

Preparation and Characterization of an Aromatic Polyimide and Its Use as a Selective Membrane for H₂O₂

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Selectivity behavior to electroactive and non-electroactive substances of a polyimide prepared from 2,2'-dimethyl-4,4'-diaminobiphenyl and the corresponding dianhydride was examined by electrochemical methods. From the excellent electrochemical findings obtained, it was observed that polyimide film was only permeable to hydrogen peroxide among the substances examined. Therefore, it is claimed that the mentioned polymeric film can be successfully used as a hydrogen peroxide-selective membrane in the presence of electroactive and non-electroactive interferents.

Key Words: Polyimide, thermally stable polymers, polymeric sensor.

Introduction

Polymeric films have been widely used to immobilize enzymes¹⁻⁴. One of the most important problems faced in hydrogen peroxide detecting enzymatic biosensor applications is the presence of interferents. Electroactive interferents such as ascorbic acid and oxalic acid contribute to the anodic signal measured for hydrogen peroxide, while non-electroactive interferents such as lactose, sucrose and urea foul the electrode surface. This interference problem can be overcome by using various polymeric coatings.

Polyimides are well known for their excellent thermal and oxidative stability, as well as their exceptional mechanical properties⁵⁻¹². The need for thermally stable membranes has raised the possibility of using polyimides with appropriate ion-conducting sites. However, it is well known that in order to obtain polymers that exhibit high selectivity and permeability it is necessary to synthesize structures with stiff backbone chains and with chain packing so as to produce a very narrow free-volume distribution. In other words, it is necessary to generate polymeric molecular sieves. The high rigidity of polyimides, their suitable polarity and their high chemical resistance due to high thermo- and chemical stability plus the capability of forming hydrogen bonds explain why these polymers can be used as membranes¹³⁻¹⁷.

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Of the various alternative design novel processable polyimides, some general approaches have been universally adopted: the introduction of aliphatic or another kind of flexible segment, which reduces chain stiffness; the introduction of bulky side chain substituents; which help in the separation of polymer chains and hinder molecular packing and crystallization; and the use of enlarged monomers containing angular bonds, which suppress coplanar structures. However, factors leading to better solubility or lower T_g or melting temperatures in a polymer often conflict with other important requirements, such as mechanical properties, thermal resistance or chemical resistance. Therefore, an adjusted degree of modification should be applied to optimize the balance of properties^{18–23}.

In the present paper, the use of a chemically prepared polyimide film as a hydrogen peroxide-selective membrane in the presence of the mentioned electroactive and non-electroactive interferents was investigated.

Experimental

Materials

NMP was distilled over CaH₂ under reduced pressure and stored over 4 Å molecular sieves. Reagent grade pyromellitic dianhydride (PMDA) was sublimed at 250 °C under reduced pressure and dried under vacuum at 120 °C prior to use. The diamine (Merck) was purified via recrystallization from ethanol to give shiny crystals. H₂O₂, ascorbic acid, oxalic acid, lactose, sucrose and urea were of analytical grade and purchased from Sigma. All aqueous solutions were prepared with deionized and doubly distilled water. Permselectivity experiments were performed in PBS (phosphate buffer salts, pH 7).

Instrumentation

Infrared spectra were recorded as KBr pellets in the range 4000–400 cm⁻¹ on an Ati Unicam Mattson 1000 Fourier Transform Infrared Spectrometer. Microanalyses were performed by TÜBİTAK (Ankara). Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively. Inherent viscosity ($\eta_{inh} = \ln \eta_r / c$ at polymer concentration of 0.5 g/dL) was measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent.

GPC analyses were performed at 30 °C using NMP as eluent at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system, with PL gel 5 μ m 10E5A° column) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses 200–1,200,000 Da) using GPC software for the determination of the average molecular mass and the polydispersity of the polymer.

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and time-base (TB) experiments were carried out with a BAS 100W (Bioanalytical Systems, Inc. West Lafayette, IN, USA) electrochemical analyzer by using the standard 3-electrode system consisting of a Pt disk (1.6 mm diameter) as the working electrode and a Ag/AgCl reference electrode together with a Pt wire coil as an auxiliary electrode.

Polyimide Synthesis

Polyimide synthesis was performed as follows: 2,2'-dimethyl-4,4'-diaminobiphenyl, (1.06 g, 5 mmol) was dissolved in NMP (15 mL) in a 50 mL Schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. PMDA (1.09 g, 5 mmol) was added to the amine solution, followed by stirring overnight to give a viscous solution. After being stirred for 3 h, the solution was heated to reflux at 200 °C for 15 h. During the polymerization process, the water generated from the imidization was allowed to distill from the reaction mixture together with 1-2 mL of xylene. After being allowed to cool to ambient temperature, the solution was diluted with NMP and then slowly added to a vigorously stirred solution of 95% ethanol. The precipitated polymer was collected via filtration, washed with ethanol, and dried under reduced pressure at 150 °C. The polymer was isolated with 93% yield.

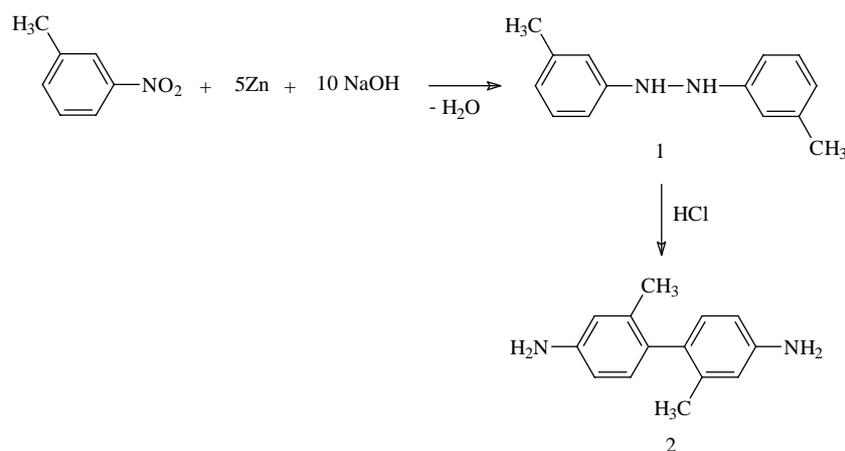
IR (KBr): (cm^{-1}) 3035, 2912, 2832, 1778, 1722, 1608, 1508, 1444, 1330, 1070, 827, 725, 519. Analytically calculated for $(\text{C}_{24}\text{H}_{14}\text{O}_4\text{N}_2)_n$, (394.38) $_n$ C: 73.09; H: 3.58; N: 7.10. Found: C: 72.94; H: 3.65; N: 7.02.

Preparation of polyimide-coated electrode and its permselectivity measurements

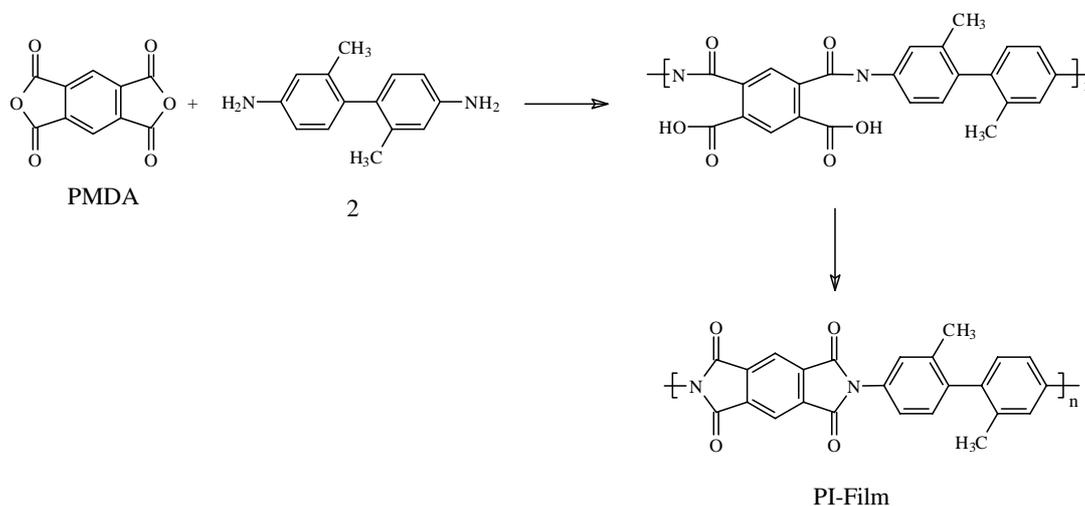
Before coating, the Pt disk electrode was cleaned according to the standard procedure and polished with aqueous alumina slurry down to 0.05 μm . Then 20 μL of polymer solution prepared by dissolving 70 mg of polyimide in 2 mL of NMP was dropped onto the surface of the Pt electrode and allowed to dry at room temperature for about 3 days. CV, DPV and TB measurements were obtained in the PBS solution, which was kept under gentle stirring at room temperature. Prior to amperometric measurements, the background current was allowed to decay to a steady state. Then amperometric behavior obtained by injection of the relevant substances was recorded as a function of time.

Results and Discussion

The aromatic polyimide synthesized from 2,2'-dimethyl-4,4'-diaminobiphenyl prepared by 3,3'-dimethylhydrozobiphenyl in the presence of an acid catalyst according to the literature²⁴ showed excellent film forming properties (Schemes 1 and 2). To determine the optimal conditions for polymerization, the polymerization of 2,2'-dimethyl-4,4'-diaminobiphenyl with PMDA was studied in detail. Table 1 summarizes some physicochemical properties of the polymer obtained. On the basis of these results, the polymerization of the monomer with the corresponding anhydride was performed in NMP at high temperatures. The FT-IR spectra showed characteristic absorption bands for aliphatic C-H stretching frequencies at 2832-2912 cm^{-1} , sym. imide ν (C=O) at 1722 cm^{-1} , asym. imide ν (C=O) at 1778 cm^{-1} , C-N imide ring deformation at near 1070 cm^{-1} and C-N bending at 725 cm^{-1} .



Scheme 1. Synthesis of 2,2'-dimethyl-4,4'-diaminobiphenyl.



Scheme 2. Synthesis of polyimide.

Table 1. Physicochemical properties of polyimide.

Basic properties						
Yield (%)	d (g/cm ³) ^a	η (dL/g) ^b	Mn $\times 10^{-5}$	Mw $\times 10^{-5}$	HI	Film
93	1.45	2.15	1.70	3.68	2.161	Transparent
Solubility ^c						
NMP	DMF	DMAc	Ether	THF	Hexane	DMSO
+	±	+	-	±	-	±

a. Determined by suspension method at 30 °C.

b. Measured at a concentration of 0.5 g/dL in NMP at 30 °C using an Ubbelohde viscometer.

c. (Solubility tested at 2% solid concentration; + soluble at room temperature; ± soluble upon heating; - insoluble).

The molecular weight of polymer having inherent viscosity near 2.15 dL/g was determined with GPC. The results showed that the Mn and Mw values were 170,000 and 368,000 with respect to polystyrene standards, respectively, and the ratio Mw/Mn was about 2.16.

Thermal properties evaluated by differential thermal analysis (DTA), differential scanning calorimeter (DSC) and thermogravimetry (TGA) techniques are listed in Table 2. A 10% weight loss in nitrogen was

observed at 581 °C. Tg measured by DSC is also shown in Table 2. The polyimide prepared from PMDA had a relatively high Tg because of its rigid structure.

Table 2. Thermal properties of polyimide.

TGA Analysis					
Atmosphere	On set	End set	10% ^a	Char ^b	IDT ^c
Air	475	678	558	14	482
nitrogen	531	692	581	51	542
DTA Analysis ^d					
TDP ^e	On set	End set	Heat (kJ/g)		
595	459	623	8.83		
DSC Analysis					
Tg (°C) ^f	On set	End set	Transition (mW)		
417	400.50	433.14	-2.26		

- Temperature of 10% weight loss was assessed by TGA at a heating rate of 10 °C/min.
- Assessed by TGA at 800 °C.
- IDT (initial decomposition temperature) is the temperature at which an initial loss of mass is observed.
- DTA thermogram of polyimide with a heating rate of 10 °C/min in air atmosphere.
- TDP (thermal decomposition peak).
- Determined by DSC in N₂ atmosphere.

As mentioned at the beginning of the paper, the main objective was to develop a permselective polymeric membrane that blocks the mentioned interferents efficiently and permits H₂O₂ penetration to the electrode surface. Therefore, the voltammetric behavior to the mentioned interferents and hydrogen peroxide of the bare and the polyimide film electrode at the suitable thickness was systematically investigated.

Figure 1-3 compares the cyclic behavior of ascorbic acid, oxalic acid and hydrogen peroxide at the bare Pt and polyimide-coated electrode. From Figure 1, it is clearly seen that electrochemical activity of the electroactive ascorbic acid in the potential region examined is completely suppressed at the film-coated electrode when compared with that on the bare electrode. Similar behavior has also been observed for another electroactive interferent, oxalic acid (Figure 2). In contrast, it can be seen from Figure 3 that CV obtained with the bare electrode for hydrogen peroxide is similar to that of the polymer electrode. These findings were also supported with DPVs. Furthermore, in order to check whether hydrogen peroxide permeates through the polymeric film in the presence of the electroactive and non-electroactive interferents, the steady-state amperometric responses to ascorbic acid, oxalic acid, lactose, sucrose, urea and hydrogen peroxide of the polymeric electrode were examined as a function of time. Figure 4 shows that, as expected, the polymeric film was insensitive to injections of the interferents examined. However, when hydrogen peroxide was injected into the PBS solution, excellent amperometric responses were observed. The response of the polymeric sensor was also fast (< 3 s). A calibration curve and its linear relation for H₂O₂ are seen in Figure 5. This linear relationship between the H₂O₂ concentration and the amperometric response is important for amperometric biosensor applications. In addition, it was observed that the sensor responded to H₂O₂ injections for 28 days.

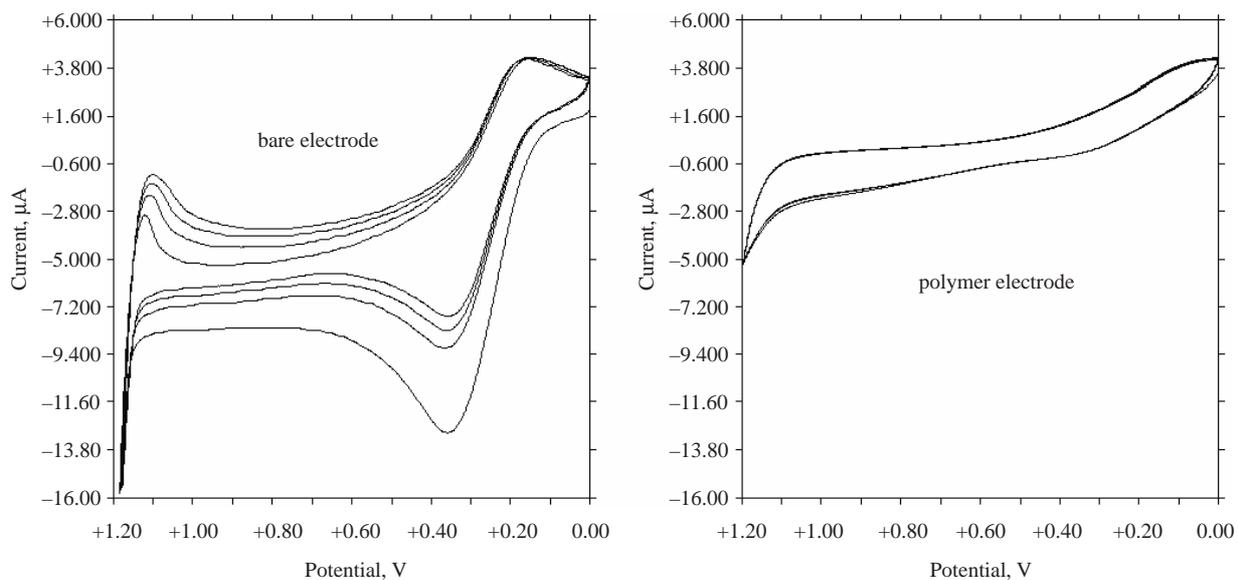


Figure 1. CVs of 4 mM ascorbic acid at the bare Pt and polymer electrode.

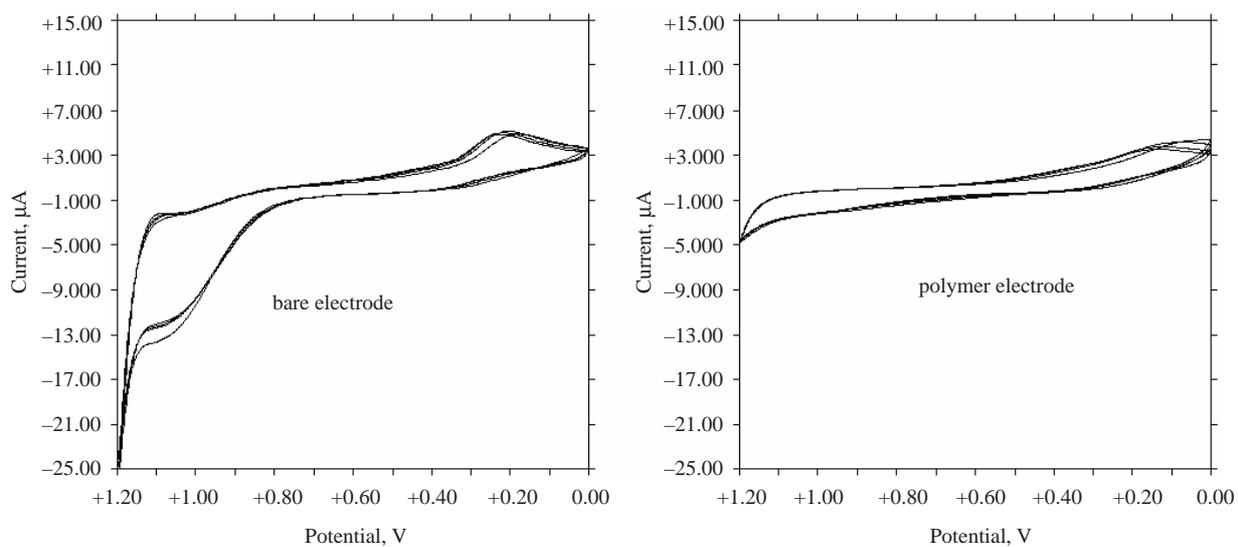


Figure 2. CVs of 4 mM oxalic acid at the bare Pt and polymer electrode.

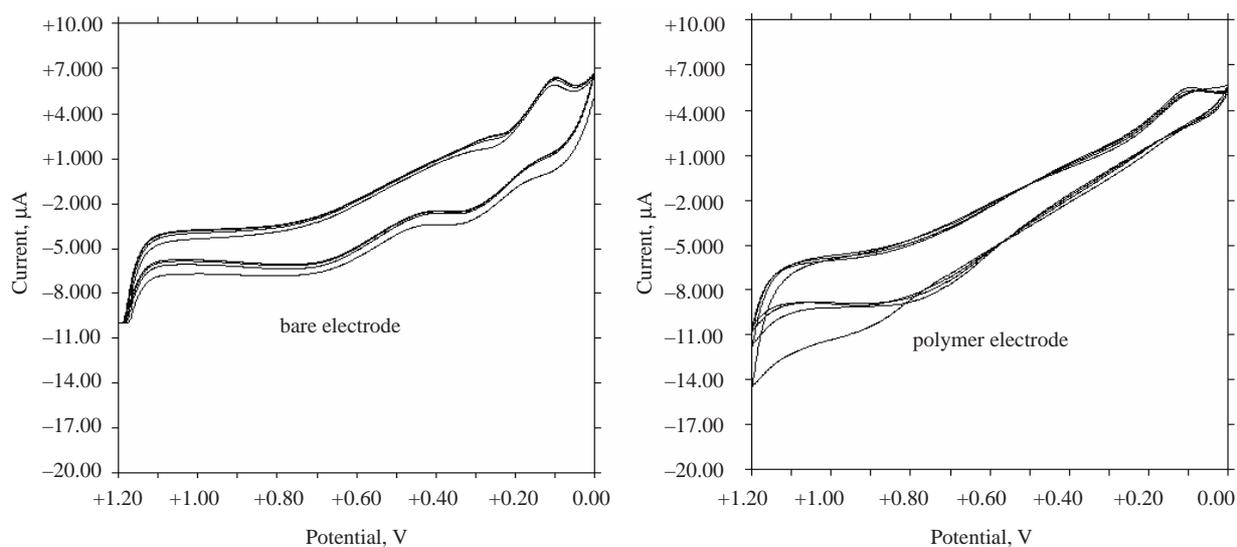


Figure 3. CVs of 4 mM H_2O_2 at the bare Pt and polymer electrode.

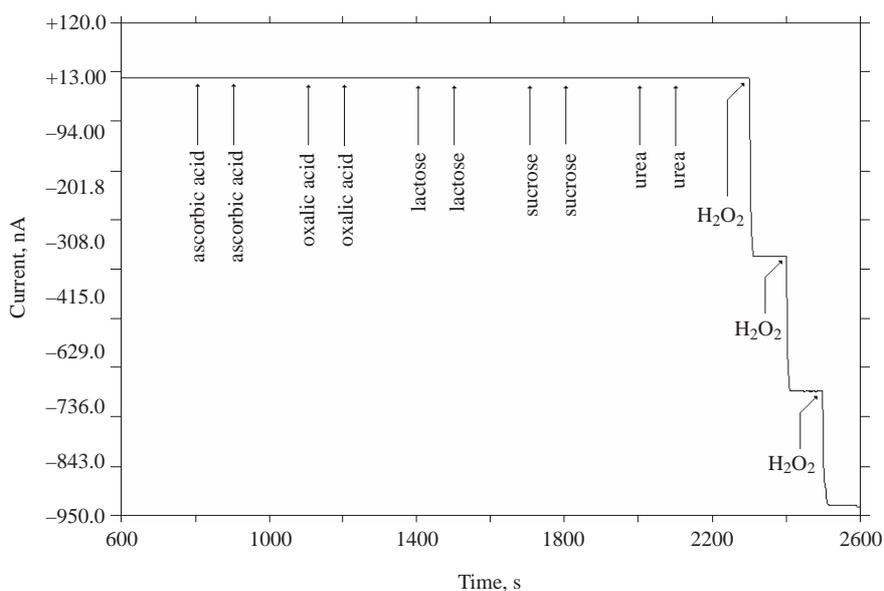


Figure 4. The permselectivity of the polymer electrode. Each injection corresponds to 2 mM of the substance indicated.

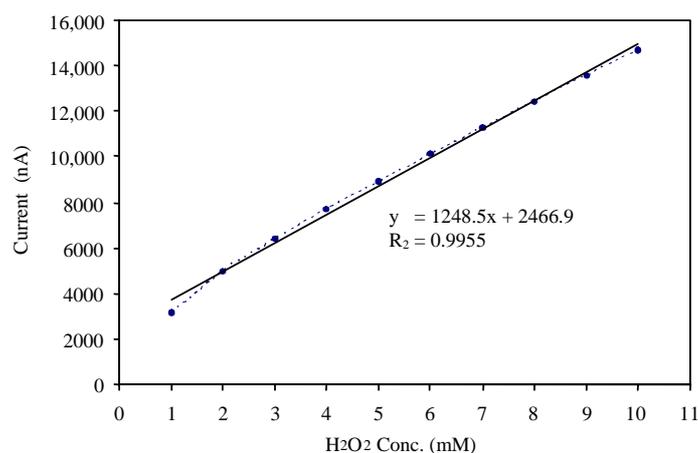


Figure 5. Calibration curve (dashed line) and its linear relation (solid line) for H₂O₂ in the presence of electroactive and non-electroactive interferences of the polymer electrode.

Conclusion

An aromatic diamine containing methyl side groups was used to prepare N-methylpyrrolidone soluble, 5-membered ring polyimide. High molecular weight film-forming polymers with controlled degrees of polymerization were prepared by varying the stoichiometric ratio of diamine. Solution cast films of the polyimides tested for their permselective character toward H₂O₂ showed that polyimides with methyl moieties could be used as a selective membrane for H₂O₂.

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