

**Synthesis and characterization of polyimides from  
1,3-Bis(3-aminophenoxy-4'-benzoyl)benzene(1,3,3'-BABB)**

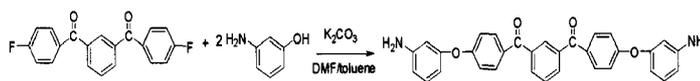
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**Introduction.**

The synthesis of thermoplastic and thermally stable aromatic polyimides is of prime interest. In the 1990s, melt-processable semicrystalline polyimide AURUMTM with high glass transition temperature ( $T_g = 250^\circ\text{C}$ ) and high melting temperature ( $T_m = 388^\circ\text{C}$ ) was successfully developed and commercialized by scientists of Mitsui Chemicals, Inc[1]. Ever since then, efficient approaches to lower the glass transition temperature and melting transition temperature have been introduced based on the modification of polymer structure. Much effort has been carried out in designing and synthesizing new dianhydrides and diamines[2]. Incorporation of flexible units such as  $-\text{O}-$ ,  $\text{C}=\text{O}$ ,  $-\text{SO}_2-$ , as well as the introduction of meta-substituted aromatic rings are the most promising approaches to overcome those processing problems. The purpose of our research work is focusing on the development of thermoplastic aromatic polyimides having lower glass transition temperatures while maintain good thermal and thermal-oxidative stabilities, excellent mechanical properties.

**Experimental.**

*Materials:* All reagents were commercially available (>99%) and used as received. The solvents were vacuum-distilled after drying over calcium hydride. The diamine monomer 1, 3-Bis(3-aminophenoxy-4'-benzoyl)benzene (1,3,3'-BABB) was successfully synthesized via nucleophilic substitution reaction in our lab(Scheme 1), with a yield of 64.4% and mp 142-146°C.



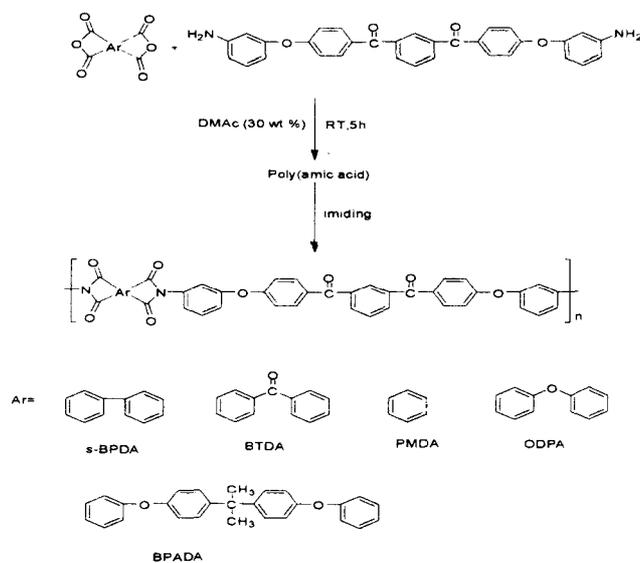
**Scheme 1.** Synthesis of the diamine monomer 1,3,3'-BABB

*Synthesis of novel thermoplastic and thermally stable Polyimides:* A series of thermally stable polyimides based on 1,3,3'-BABB and several dianhydrides were prepared via a conventional two-step polycondensation(Scheme 2).

**Results and Discussion.**

The main aim of this study is the preparation of kind of thermoplastic polyimides with lower glass transition temperature without sacrificing their thermal stabilities. By considering the excellent thermoplastic behavior of poly(ether ketone)s, which is also a kind of high performance plastic with good thermal stability, a diamine monomer containing aryl-ether and aryl-ketone structures was designed and synthesized. It is expected that the flexible ether unit and the m-substituted aromatic rings would lead to a much lower glass transition temperature, while the rigid aryl-ketone moisture could maintain the thermal stability of the polyimides based on 1,3,3'-BABB .

*Synthesis of novel thermoplastic and thermally stable Polyimides (Scheme 2):* first, 1,3,3'-BABB and distilled DMAc were charged into a conical flask equipped with magnetic stirrer. After the diamine was dissolved, calculated amounts of dianhydride were added gradually, with a final solid concentration controlled to 30 wt %. The polyamic acid solution was casted onto a clean, dry glass plate with blade set at 0.50mm. After the solvent was removed by drying in an oven , then a thermal imidization was performed in vacuum oven at 200°C、250°C、300°C, respectively, and then cooled to room temperature.



Scheme 2. Synthetic scheme of polyimides based on 1,3,3'-BABB

The polyimides films were characterized with DSC, TGA, and their optical, mechanical properties, water absorption were also evaluated.

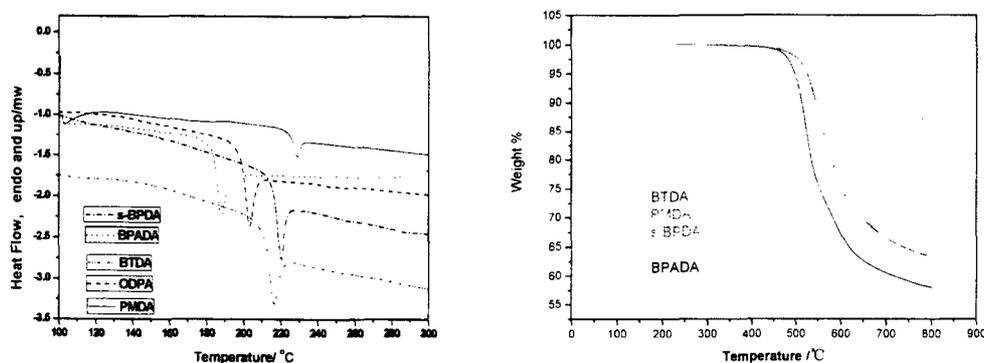


Figure 1 (a) DSC diagrams of polyimides ;

(b) TGA traces of polyimides in N<sub>2</sub> atmosphere

The T<sub>g</sub> was determined in N<sub>2</sub> atmosphere by using DSC with a heating rate of 10°C/min. The thermal stabilities of the polyimide films were estimated by the 5% (T5) and 10% (T10) weight loss temperature measured by TGA with a heating rate of 5°C/min in N<sub>2</sub> atmosphere. The results are listed in Table 1. All of the films show lower T<sub>g</sub>s (180-225°C) because of the flexible molecule chain due to the ether and the *m*-substituted aromatic rings in the diamine. The PI made from BPADA shows the lowest T<sub>g</sub>, which suggests that the bulky methyl groups in the BPADA units could increase free volume and lower the interaction between polymer chains. The stick structure of the PMDA and BPADA increase the interaction between polymer chains, therefore leading to higher T<sub>g</sub>s. The T<sub>g</sub> PI-PMDA > PI-s-BPDA > PI-BTDA > PI-ODPA > PI-BPADA, which accords with the rigidity of the dianhydrides.

The thermal stability of the polyimide films were estimated by the 5% (T5) and 10% (T10) weight loss temperature measured by a thermogravimetric analyzer (TGA) at a heating rate of 5°C/min in N<sub>2</sub> and air atmosphere. The results are tabulated in Table 1 and the typical TGA curves are reproduced in Figure 1(b). All of the films exhibited good thermal stability, the polyimides have a 10% weight loss temperature in the range of 513 - 560°C in N<sub>2</sub>, 523-567 °C in air, while some of them showed a 5% weight loss temperature reach at 542°C in N<sub>2</sub>, indicating that introduction of the flexible structure in the monomer did not sacrifice their thermal and thermo-oxidative stabilities, when the rigid aryl-ketone structure together with the thermal stable aromatic rings as well as the symmetric structures of the polymer backbones all contributed to the thermal stability. The

temperatures at which a weight loss of 5% (Td,5%) and 10% (Td,10%) occurred were recorded, along with the char yield at 800 °C

**Table 1.** Thermal Data of PI films in nitrogen

samples	Decomp onset(°C)	Tg (°C)	Td 5% (°C)a	Td 10% (°C)b	Char yield at 800 °C(%)
PI-BPADA	479	184	497	513	58
PI-ODPA	495	198	496	520	59
PI-BTDA	518	211	525	544	64
PI-s-BPDA	537	216	542	560	63
PI-PMDA	518	225	524	541	59

The mechanical properties of the polyimides films were studied by using a tensile tester and evaluated with their stress - strain profiles. The results are shown in **Table 2**. The polyimides have tensile strength at break ranging from 105 to 133 MPa, elongations at break of 8.8 - 167.9% and initial modulus of 2.6-3.1 GPa, which indicated that the PIs containing ether and carbonyl linkages have excellent toughness. As shown in **Table 2**, the Elongation at break of polyimide based on PMDA is much higher than other polyimides and the Elongation at break of polyimide based on BPADA is the lowest, which is probably due to the different flexibilities of the dianhydrides, less flexible dianhydride structure would lead to a more ordered and closer stacking of the polymer chains.

**Table 2.** Mechanical properties of polyimides at room temperature

samples	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)
PI-BPADA	113.0	3.0	8.8
PI-ODPA	123.3	3.1	28.6
PI-BTDA	133.3	3.1	21.3
PI-s-BPDA	122.9	3.1	38.5
PI-PMDA	105.0	2.6	167.9

It is very interesting to find all polyimides films showed a remarkable thermoplastic behavior when evaluated their mechanical properties 20°C above their Tgs. The results are reported in **Table 3**. The tensile modulus and tensile strength were depressed obviously, and the values of elongation at break were increased clearly.

**Table 3.** Thermal mechanical properties of polyimides

samples	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)
PI-BPADA	2.21	3.64	1314.9
PI-ODPA	3.79	4.03	689.6
PI-BTDA	7.59	83.61	287.0
PI-s-BPDA	3.51	6.10	556.5
PI-PMDA	4.01	2.99	1274.66

The optical data of PI films were listed in Table 4. It is easily to see from **Figure 2** that all the films exhibit high transparency. BTDA/BABB is brown and has low transparency in the visible region despite its  $\lambda_0$  being close to those of

PMDA/BABB and BPDA/BABB, the latter two polyimides are yellow. The deep color of the polyimide prepared from BTDA can be explained by cross-linking reactions between the benzophenone and C=O groups. The ODPA/BABB, BPADA/BABB are shallow yellow, and have the similar transparency (88%), but the ODPA/BABB and BPADA/BABB have the minimum  $\lambda_0$ , just because the ODPA and BPADA have a lower electron affinity (EA 1.30) than BPDA(EA 1.38), BTDA(EA 1.55), PMDA(EA 1.90). The colors of the polyimides accord with the electron affinity of the dianhydrides. This also can be explained with the charge transfer complex (CTC) formation between polymer chains: as the C=O group in BTDA increase the charge transfer complex (CTC) effect of intra-molecular, which lead to a deeper color. The ODPA and BPADA could obtain colorless polyimides with the ether linkages reduce the CTC effect.

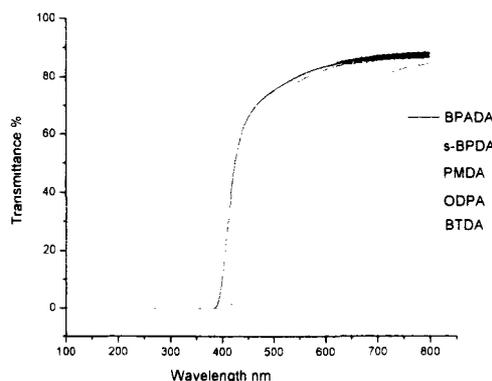


Figure 2. UV-Vis absorption spectra of the polyimide films

The results of water absorption were listed in Table 4. Put the dry films which have been weighted ( $m_0$ ) into the water at room temperature for 24 hours, then wipe up the water on the surface of the films and weight them ( $m$ ). We calculate the water absorption with this formula:  $(m-m_0)/m_0$ . From the results we can see that the water absorption of the polyimide films is very low than reported, which could be attributed to the existence of the aryl-ether moieties in the polymer backbone. Furthermore, the water absorption decreased just at the same order as the aryl-ether and the aromatic rings contents in the dianhydride structure increased: BPADA > BPDA > ODPA > BTDA > PMDA.

Table 4. Optical Data and water absorption of PI films

samples	color	UV(%)	$\lambda_0$ (nm)	Water absorption%
PI-BPADA	shallow yellow	88.0	378	0.27
PI-ODPA	shallow yellow	87.9	364.5	0.55
PI- BTDA	brown	84.5	391	0.62
PI- s-BPDA	yellow	87.5	388	0.46
PI-PMDA	yellow	87.2	396	0.89

### Conclusions.

A novel series of polyimides with low glass transition temperature and outstanding mechanical properties and thermal stability have been successfully synthesized.

### References.

- [1] S.Tamai\*, T.Kuroki, A.Shibuya, A.Yamaguchi, Polymer 42, 2373-2378,2001
- [2] Shahram Mehdipour-Ataei, Yaghoob Sarrafi, Mehdi Hatami, European Polymer Journal,40,2009-2015,2004