

# Synthesis and Characterization of Novel Polyimides Based on 2,6-bis(m-Amino Phenoxy) Benzoyl Naphthalene

R.D. Toker Öztürk\*, Nilhan Kayaman-Apohan, Atilla Gungor

Department of Chemistry, Faculty of Art & Science, Marmara University, 34722 Göztepe-Istanbul, Turkey  
 deniztoker84@hotmail.com.tr

It is well known that aromatic polyimides (PIs) have found wide applications in many industrial fields due to their excellent thermal stability, high mechanical strength, high stability to ionizing, good film forming ability, and superior chemical resistance. In this work we synthesized a novel monomer containing naphthalene, 2,6-Bis(m-amino phenoxy) benzoyl naphthalene. A series of novel polyimide based on 2,6-Bis(m-amino phenoxy) benzoyl naphthalene were prepared. FTIR was used to identify the novel synthesized monomer and polyimides. Polyimides were synthesized via the known two-step process; preparation of poly(amic-acid) in DMAc, followed by thermal imidization. TGA was used to measure the thermal properties. Mechanical properties of the free films were determined by standard tensile stress-strain tests.

## 1. Introduction

The growth of modern technology has posed a constantly increasing need for materials that can perform well under harsh conditions, such as elevated temperatures. Polyimides belong to the important class of organic materials known as "high performance" polymers due to their exceptionally high thermo-oxidative stability (Silion et al. 1999) (Ratta, V. et al. 2000). It is well known that aromatic polyimides have found wide applications in many industrial fields due to their excellent thermal stability, high mechanical strength, high stability to ionizing, good film forming ability, and superior chemical resistance. Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other uses for these polymers such as adhesives, gas separation membranes, fuel cell membranes, composite matrices, coatings, and foams are rapidly increasing.

Naphthalene is a bicyclic aromatic molecule. Due to their lower ring strain, six-membered ring (naphthalenic) polyimides have superior chemical and thermal stability compared to the more common five membered ring (benzyl) polyimides. Polyimides containing naphthalene structure create fully aromatic construction. Fully aromatic polyimides containing naphthalene have rigid chains and strong interchain interactions. However, when sulfonated phthalic polyimides are used for proton exchange membranes in fuel cells, they quickly degrade, whereas it has been recognized that naphthalenic polyimides are much more stable in fuel cell environments (Detallante, V. et al. 2002) (Meyer, G. Et al. 2005).

General correlation between the properties aromatic polyimides and the chemical structure of their repeat unit can be established. If they are dividing in to several groups based on the presence of hetero atom for various groups, between the aromatic rings and their position in relation to the imide rings. They break the conjugation of the chain and act as internal 'hinges' allowing the mutual rotation of adjacent rigid elements of the macromolecules. For example aromatic ether linkages inserted into polymer main chains can lower the energy of internal rotation significantly ( Zhuang, H. Et al.1998).

Introduction of flexible ether (-O-) groups, in the polyimide backbone leads to a decreased glass transition temperature and an enhanced moldability.

The goal of better thermal stability together with retained good processability may be achieved in preparing wholly aromatic poly(ether imide)s containing asymmetric, such as meta- and orthocatenated, aromatic units.

In this work we synthesized a novel monomer containing naphthalene, 2,6-Bis(m-amino phenoxy) benzoyl naphthalene. A series of novel polyimide based on 2,6-Bis(m-amino phenoxy) benzoyl naphthalene were prepared. FTIR were used to identify the novel synthesized monomer and polyimids.

therefore, we investigated the mechanical and thermal properties of polyimides prepared from 2,6-Bis(m-amino phenoxy) benzoyl naphthalene and dianhydrides which are Pyromellitic dianhydride (PMDA), 4,4'-Oxydiphthalic anhydride(ODPA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,3',4,4'-benzophenon tetracarboxylic dianhydride(BTDA).

## 2. Experimental Part

### 2.1. Materials

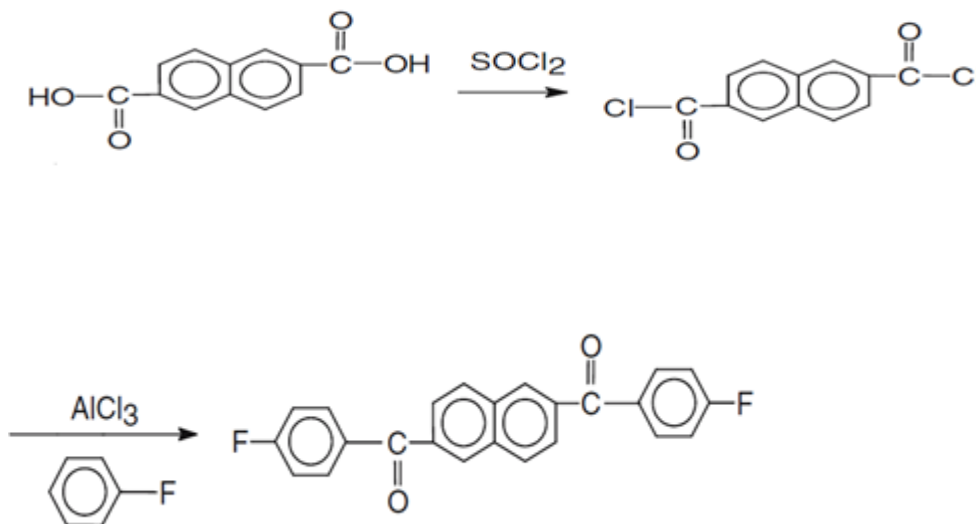
4,4' Diaminodiphenylether (Merck), 3,3',4,4' Benzophenonetetracarboxylic dianhydride(Arcos Organics), Dimethyl 2,6-bis naphthalen dicarboxylate( Amoco Chemical Company), Thionyl chloride (Merck), N,N' Dimethyl Acetamide (DMAc) (Merck), Other chemicals were purchased from Fluka.

### 2.2. Characterization

The infrared spectra were recorded on Perkin Elmer spectrum 100 Model ATR FT-IR Spectrometer. The transition mode was used and the wavenumber range was set from 4000 to 400  $\text{cm}^{-1}$ . The thermal decomposition behavior of polyimide films was determined using a Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. Mechanical properties of the polyimide films were determined by standard tensile stress-strain tests in order to measure the ultimate tensile strength, the modulus and elongation at break. Stress-strain measurements were carried out at room temperature by using a universal test machine (Zwick Rolle, 500N).

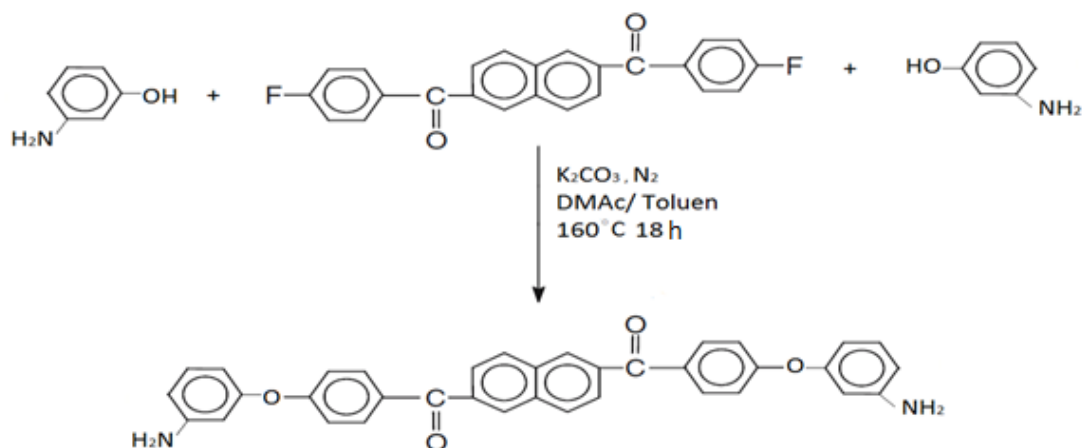
### 2.3. Synthesis of 2,6-bis(4,4'-fluorobenzoyl)naphthalene

2,6-bis naphthalen dicarboxylic acid was obtained by deesterification of 2,6-bis naphthalene dicarboxylic acid dimethyl ester with NaOH. Thionyl chloride was poured into a round-bottomed flask containing 2,6-bis naphthalenedicarboxylic acid and the reaction mixture was refluxed. The excess thionyl chloride was, then, removed vacuum distillations. A yellow solid, 2,6-bis naphthalene dicarboxylic acid chloride was obtained and, further, dried under vacuum. Anhydrous powdered aluminium chloride was added during suspension of 2,6-bis naphthalene dicarboxylic acid chloride in fluorobenzene. The reaction mixture was poured into cold aqueous hydrochloric acid, then the water was decanted off and the residue was washed several times with water. Finally, the product was recrystallized from toluene and dried under vacuum at to afford white crystals.



### 2.4. Synthesis of 2,6-bis (m-aminophenoxy) benzoyl naphthalene

To a three-neck round-bottom flask equipped with a magnetical stirrer, nitrogen inlet, and a Deane Stark trap were added 2,6-bis(4,4'-fluorobenzoyl)naphthalene, 3-aminophenol, potassium carbonate, DMAc and toluene. The reaction mixture was heated and continued stirring. After reaction was complete, toluene was removed from the reaction and cooled to room temperature. The reaction yield was 80%.



### 2.5. Preparation of Polyimides

The polyimides were prepared from diamine 2,6-bis (m-aminophenoxy) benzoyl naphthalene (nafta) and four commercially available dianhydrides: 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), Pyromellitic Dianhydride (PMDA), 2,2'-Bis-(3,4-Dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), 4,4-Oxydiphthalic Anhydride (ODPA) by a conventional two-step synthetic method (table 1).<sup>7</sup> DMAc were placed into a 100-mL three-neck flask under nitrogen purge. The mixture was stirred until the solution was clear. Equal molar amounts of solid dianhydrides were added to the 2,6-bis (m-aminophenoxy) benzoyl naphthalene solution to make a solution with a solid content of 20%. The reaction mixture was stirred for 24 h at room temperature to give a transparent yellow viscous solution of PAA. The viscous PAA solution was spread on a glass plate. The films were then stage-dried in an air oven.

Table 1: Polyimide films formulation

Homo Polyimide	Nafta	BTDA	PMDA	6FDA	ODPA
Nafta-BTDA	1eq mol	1eq mol			
Nafta-PMDA	1eq mol		1eq mol		
Nafta-6FDA	1eq mol			1eq mol	
Nafta-ODPA	1eq mol				1eq mol

### 3. Results

In figure 1(a), the key structural features in FT-IR spectrum of 2,6-bis(4,4'-fluoro benzoyl) naphthalene include the following absorption: aromatic C-H stretching vibration,  $3123\text{ cm}^{-1}$ , ketone C=O stretching vibration,  $1646\text{ cm}^{-1}$ , aromatic C=C stretching vibration,  $1595\text{ cm}^{-1}$ , C-F stretching vibration,  $1154\text{ cm}^{-1}$ . In figure 1(b), the key structural features in FT-IR spectrum of 2,6-bis (m-aminophenoxy) benzoyl naphthalene include -NH asymmetrical and symmetrical stretch,  $3392\text{-}3366\text{ cm}^{-1}$ .

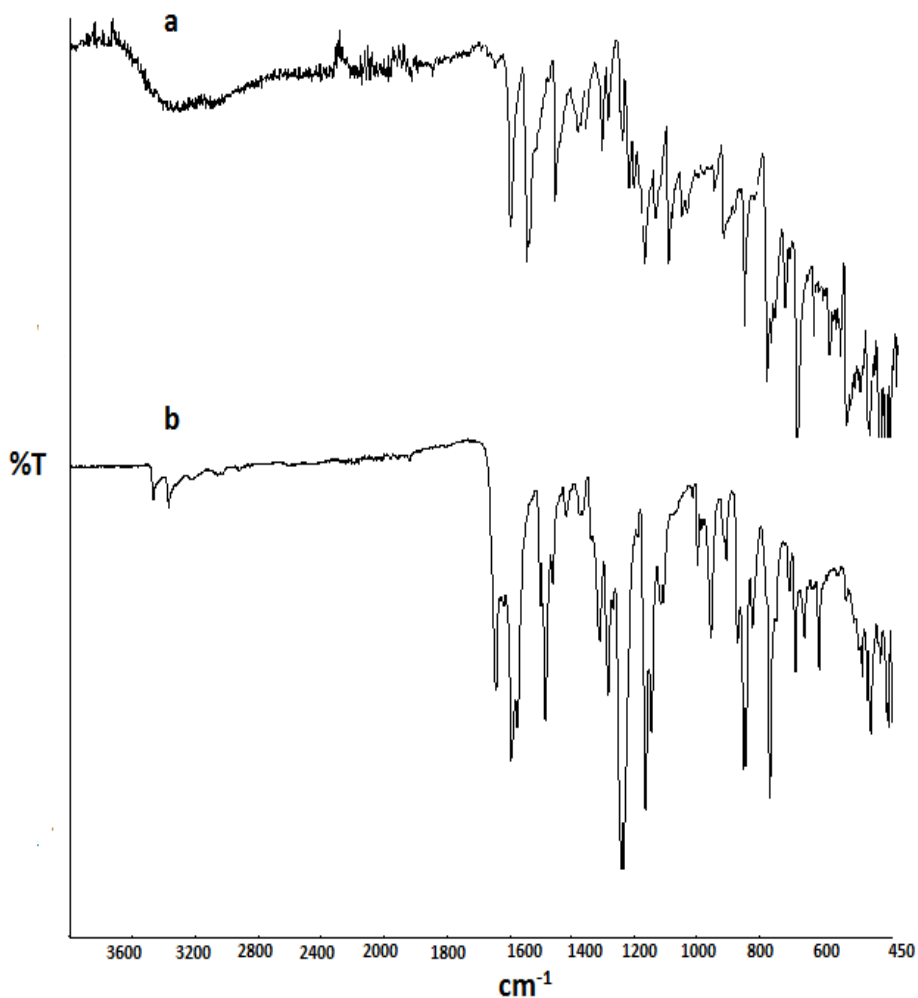


Figure 1: ATR-FTIR spectrum of (a) 2,6-bis(4,4'-fluorobenzoyl)naphthalene and (b) 2,6-bis(m-aminophenoxy) benzoyl naphthalen

The formation of polyimides was confirmed with IR analysis. Figure 2 demonstrates typical set of IR spectra for polyimides. All the polyimides exhibited characteristic imide group absorptions around 1779 cm<sup>-1</sup> and 1714 cm<sup>-1</sup> (typical of imide carbonyl asymmetrical and symmetrical stretch), 1360 - 1366 cm<sup>-1</sup> (C-N stretch). The disappearance of amide, carboxyl bands and 1540 cm<sup>-1</sup> (-NHCO- stretch) indicated a virtually complete conversion of the polyamic acid (PAA) precursor into polyimide.

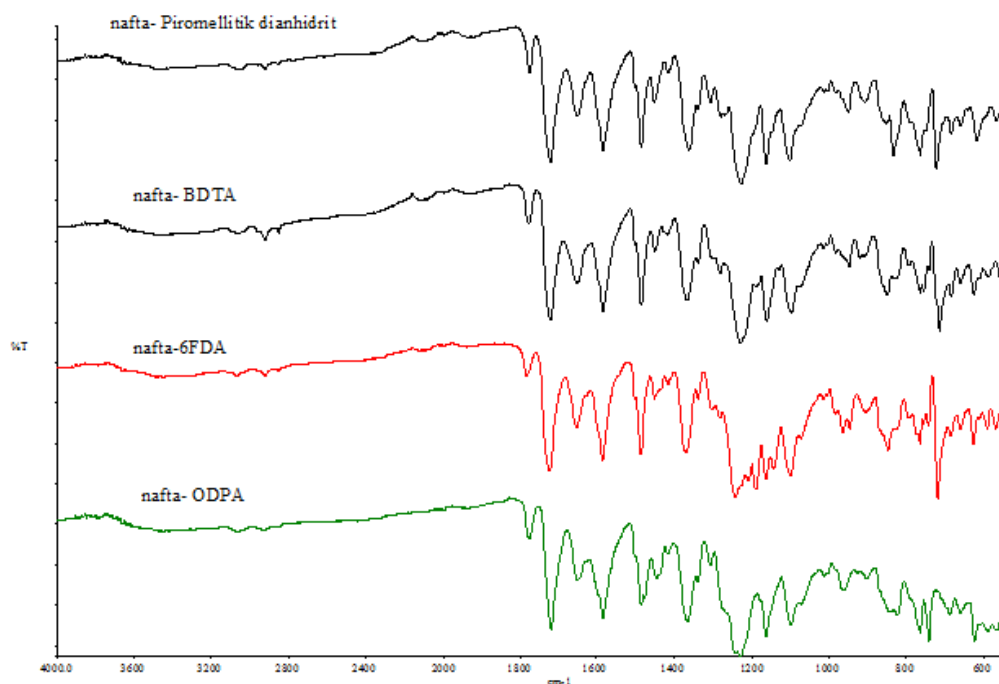


Figure 2: ATR-FTIR spectrum of polyimide films

Thermal properties of the polyimides were evaluated by means thermo-gravimetric analysis (TGA). Thermo-oxidative stabilities of the polymers were determined by thermogravimetric analysis in air. Figure 3 shows TGA curves of the novel naphthalene based polyimides under air atmosphere and the initial thermal decomposition temperatures (Td) were determined in the range of 500 to 522 °C in air for all polyimides tested. The results of thermal analysis demonstrate that the resulting polyimides should hold excellent thermal stability, which would be facilitated to their application.

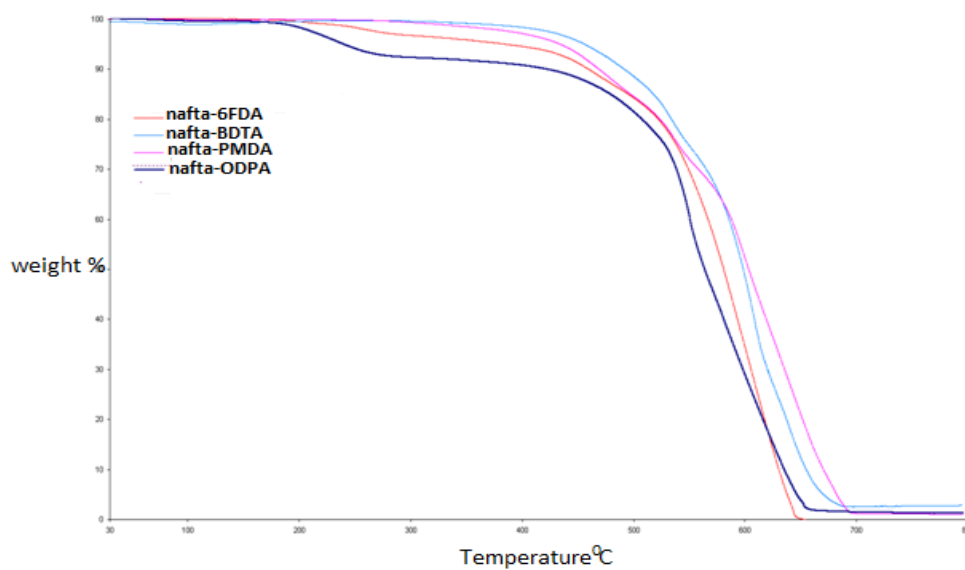


Figure 3: TGA thermograms of the all samples in air atmosphere.

The mechanical properties of naphthalene containing homo polyimide films were measured and the evaluated data as Young's modulus (E), tensile strength ( $\sigma$ ), and elongation at break ( $\epsilon$ ) are displayed in Table 2. All films were strong and flexible. The polyimide films had tensile strengths of 34,95 -55,59 Mpa, Young modulus of 1089,66-897,38 Mpa, and Elongation at break of 4,35-6,96%, indicating that they are strong materials.

Table 2: The mechanical properties of polyimide films

Formulation	Young -modulus Mpa	Tensile Strength Mpa	Elongation at break (%)
Nafta-6FDA	1089,66	34,95	4,35
Nafta-BTDA	1070,86	55,59	6,77
Nafta-PMDA	897,38	43,57	6,96
Nafta-ODA	908,38	42,30	4,99

#### 4. Conclusions

A new diamine- monomer containing naphthalene, 2,6-bis (m-aminophenoxy) benzoyl naphthalene has been successfully synthesized via three step reaction. Four polyimides containing naphthalene have been prepared from 2,6-bis (m-aminophenoxy) benzoyl naphthalene via thermal imidization. Because of the incorporation of naphthalene and imide group, the resulting polyimides exhibited outstanding thermal properties in air. These novel polyimides have high tensile strengths, high module and low elongation at break. Therefore, these polymers may be potential candidates for high temperature membranes, microelectronic devices.

#### References

- Sillion, B., Verdet, L., 1991, Heat Resistant Polymers for Electronics Applications in Polyimides and other High-Temperature Polymers, Abadie M.J.M, Elsevier,367-368.
- Ratta, V., Ayambem, A., Young, R., McGrath, J.E., Wilkes, G.L., 2000, Thermal Stability, Crystallization Kinetics and Morphology of a New Semicrystalline Polyimide Based on 1,3-Bis(4-aminophenoxy) benzene and 3,3',4,4'-Biphenonetetracarboxylic Dianhydride, *Polymer*, 41, 8121-8138.
- Detallante, V., Langevin, D., Chappay, C; Metayer, M., Mercier R., Pineri, M., 2002, Kinetics of Water Vapor Sorption in Sulfoated Polyimide Membranes, *Desalination*, 148, 333-339.
- Meyer, G., Gebel, G., Gonon, L., Capron, P., Marscaq, D., Marestin, C., Mercier,R., 2005, Degradation of Sulfonated Polyimide Membranes in Fuel Cell Conditions, *Journal of Power Sources*,1-9.
- Zhuang, H., 1998, Synthesis and Characterization of Aryl Phosphine Oxide Containing Thermoplastic Polyimides and Thermosetting Polyimides with Controlled Reactivity, PhD Thesis, 6-25.