

Substituted Aliphatic Polybenzimidazoles as Membrane Separator Materials

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Synopsis

When initially evaluated as potential membrane separators for a heat-sterilizable silver-zinc battery, aliphatic polybenzimidazoles (PBI) proved to be unsatisfactory because of their excessively high resistivity. Later, various polymer modifications such as sulfonation, *N*-hydroxyethylation, *N*-cyanoethylation, and *N*-carboxyethylation were made in an attempt to increase the hydrophilicity of the PBI's. As a result of these efforts, an *N*-carboxyethylated, suberic acid-based PBI shows promise as a sterilizable battery separator material.

INTRODUCTION

The demands placed on space vehicles and associated hardware are becoming proportionally more stringent as they encounter a wider range of difficult environmental conditions. Advanced materials obviously are required to meet these demands, but many are not commercially available and must be specially prepared for a particular end application. Such is the case for the Voyager space vehicle, which is designed to land on Mars.

Part of the Voyager mission is concerned with determining whether or not life forms exist on that planet. Since the contaminants from Earth could seriously interfere with this investigation, the entire landing vehicle must be sterilized. The most effective method of sterilization known is through the application of heat. Problems are created by heat sterilization, however, one of which is related to the silver-zinc batteries commonly used in space vehicles because cellophane currently serves as the membrane separator in these batteries. The difficulty lies in the fact that this material disintegrates when sterilized in the presence of the 40% potassium hydroxide electrolyte.

It is apparent that a new separator material is needed. The development of such a material, however, must be governed by the following stringent requirements established by the Jet Propulsion Laboratory: hydrolytic stability in 40% potassium hydroxide for a thermal cycle of 64 hr at 135°C; specific resistance of 150 ohm-cm or less; silver and zinc diffusion rates comparable to those provided by cellophane; resistance to the oxidative species present in the cell under sterilization conditions; an electrolyte diffusion rate comparable to that provided by cellophane.

The approach taken to meet these requirements was through chemical modification of an existing polymer, a convenient route for obtaining specific properties when other routes are unfeasible. Fettes,¹ for example, lists several useful methods for chemically modifying polymers, including halogenation, hydrolysis, coupling, oxidation, alkylation, and surface reactions. A more specific example would be the polyamides, which have been *N*-alkylated with ethylene oxide^{1,2} and formaldehyde² to improve solubility and flexibility.

EXPERIMENTAL

Polymers

Aliphatic polybenzimidazoles were prepared as described in an earlier publication.³

Polymer Modifications

Sulfonation. Poly-2,2'-octamethylene-5,5'-bibenzimidazole was dissolved in 200 ml of concentrated sulfuric acid and warmed to 60°C. Chlorosulfonic acid (30 ml) was added cautiously, and the mixture was heated to and maintained at a temperature of 60–70°C for 1½ hr. After the solution was poured into water, washed thoroughly, and dried, 19 g of product was obtained. The degree of sulfonation was determined by collecting in effluent HCl gas in a caustic trap, then back titrating.

***N*-Hydroxyethylation.** A typical procedure for the *N*-hydroxyethylation of poly-2,2'-octamethylene-5,5'-bibenzimidazole follows. Sodium hydride (1.61 g, 0.066 mole) was added to a solution of the PBI polymer (4.0 g) in 110 ml of dimethylacetamide (DMAC). A tan precipitate immediately formed, accompanied by gas evolution. After the mixture had been stirred for ½ hr at room temperature, a solution of 2-bromoethanol (3.0 g, 0.024 mole) in DMAC (10 ml) was added over a 15 min period. The slurry was warmed and maintained at 60°C for 45 min, cooled, and poured into anhydrous ethanol. The cloudy orange solution was neutralized with acetic acid, the precipitate filtered and dried to yield 3.2 g of tough, tan polymer. The inherent viscosity (0.5% in sulfuric acid at 25°C) was 0.92. The polymer failed to form a 1% solution in DMAC after refluxing for 4 hr, whereas the starting material formed a 5% solution upon slight warming. However, a tough, flexible film of the modified polymer could be cast from a 2% solution in *m*-cresol. The degree of hydroxyethylation was found to be 83% as determined by elemental analysis (calcd % oxygen = 7.42, found = 6.20).

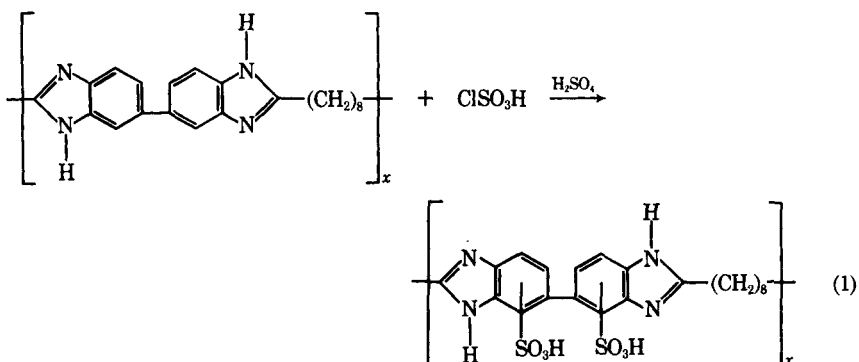
***N*-Cyanoethylation.** The following is typical of the procedure used for the *N*-cyanoethylation of poly-2,2'-hexamethylene-5,5'-bibenzimidazole. The polymer (40 g) was dissolved in DMAC (250 ml) at 100°C then cooled to 70°C. Acrylonitrile (28 ml) in DMAC (42 ml) was added slowly and the mixture heated at 95°C for 1 hr. Sodium methoxide (0.2 g) in DMAC

(20 ml) was added, and the solution was stirred at 105°C for 2½ hr, then for ¾ hr at 160°C. Excess nitrile was removed by distillation. An infrared spectrum of the polymer displayed a typical nitrile peak at 4.65 μ . The degree of cyanoethylation was determined on the hydrolyzed product by using the neutralization equivalent (NE) and found to be 95% (calcd NE = 218, found = 230).

RESULTS AND DISCUSSION

Poly-2,2'-octamethylene-5,5'-bibenzimidazole was evaluated as a potential battery separator material. This aliphatic PBI displayed high resistance to oxidation and to alkaline hydrolysis at 145°C; however, its specific resistance was in excess of the minimum requirement of 150 ohm-cm (Table I).

A convenient way to lower the resistivity of the PBI is through chemical modification of the polymer with hydrophilic and ion-exchanging functional groups. One method of introducing hydrophilicity into the polymer is by sulfonation [eq. (1)].



Accordingly, poly-2,2'-octamethylene-5,5'-bibenzimidazole was sulfonated, but was found to be unsatisfactory as a battery separator. The modified polymer was insoluble in all solvents except sulfuric acid, and the polymer decomposed when heated in a press.

TABLE I
Properties of Poly-2,2'-octamethylene-5,5'-bibenzimidazole Film

Test conditions	Tensile strength, psi	Pickup, wt-%	Resistivity, ohm-cm
None (control)	7400	—	—
Three heat cycles, 36 hr each at 145°C in 40% KOH	8300	15.1	16.6×10^5
Three heat cycles, 36 hr each at 145°C in 40% KOH saturated with Ag ₂ O	6000	—	—

TABLE II
Effect of Sterilization on *N*-Hydroxyethylated
Poly-2,2'-octamethylene-5,5'-bibenzimidazole

Polymer	Properties after 36 hr at 145° in 40% KOH			
	Dry tensile strength, psi	Wet tensile strength, psi	Electrolyte pickup, %	Specific resistance, ohm-cm
Unmodified PBI polymer	7400	8300	15.1	16.6×10^5
25% Hydroxyethylated PBI polymer	7700	4800	11.7	13.6×10^4
84% Hydroxyethylated PBI polymer	3800	3100	47.5	81.2×10^3

TABLE III
Effect of Sterilization on Carboxyethylated
Poly-2,2'-octamethylene-5,5'-bibenzimidazole

Polymer	Properties after 36 hr at 145°C in 40% KOH			
	Dry tensile strength, psi	Wet tensile strength, psi	Electrolyte pickup, %	Specific resistance, ohm-cm
Unmodified polymer	7400	8300	15.1	16.6×10^5
Carboxyethylated PBI polymer	6900	2000 ^a	90.0	1340

^a Decreased tensile strength is a result of increased volume due to swelling of polymer.

TABLE IV
Rate of Silver Diffusion and Pickup of Sterilized
Poly-2,2'-octamethylene-5,5'-bis-1(β -carboxyethyl)benzimidazole Film

Film sample	Rate of silver diffusion, g/hr/in. ²	Rate of silver pickup, g/hr/in. ²
Modified PBI	4.7×10^{-9}	6.8×10^{-7}
Cellophane	1.6×10^{-3}	11×10^{-6}

While the carboxyethylated sebacic acid based PBI did not pass the specific resistance requirement of 150 ohm-cm, it did represent a substantial improvement over the unmodified polymer. In order to compare this modified polymer with cellophane, the conventional separator now used, the rate of silver diffusion and pickup was determined by the method given by Dirkse.⁴ The carboxyethyl-modified sebacic acid based polymer proved to be superior to cellophane (Table IV).

A method of further reducing the resistivity of the carboxyethyl modified PBI's is to employ shorter chain acids when preparing the aliphatic PBI. Such a polymer, when modified, would contain more functional groups per unit weight.

A flexible aliphatic PBI based on suberic acid and diaminobenzidine was prepared, then cyanoethylated. It was subsequently cast into films, hydrolyzed, and sterilized. This modified polymer met the specific resistance requirement, as shown in Table V.

TABLE V
Effect of Sterilization on Poly-2,2'-hexamethylene-5,5'-bis-
1(β -carboxyethyl)benzimidazole

Tensile strength, psi	Tensile strength after sterilization, psi	Electrolyte pickup, %	Avg specific resistance, ohm-cm
10,600	920 ^a	260	90

^a Decreased tensile strength is a result of increased volume due to swelling of polymer.

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

The authors wish to thank Richard Rafter for his assistance, Richard Empey for the test data, and Edward Harrison and Jerome Hollander for their valuable comments.

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Received July 16, 1968