Polymer Bulletin 51, 351–358 (2004)
DOI 10.1007/s00289-004-0239-3

Polymer Bulletin

Synthesis, Characterization and Dopamine Selectivity of 1,4-bis(3-aminopropyl)piperazine - Containing Polyimide

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Received: 22 December 2003/Revised version: 15 January 2004/ Accepted: 1 March 2004

Summary

A novel polyimide prepared from 1,4-bis(3-aminopropyl) piperazine and pyromellitic dianhydride (PMDA) was characterized by thermal, FTIR, GPC and microanalysis techniques. Thermal properties of the polyimide were evaluated by differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TGA). Moreover, platinum electrodes were covered with this polyimide and permeation properties of the resulting polyimide-coated electrodes to dopamine and ascorbic acid were examined by electrochemical method. On the basis of the permselectivity data obtained, it was found that the polyimide-coated electrode exhibited selective permeation for dopamine while blocking ascorbic acid.

Key words: Polyimide, synthesis, permselective membrane, dopamine.

Introduction

Polyimides represent an important class of high performance polymeric materials and have found wide applications in aerospace, microelectronics and membrane separation industries. Comparing with common polymers, polyimide posses many outstanding key properties such as high mechanical strength, high modulus, unusual thermo-oxidative stability, excellent electrical properties and superior chemical resistance. Polyimides are usually prepared by the so-called two-step method in which a dianhydride and a diamine are allowed to undergo condensation polymerization to form a polyamic acid precursor and subsequently the precursor is converted thermally or chemically to the final polyimide [1-5]. Due to their chemical stability, polyimides are inert against chemical reaction and are unaffected with common organic solvents. On the other hand, in recent years, determination of dopamine has gained considerable interest because of its clinically importance [6-10]. Dopamine is one of the most important neurotransmitters in central nervous system (CNS) and regulates neural interactions. This regulation is proportional to the concentration of dopamine released to the neurons. However, the electrochemical determination of dopamine in CNS is difficult because the presence of ascorbic acid reduces the sensitivity and selectivity of dopamine [11,12].

In the present paper, a novel piperazine - containing polyimide was synthesized and characterized by thermal, FTIR, GPC and microanalysis techniques. Furthermore, it was also examined whether this polyimide film can be used as dopamine selective polymeric membrane.

Experimental

Materials

All chemicals for synthesis were purchased form Aldrich and used after purification. NMP was purified by distillation over CaH_2 under a nitrogen atmosphere and stored over 4Å 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. Dopamine hydrochloride and ascorbic acid were analytic grade and purchased from Merck. All Solutions for amperometric tests were prepared with deionized and doubly distilled water. Ascorbic acid and dopamine solutions were prepared freshly for each experiment. 0.1 M KCl solution was used as an electrolyte.

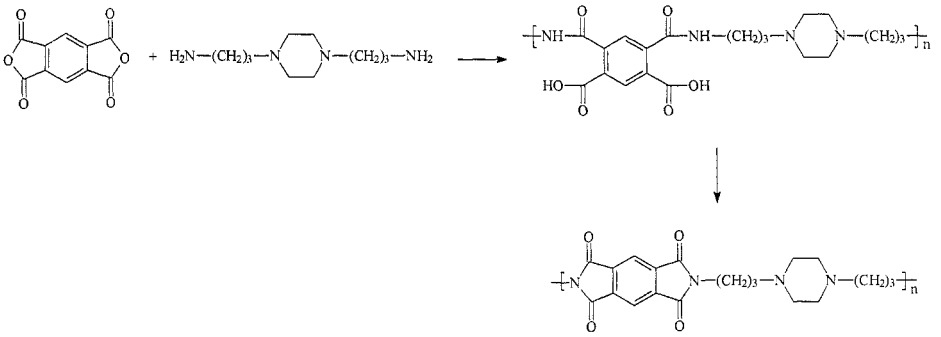
Instrumentation

FTIR 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 the TÜBİTAK (Ankara). Differential scanning calorimeter (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively. DSC analysis was completed in a dry nitrogen atmosphere and the heating rate was 10°C.min^{-1}. Inherent viscosities (η_{inh}= $ln\eta_r/c$ at polymer concentration of 0.5 g/dL) were 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 eluant at a flow rate of 0.5 mL min^{-1}. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses between 200-1200000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer sample. Amperometric measurements were made with a BAS 100W (Bioanalytical Systems, Inc. West Lafeyette, IN, USA) electrochemical analyzer. For this reason, a three-electrode cell system consisting of a Pt disc (2 mm diameter) as working electrode and a Pt coil as an auxiliary electrode together with an Ag/AgCl reference electrode was used.

Synthesis of polyimide

The polymer synthesis is shown in scheme 1. A typical polyimide synthesis was performed as follows: 1,4-bis(3-aminopropyl) piperazine (8,13g, 4.15mmol) was dissolved in 15mL NMP in a 100 mL schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. PMDA (0.9g, 4.15 mmol) was added to the amine solution that was stirred overnight to give a viscous solution. The mixture was heated to 70 °C, 5 mL xylene added and refluxed for 3h. Following the removal of xylene by distillation, the reaction mixture was cooled to room temperature and precipitated into large excess of methanol. The dark amber

product was maintained at 220-230°C under nitrogen for 2h and dried at 100°C under vacuum. The yield was 90%. Analytically calculated for $(C_{20}H_{22}N_4O_4)_n$ $(382,42)_n$: C, 62,8; H, 5,79; N, 14,65. Found: C, 63,1; H, 5,68; N, 14,45.



Scheme 1. Synthesis of piperazine - containing polyimide.

Preparation of Polymer coated electrode and its amperometric measurements

Prior to coating, the platinum disc electrodes to be used as a substrate were cleaned according to the standard procedure [13] and polished with aqueous alumina slurry down to 0,05 μm. Polymer solution was prepared by dissolving 70 mg polymer in 2 ml NMP. Then, 20 μl polymer solution was dropped onto the surface of Pt electrode and allowed to dry at room temperature for about 48 h. Figure 5A-D shows the amperometric responses of the polymer-coated electrodes prepared with 20, 40, 60 and 80 μl of polymer solution, respectively. The amperometric responses of the bare or the polymer-coated electrodes to the electroactive substances (dopamine and ascorbic acid) were measured by time-base technique. Before the injection of electroactive substances into the KCl solution, solution was kept under gentle stirring at room temperature and the background current was allowed to decay to a steady state value. Then, the anodic current obtained by the oxidation of electroactive substances was measured as a function of time.

Results and Discussion

IR spectroscopy allows the monitoring of the imide ring formation during thermal imidization. Figure 1 shows FTIR spectra of monomers and polyimide. The characteristic absorption bands of the imide ring were observed near 1774 cm^{-1} (asymmetrical imide ν (C=O) stretching), 1724 cm^{-1} (symmetrical imide ν (C=O) stretching), 1371 cm^{-1} (C-N imide stretching), 1055 cm^{-1} (imide ring deformation) and 730 cm^{-1} (C-N bending). The FT-IR spectrum of polyimide showed that aliphatic C-H stretching frequencies were appeared between 2850-2930 cm^{-1} [14-17].

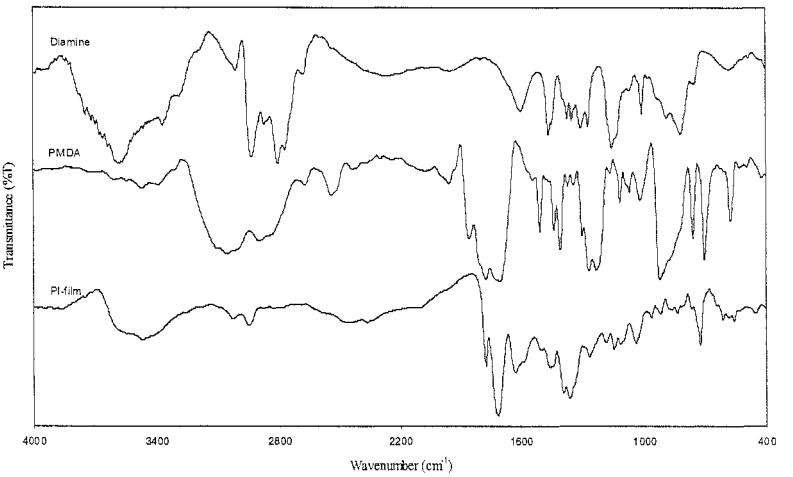


Figure 1. FTIR spectra for monomers and polyimide.

The solubility of polyimide was tested and the results were given in Table 1. Polyimide was soluble in polar aprotic solvents but insoluble in THF and apolar solvents at room temperature. The good solubility toward test solvents was attributed to the linear structure of the monomer. It may also be a result of the presence of the aliphatic heterocyclic groups that decrease interchain interaction of rigid aromatic repeating units, resulting in improved solubility, but lowering glass transition temperature. The thermal properties of the polyimide were evaluated by DSC, DTA and TGA. The thermal behavior data of polymer are listed in Table 2. DTA and DSC analysis of the polyimide were given in Figure 2, respectively. DSC measurement was conducted with a heating rate of 10°C min^{-1} in nitrogen. Glass transition temperature (T_g) of the polyimide was found as 81 °C. This value is lower than generally polyimides because of the polymer structure [18].

Table 1. Basic properties of polyimide

Basic properties						
Yield (%)	d (g/cm^3)[a]	η (dL/g)[b]	$M_n \times 10^{-5}$ [c]	$M_w \times 10^{-5}$ [c]	HI	Film
89	1,42	1,92	2.94	3,47	1,18	Transparent
Solubility[d]						
NMP	DMF	DMAc	DMSO	THF	Hexane	Ether
+	+	+	+	±	-	-

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. Measured by GPC in NMP, polystyrene was used as standard.
d. (Solubility tested at 2% solid concentration; + soluble at room temperature; ± soluble upon heating; - insoluble)

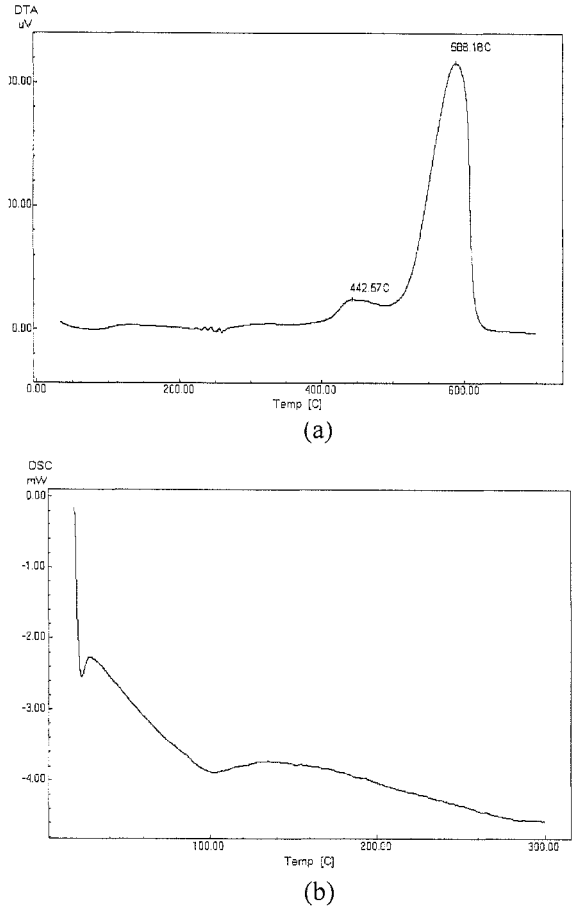


Figure 2. DTA (a) and DSC (b) curves for polyimide, with a heating rate of 10°C/min.

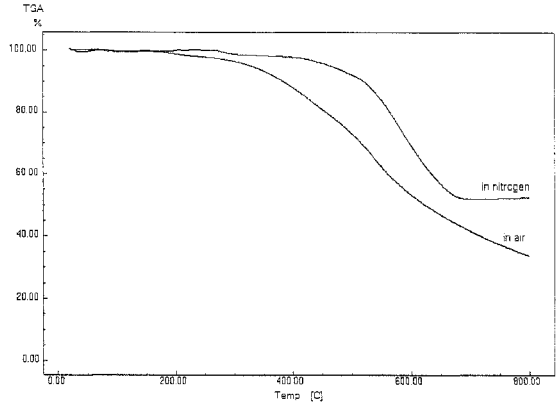


Figure 3. TGA curves for polyimide, with a heating rate of 10°C/min.

The thermal stability of polyimide was evaluated by TGA. The temperatures of 10% weight loss in nitrogen and air atmospheres were determined from original thermograms (Figure 3). The polyimide started to lose weight because of thermal degradation around 523°C in nitrogen atmosphere. Char yields of polyimide at 800°C were in the % 53, which was good polyimide.

Table 2. Thermal properties of polyimide

TGA Analyses [a]					
Atmosphere	On set	End set	% 10[b]	Char	IDT[c]
Air	320	598	365	34	390
Nitrogen	402	684	523	53	433
DTA Analysis[d]					
TDP[e]	On set		End set	Heat (kJ/g)	
588	502		628	5,96	
DSC Analysis					
Tg (°C)[f]	On set		End set	Transition (mW)	
81	31		95	-1,61	

a. Temperature of 10% weight loss was assessed by TGA at a heating rate of 10 °C/min.
b. Assessed by TGA at 800 °C in N_2 and air atmosphere.
c. IDT (initial decomposition temperature) is the temperature at which an initial loss of mass observed.
d. DTA thermogram of polyimide with a heating rate of 10°C/min in an air atmosphere.
e. TDP (thermal decomposition peak)
f. Determined by DSC in N_2 atmosphere.

Dopamine Selectivity of Polymeric electrode

Figure 4 shows the amperometric responses of the bare Pt electrode to electroactive dopamine and ascorbic acid. As can be easily seen from this figure, it is impossible to overcome the interference from ascorbic acid with uncoated electrode.

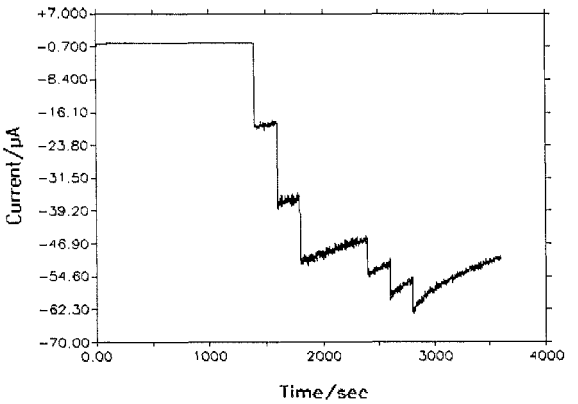


Figure 4. The amperometric responses of the bare Pt electrode to dopamine and ascorbic acid. (The first three and the end three injections belong to dopamine and ascorbic acid, respectively. Each step corresponds to 2 mM of the relevant substance).

According to our experience, however, this interference problem can be overcome by using a suitable permselective polymeric membrane. In the previous papers [19-21], we have reported that some electropolymerized films could be used successfully as a dopamine selective polymeric membrane in the presence of ascorbic acid.

In order to examine whether the chemically prepared polyimide film is permeable to the electroactive species such as dopamine and ascorbic acid or not, the steady-state amperometric responses of the polymeric films at the different thicknesses to dopamine and ascorbic acid were investigated.

Figure 5A-D compares the steady-state amperometric responses of the polymer electrodes to dopamine and ascorbic acid. The proportionality depicted in the mentioned figure confirms that the permeation of the electroactive species through polymeric membrane was decreased with the increasing film thickness.

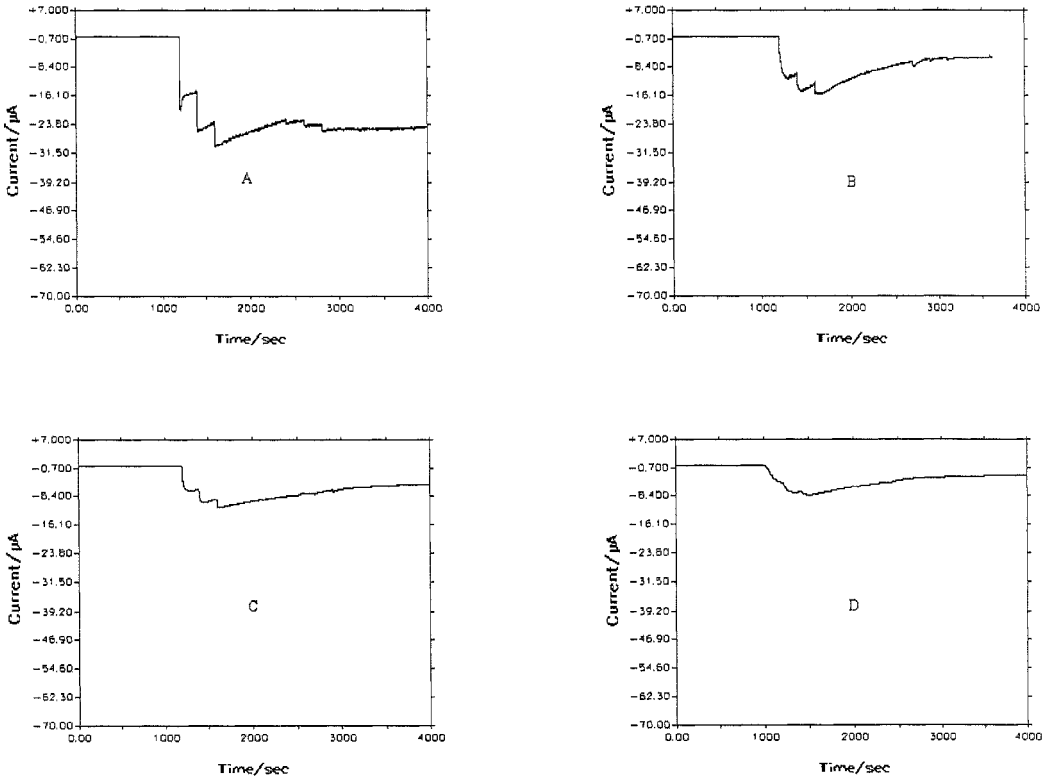


Figure 5. Relationship between the permeability of dopamine and ascorbic acid and thickness of the polymer-coated electrodes prepared with 20 (A), 40 (B), 60 (C) and 80 (D) μl of polymer solution. Injections were made as stated in Figure 4. Each injection corresponds to 2 mM of the relevant substance).

Conclusion

In brief, piperazine - containing polyimide was synthesized from 1,4-bis (3-aminopropyl) piperazine and pyromellitic dianhydride. The resulting polyimide was characterized by thermal, FTIR, GPC and microanalysis techniques. Furthermore, permselective behavior of Pt electrodes coated with polyimide to dopamine was also examined. From permselectivity results, it has been demonstrated the effectiveness of the polymeric film in reducing the amperometric responses from ascorbic acid interference, when compared with the bare electrode.

References

1. Gosh MK, Mittal KL (1996) Polyimides: Fundamentals and Appl., Marcel Decker, NY.
2. Fang J, Tanaka K, Katy H, Okamoto K (2000) J. Polym.Sci.: Part A : Polym. Chem. 38:895
3. Bannered S, Madera MK, Saluki AK, Jaywalk DK (2003) Polymer 44:613
4. Seino H, Mochizuki A, Ueda M (1999) J. Polym. Sci.: Part A: Polym. Chem.37:3584.
5. Yang CP, Hsiao SH, Yang HW (2000) Macromol. Chem.Phys. 201:409
6. Nikolelis DP, Petropoulou SSE, Pergel E, Toth K (2002) Electroanal. 14 (11):783
7. Nikolelis DP, Theoharis G (2003) Bioelectrochemistry 59 (1-2):107
8. Nikolelis DP, Petropoulou SSE (2002) Biochimica et Biophysica Acta Biomemebranes 1558 (2):238
9. Roy PR, Okajima T, Ohsaka T (2003) Bioelectrochemistry 59 (1-2):11
10. Shankaran DR, Uehara N, Kato T (2003) Analytica Chim. Acta 478:321
11. Niwa O, Morita M, Tabei H (1991) Electroanalysis 3:163
12. Kaneko H, Yamada M, Aoki K (1990) Analytical Sciences 6:439
13. Gileadi E, Kirowa-Eisner E, Penciner J (1975) in Interfacial Electrochemistry. An Experimental Approach, Addison-Wesley, Reading
14. Vora HR, Goh SH, Chung TS (2000) Polymer Engineering and Science 40:1318
15. Seçkin T, Köytepe S, Özdemir İ, Çetinkaya B (2003) J.of Inorg. and Organomet. Polym. 13:9
16. Seçkin T, Köytepe S, Çetinkaya B, Özdemir İ, Yigit B (2003) Designed Monomers and Polymers 6(2):175
17. Seçkin T, Çetinkaya E, Köytepe S, Yigit B (2003) Polym. Bull. 50:139
18. Huang HW, Kaneko TI, Horie K, Watanabe J (1999) Polymer 40:3821
19. Erdogdu G, Ekinci E, Karagözler AE (2000) Polym. Bull. 44:195
20. Ekinci E, Erdogdu G, Karagözler AE (2000) Polym. Bull. 44:547
21. Ekinci E, Erdogdu G, Karagözler AE (2001) J. Appl. Polym. Sci. 79:327