature. The solution was vigorously stirred and examined after 30 minutes. The results are reported in Tables VIII-IX.

2. Fourier Transform Infrared Spectroscopy.

Infrared absorbance spectra as KBr pellets were obtained using a Perkin-Elmer model 1750 Fourier transform infrared spectrophotometer. Twenty scans at a resolution of 2 cm^{-1} were signal averaged before Fourier transformation.

3. Nuclear Magnetic Resonance Spectroscopy.

Proton NMR spectra were obtained by using VARIAN EM 360 nuclear magnetic resonance spectrometer at room temperature. Carbon-13 solid NMR were recorded on VXR-200 at 50 MHz using tetramethylsilane as an internal standard.

4. Differential Scanning Calorimetry.

DSC measurements under N_2 atmosphere were conducted over a 25°C to 500°C temperature range using PERKIN-ELMER DSC-2 with a data station interface. The heating rate was

10°C per min with temperature precision ± 0.2°C and the sample weight was in the range of 5-10 mg. Temperature and enthalphy calibrations were done with indium and tin standards.

5. Thermogravimetric Analysis.

TGA was conducted with a PERKIN-ELMER TG/S/2 thermogravimetric analyzer in a N_2 atmosphere and at a 10°C per min heating rate.

6. Gel Permeation Chromatography.

Molecular weights of polymers prepared via ethylene carbonate route were measured with a modified high pressure liquid chromatography (HPLC) system equipped with a u-spherogel (10^4 angstrom pore size) column (Beckman). A range of narrow molecular weight polystyrene samples (10200, 34500, 305500, and 470000) were used as calibration standards. The eluting solvent used was DMF and flow rate was set at 0.5 ml/min at room temperature. Chromatographed samples were detected with a Fresnel refractive index detector (refractive index range 1.35 to 1.45 units) at a concentration of 0.3% w/v. Samples were passed through a membrane filter (Nylon 66, 0.45 microns) before injection.

Molecular weights of polymers prepared via 2-chloroethanol route were measured on a different gel permeation chromatograph (Waters 6000 pump) equipped with

two columns (500 and 10,000 angstrom pore size). Polystyrene standards (800 and 402,000) were used for calibration. The eluting solvent used was tetrahydrofuran (THF) and flow rate was set at 1.0 ml/min at room temperature. Chromatographed samples were detected with a differential refractometer R401 (Waters) detector at a concentration of 0.3% w/v.

IV. RESULTS AND DISCUSSION

A. THE PREPARATION OF 2,2'-BIIMIDAZOLE

The preparation of 2,2'-biimidazole from ammonia and glyoxal proceeded very rapidly and without difficulty. However, the yields were low (8-13%) which can be explained based on the numerous side products being formed by competing reactions [14].

It was found that the precipitate must be removed from the reaction mixture as soon as it was formed, otherwise more unwanted contaminants are allowed to form making it more difficult to obtain a pure biimidazole.

Some of the characteristics of biimidazole observed were its high and low solubility in HCl and water, respectively. Its low solubility can be explained in terms of hydrogen bonding between the pyridine nitrogen of a biimidazole molecule and the imino hydrogen of another biimidazole molecule as shown below. However, the formation of HCl-Biimidazole salt solubilizes it in water.
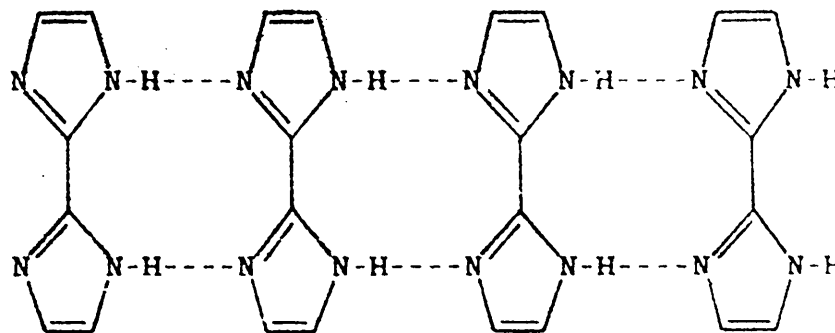
Such an association occurs only in a non-acidic solvent such as water. Non-associations develop in the presence of highly acidic solvents such as HCl [18]. The high melting point above 300°C may be attributed to this type of association as well.

The composition of the recrystallized biimidazole was determined by elemental analysis. The experimental results agree within 0.48% relative error compared to theoretical values. The results are given in Table III.

The infrared spectrum shown in Figure 8 is dominated by a broad intense absorption from 3200 to 2500 cm^{-1} assigned to hydrogen-bonded N-H stretching.

TABLE III

ELEMENTAL ANALYSIS OF 2,2'-BIIMIDAZOLE

	Theoretical	Experimental	% Relative Error
% C	53.73	53.77	0.07
% H	4.48	4.48	0
% N	41.77	41.57	0.48
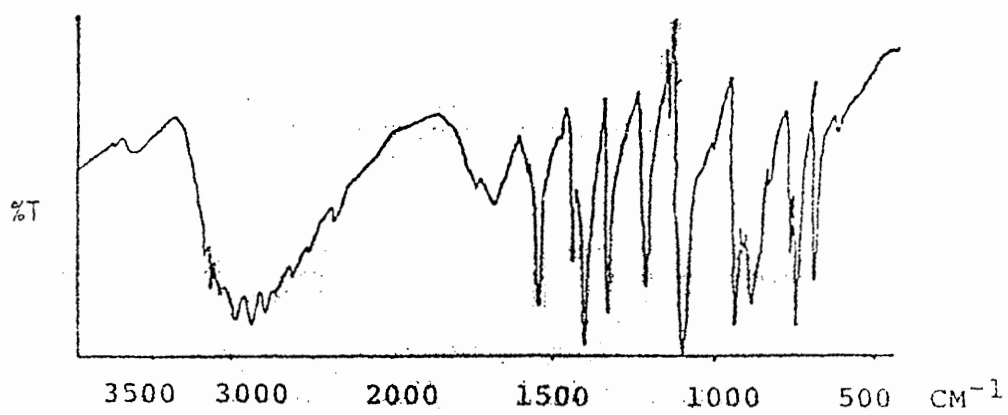
Figure 8.   IR Spectrum of 2,2'-Biimidazole

B. THE PREPARATION OF 1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE

1. Ethylene Carbonate Route.

Optimum reaction conditions for the hydroxyethylation of 2,2'-biimidazole using ethylene carbonate as the hydroxyethylating agent were observed at 99°C and 3.0 hr total reaction time. KI was chosen as the catalyst based on Yoshino's observations [6]. It was observed that when mixing was not appropriate the yields were lower. Again, competing reactions forming other products may lower the yield of the dihydroxy product. It has been reported that ethylene carbonate forms monoethylene glycol ether in hydroxyethylation reactions [20]. It is possible that for biimidazole the following reaction could occur:

$$2,2'\text{-Biimidazole} + \text{(ethylene carbonate)} \longrightarrow \text{(dihydroxyethyl biimidazole)} + CO_2$$
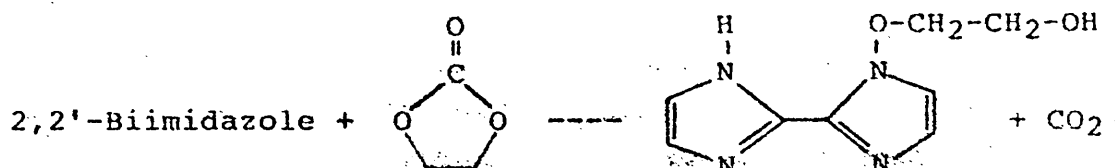
A dark brown, highly crude hydroxyethylated biimidazole was collected (60-70% yield). Effective isolation of the dihydroxyl from unreacted ethylene carbonate was difficult to achieve. Purification of hydroxyethylated biimidazole was carried out by first treating the crude product with decolorizing carbon until a light yellow oily product was obtained. Then the reaction mixture was eluted through a

chromatograph column (100 cm in length and 5.0 cm in diameter), packed with silica (Grade 12:28-200 mesh from Aldrich) using solvent mixtures of methanol/water (55:45) and acetone. Thin layer chromatograph (TLC) of the treated material showed the presence of a big, dark spot and a small light spot (Figure 9). High pressure liquid chromatograph (HPLC) of the diol in methanol/water (40/60) mixture showed two peaks. This indicates the presence of impurity in the sample. The proton NMR spectrum (Figure 10) also shows a chemical shift at 3.55 ppm which can not be accounted for. Table IV, column (1) summarizes the chemical shifts of Figure 10 . Figure 11 represents the C-13 NMR of the impure hydroxyethylated biimidazole and the corresponding chemical shifts are listed in Table V, column (1). The ring carbons at positions 2, 4 and 5 show resonances at 137.5, 127.2 and 122.98 ppm respectively; and ethyl carbons at 49.21 and 61.09 ppm. A number of extra peaks are observed probably due to the presence of impurities in the sample. Elemental analysis of this product is shown in Table VI, column (1).

Several methods of isolation were attempted to purify the hydroxyethylated biimidazole. Treatment of the crude product with n-butanol effectively removes excess ethylene carbonate from the sample. However, TLC, HPLC and NMR analyses show that impurity is still present. Ultracentrifugation and salting out methods failed to yield a pure product.
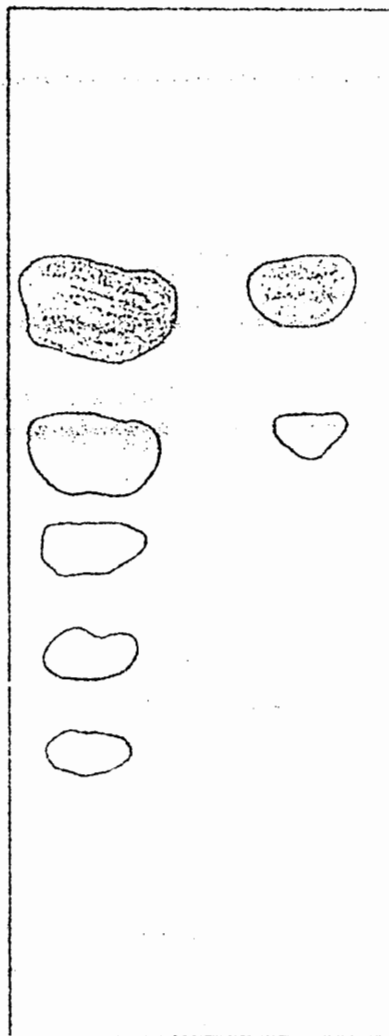
Figure 9.   Thin Layer Chromatograph of
             1,1'-Dihydroxyethyl-2,2'-Biimidazole
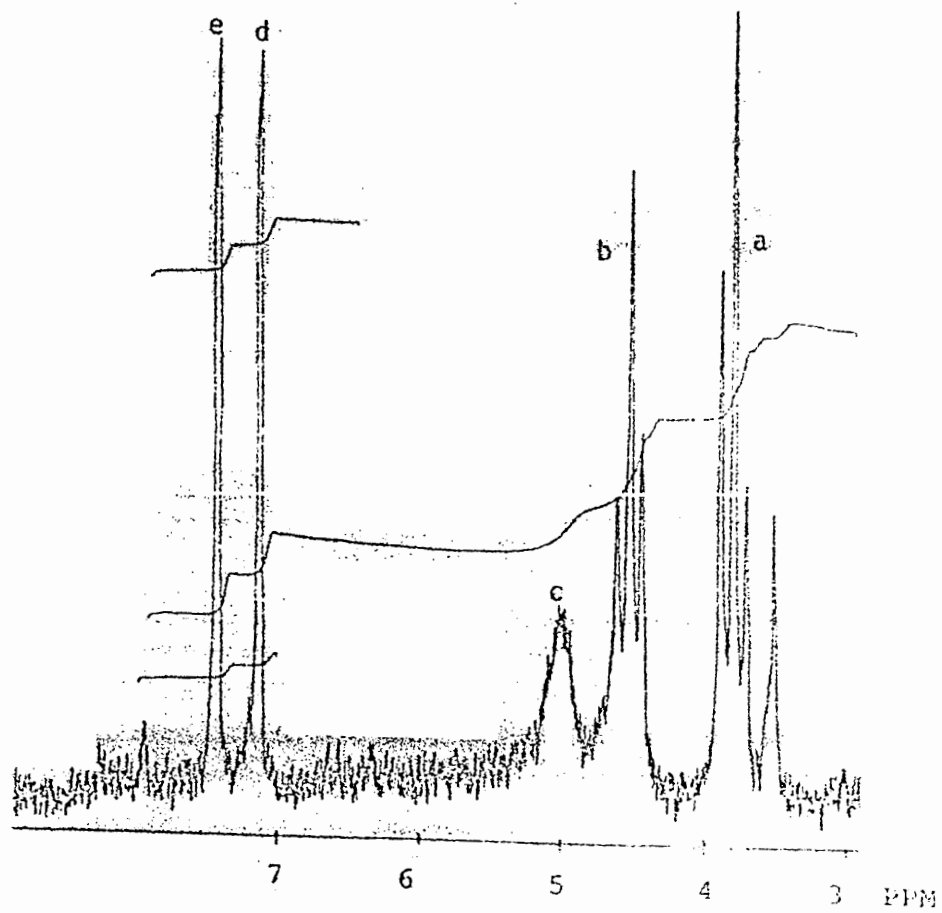
Figure 10. H-NMR Spectrum of 1,1'-Dihydroxyethyl-
2,2'-Biimidazole via Ethylene Carbonate Route
(in DMSO-d_6)

TABLE IV

1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE 60 MHZ PROTON
NMR SPECTRUM ANALYSIS

Hydrogen	Chemical Shift (PPM)	
	(1) (in DMSO-d$_6$)	(2) (in D$_2$O)
a	3.75 - 3.9(t)	3.7-3.9(t)
b	4.5 - 4.63(t)	4.25-4.4(t)
c	5.0(s)	4.8(s)
d	7.15(d)	7.2(s)
e	7.45(d)	7.4(s)

Ratio of a:b:c:d:e: = 2:2:1:1:1

Column (1)= Prepared via ethylene carbonate route

Column (2)= Prepared via 2-chloroethanol route

s = singlet; d = doublet; t = triplet
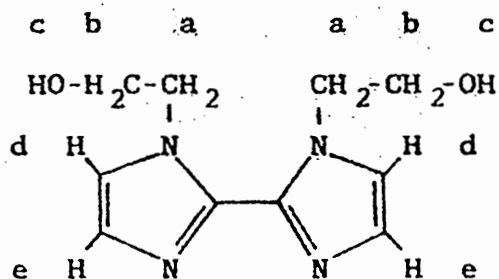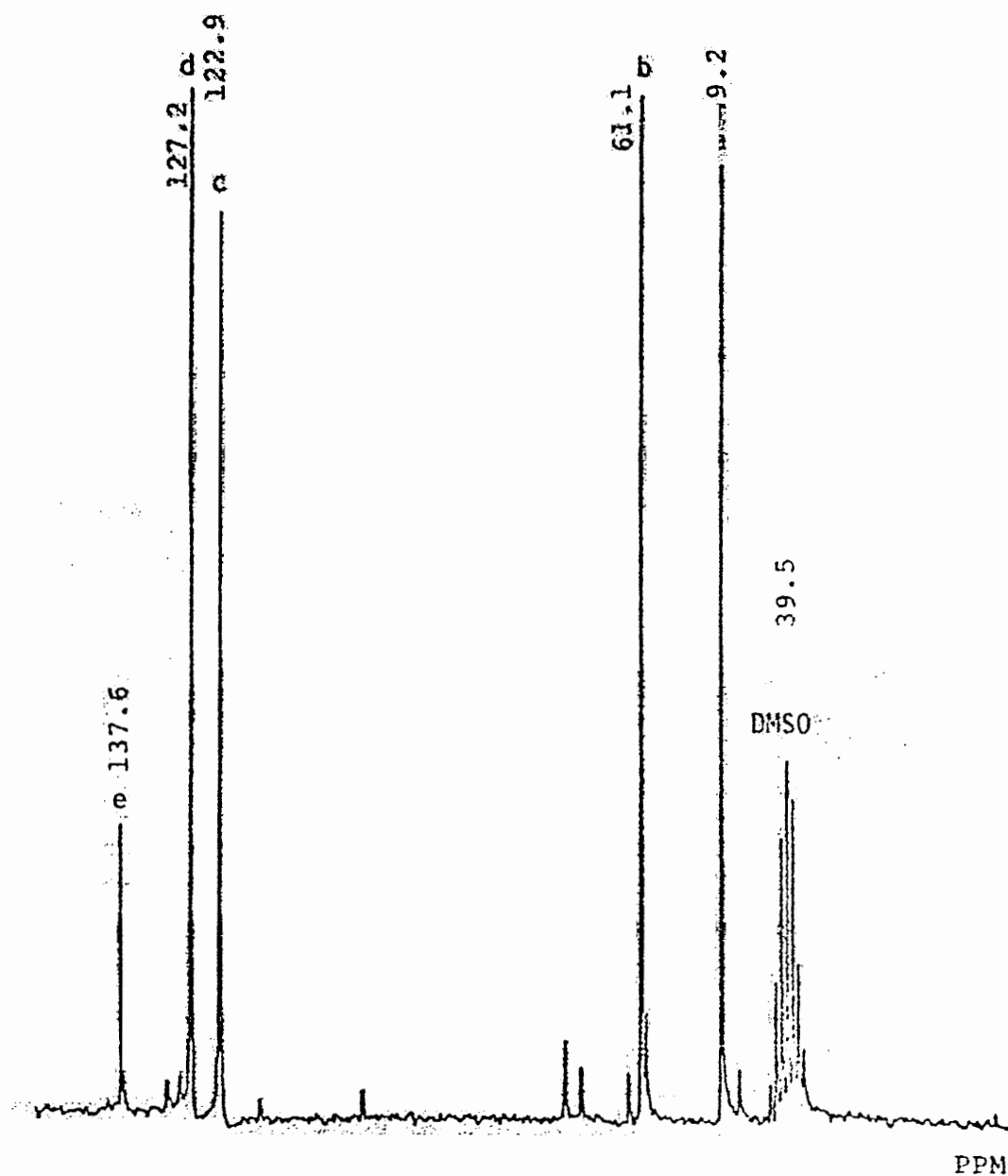
```
   c  b  a        a  b  c
  HO-H2C-CH2    CH2-CH2-OH
 d H   N         N   H d
      ...
 e H   N         N   H e
```

Figure 11. C-13 NMR Spectrum of 1,1'-Dihydroxyethyl-
2,2'-Biimidazole via Ethylene Carbonate Route
(in DMSO-d_6)

TABLE V

1,1'-DIHYDROXYETHYL-2,2'-BIIMIDAZOLE

C-13 NMR SPECTRUM ANALYSIS (in DMSO-d6)

Carbon	Chemical Shift (PPM)	
	(1)	(2)
a	49.2	49.2
b	61.1	61.1
c	122.9	122.9
d	127.2	127.3
e	137.6	137.7

Column (1)= Prepared via ethylene carbonate route

Column (2)= Prepared via 2-chloroethanol route
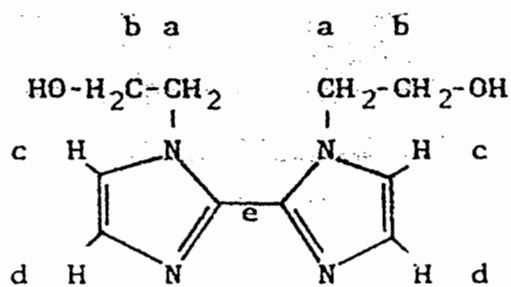
TABLE VI

ELEMENTAL ANALYSIS OF 1,1'-DIHYDROXYETHYL-

2,2'-BIIMIDAZOLE

	Theoretical	Experimental	
		(1)	(2)
%C	54.04	52.12	54.00
%H	6.35	6.48	6.42
%O	14.40	18.72	14.46
%N	25.21	22.68	25.42

Column (1)= Prepared via ethylene carbonate route

Column (2)= Prepared via 2-chloroethanol route

2.   2-Chloroethanol Route.

The method with 2-chloroethanol yielded a pure product.
High pressure liquid chromatographs (HPLC) in methanol/water
(40/60) mixtures of the dihydroxy material show only one
peak. Its composition was determined by elemental analysis.
The experimental results agree within 0.22% difference
compared to theoretical values, as shown in Table VI, column
(2).   Figure 12 and 13 represent the proton and C-13 NMR
spectra of pure hydroxyethylated biimidazole respectively.
The chemical shifts for H and C-13 NMR spectra are
summarized in Table IV, column (2) and Table V, column (2)
respectively.   The ring hydrogens are assigned to singlet
resonances at 7.2 and 7.4 ppm; ethyl hydrogens are
identified with triplet resonances at 3.7-3.9 and 4.25-4.4
ppm. The hydroxyl hydrogen shows a peak at 4.8 ppm.   The
integrated NMR spectrum of Figure 12 shows a hydrogen ratio
of 1:1:2:2:1 assigned to ring, ethyl and hydroxyl hydrogens
respectively. Although the hydroxyl hydrogen peak in Figure
12 is sharper and has higher peak height than the hydroxyl
hydrogen in Figure 10, the ratios of the integrated areas of
the peaks in both spectra are the same. The C-13 NMR
spectrum shows the absence of any impurity in the diol as
seen in Figure 13.   The infrared spectrum shown in Figure 14
is characterized by a strong, broad band at 3283 cm [1]
assigned to hydrogen-bonded O-H stretching. The rest of
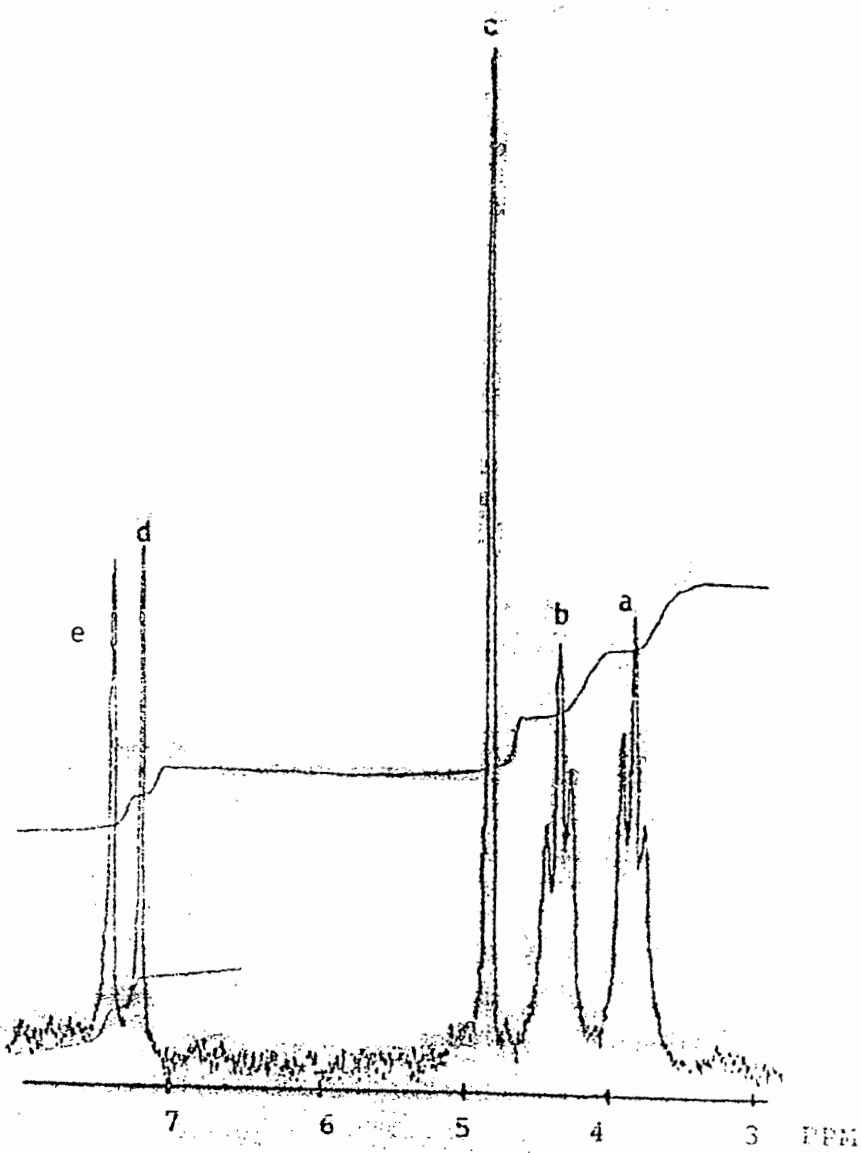
Figure 12. H-NMR Spectrum of 1,1'-Dihydroxyethyl-2,2'-Biimidazole via 2-Chloroethanol Route (in D_2O)
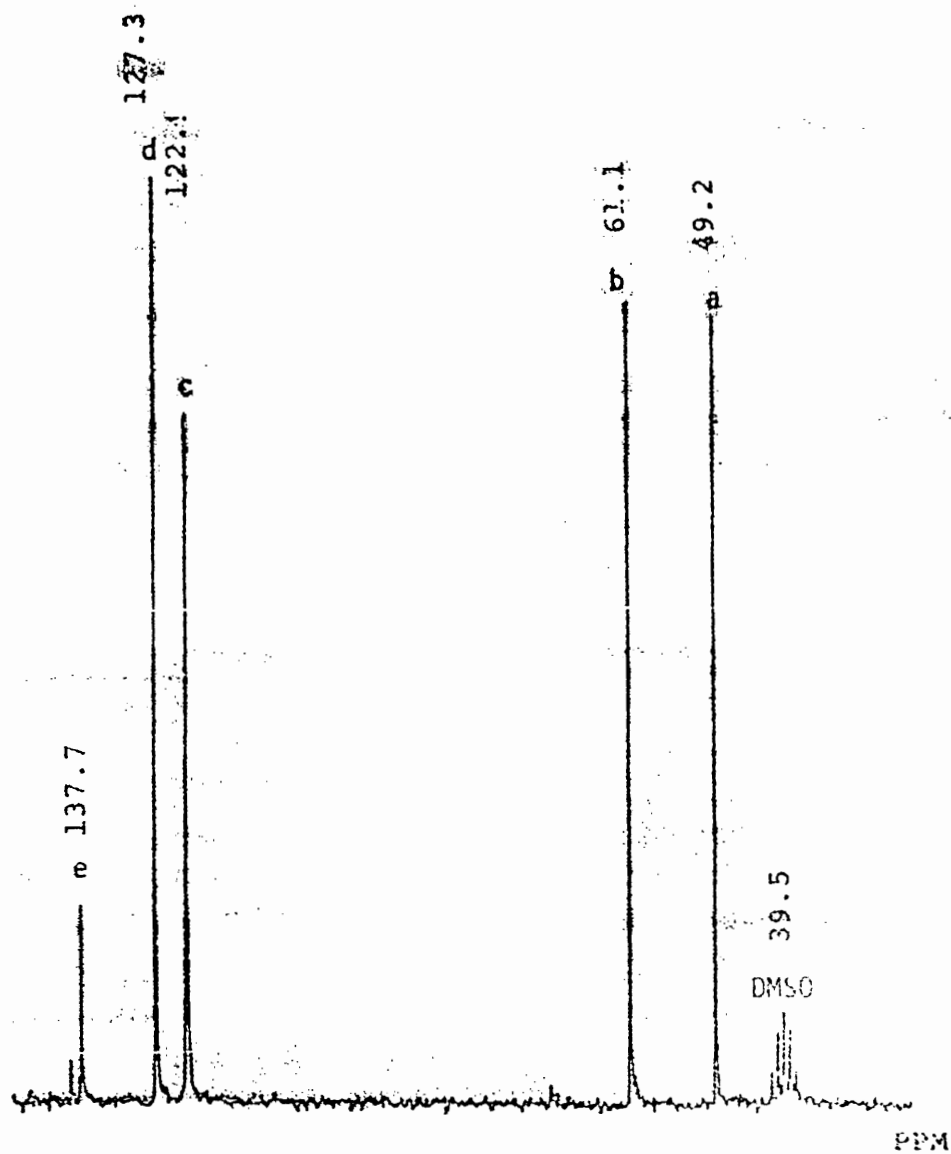
Figure 13. C-13 NMR Spectrum of 1,1'-Dihydroxyethyl-
2,2'-Biimidazole via 2-Chloroethanol Reat-
(in DMSO-d$_6$)
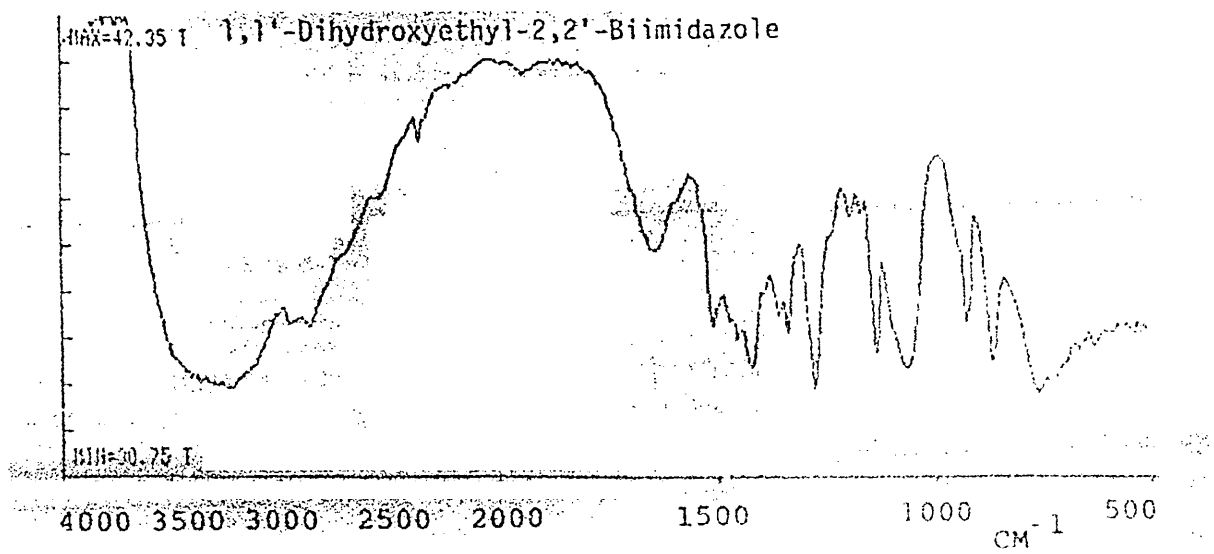
Figure 14.   IR Spectrum of 1,1'-Dihydroxyethyl-2,2'-Biimidazole

the spectrum was analyzed according to frequencies given by Morrison and Boyd [17] and are listed in Table VII.

C. THE PREPARATION OF POLYCARBONATES

Table I summmarizes the conditions used in the synthesis of polycarbonates. The reactions in the preparation of these polycarbonates were carried out in two ways: transesterification in the melt and in solution polymerization. It is possible to produce polycarbonates by the transesterification in the melt. However, the high viscosity of the melt of the polycarbonate formed prevents the production of a polymer of molecular weight above 10,000. This indicates that the use of sodium methoxide or titanium tetrachloride as catalysts has little effect.

The polymerization reaction was carried out by transesterification in solution to increase the molecular weight of the polycarbonate. Polymerization reactions carried out with an equimolar ratio of diol and diphenyl carbonate using titanium tetrachloride as catalyst gave the highest molecular weight. Table VIII lists the results obtained for the yield and physical form of the polymer and method of isolation.

TABLE VII

1,1'-DIHYDROXYETHYL-2,2-BIIMIDAZOLE

INFRARED ASSIGNMENTS

Bond	Frequency (CM^{-1})
O-H	3283
C-H	2943 - 2858
C-O	1063
C---C	1646
C-N Aromatic	1361
C-H Aromatic in plane bending	1276, 1134, 1063
out of plane bending	928, 865, 758

TABLE VIII

YIELD, PHYSICAL FORM AND METHOD OF ISOLATION

OF POLYCARBONATES

Sample	Yield (g)	Physical Form	Isolation Method
PC-1	0.6640	gum	none
PC-2	0.3870	gum	none
PC-3	0.3710	gum	none
PC-4	0.7070	gum	none
PC-5	0.2300	gum	none
PC-6	0.4360	gum	none
PC-I	2.2358	solid	a
PC-II	3.0106	gum	a
PC-III	1.5192	powder	a
PC-IV	1.8376	gum	b
PC-V	1.9802	gum	b
PC-VI	1.2634	gum	b
PC-VII	2.4328	gum	a
PC-VIII	2.6370	solid	a
PC-IX	1.8170	solid	a
PC-X	1.6388	gum	b
PC-XI	0.5910	gum	b
PC-XII	0.7455	gum	b

TABLE VIII (cont.)

Sample	Yield (g)	Physical Form	Isolation Method
PC-XIII	5.8172	solid	a
PC-XIV	2.2638	solid	a
PC-XV	5.2907	solid	a
PC-XVI	0.7913	gum	b
PC-XVII	0.962	gum	b
PC-XVIII	0.8441	powder	a

a : Precipitated from solution using water

as solvent and dried in vacuum oven for 1 week.

b : Solvent evaporated in vacuum oven.

The observation that polycarbonates of molecular weight range of 7,943- 17,782 for reaction conditions where the diol/carbonate ratio was varied to 2:1 and 1:2 indicates that the consideration of the role of the catalyst and possible formation of intermediate oligomers can give rise to polymer formation. The following sequence of interactions are suggested:

$$HO\text{-}R'\text{-}OH + {}^-OMe \rightleftharpoons HO\text{-}R'\text{-}O^- + CH_3OH \qquad (6)$$

$$\underset{\displaystyle RO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR + {}^-O\text{-}R'\text{-}OH \rightleftharpoons RO\text{-}\underset{\underset{\displaystyle O\text{-}R'\text{-}OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}\text{-}O\text{-}R}{} \qquad (7)$$

$$RO\text{-}\underset{\underset{\displaystyle O\text{-}R'\text{-}OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}\text{-}OR \rightleftharpoons R\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R'\text{-}OH + {}^-OR \qquad (8)$$

$$\text{I}$$

$${}^-OR + CH_3OH \rightleftharpoons {}^-OCH_3 + R\text{-}OH \qquad (9)$$
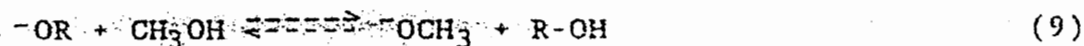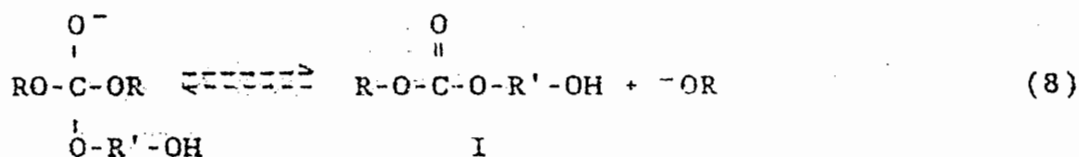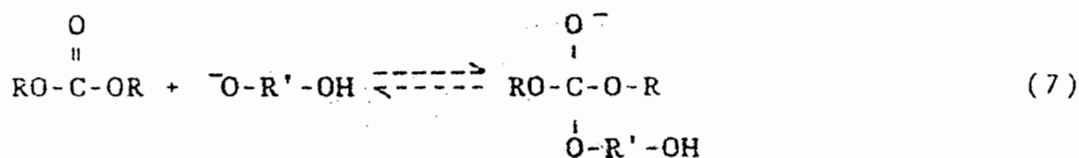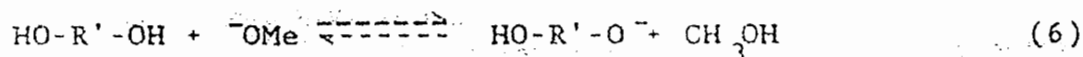
This alcohol-carbonate unit (I) can now react with either a diol or a carbonate as shown in equation (10) and (11).

$$RO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R'\text{-}OH + HO\text{-}R'\text{-}OH \rightleftharpoons HO\text{-}R'\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}R'\text{-}OH + R\text{-}OH$$

$$\text{II} \qquad (10)$$

$$
\overset{\text{O}}{\underset{\|}{}} \qquad \overset{\text{O}}{\underset{\|}{}} \qquad \overset{\text{O}}{\underset{\|}{}} \qquad \overset{\text{O}}{\underset{\|}{}}
$$

$$
\text{RO-C-O-R'-OH} + \text{RO-C-OR} \quad \rightleftharpoons \quad \text{RO-C-O-R'-O-C-OR} + \text{R-OH}
$$

$$
\text{III} \qquad (11)
$$
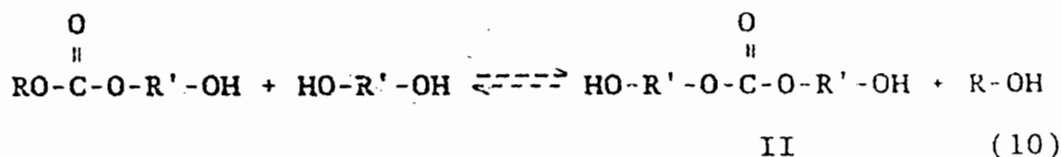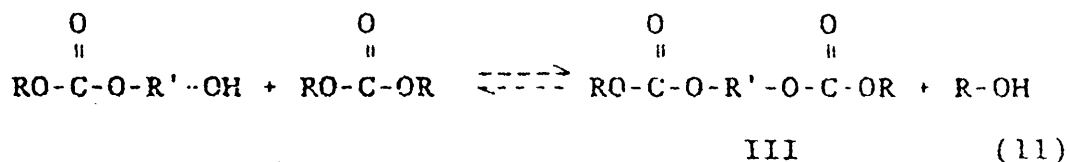
The chain capped with the two alcohol groups (II) can now condense with a molecule containing a carbonate group, while the molecule capped with two carbonate functional groups (III) can react with a molecule containing an alcohol functional group as shown in equation (12).
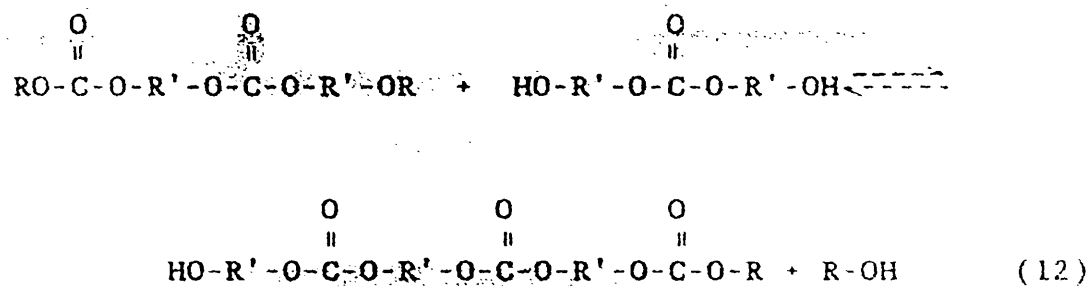
$$
\overset{\text{O}}{\underset{\|}{}} \qquad \overset{\text{O}}{\underset{\|}{}} \qquad\qquad\qquad \overset{\text{O}}{\underset{\|}{}}
$$

$$
\text{RO-C-O-R'-O-C-O-R'-OR} + \text{HO-R'-O-C-O-R'-OH} \rightleftharpoons
$$

$$
\overset{\text{O}}{\underset{\|}{}} \qquad\quad \overset{\text{O}}{\underset{\|}{}} \qquad\quad \overset{\text{O}}{\underset{\|}{}}
$$

$$
\text{HO-R'-O-C-O-R'-O-C-O-R'-O-C-O-R} + \text{R-OH} \qquad (12)
$$

This continues through the monomer matrix wherever molecules of different functionalities having the necessary energy of activation and correct geometry collide. The net result is the formation of dimer, trimer, tetramer, etc. and eventually a polymer.

D. CHARACTERIZATION OF POLYCARBONATES

1. Solubility.

Polycarbonates obtained either by transesterification in the melt or by polycondensation in solution in any ratio without catalyst were soluble in most commonly employed solvents (as shown in Appendices A and B). Similar results were observed for polycarbonates obtained by using basic catalyst (NaOMe). This indicates that the polymers are linear and that there is no cross-linking in the backbone. On the other hand, polycarbonates obtained by using titanium tetrachloride showed little or no solubility in most solvents. This could indicate some degree of crystallinity and/or crosslinking in the polymers possibly from titanium incorporation. Crystallinity leads to high physical strength and increased solvent and chemical resistance.

2. Infrared Spectra.

Figures 15 through 21 show the infrared absorption spectra of a series of polycarbonates. The gum and viscous liquid samples were analyzed as films on AgCl cells, the solid on KBr pellets. A number of characteristic bands reoccur in the infrared spectra of all the polycarbonates assigned as shown in Table IX. The observed decreased in intensity of strong O-H absoption band from 3114-3315 cm^{-1}
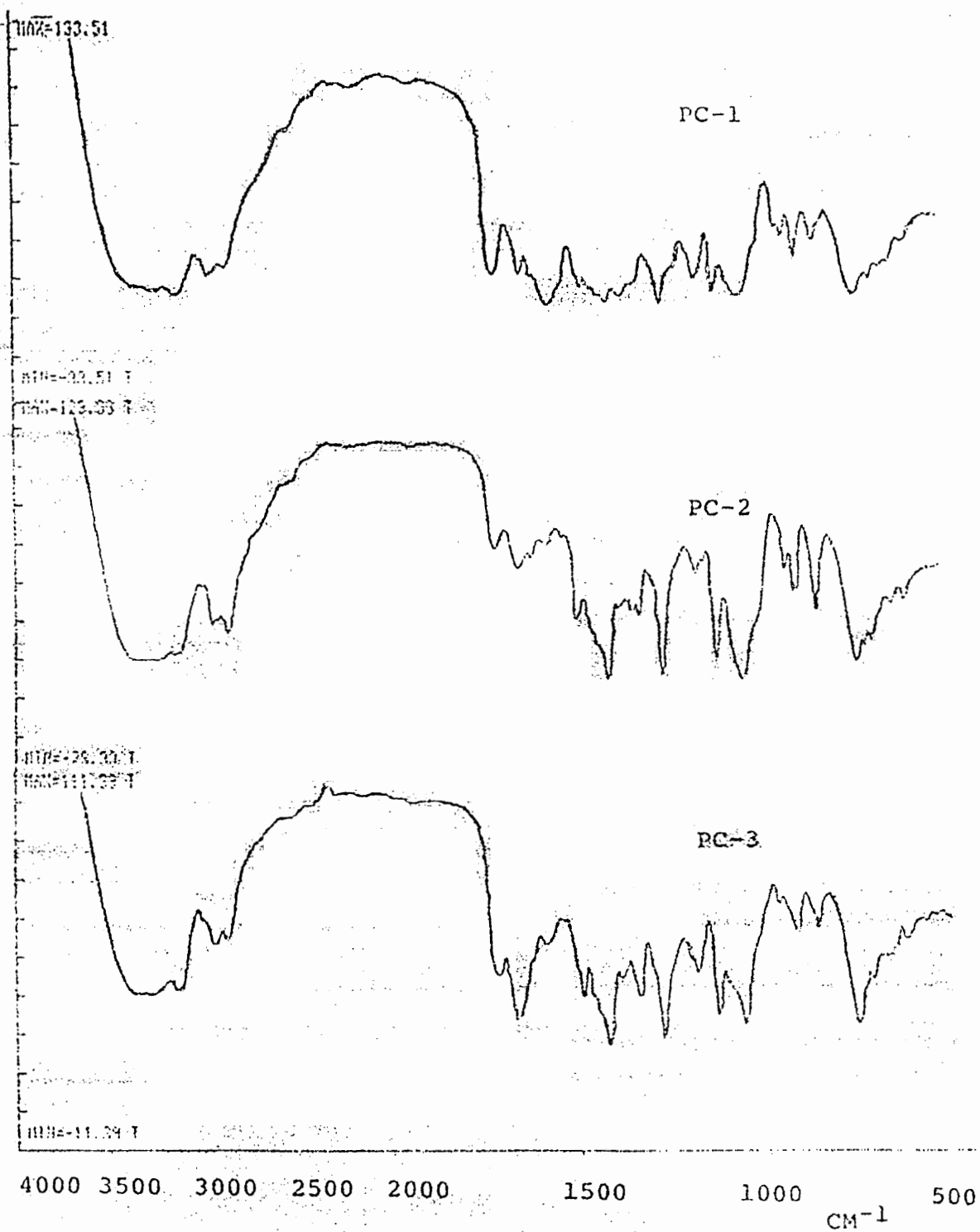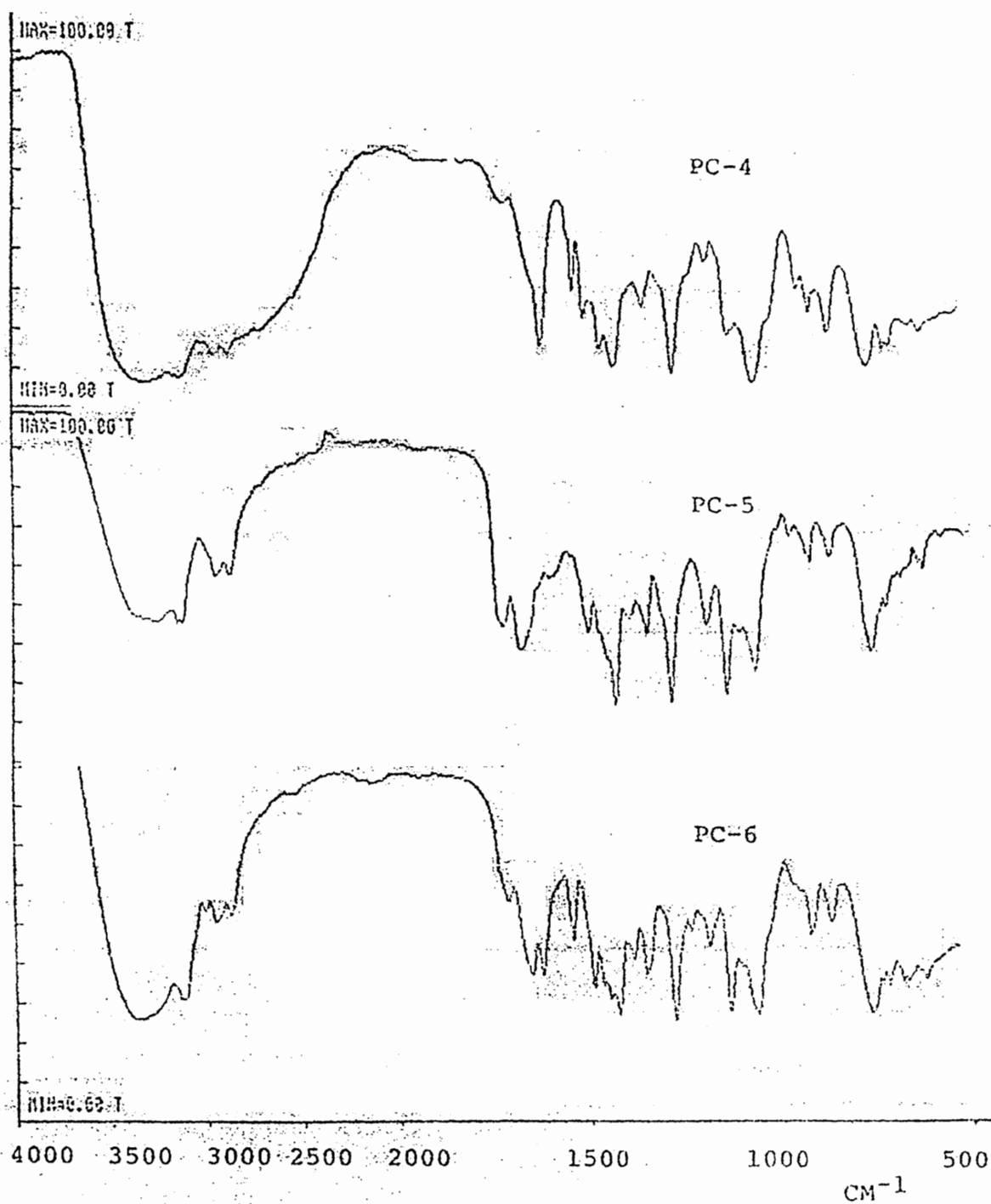
Figure 15. IR Spectra of PC-1, PC-2 and PC-3

Figure 16. IR Spectra of PC-4, PC-5 and PC-6
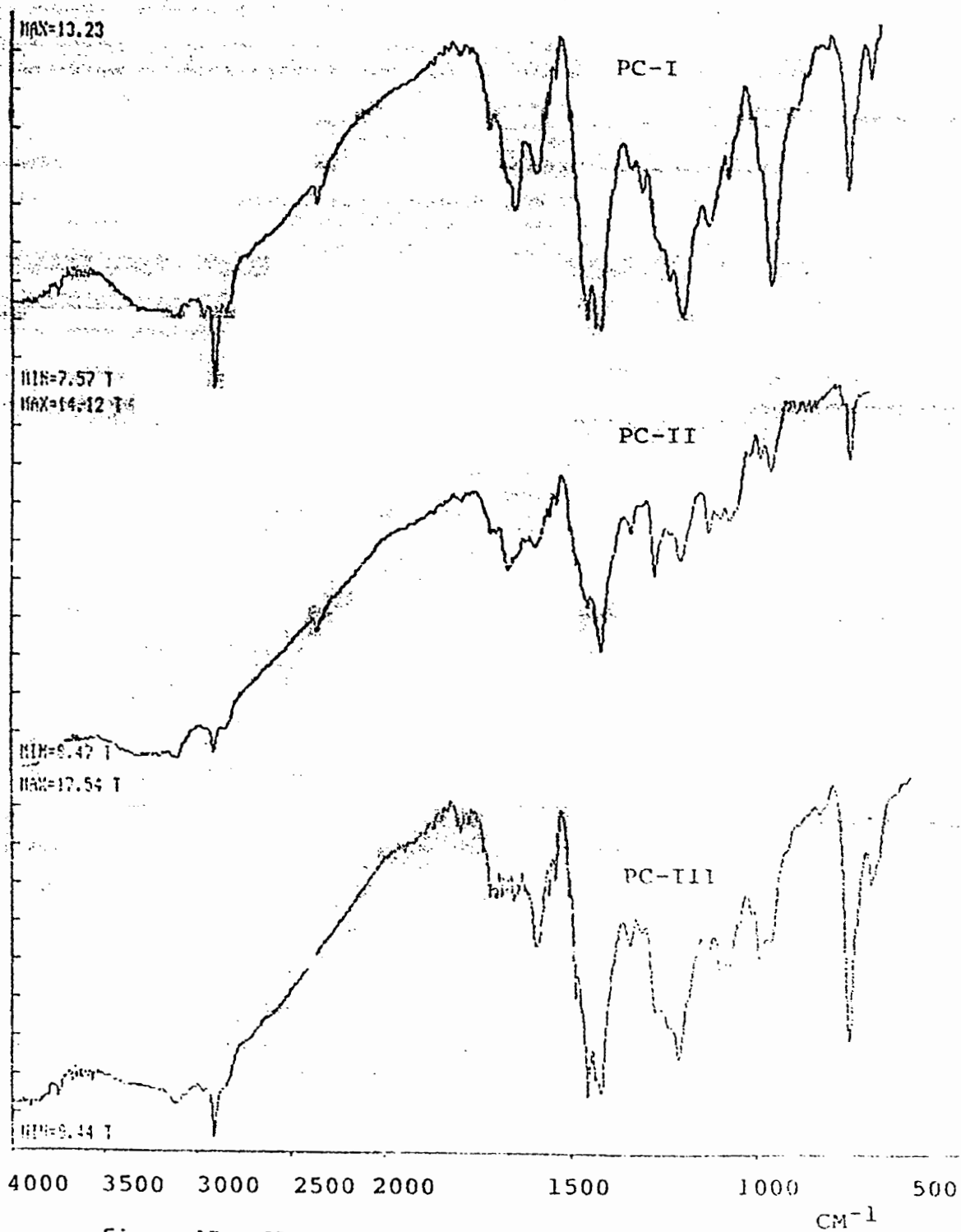
Figure 17. IR Spectra of PC-I, PC-II and PC-III
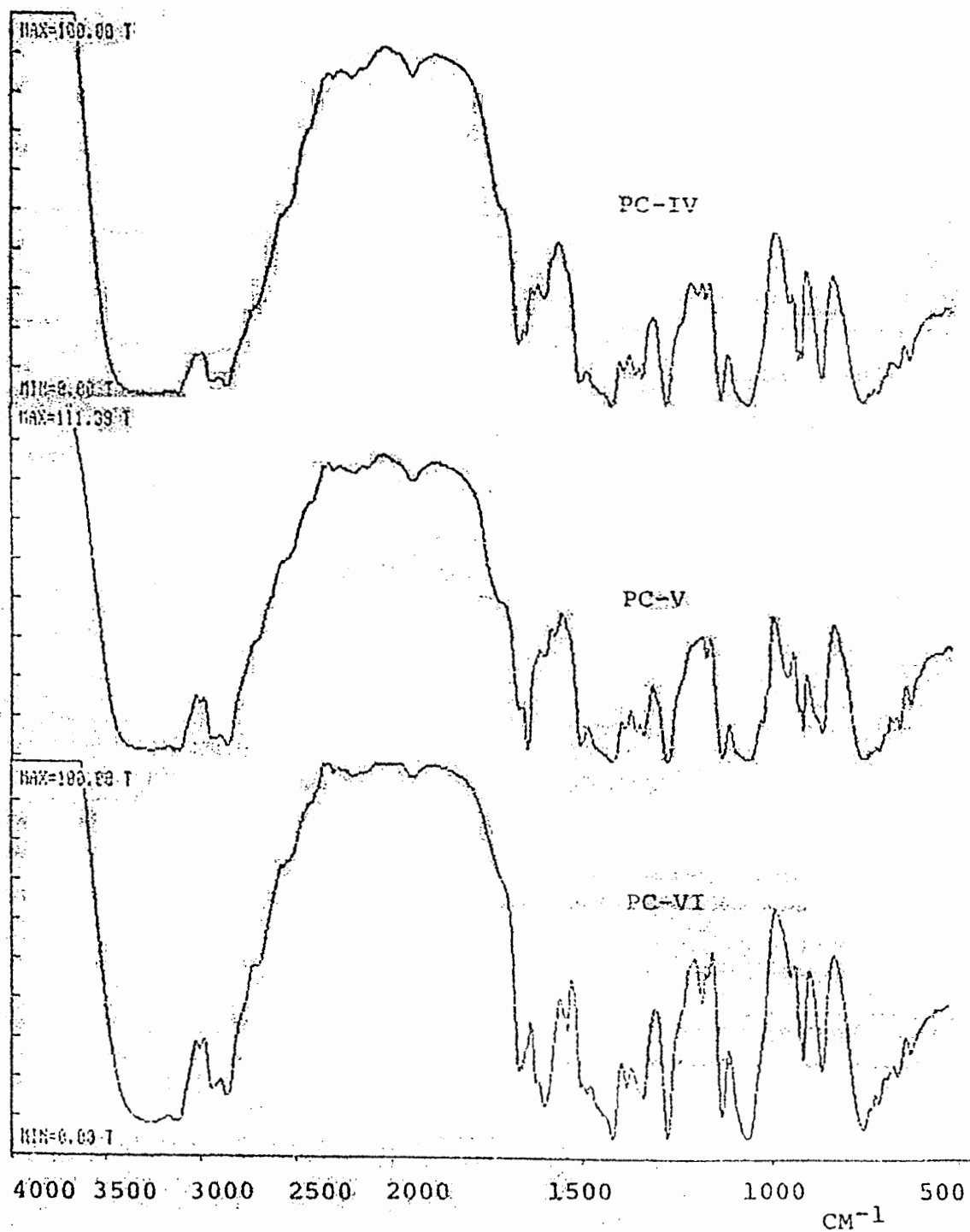
Figure 18. IR Spectra of PC-IV, PC-V and PC-VI
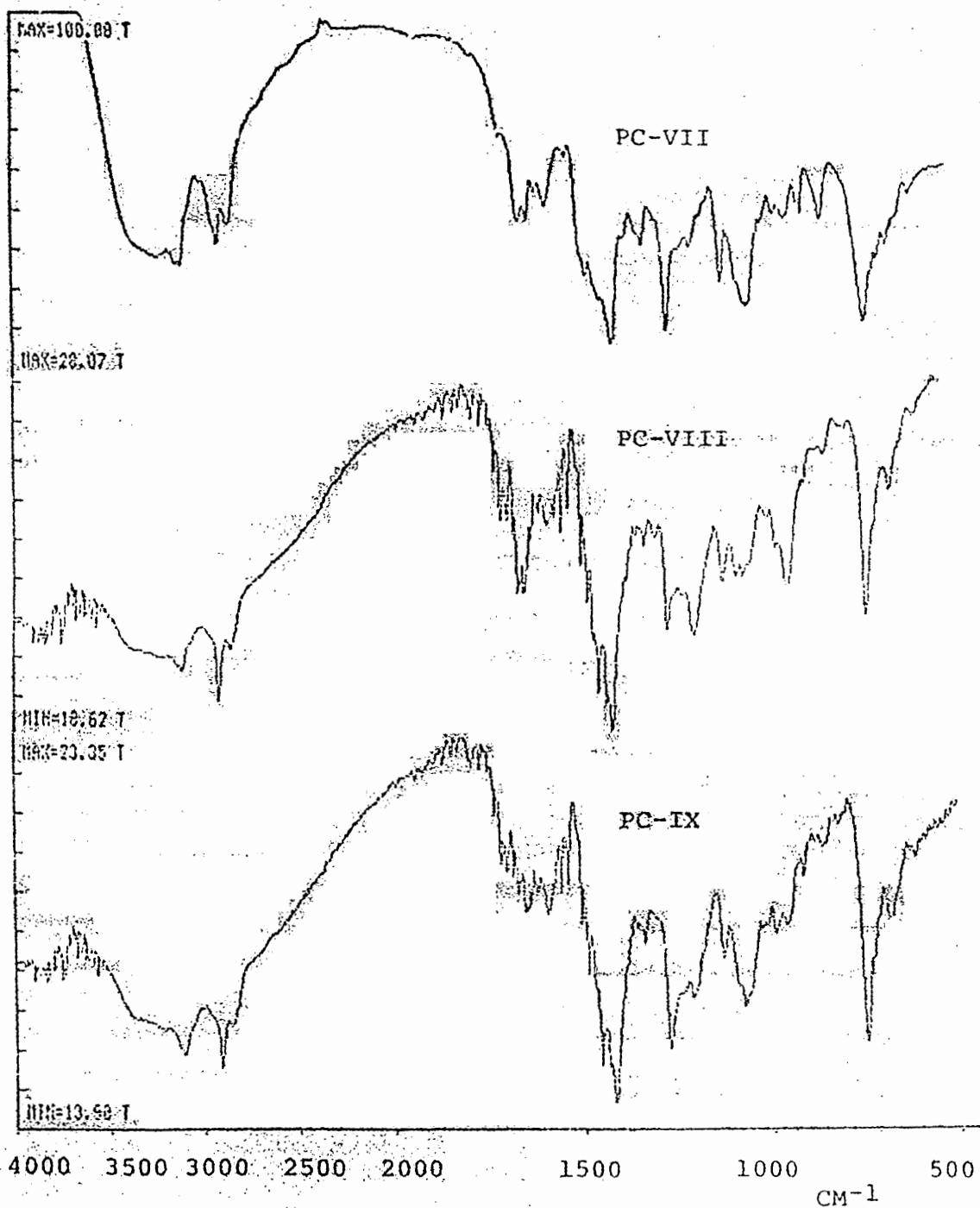
Figure 19. IR Spectra of PC-VII, PC-VIII and PC-IX
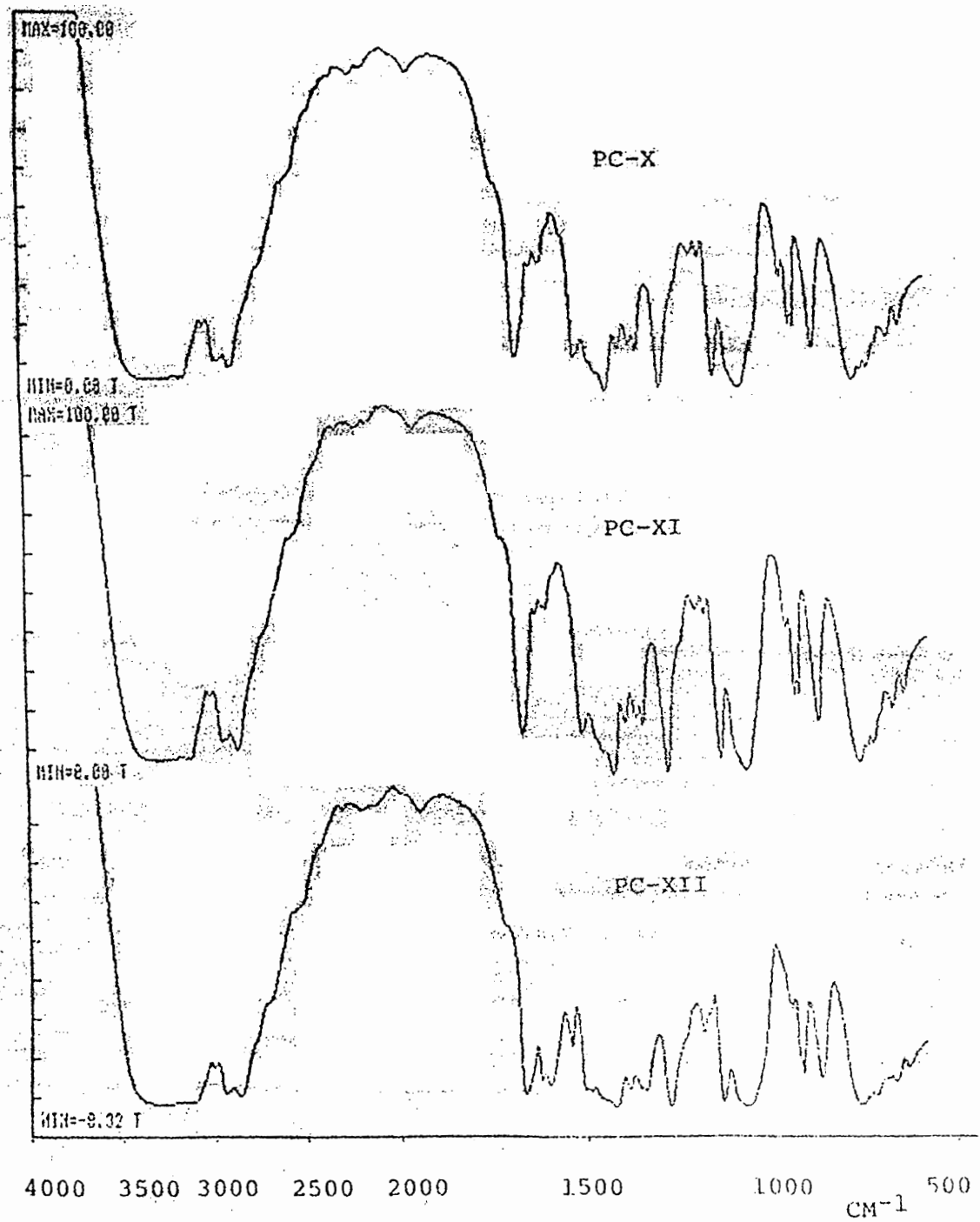
Figure 20. IR Spectra of PC-X, PC-XI and PC-XII
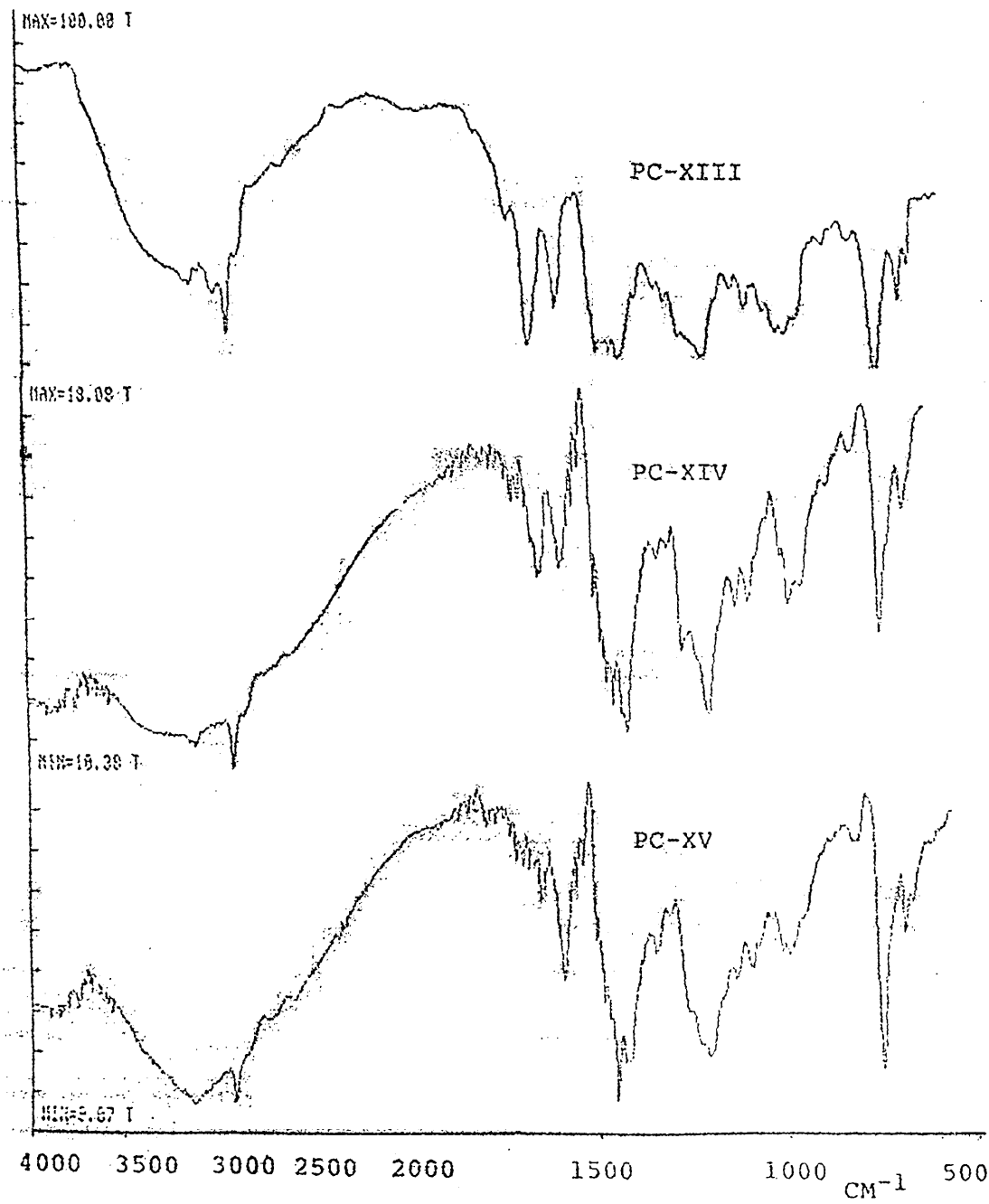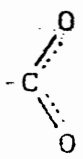
Figure 21. IR Spectra of PC-XIII, PC-XIV and PC-XV

TABLE IX

INFRARED ASSIGNMENTS OF POLYCARBONATES

Bond	Frequency (CM^{-1})
O-H	3315 - 3114
C-H	2953 - 2861
$-C \begin{smallmatrix} O \\ O \end{smallmatrix}$	1718 - 1663
C-O	1068 - 1061
C...C	1671 - 1646
C-N Aromatic	1357 - 1340
C-H Aromatic in plane bending	1136 - 1133
	1276 - 1280
out of plane bending	769 - 757
	867 - 872

for samples where diphenyl carbonate was used as initial carbonate is interpreted to indicate that diphenyl carbonate is more reactive than diethyl carbonate. The rest of the spectrum was analyzed according to frequencies given by Morrison and Boyd [17] and Silverstein [37].

3. NMR.

The proton NMR spectra of polycarbonates prepared by the reaction of 1,1'-dihydroxyethyl-2,2'-biimidazole and carbonate in a 1:1, 2:1, and 1:2 diol to carbonate ratio were obtained using deuterated acetic acid as solvent (Figures 22-24). The proton absorptions are summarized in Tables X. According to the proposed structure for 1:1, 2:1, and 1:2 diol to carbonate reacting ratios to form polymers. labels have been assigned to the different proton environments as shown in Figure 25-27. There seems to be a trend in the spectra obtained for polymers prepared where the ratio of diol to carbonate was varied from 1:1 to 2:1 and 1:2. The spectra obtained for polymers PC-V and PC-VI where the ratio of diol to carbonate is 1:1, have close similarity. The ring hydrogens are assigned to 7.4 and 7.5 ppm; ethyl hydrogens are identified with peaks at 3.8 and 4.3 ppm. The integrated spectra gives a hydrogen ratio of 1:1:2:2 assigned to ring and ethyl hydrogens respectively. The peak appearing at 2.7 ppm is due to the solvent (DMF). All these spectra show broad peaks probably due to the high
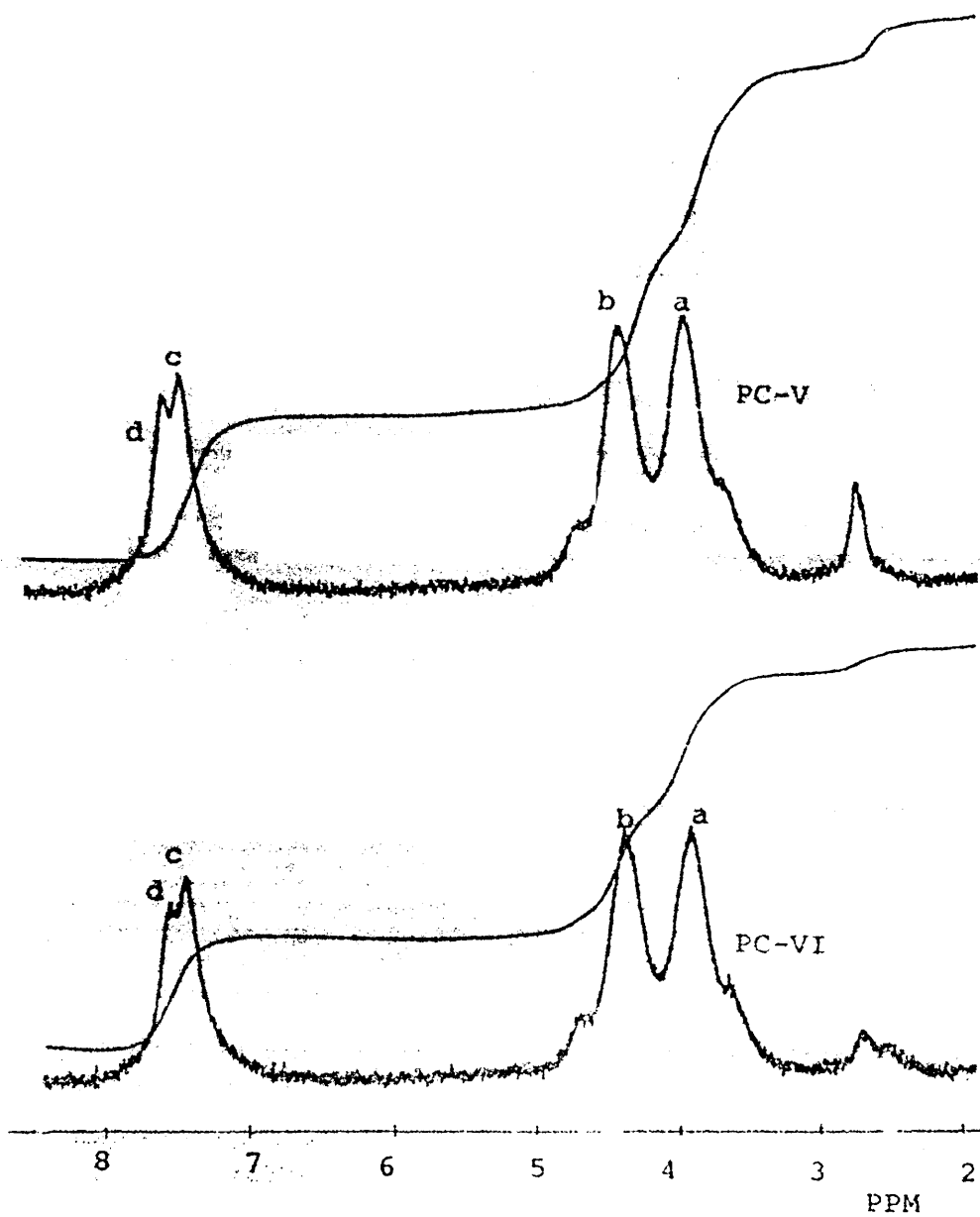
Figure 22. H-NMR Spectra of PC-V and PC-VI
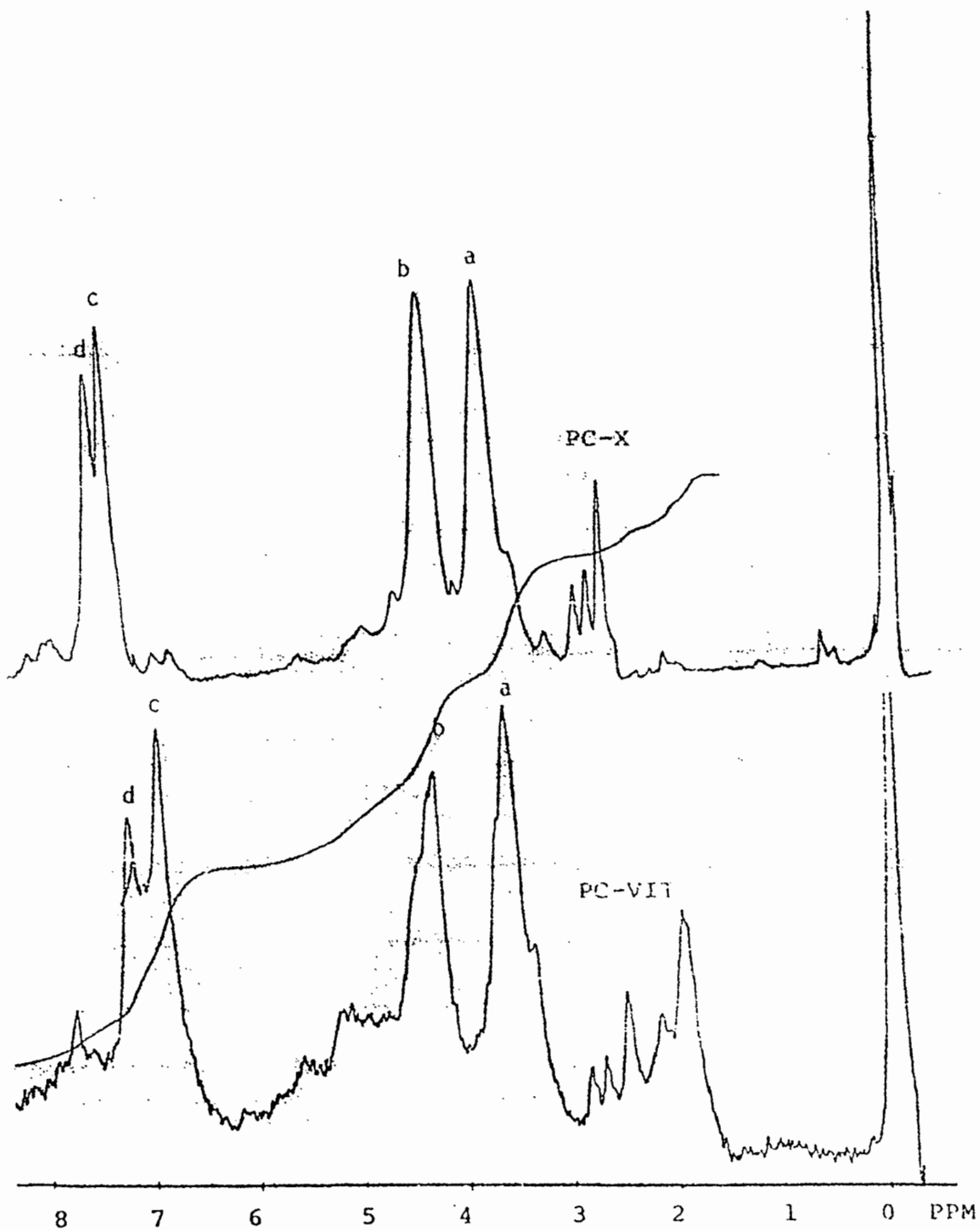
Figure 23. H-NMR Spectra of PC-VII and PC-X
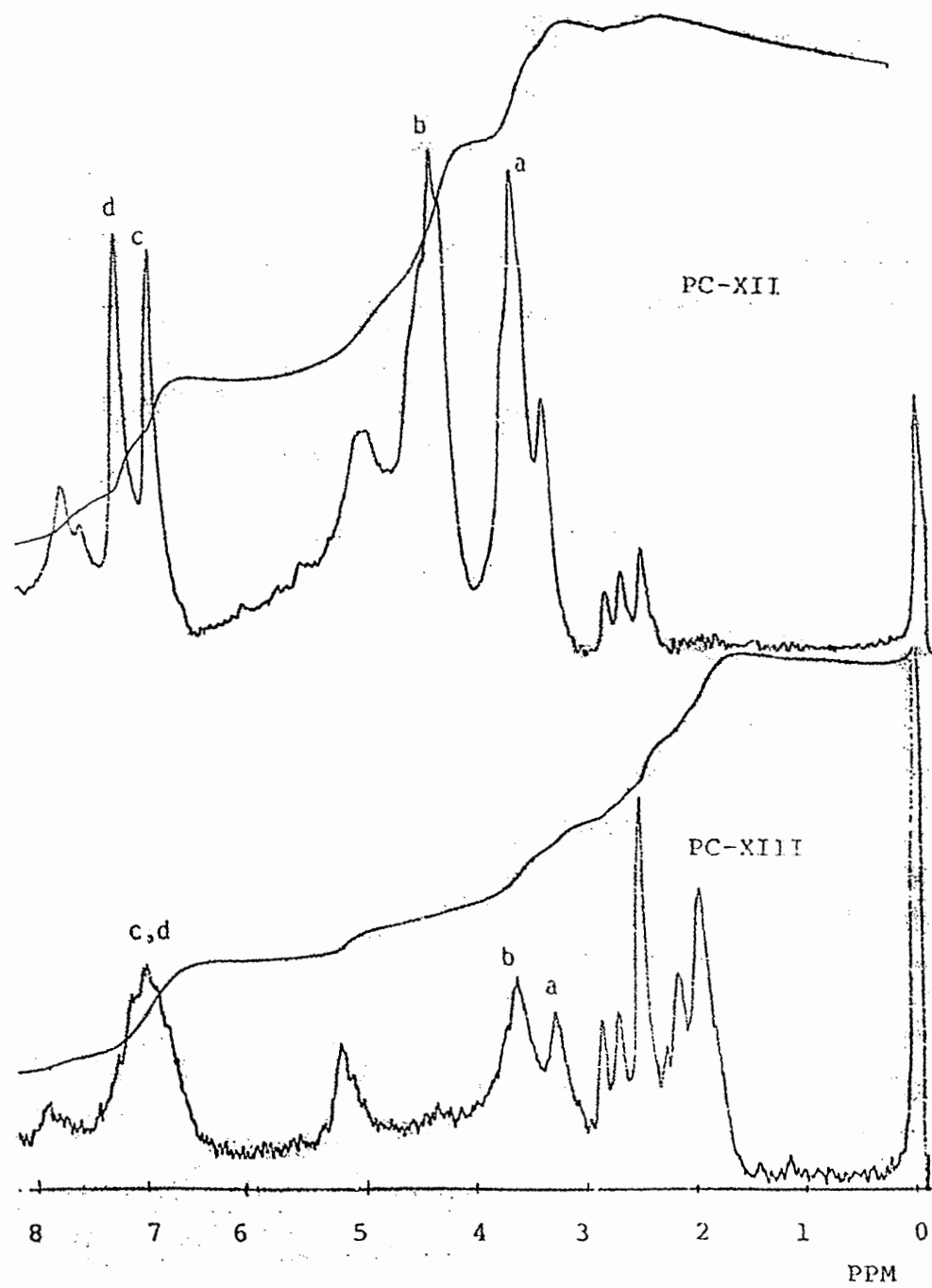
Figure 24. H-NMR Spectra of PC-XII and PC-XIII

TABLE X

SUMMARY OF PROTON NMR ABSORPTIONS OF POLYCARBONATES

Sample	Chemical Shift (PPM)			
	a	b	c	d
PC-V	3.85	4.3	7.4	7.5
PC-VI	3.9	4.3	7.4	7.55
PC-VII	3.65	4.3	6.9	7.2
PC-X	3.8	4.4	7.4	7.5
PC-XII	3.5	4.2	6.8	7.2
PC-XIII	3.6	5.2	7.0	7.0
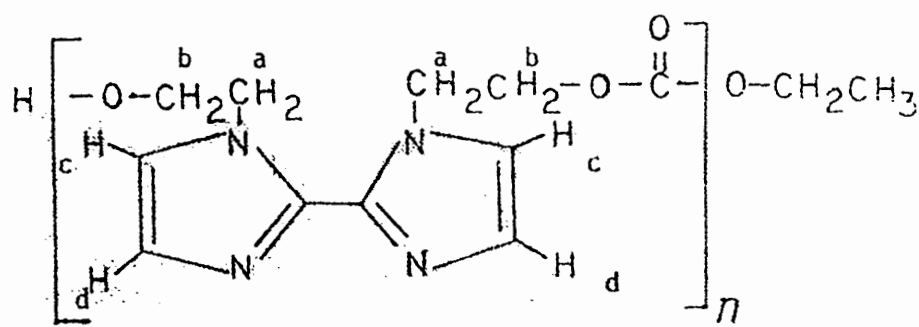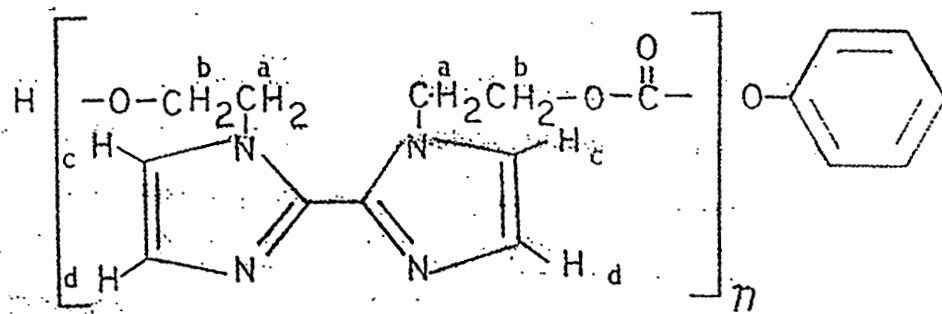
Figure 25.   Proposed Structure for
              1:1 Diol:Carbonate Ratio
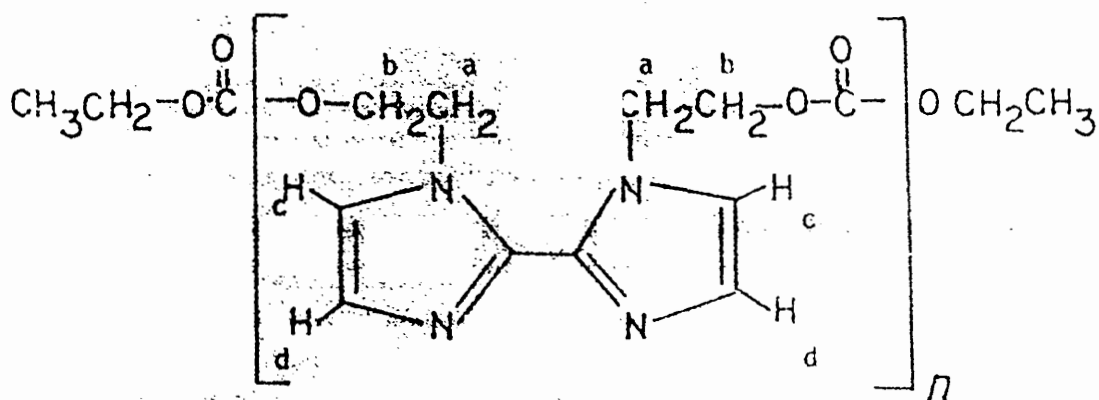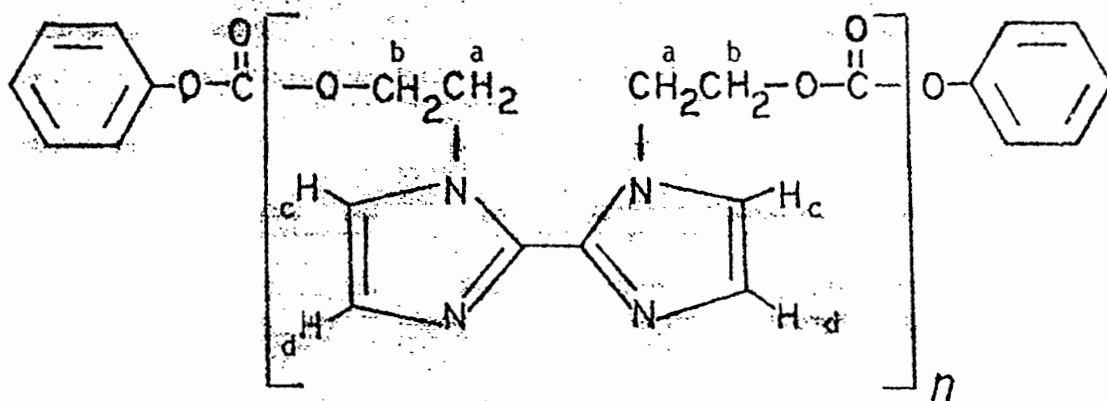
Figure 26. Proposed Structure for
1:2 Diol:Carbonate Ratio
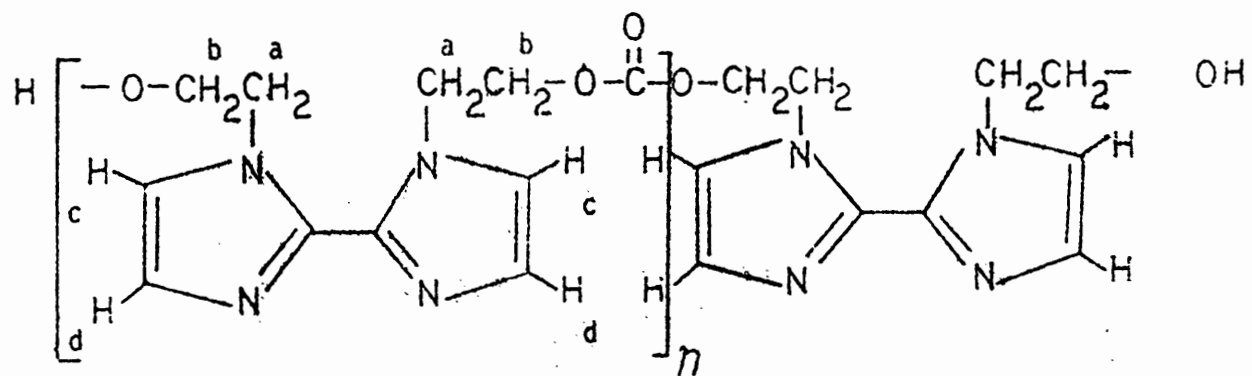
Figure 27.   Proposed Structure for 2:1 Diol:Carbonate Ratio

viscosity of the polymer solution. The spectra of PC-VII, PC-X and PC-XII prepared using a ratio of 2:1 diol to carbonate also have close similarity. Several extra peaks are observed in all these spectra due to the solvent and impurities. Impurities that could be present are phenol and ethanol (by-products), diethyl carbonate (reactant) and water (use for precipitation). The spectra of PC-XIII has poor resolution due to the presence of lot of impurities. Figure 28 shows a C-13 NMR spectrum of PC-III using VXR-200 at 50 MHz. Tetramethylsilane (TMS) was used as standard. The carbonyl carbon was identified at 153.4 ppm. The aromatic carbons absorb at 137.5, 129.0 and 116.5 ppm and the aliphatic carbons at 30.4 and 15.2 ppm. The proton NMR spectrum of the THF-soluble polymer (PC-I) is shown in Figure 29 using DMSO- d_6 as solvent. The spectrum was ran on a 100MHz JEOL FX-100 NMR instrument.

4. DSC.

Figure 30 shows no obvious glass transition and melting temperature in samples PC-I, III, IX, and XV. While Figure 31 shows a broad melting range for samples PC-II, VIII, and XIV using NaOMe as catalyst. No well-defined melting point indicates a low degree of crystallization. Somewhere above the second-order transition temperature they begin to soften and their transition from the solid to the liquid state occurs at 280- 330°C. It is quite difficult to pinpoint the exact moment of transition from solid to liquid by any one
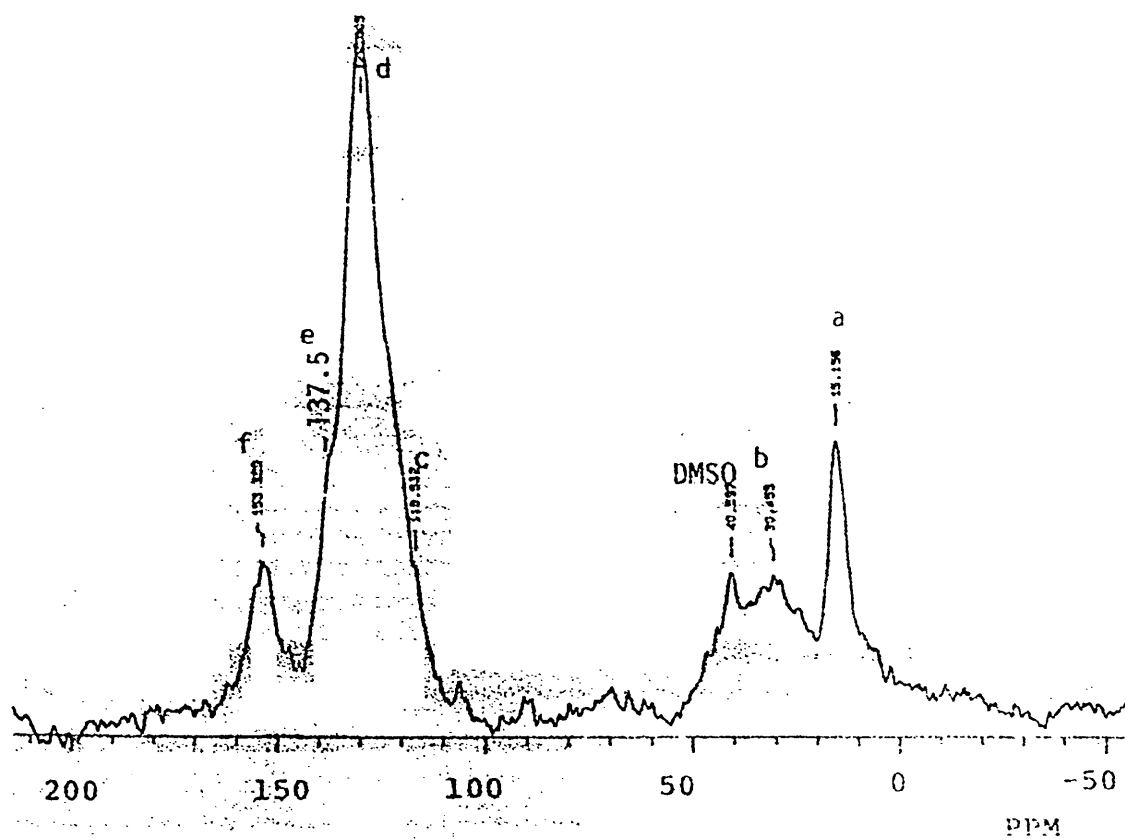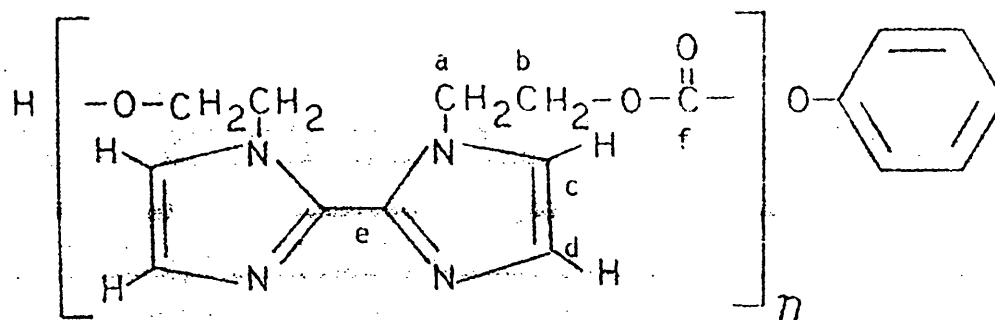
Figure 28. Solid Carbon-13 NMR Spectrum of PC-III
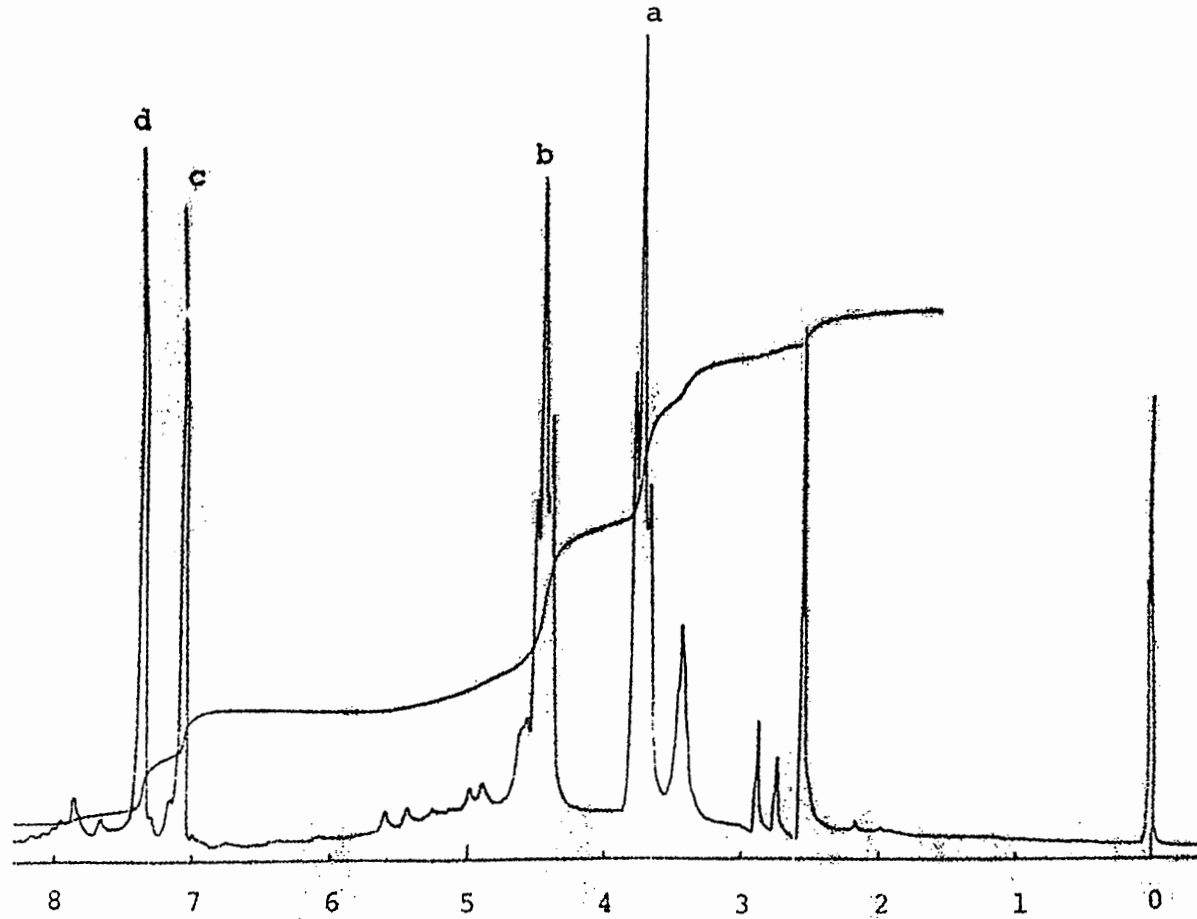
Figure 29. H-NMR Spectrum of PC-I
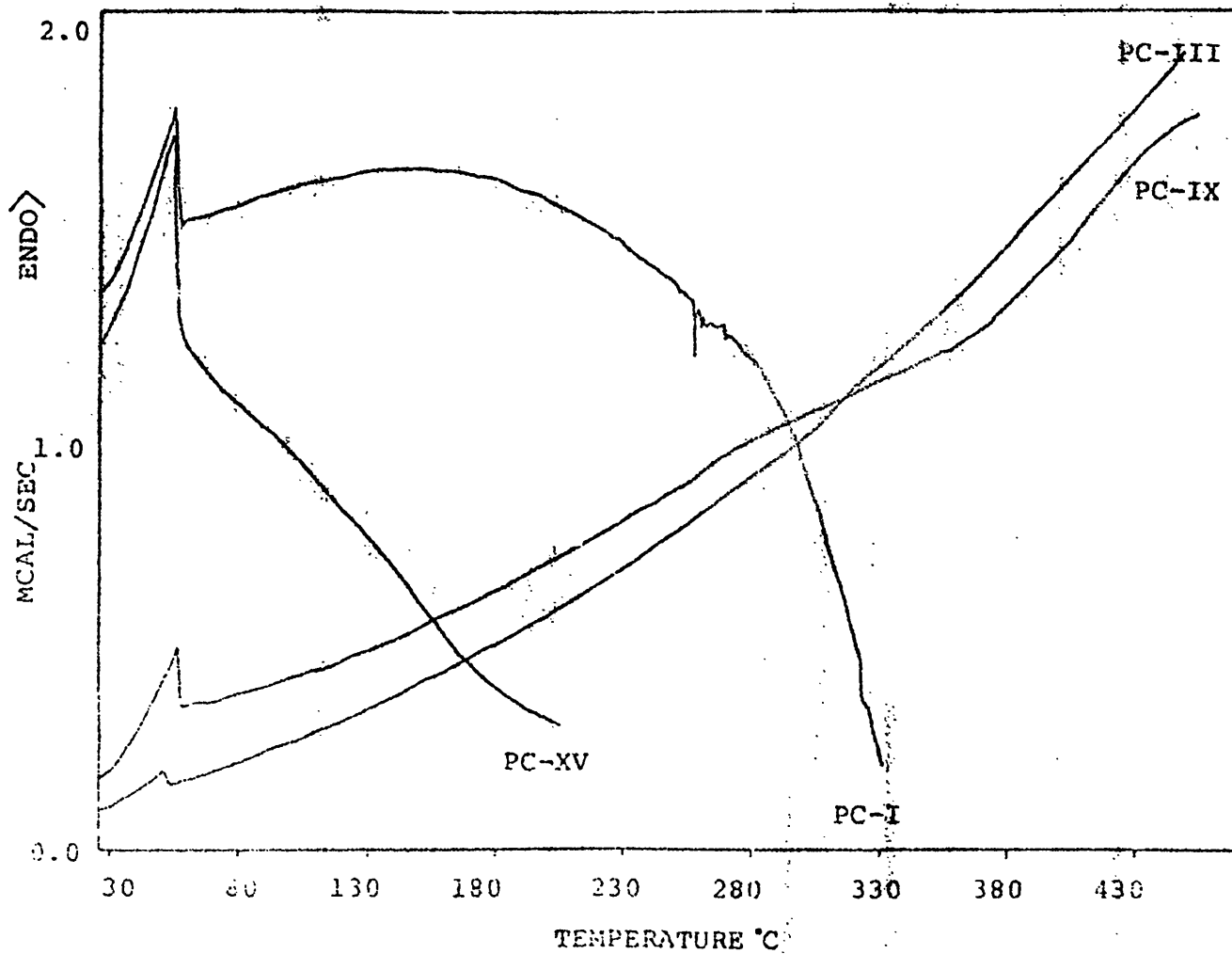
Figure 30. DSC Results of PC-I, PC-III, PC-IX and PC-XV
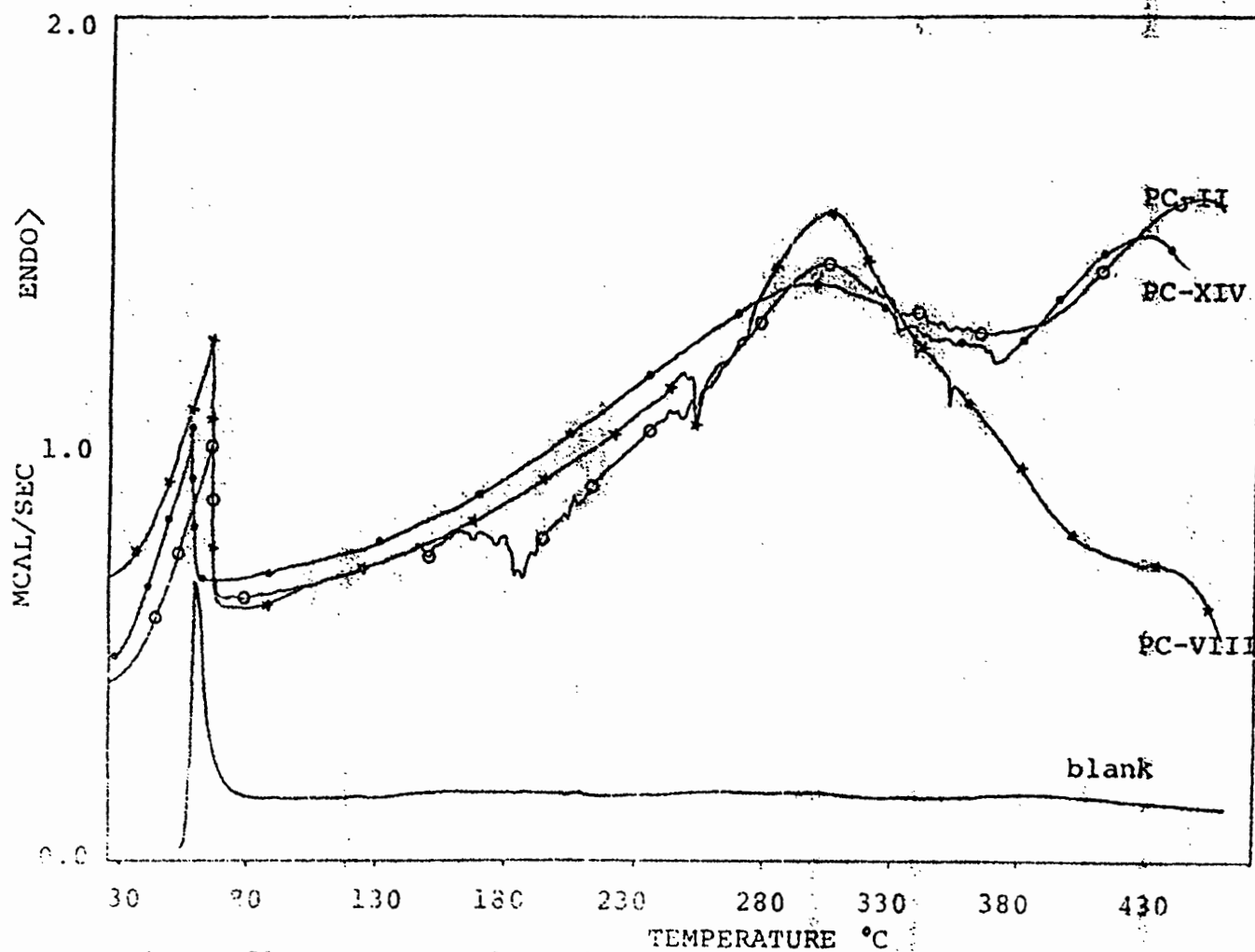
Figure 31. DSC Results of PC-II, PC-VIII and PC-XIV

of the conventional methods for melting point determination. This is because the melt viscosity of the polycarbonates is extremely high in the vicinity of the melting point. The transition occuring at around 50°C in all the DSC measurements is a function of the instrument. This was observed when a blank was run under the same temperature range (Figure 31).

5. TGA.

The results of TGA analysis are given in Table XI and Figure 32. The polymers heated at a rate of 10 C per min undergo less than 9% decomposition below 200 C.

6. Molecular Weight.

Molecular weights of polymers (prepared via ethylene carbonate route) are reported in Table XII. There is a significant increase in the molecular weights when reactions were carried out in solution than by transesterification in the melt. Higher molecular weights were obtained when diphenyl carbonate was used compared to diethyl carbonate. This indicates that transesterification of the hydroxyethylated diol with diethyl carbonate is relatively slow compared to diphenyl carbonate, even at high temperature (210°C) in the presence of catalysts. The

TABLE XI

TGA ANALYSIS OF POLYCARBONATES

Polymer	Temperature($^{\circ}$C) / % Weight loss							
	150	200	250	300	350	400	450	475
PC-I	0.5%	3.0%	10%	23%	30%	34%	38%	40%
PC-II	0.4%	2.4%	8%	22%	28%	32%	35%	37%
PC-III	1.4%	4.6%	14%	18%	24%	28%	34%	38%
PC-IV	2.7%	8.5%	14%	17%	22%	25%	31%	34%

Note: % Weight loss were measured by heating samples
at a rate of 10°C/min.
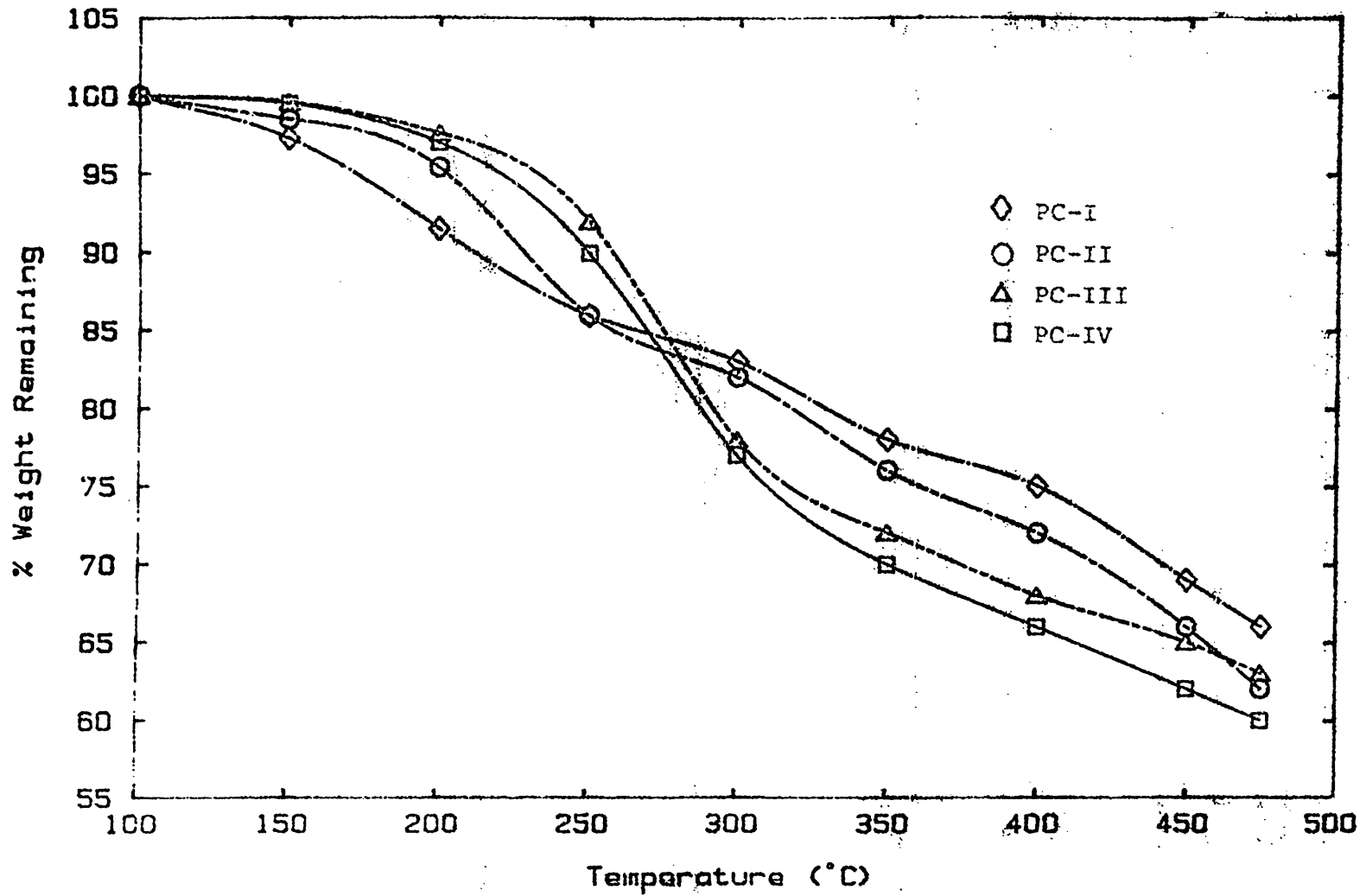
Figure 32 .   TGA Analysis of Polycarbonates

TABLE XII

MOLECULAR WEIGHT DISTRIBUTION OF POLYCARBONATES

Polymer(a)	Distance (cm)	Peak Molecular Weight $(x10^3)$
PC-1	> 12	< 10.0
PC-2	≥ 12	< 10.0
PC-3	> 12	< 10.0
PC-4	> 12	< 10.0
PC-5	> 12	< 10.0
PC-6	> 12	10.0
PC-I	10.2	13.3
PC-II	10.3	11.9
PC-III	9.5	26.6
PC-IV	10.4	10.6
PC-V	10.5	10.0
PC-VI	10.6	8.9*
PC-VII	9.8	17.8
PC-VIII	10.2	13.3
PC-IX	10.0	16.6
PC-X	10.6	8.9*
PC-XI	10.55	9.4*
PC-XII	10.7	7.9*

TABLE XII (cont.)

Polymer(a)	Distance (cm)	Peak Molecular Weight $(x10^3)$
PC-XIII	10.2	13.3
PC-XIV	10.3	11.9
PC-XV	10.5	10.0

a: Diol prepared via ethylene carbonate route

*: Extrapolated Value

Note: The reported molecular weights are relative to Polystyrene standards.

highest molecular weight of 26,600 was obtained with the following reaction conditions: a 1:1 diol to diphenyl carbonate ratio, $TiCl_4$ as catalyst and DMSO as solvent.

Comparison of the molecular weights of polymers obtained where the diol was prepared via ethylene carbonate route as compared to that prepared via 2-chloroethanol route is given in Table XIII. The polymers PC-(I,II,III) were prepared from a diol containing some impurities. While PC-(XVI,XVII,XVIII) were prepared from a pure diol. The molecular weights of the polymers prepared without catalyst (PC-I and PC-XVI) and that prepared with NaOMe as catalyst (PC-II and PC-XVII) were observed to be approximately the same. This suggests that impurity in the monomer (diol) represents a very small fraction of the diol composition and that it apparently has a minimum effect on the polymerization process. However, there is an increase in the molecular weight of PC-XVIII as compared to PC-III. The observed increase in the molecular weight of PC-XVIII is probably due to increased efficiency of $TiCl_4$ catalyst in polymer synthesis using a pure monomer (diol).

TABLE XIII

MOLECULAR WEIGHT COMPARISON OF POLYCARBONATES

Polymer	Mn (x10^{-3})	Mw (x10^3)	Peak Molecular Weight(x10^3)
PC-I	10.9	11.8	12.1
PC-XVI	11.4	12.4	12.6
PC-II	10.2	11.4	11.5
PC-XVII	11.0	11.8	11.9
PC-III	23.2	25.0	25.8
PC-XVIII	35.5	38.3	37.6

PC-(I,II,III): Diol prepared via ethylene carbonate route

PC-(XVI,XVII,XVIII): Diol prepared via 2-chloroethanol route

Mn: Number average molecular weight

Mw: Weight average molecular weight

Note: The reported molecular weights are relative to

Polystyrene standards.

V. CONCLUSION

Linear polycarbonates can be synthesized by the acid or base-catalyzed transesterification reaction of 1,1'-dihydroxyethyl-2,2'-biimidazole and diphenyl or diethyl carbonates. Solution polymerizations carried out in DMSO or DMF promote a higher molecular weight than the reactions without solvent. A pure monomer (diol) is obtained by using 2-chloroethanol as the hydroxyethylating agent. There is no significant difference in the molecular weights obtained for polymers where the monomer (diol) was pure as compared to the polymers where the monomer contains impurities. This is observed only for polymers which are synthesized by non-catalyzed and base-catalyzed (NaOMe) reactions. However, there is a significant increase in the molecular weight of the polymer prepared by using a pure diol as compared to the polymer prepared by using an impure diol where titanium tetrachloride is used as catalyst. The polymers obtained both in the presence and in the absence of NaOMe catalyst were soluble in most commonly employed solvents. This indicates that the polymers are linear and no cross-linking in the backbone. DSC results showed a broad melting range (280- 330°C) indicating low degree of crystallinity. TGA results showed that the polymers undergo less than 9% decomposition below 200°C. Because of the well known metal binding ability of the biimidazole functionality, its evaluation as an electrically conductive polymer has high priority in the future. Also, synthesis of copolycarbonates

of 1,1'-dihydroxyethyl-2,2'-biimidazole and other aromatic compounds such as bisphenol A or aliphatic dihydroxy compounds should be investigated. It would be interesting to know, as a continuation of this work, whether titanium has been incorporated into those polymers prepared by using titanium tetrachloride as catalyst.

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VITA

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She has been enrolled in the Graduate School of the University of Missouri-Rolla since January 1985.

APPENDIX A

SOLUBILITY OF POLYCARBONATES IN METHANOL, METHYLENE CHLORIDE, THF AND DMF

Solvent	Methanol	Methylene Chloride	THF	DMF
PC-1	ss	s	s	s
PC-2	s	ss	ss	s
PC-3	s	ss	I	s
PC-4	s	I	I	s
PC-5	s	ss	I	s
PC-6	s	I	I	s
PC-I	I	s	ss	s
PC-II	I	s	ss	s
PC-III	I	ss	ss	s
PC-IV	s	s	s	s
PC-V	s	s	s	s
PC-VI	ss	s	I	s
PC-VII	ss	s	s	s
PC-VIII	I	s	s	s
PC-IX	I	ss	I	s
PC-X	s	s	s	s
PC-XI	s	s	s	s
PC-XII	ss	s	I	s

Solvent	Methanol	Methylene Chloride	THF	DMF
PC-XIII	I	s	ss	s
PC-XIV	I	I	ss	ss
PC-XV	I	I	I	ss
PC-XVI	I	ss	ss	ss
PC-XVII	I	ss	ss	ss
PC-XVIII	I	I	ss	ss

I : Insoluble

s : soluble

ss : slighly soluble

APPENDIX B

SOLUBILITY OF POLYCARBONATES IN DMSO, ACETIC ACID AND CHLOROFORM

Solvent	DMSO	Acetic acid	Chloroform
PC-1	s	ss	s
PC-2	s	s	ss
PC-3	s	ss	ss
PC-4	ss	I	I
PC-5	s	s	I
PC-6	I	ss	I
PC-I	s	s	s
PC-II	s	s	s
PC-III	ss	I	I
PC-IV	s	s	s
PC-V	s	s	s
PC-VI	s	s	s
PC-VII	s	s	s
PC-VIII	s	s	s
PC-IX	s	s	s
PC-X	s	s	s
PC-XI	s	s	s
PC-XII	s	s	s

Solvent	DMSO	Acetic acid	Chloroform
PC-XIII	s	I	s
PC-XIV	I	I	I
PC-XV	I	I	I
PC-XVI	s	s	ss
PC-XVII	s	s	ss
PC-XVIII	ss	I	I

I : Insoluble

s : soluble

ss : slighly soluble