

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

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Abstract

Diamine 1,3-Bis(3-aminophenoxy-4'-benzoyl)benzene (1,3,3'-BABB) was successfully synthesized via nucleophilic substitution reaction of 3-aminophenol and 1,3-bis(4-fluorobenzoyl) benzene. A series of thermally stable polyimides based on 1,3,3'-BABB and dianhydrides, s-BPDA, BTDA, ODPDA, PMDA, BPADA were prepared via a conventional two-step synthesis. The polyimides were characterized by DSC, TGA, UV-vis absorption, XRD, water absorption, inherent viscosity, mechanical properties. Owing to the diamine containing the aether bonds and carbonyl the polyimides exhibited low glass-transition temperatures and high UV permeation.

1. Introduction

Aromatic polyimides (PI) have been widely utilized in industrial applications such as automobile and aircraft parts, electronic packaging, films, adhesives, and matrix materials for composite materials due to their outstanding mechanical, thermal stability, dielectric and adhesive properties, chemical resistance and dimensional stability [1]. However the technological and industrial application of rigid polyimides are limited by processing difficulties due to their high melting or glass transition temperatures and lack of solubility in most organic solvents. Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors.

In 1970s, high performance thermoplastic PIs were developed at NASA Langley Research Centre. The early versions of thermoplastic PIs were difficult to process because they were insoluble in most organic solvents and infusible at elevated temperatures. Most of the thermoplastic PIs have T_g in excess of 300°C and melt temperature T_m above 400°C . To process such PIs, very high temperatures ($>400^\circ\text{C}$) are required, which causes the degradation of the polymer [2]. Most high performance thermoplastic PIs exhibit viscoelastic solid-like behavior. They require high consolidation pressures to attain wetting of the adhered surface even at temperatures higher than T_g . Application of very high pressure results in 'flow-out' of the resin from the bonded area, resulting in non-uniform bond line thickness.

The synthesis of thermoplastic and thermally stable aromatic polyimides is of prime interest. In the 1990s, melt-processable semicrystalline polyimide AURUMTM having 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.

The 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 achieved in designing and synthesizing new dianhydrides and diamines, 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 important approaches to overcome those processing

problems. The goal of this research work is to focus on the development of polyimide having low glass temperature and good thermal stability. In this research we synthesize diamine 1,3-Bis(3-aminophenoxy-4'-benzoyl) Benzene (BABB) containing ether and carbonyl linkages with 3-Aminophenoyl and 1,3-Bis(4-fluorobenzoyl)benzene. Then a series of PAA (Poly amic acid) were prepared with BABB and 3,3',4,4'-Biphenyl-tetracarboxylic acid dianhydride (s-BPDA), 4,4'-oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), Benzophenonetetracarboxylic dianhydride (BTDA), 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA). Finally, the PI films were prepared with thermal imidization from PAA. In the work, we provide the degree of crystallization, glass transition, thermal decomposability, water absorption, mechanism properties, UV/vis permeation characteristics of the resulting films. All the films have low glass transition temperature (180-220°C) and excellent transparency due to the diamine containing ether and carbonyl linkages. And that all the films exhibit excellent resistance to a wide range of chemicals, high mechanical properties.

2. Experimental

2.1 Materials: 3-AP, Na₂CO₃;99%, 1,3,4-FPEB, s-BPDA, BTDA, ODPA, PMDA, BPADA were commercial and used as received. DMF, DMAc, toluene, were vacuum-distilled after drying over calcium hydride.

2.2 Monmer Characterization:

Infrared spectra were obtained on an OPUS FTIR spectrometer.

¹H NMR spectra was obtained on A Bruker 300.

Mass spectrum was obtained on an AXIMA-CFR COMPACT.

Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC 821e thermal analyzer with the sample sealed in an aluminum pan.

Elemental analysis was performed with Perkin Elmer 2400 CHN analyzer.

2.3 Polymer Characterization:

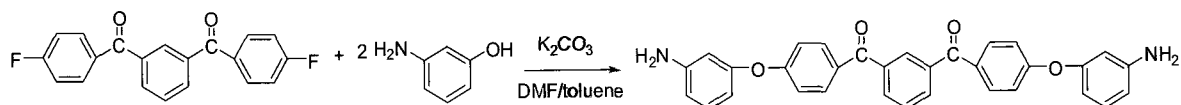
Glass transition temperatures (T_g) were determined with DSC at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Inherent viscosities (η_{inh}) were obtained on 0.5 g/dL polyimide solutions in N,N-Dimethylacetamide (DMAc) at 25°C. Dynamic thermogravimetric analysis (TGA) was performed on a PerkinElmer (TGA-7) thermogravimetric analyzer with Pyris data collection and analysis software for Windows. Films samples at a heating rate of 5 °C min⁻¹ in nitrogen atmosphere at a flow rate of 25 cm³/min. UV/vis spectra were obtained on thin films using a UV/vis 2501 spectrometer. Tensile properties such as the tensile modulus, tensile strength and elongation of the films at break were measured as the average using specimens on a Daojing AG-I tensile apparatus.

2.4 Synthesis and Characterization of 1,3-Bis(3-aminophenoxy-4'-benzoyl) Benzene (1,3,3'-BABB)

3-Aminophenoyl (0.220mol) was dissolved in a solution of N,N-dimethylformamide (150ml) and toluene (30ml) in a 250ml three-neck flask equipped with a magnetic stir, thermometer, N₂ gas inlet, Dean-Stark trap and condenser. Powdered anhydrous potassium carbonate (34.75g,0.250mol) was added and water was removed by azeotropic distillation with toluene. Then 1,3-Bis(4-fluorobenzoyl)benzene (323.00g,0.01mol) was added and the

reaction mixture stirred at 130-150°C for 8-15h. The mixture was allowed to cool and subsequently added to water to precipitate a solid which was collected by filtration and dried in vacuum oven at 40°C. Recrystallization from the mixture of water and methanol afforded 1,3-Bis(3-aminophenoxy-4'-benzoyl) benzene (3.22g, 64.4%) (Scheme 1) .

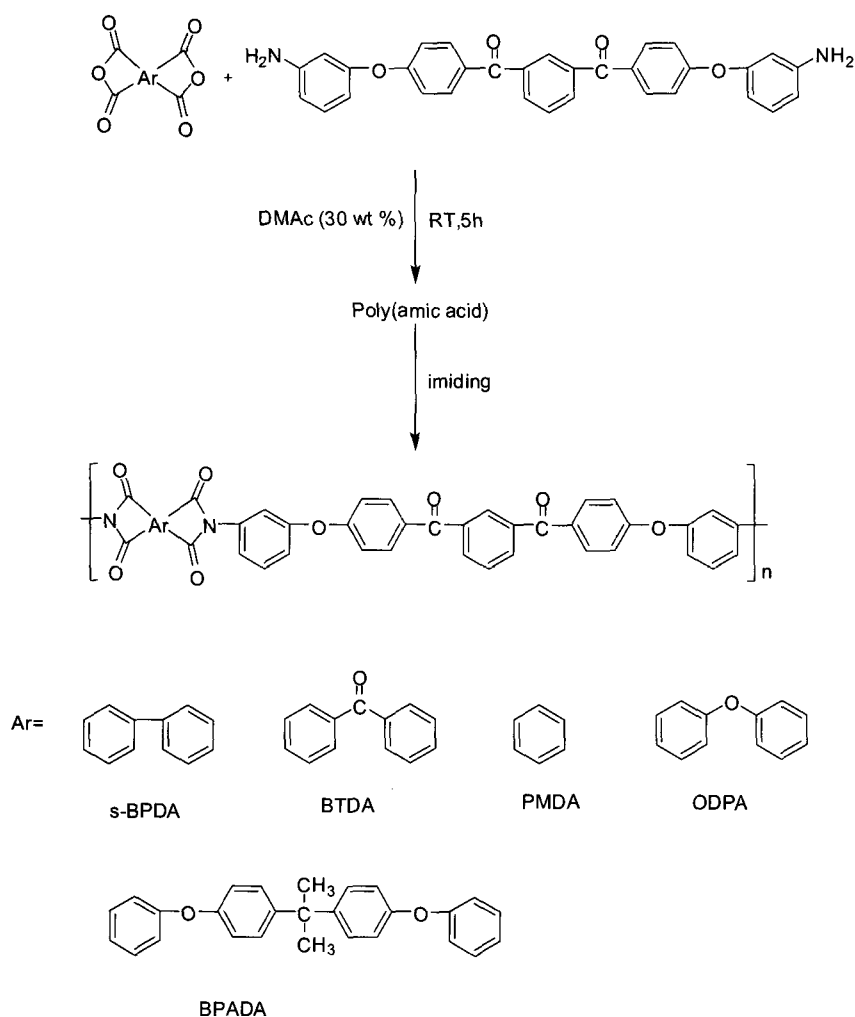
Yield:64.4%, mp 142-146°C. IR (KBr)3467,3379cm⁻¹(s,NH₂),1641 cm⁻¹ (vs ,sharp ,C=O).¹H NMR(DMSO) δ5.3 (s,4H,NH₂), 6.2-8.2(m,20H,aromatic).Elemental analysis calculated for C₃₂H₂₄N₂O₄: C, 76.78%; N, 5.60%; H, 4.83%; O ,12.79%. Found: C,76.77%; N,5.62%; H, 4.88%;O, 12.73%. HPLC: 99.9%. The diamine melting point temperature is 146 °C



Scheme 1. Preparation of 1,3-Bis(3-aminophenoxy-4'-benzoyl)benzene

2.5 Synthesis and Characterization of the Poly (amic acid) solutions

All poly(amic acid) solutions with 1,3,3'-BABB and commercial dianhydrides (PMDA, ODPDA, BTDA, s-BPDA and BPADA) were prepared via the two-step process: the synthesis of poly(amic acid) followed by (Scheme 2). First, 1,3,3'-BABB and distilled DMAc were charged into a conical flask-dried with magnetic stirrer. After the diamine was dissolved, calculated amounts of dianhydride were added gradually, with the solid concentration controlled to 30 wt %. The Scheme 2 is representative for the preparation of all polymers.



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

2.6 PI films Preparation and Characterization

The polyamic acids were casted onto clean, dry plate glasses using a blade set at 0.50mm. After the solvent was removed by drying in common oven at 50 °C for 2h, 80 °C for 2h, 100 °C for 4h, 120°C for 2h, 150°C for 1h, and 180°C for 1h, then the thermal imidization of poly(amic acid) films was performed in vacuum oven at 200°C for 1h, 250°C for 1h, 300°C for 1h and then cooled to room temperature. Removal of the cured films from the plates was aided by immersion in cool water.

3. Results and Discussion

The main aim of this study was to prepare polyimides with low glass transition temperature without sacrificing their thermal stability. So synthesis of a diamine with ether bonds and meta-substituted aromatic rings units was considered. BABB has symmetric structure without any weak linkages were considered for increasing of the thermal stability. Also, presence of flexible ether and meta-substituted aromatic rings units were considered for lower the glass transition temperature.

3.1 Inherent viscosities of PAA solutions

The inherent viscosities data of the polyimides are listed in table 1. The inherent viscosities data of the polyimides are listed in table 1. The inherent viscosity is a good criterion for estimation of molecular weight, the prepared polyimides showed reasonable molecular weights. As the stiff chains of dianhydrides BPDA and PMDA, the η_{inh} of BABB/BPDA and BABB/PMDA are higher than others.

Table 1. Characterization of Polyimides

Samples	η_{inh}^a (g/dL)	Tensile Strength ^b (MPa)	Tensile Modulus ^b (GPa)	Elongation at break ^b (%)
ABB/BPADA	0.4	113.0	3.0	8.8
BABB/ODPA	0.4	123.3	3.1	28.6
BABB/BTDA	0.4	133.3	3.1	21.3
BABB/s-BPDA	0.83	122.9	3.1	38.5
BABB/PMDA	0.6	105.0	2.6	167.9

a Inherent viscosity of PAA measured with 0.5g/dL in DMAc at 25°C.

b Measured at room temperature in air at a drawing rate of 8 mm/min.

3.2 Solubility of polyimides

The solubility behavior of the polyimides generally depends on their chain packing density and intermolecular interactions, which are affected by the rigidity symmetry and regularity of the molecular backbone. All of the films exhibited indiscernible in NMP, m-cresol, DMAc, chloroform etc organic solvents examined in this study and exhibit high chemical resistance. This nature can be explained by the strong interaction between polymer chains that are highly stacked on each other because of the rigidity of the dianhydrides in polymer backbone.

3.3 Thermal properties of polyimides

The glass transition temperature (T_g) was determined in N_2 using dynamic mechanical thermal analyzer with a heating rate of 10°C/min. The typical DSC curves are shown in Figure 1 and the results are listed in Table 2. All of the films show low glass transition temperatures (180-220°C) on the DSC thermograms because of the flexible molecule chain due to the ether and carbonyl linkages in the diamine. The PI made from BPADA shows the lowest glass transition temperature, it 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 BPDA increase the interaction between polymer chains, therefore leading to the higher glass transition temperatures. The glass transition temperatures BABB/PMDA > BABB/s-BPDA > BABB/BTDA > BABB/ODPA > BABB/BPADA, it accords with the rigidity of the dianhydrides.

The thermal stability of the polyimide films were estimated by the 5% (T_5) and 10% (T_{10}) weight loss temperature measured by a thermogravimetric analyzer (TGA) at a heating rate of 5°C/min in N_2 atmosphere. The results are tabulated in Table 2 and the typical TGA curves are reproduced in Figure 2. 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_2 , while some of them

showed 5% weight loss temperature reach at 542°C, indicating that introduction of the flexible structure in the monomer could lower the glass transition temperature and do not sacrifice thermal and thermooxidative stabilities of the polyimides. As the phenylation of backbone, avoid of weak linkages and symmetry of the structures were most important structural modification for increasing of the thermal stability. The temperatures at which a weight loss of 5% (T_d , 5%) and 10% (T_d , 10%) occurred were recorded, along with the char yield at 800 °C (Table 2).

Table 2 Thermal Data of PI films

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

^a Temperature at 5 wt% loss. ^b Temperature at 10 wt% loss.

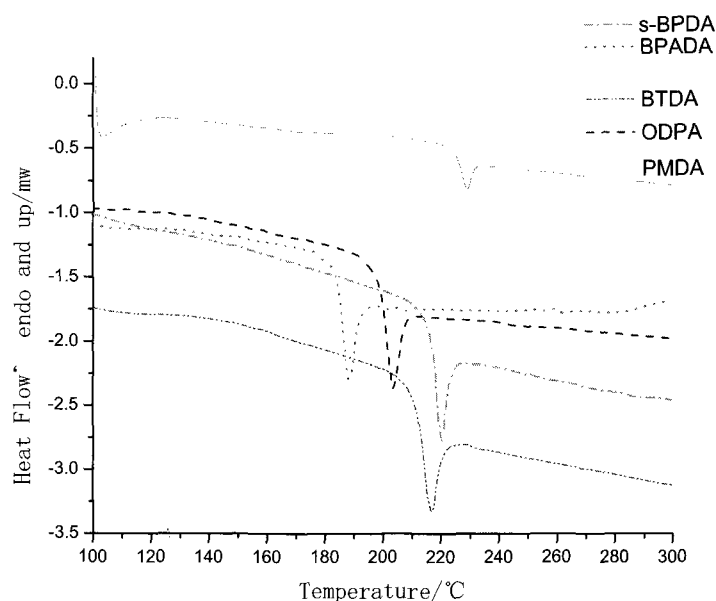


Figure 1 DSC diagrams of polyimides with the heating rate of 10°C/min under nitrogen atmosphere

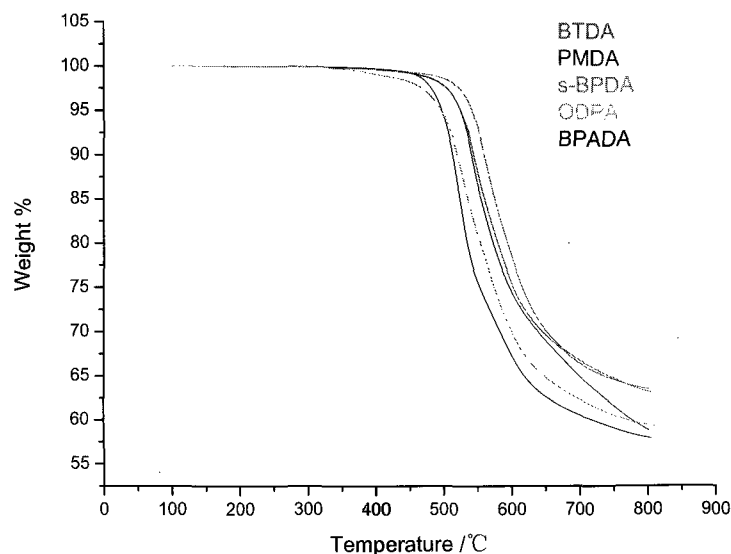


Figure 2 TGA traces of polyimides with the heating rate of 5°C/min under nitrogen atmosphere

3.4 Mechanical properties of polyimides

The mechanical properties of the polyimide films were determined using a tensile tester and were evaluated using their stress – strain profiles. The results are reported in Table 1. The polyimides have tensile strength at break of 105-133 MPa, elongations at break of 8.8 – 167.9% and initial modulus of 2.6-3.1 GPa, indicating the PIs containing ether and carbonyl linkages have excellent toughness. As shown in Table 1, 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, this due to the flexibility of the dianhydride, when the polymer chains from the random to the melodic, the flexible chains form the crystal easily, since the film made from BPADA has the higher orderliness.

3.5 Optical Properties of the Polyimides

UV/vis spectra were obtained on thin films using a UV/vis 2501 spectrometer (Figure 3, Table 3). Figure 3 shows UV-Vis absorption spectra of the polyimides derived from BABB and five kinds of conventional dianhydrides. Table 3 lists the color, maximum transparency, and the minimum λ_0 . All the films exhibit high transparency. ODPA/BABB, BPADA/BABB, BPDA/BABB polyimides exhibit higher transparency at shorter wavelengths (400-450nm) than PMDA/BABB and BTDA/BABB. BTDA/BABB is brown and has low transparency in the visible region despite its λ_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 occurring at benzophenone C=O groups. The ODPA/BABB, BPADA/BABB are shallow yellow, and have the approximative transparency (88%), but the ODPA/BABB have the minimum λ_0 , this because the ODPA have the lower electron affinity (EA 1.30) than BPDA(EA 1.38), BTDA(EA 1.55), PMDA(EA 1.90). The color of the polyimides accord with the electron affinity of the dianhydrides.

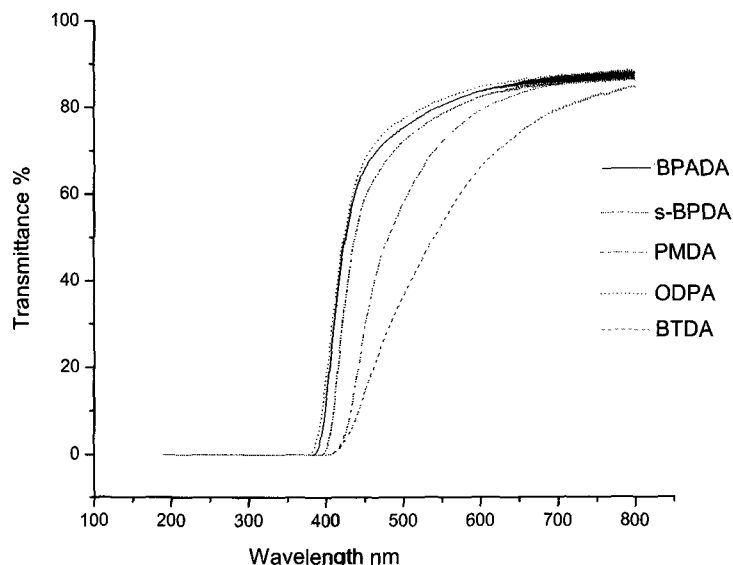


Figure3 UV-Vis absorption spectra of the polyimide films

Table 3. Optical Data of PI films

samples	color	UV(%)	$\lambda_0(\text{nm})$	Water absorption%
BABB-BPADA	shallow yellow	88.0	378	0.4
BABB-ODPA	shallow yellow	87.9	364.5	2.4
BABB- s-BPDA	yellow	87.5	388	0.1
BABB-PMDA	yellow	87.2	396	1.4
BABB- BTDA	brown	84.5	391	0.2

3.6 Water absorption

The results of water absorption were listed in table 3. 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 absorptions of the polyimide films are very low. The ODPA/BABB film's water absorption is higher than other films because there is an ether bond in the 4,4'-oxydiphthalic anhydride. As the rigidity structure of the s-BPDA, the polyimide BABB/s-BPDA film's water absorption is the lowest.

3.7 The crystalline of polyimides

To evaluate the amount of crystalline in the polyimides, the wide-angle X-ray diffraction pattern of the polyimides in the region of $2\theta = 10 - 60^\circ$ at room temperature were studied. The crystalline of the polymers was negligible and therefore, they were almost amorphous. The representative wide-angle X-ray diffractogram of the polymers was shown in Fig9.

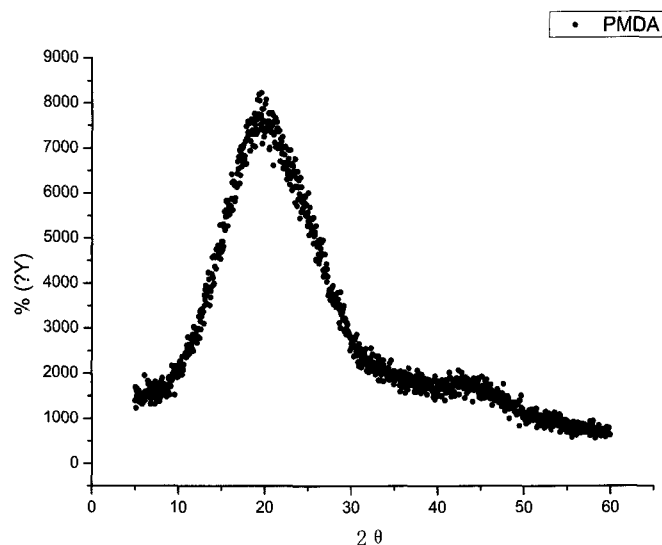


Fig9. Wide-angle X-ray diffraction pattern of BABB/PMDA.

4. Conclusions

The diamine BABB was synthesized through nucleophilic substitution reaction with 3-aminophenol instead of 3-nitrophenol and FPEB in the presence of sodium carbonate. This method avoided the reductive process contrast with 3-nitrophenol, thus it has a high yield. The synthesis and characterization of polyimides based on BABB and several aromatic dianhydrides have been reported. The polyimide films show low glass transition temperature between 180-220 °C and also exhibit the outstanding mechanical properties and thermooxidative stability. The films were insoluble in common organic solvents, exhibiting high chemical resistance. The characteristics were considered to be due to the introduction of the ether and carbonyl linkages into the polymer backbone.

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