

Aliphatic Heterocyclic Polymers

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Synopsis

Aliphatic polybenzoxazoles, polybenzothiazoles, and polybenzimidazoles have been prepared by three methods: in poly(phosphoric acid), by the polyamide precursor, and by melt polymerization. The melt polymerization method was found to be the most satisfactory. All of the aliphatic heterocyclic polymers had excellent thermal stability, resistance to alkaline hydrolysis, high glass transition temperatures, and a high degree of flexibility. The only class of polymer found having any degree of solubility, however, was the polybenzimidazoles. Aliphatic polybenzimidazole films were prepared by solution casting. These films were found to be extremely flexible at ambient and cryogenic temperatures. The films were unaffected by alkaline hydrolysis, even in an oxidizing medium. A molding prepared from the aliphatic polybenzimidazole had excellent physical properties at both cryogenic and room temperature.

INTRODUCTION

An aliphatic polybenzoxazole prepared by the melt condensation of 3,3'-dihydroxybenzidine with sebacic acid has been reported¹ which had an inherent viscosity of 0.53 (0.5% in *m*-cresol). Imai and co-workers² prepared the same polymer having an inherent viscosity of 0.40 (0.2 g./100 ml. of conc. H₂SO₄) via condensation in poly(phosphoric acid). These polymers reportedly are soluble in *m*-cresol or formic acid, but become severely degraded by alkaline or acidic hydrolysis.

Imai and co-workers² also reported upon the preparation of an aliphatic polybenzothiazole by the condensation of 3,3'-dimercaptobenzidine dihydrochloride with sebacic acid in poly(phosphoric acid) as solvent. This polymer had an inherent viscosity of 0.31 (0.2 g./100 ml. of conc. H₂SO₄), and was reportedly soluble in *m*-cresol or formic acid. It was also seriously degraded by acid hydrolysis.

A polyalkylene benzimidazole, prepared by the melt condensation of 3,3'-diaminobenzidine with sebacic acid, was reported by Brinker.³ This polymer had an inherent viscosity of 1.05 (0.5% in *m*-cresol). Iwakura and workers⁴ prepared the same polymer having an inherent viscosity of 0.69-2.54 (0.2 g./100 ml. of conc. H₂SO₄) via condensation in poly(phosphoric acid).

The purpose of this paper is to compare the properties of these three classes of high molecular weight aliphatic heterocyclic polymers; particular emphasis is placed on their film-forming characteristics.

EXPERIMENTAL

Preparation of Polyalkylene Heterocyclic Polymers in Poly(phosphoric Acid)

Poly(phosphoric acid) (515 g.) was deoxygenated by being heated to 190–200°C. under vacuum, purged with nitrogen, then cooled to room temperature under nitrogen. The amine (0.1 mole) was added, and the system again was purged with nitrogen by evacuation and flushing. The mixture was heated at 100°C. with vigorous stirring for 2 hr. to dissolve the amine. The acid component (0.1 mole), was then added and the system again purged with nitrogen. The condensation was conducted over a 4-hr. period by gradually raising the temperature from 100 to 235°C.; the temperature was maintained at 235°C. during the last hour. The viscous solution was then poured very slowly into 2 l. of rapidly stirred hot water in a Waring Blendor. The finely divided solid was then washed repeatedly with hot 5% sodium carbonate solution, followed by repeated washings with boiling water. The polymer was removed by filtration, and dried under vacuum over phosphorus pentoxide.

Preparation of Polyalkylene Heterocyclic Polymers—Polyamide Precursor Method

The diacid chloride (0.0112 mole) in dimethylacetamide (45 ml.) was added under argon during 40 min. to the amine (0.0112 mole) and sodium carbonate (0.224 mole) in dimethylacetamide (50 ml.) at 1°C. The mixture was then stirred at 2°C. for 0.5 hr, followed by 18 hr. at room temperature. The reaction mixture was poured into water, filtered, and the polymer dried over phosphorus pentoxide under high vacuum.

The precursor polymer was then ring-closed by heating it in argon to 400°C. over a period of 4 hr. and maintaining the temperature at 400°C. for 1 hr.

Melt Condensation of Aliphatic Polybenzimidazoles

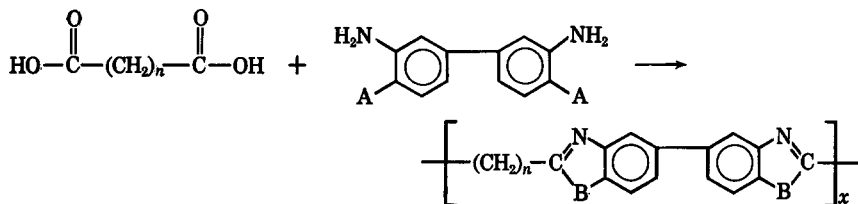
First Stage. A mixture of the diacid (0.03 mole) and 3,3'-diaminobenzidine (0.03 mole) was added to the reaction flask and then purged with nitrogen by alternate evacuation and refilling. It was then immersed in a silicone oil bath at 200–205°C. and stirred for 1 hr., during which time the polymer gradually solidified with foaming. Heating was continued for an additional 130 min. at 205–245°C. This prepolymer had an inherent viscosity of 0.1–0.3 (0.5% in conc. H_2SO_4).

Second Stage. The prepolymer from the first stage was pulverized and heated under nitrogen for 4.5 hr. at 280–305°C. The adhesion of the polymer to glass was so great that the glass reaction vessel shattered upon cooling. The inherent viscosity of this polymer was 2.19.

Polymers suitable for solution casting generally had an inherent viscosity of 0.80–1.00. These polymers were prepared by heating at 300–310°C. for 1–2 hr.

RESULTS AND DISCUSSION

Aliphatic polybenzimidazoles, polybenzoxazoles, and polybenzothiazoles were prepared as outlined below.



If A = OH, B = O (polybenzoxazole)
 If A = SH, B = S (polybenzothiazole)
 If A = NH₂, B = NH (polybenzimidazole)

Aliphatic Polybenzoxazoles

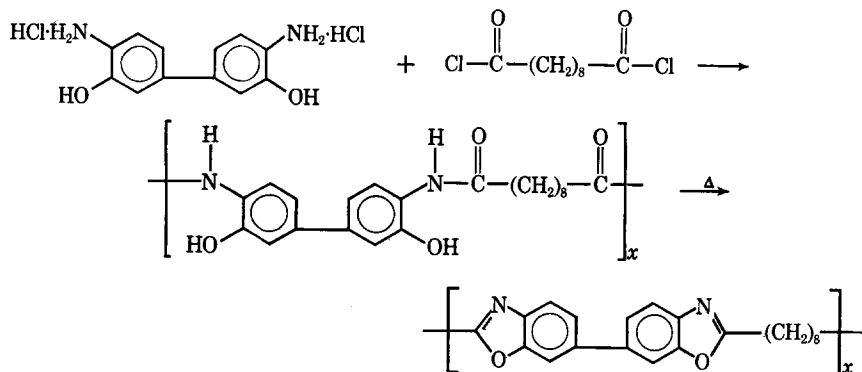
The aliphatic polybenzoxazole based on 3,3'-dihydroxybenzidine dihydrochloride and sebacic acid was prepared in poly(phosphoric acid). Isolating this polymer from the poly(phosphoric acid) was an extremely difficult and laborious task. The polymer was of such a high molecular weight that it was insoluble in all common solvents, including sulfuric acid. However, films could be prepared by hot pressing techniques. The properties of this polymer are listed in Table I.

TABLE I
 Properties of Poly-2,2'-Octamethylene-6,6'-Bibenzoxazole

Hydrolytic stability in refluxing 40% KOH after 3 hr.	Glass transition temp., °C.	Polymer fusion temp., °C.	Polymer decomposition temp. by TGA, °C.
Unaffected	350	282 at 200 psi	Helium—445 Air—345

It should be noted that this polymer was not degraded by alkaline hydrolysis, as reported previously,^{1,2} probably because of much higher molecular weight. Based on thermogravimetric analysis, the polymer is apparently sensitive to oxidation; nevertheless, its thermal stability is outstanding.

This polymer was also prepared via the polyamide precursor; i.e.,



The precursor polymer was soluble only in sulfuric acid and had an inherent viscosity of 0.43 (0.5% in conc. H_2SO_4). Higher molecular weight polybenzoxazoles could not be prepared by this method.

Due to the very limited solubility of the polybenzoxazoles, solution-cast films could not be prepared.

Aliphatic Polybenzothiazoles

The aliphatic polybenzothiazole based on 3,3'-dimercaptobenzidine dihydrochloride and sebacic acid was prepared in poly(phosphoric acid). The isolation of this polymer from the poly(phosphoric acid) was extremely difficult. This polymer also was of such a high molecular weight that it was insoluble in all common solvents, including sulfuric acid. Flexible films could be prepared by hot-pressing techniques. The properties of this polymer are listed in Table II.

TABLE II
Properties of Poly-2,2'-Octamethylene-6,6'-Bibenzothiazole

Hydrolytic stability in refluxing 40% KOH after 3 hr.	Glass transition temp., °C.	Polymer fusion temp., °C.	Polymer decomposition temp. by TGA, °C.
Unaffected	238	300 at 1000 psi	Helium—450 Air—430

It is apparent that this polymer is insensitive to oxidation, as demonstrated by thermogravimetric analysis in air. The polymer was found to have a much lower glass transition temperature (T_g) than the corresponding polybenzoxazole, as well as outstanding thermal stability.

A polybenzothiazole based on sebacic acid was prepared by the melt condensation method which had an inherent viscosity of 0.63.

The polyamide precursor route was also investigated, but high molecular weight precursor polymers could not be prepared. In addition, the low molecular weight polybenzothiazole was found to have very limited solubility.

Aliphatic Polybenzimidazoles

Aliphatic polybenzimidazoles based on 3,3'-diaminobenzidine and sebacic or glutaric acids were prepared in poly(phosphoric acid), with the usual problems in isolation. The physical characteristics of these polymers are listed in Table III.

TABLE III
Physical Characteristics of Aliphatic Polybenzimidazoles

Polymer	Hydrolytic stability in refluxing 40% KOH-3 hr. inherent viscosities ^a		Glass transition temp., °C.	Polymer fusion temp., °C.	Polymer decomposition temp. by TGA, °C.	
	Before	After			In air	In helium
Poly-2,2'-trimethylene-5,5'-bibenzimidazole	0.83	0.93	275	316 at 1000 psi	395	410
Poly-2,2'-octamethylene-5,5'-bibenzimidazole	1.43	1.63	234	307 at 170 psi	370	450

^a 0.5% in conc. H₂SO₄.

TABLE IV
Properties of Poly-2,2'-Octamethylene-5,5'-Bibenzimidazole Films

Tensile strength, psi	Tensile strength after 3 cycles, 36 hr. each at 145°C. in 40% KOH	Tensile strength after 3 cycles, 36 hr. each at 145°C. in 40% KOH saturated with Ag ₂ O
7400	8300	6000

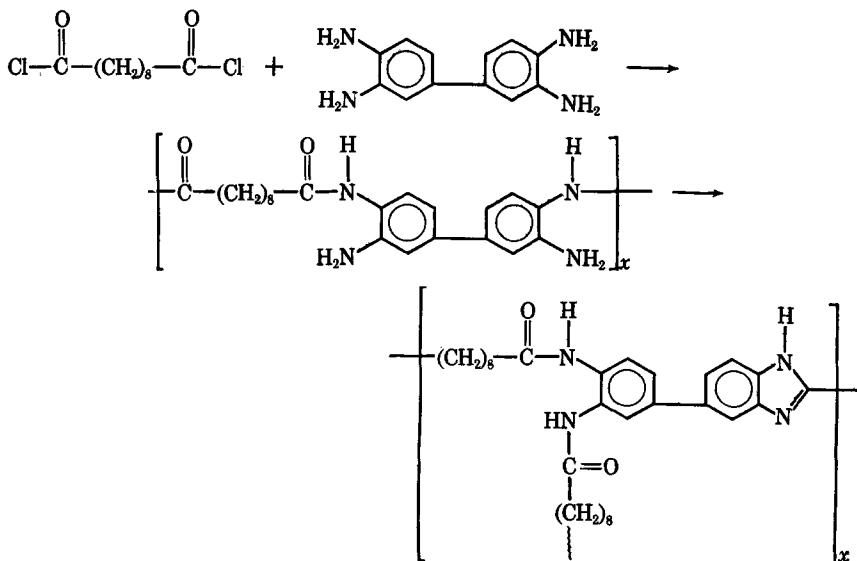
TABLE V
Properties of Molded Poly-2,2'-Octamethylene-5,5'-Bibenzimidazole

Temp.	Notched impact, ft.-lb./in. of notch	Compressive strength, psi	Compressive modulus, psi × 10 ⁶
-196°C.	0.92	85,000	10.0
R. T.	1.58	28,500	4.25

The sebacic acid-based polybenzimidazole was soluble in dimethylacetamide, *m*-cresol, sulfuric acid, and formic acid, while the glutaric acid-based polybenzimidazole was soluble only in sulfuric and formic acids.

The T_g of the aliphatic polybenzimidazole was roughly equivalent to that of the corresponding polybenzothiazole polymer, but considerably lower than that of the polybenzoxazole.

Since the preparation of the polybenzimidazole in poly(phosphoric acid) posed numerous problems with polymer purification, the polyamide precursor route was investigated. The polymers prepared by this route generally resulted in insoluble products, probably due to crosslinking, as outlined below.



Melt condensation was found to be the most satisfactory method for preparing the aliphatic polybenzimidazoles. The condensation was conducted in two stages. In the first stage, the polymer was advanced to an inherent viscosity of approximately 0.1–0.3. In the second stage, the prepolymer was advanced to the desired molecular weight. Final polymers having an inherent viscosity as high as 3.16 have been achieved, but polymers having an inherent viscosity of 0.80–1.00 have been found to be optimum for preparing films via solution coating.

Very tough, flexible films of the sebacic acid-based polybenzimidazoles have been prepared by solution casting from either dimethylacetamide or *m*-cresol. The flexibility of these films was unchanged at temperatures as low as -196°C . Additional properties of these films are listed in Table IV.

Table IV illustrates that these films were completely unaffected by alkaline hydrolysis, even in the presence of an oxidizing agent such as silver oxide.

A molding was also prepared from the sebacic acid-based polybenzimidazole. The polymer had excellent cryogenic properties, as illustrated by the data in Table V.

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100, with Dr. Ralph Lutwack acting as project officer.

The authors wish to thank Richard Empey for the test data, and Edward Harrison for his valuable criticisms.

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Résumé

Les polybenzoxazoles, polybenzothiazoles et polybenzimidazoles aliphatiques ont été préparés par trois méthodes: dans l'acide polyphosphorique, au moyen d'un précurseur polyamide et par polymérisation à l'état fondu. La méthode de polymérisation à l'état fondu a été trouvée la plus satisfaisante. Tous les polymères hétérocycliques aliphatiques ont une stabilité thermique excellente, une résistance à l'hydrolyse alcaline, une température de transition vitreuse élevée et un haut degré de flexibilité. La seule classe de polymères ayant quelques degrés de solubilité toutefois, était le polybenzimidazole. Les films de polybenzimidazole aliphatique ont été préparés par coulage de leur solution. Ces films ont été trouvés être extrêmement flexibles aux températures ambiantes et cryogéniques. Les films n'étaient pas affectés par hydrolyse alcaline, même en milieu oxydant. Un objet moulé préparé au départ du polybenzimidazole aliphatique avait des propriétés physiques excellentes à température cryogénique et à température de chambre.

Zusammenfassung

Aliphatische Polybenzoxazole, Polybenzothiazole und Polybenzimidazole wurden nach drei Methoden dargestellt: in Polyphosphorsäure, über die Polyamidvorstufe und durch Schmelzpolymerisation. Als zufriedenstellendste Methode erwies sich die Schmelzpolymerisation. Alle aliphatischen heterocyclischen Polymeren besaßen ausgezeichnete thermische Stabilität, Beständigkeit gegen alkalische Hydrolyse, hohe Glasumwandlungs-temperatur und einen hohen Grad an Biegsamkeit. Die einzige Polymerklasse mit einem gewissen Grad an Löslichkeit waren die Polybenzimidazole. Filme aus aliphatischen Polybenzimidazolen wurden durch Giessen aus Lösung hergestellt. Diese Filme waren bei Raumtemperatur und bei kryogenen Temperaturen extrem biegsam. Die Filme wurden durch alkalische Hydrolyse, selbst in einem oxydierenden Medium nicht angegriffen. Ein Formstück aus aliphatischem Polybenzimidazol besaß bei kryogener und normaler Temperatur ausgezeichnete physikalische Eigenschaften.

Received December 26, 1966

Prod. No. 1559