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Synthesis and Characterization of Polyimides with Ether Linkages

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Synopsis

A series of polyimides derived from a newly synthesized diamine, namely, 4,4'-bis(4-aminophenoxy)-2,2'-dimethylbiphenyl (BAPD), were developed and characterized. Their physical and thermal properties were compared to polyimides based on commercially available 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP).

INTRODUCTION

Polyimides have found extensive use as adhesives, electronic packing materials and matrix resins at elevated temperature. However, solubility and processability are generally major concerns when working with polyimides. One approach that has been successfully applied is, to incorporate flexible linkages along the backbones, either in the diamine or the dianhydride component. The flexible linkages include ether (-O-), methylene, ($-CH_2-$), carbonyl (C=O), sulfur (-S-), sulfone ($-SO_2-$) and isopropylidine [$-C(CH_3)_2-$] as well as hexafluoroisopropylidene [$-C(CF_3)_2-$]. Polyimides containing ether linkages prepared through phenoxy derivatives via nitro displacements, especially General Electric's polyetherimide, Ultem®, have achieved great commercial success. [1,2] Other polyimides based on commercially available phenoxy-diamines, such as 4,4'-bis(4-aminophenoxy)-biphenyl (BAPA)[3] and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) have exhibited versatile properties suitable for adhesive and film applications in electronics. However, the diamine BAPA is not soluble in most common solvents, except N-methy-2-pyrrolidinone (NMP). In recent years, noncoplanar 2,2'-substituted biphenyl diamines have been shown to enhance the solubility of polyamides[4] and polyimides[5-10] while imparting interesting physical properties towards the polymers.

The objective of this research is to introduce the 2,2'-dimethylbiphenyl moiety along with phenoxy units into the diamine structure to prepare 4,4'-bis(4-aminophenoxy)-2,2'-dimethyl biphenyl (BAPD) for polyimide synthesis. Polyimides based on BAPP will also be synthesized for a comparison. Although BAPP is a commercially available diamine, there are very few reports on the properties of its corresponding polyimides other than the patented literature.[11,12] Hopefully, the two methyl substituents on the bipheny will improve the solubility of the diamine and yield polyimides with different properties than the polyimides containing the isopropylidene [-C(CH_3)$_2$-] group between the two phenyl rings.

EXPERIMENTAL

Materials

2,2'-Dimethyl benzidine.2HCl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA), 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) were purchased from Chriskev Co. 4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride (HFDA) was obtained from Hoechst Celanese. All the dianhydrides were dried overnight at 150 °C under vacuum, before use. N-Methyl-2-pyrrolidinone (NMP), obtained from Aldrich, was distilled over phosphorus pentoxide under vacuum, prior to polymerization.

Synthesis of Diamine Monomer

Synthesis of 2,2'-dimethyl-4,4'-biphenol **(2)**
To a 1000 mL flask, 2,2'-dimethylbenzidine dihydrochloride (53.4 g, 0.14 mol.) **(1)** was added as wet cakes (contained 26% moisture) as received along with 200 mLof distilled water and 30 mL of conc. HCl. The resulting heterogeneous reaction mixture was stirred at 0 °C. Then a solution of sodium nitrite (22.77 g, 0.33 mol.) in 40 mL of water was added dropwise to the above solution over a period of 1 hour at 0 °C under nitrogen to form a diazonium salt. Separately, a two phase solution containing 75 mL of sulfuric acid in 250 mL of water and 125 mL of 1,2 dichloroethane in a 2000 mL round-bottom flask were stirred vigorously into a one phase system at 85-90 °C. Then the diazonium solution was added dropwise to the above two-phase solution with very efficient stirring for 1-2 hours until no more nitrogen was evolved due to the decomposition of diazonium salts. (During the process, the diazonium salts decomposed with aq. sulfuric acid to form the biphenol which was immediately extracted to the organic layer). The reaction mixture was cooled down, and the organic layer was separated and dried over magnesium sulfate. The solvent was concentrated to half of its original volume and then cooled in a refrigerator overnight to induce crystallization. The resulting solids were collected and washed with 1,2-dichloroethane/hexane = 15/85 to remove the dark color impurities to afford 19.66 g (62%) as the first crop. mp = 106-108°C (lit.[13] mp = 122-124 °C), TLC(SiO_2): Rf = 0.09 (EtOAc/hexane = 15/85)

Synthesis of 4,4'-bis(4-nitrophenoxy)-2,2'-dimethylbiphenyl (**3**)

2,2'-Dimethylbiphenol (**2**) (42.8 g , 0.2 mol.) was dissolved in 250 mL of N,N-dimethylformamide (DMF), and then potassium carbonate (60.8 g, 0.44 mol.) and 4-fluoro-nitrobenzene (59.22 g, 0.42 mol.) were added. The reaction mixture was heated to reflux for 20 hours overnight. The reaction mixture was filtered to remove potassium carbonate, then the solution was concentrated to 1/3 of its original volume in a rotary evaporator. Subsequently, water was added to the DMF solution to precipitate out the product in quantitative yield, and then the product was washed with ethanol to remove any trace of unreacted 4-fluoro-nitrobenzene. The crude product (mp = 146-147 °C) is pure enough for next step. TLC(SiO_2): Rf = 0.36 (EtOAc/hexane = 15/85), elemental analysis for $C_{26}H_{20}N_2O_6$ calcd: C 68.41% ; H 4.38% ; N 6.14%
found : C 68.26% ; H 4.43% ; N 6.17%

Synthesis of 4,4'-bis(4-aminophenoxy)-2,2'-dimethylbiphenyl (**4**)
4,4'-Bis(4-nitrophenoxy)-2,2'-dimethylbiphenyl (80g,) was dissolved in 350 ml of DMF and added carefully to a hydrogenation bottle containing 8 gm of 5% Pt/C (adding catalysts to a solution might cause fire due to the presence of vapor). The solution was subjected to hydrogenation at 100 °C for 3 hours. Then 100 ml of water and 3 g of decolorizing charcoal were added and heated for 5 min. The solution was then filtered through a Celite pad and 1000 ml of water was added. The reaction mixture became a mixture of fluffy solid and a sticky resin and was stirred for 1 hour to give a tan colored solid. The solid was removed by filtration, crushed with a mortar and pestle and then stirred with 1000 ml of water for 1 hour. The solid was collected by filtration and dried to afford 59.2 g (85%) of the product. mp = 140 °C, TLC (SiO_2): Rf = 0.7 (CH_3OH/CH_2Cl_2 = 10/90), elemental analysis for $C_{26}H_{24}N_2O_2$,
calcd. : C 78.67% ; H 6.10% ; N 7.06% , found : C 78.32% ; H 6.13% ; N 6.81%

Polymerization

The polymerization was accomplished by reacting a dianhydride, such as 4,4'-(hexafluoroisopropylidene)-diphthaic anhydride (HFDA) with an equal molar amount of either 4,4'-bis(4-aminophenoxy)-2,2'-dimethylbiphenyl (BAPD) or BAPP in dry NMP (10-15% solid content) overnight with vigorous stirring under nitrogen. The resulting poly(amic acid) was then heated to 180 °C for 3-4 hour to complete the imidization. Some of the poly(amic acids) solutions, such as BTDA-BAPP formed highly viscous solution, due to ionization of the poly(amic acid) which causes chain expansion and entanglements similar to the polyelectrolyte effect.[14] However, upon imidization the viscosity dropped back to normal. The resulting polyimide solution was precipitated out from 95% ethanol to yield polymers ranging from fiberous to powdery texture. The color of the polymers varied from tan to colorless.

Instrumentation

Pressurized differential scanning calorimetry (DSC) was performed on a DuPont 910 differntial scanning calorimeter at 10 °C per min. under 200 psi. Thermal mechanical analysis was carried out on TA Instruments 2940 dynamic mechanical analyzer at 10 °C per min., using an expansion probe with a 5 gm load. Thermogravimetric analysis was measured on TA Instruments 2950 thermogravimetric analyzer at 10 °C per min. The intrinsic viscosities were measured in a Ubbelhde capillary viscometer at 30 °C, using either N-methyl-2-pyrrolidinone or m-cresol as the solvents.

RESULTS AND DISCUSSION

Polyelectrolyte Effect

An interesting phenomenum appeared in the synthesis of BTDA-BAPP polymer. During the preparation of the poly(amic acid) at room temperature overnight, the solution became very viscous. One third portion of the in situ poly(amic acid) was removed and its inherent viscosity (η_{inh})was determined to be 1.89 dL/g. Another one third of poly(amic acid) was precipitated from ethanol and dried at 35 °C under vacuum overnight, which displayed an inherent viscosity of 1.24 dL/g after redissolving in NMP. The remaining 1/3 of the poly(amic acid) was heated to 180-190 °C for 3 hours to complete the imidization. During the transition of poly(amic acids) into polyimides, the viscosity of the solution dropped dramatically; and the resulting polyimde yielded an inherent viscosity of 0.4 dL/g. This kind of behavior is attributed to the ionization of poly(amic acids), promoted by the trace amount of deleterious amine present in the amide solvents.[15] The negative charges of the carboxylates on the poly(amic acids) create repulsion, thus causing the expansion of hydrodynamic volume of the polymer which leads to higher viscosity for in-situ poly(amic acids). In fact, this is a typical polyelectrolete effects. The precipitated poly(amic acid), on the other hand, was semi-purified to be free from the impurities of the reaction mixture. Therefore, its extent of ionization and polyelectrolyte effect are less pronounced (Fig. 3) as indicated by the slight drop in viscosity, since the redissoved poly(amic acid) solution could still contain trace amount of amine from distilled NMP. After the imidization, the polyimide would not be ionized; therefore, the hydrodynamic volume of the polymer essentially collapses, leading to much lower viscosity in polyimides. However, this is not to say that the polyimide in NMP is totally free from the polyelectrolyte effect, since it is well recognized that one needs to add LiCl or LiBr to the dry NMP for molecualr weight determination by gel permeation chromatography (GPC)[16]. The LiBr could neutralize any residual uncyclized poly(amic acids), and removal of water would inhibit ionization, thus minimizing the polyelectrolyte effect and the expansion of polymer's hydrodynamic volume.

Thermal analysis

As listed in Table 1, the BTDA-BAPD and BPDA-BAPD are not soluble in NMP like the rest of these two series of polyimides, although BAPD is more soluble than BAPP as an diamine. This might be attributed to the more rigid nature of the biphenyl moiety in BAPD, relative to the flexible isopropylidene group in BAPP, as well as the fact that these two polyimides exhibited higher viscosity -- thus implied higher molecular weight, although the more rigid backbone could also contribute to higher viscosity. Initial DSC thermal analysis performed on these polyimides in their as-precipitated states showed that only BTDA-BAPP was crystalline (T_m=288°C), probably due to the combination of semi-flexible carbonyl group in BTDA and the flexible isopropylidene group in BAPP, since HFDA-BAPP which contained two flexible linkages (an isopropylidene and a hexafluroisopropylidene) remained amorphous. However, the glass transition temperatures (T_g's) for the remaining of BAPD and BAPP containing polyimides were difficult to discern from their DSC thermograms. Nevertheless, after compression-molding these polyimide in a preheated press at 360 °C to make pellets and then cooling to ambient temperature, these samples displayed comparable, but distinctive T_g's, either by TMA or DSC (Table 2). The TGA results for 5% weight loss under nitrogen between BAPD and BAPP based polyimides varied slightly, but they were not drastically different from each other.

Conclusion

The introduction of 2,2'-dimethyl biphenyl moiety along with the ether linkages in BAPD diamine, produces exclusively amorphous polyimides, because the methyl substituents disrupt crystal packing. On the other hand, the BTDA-BAPP polyimide can be crystalline, although other BAPP-based polyimides remained amorphous. The TMA, DSC and TGA thermal analysis showed that both the BAPD and BAPP based polyimides displayed comparable glass transition temperatures (T_g's) and thermal stability. These results clearly indicate that the placement of two methyl groups on the 2,2'-positions of the biphenyl in addition to phenoxy moieties in the diamine BAPD, induced a similar effect in polyimides, as putting the two methyl groups in the more flexible isopropylidene group between two phenyl rings like BAPP.

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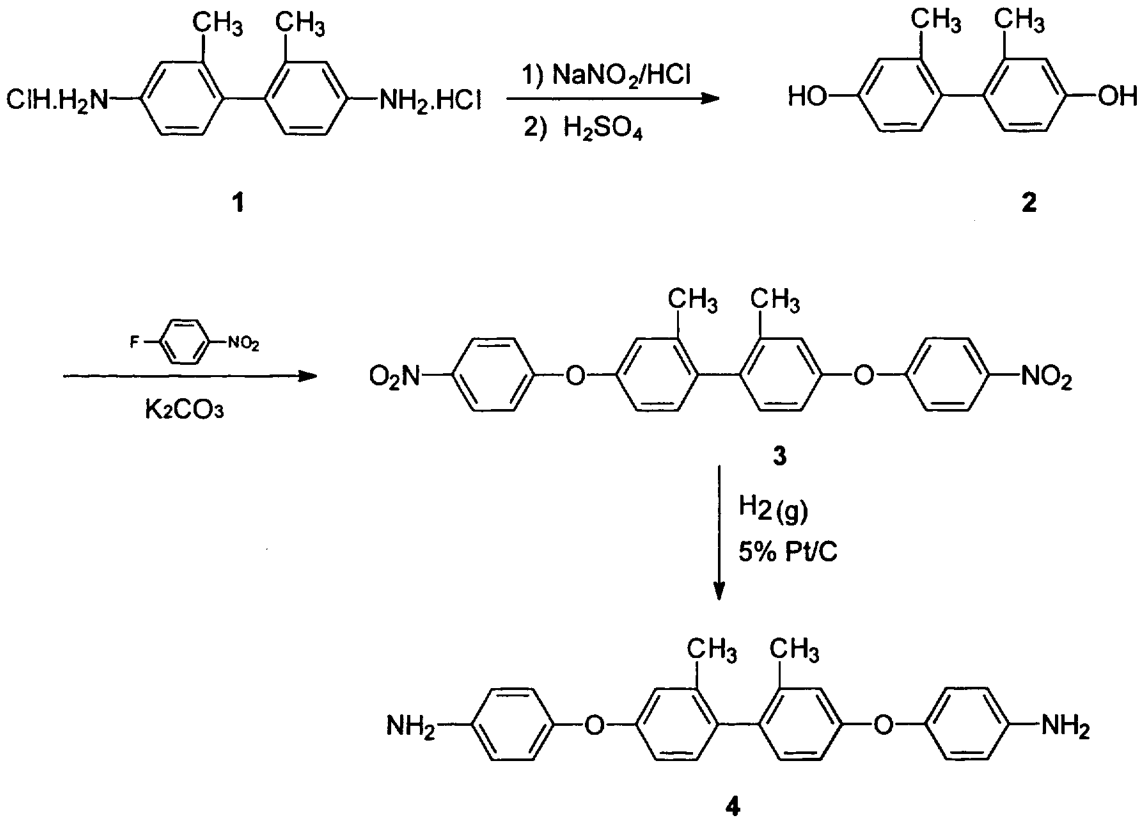
Figure 1 Synthesis of 4,4'-bis(4-aminophenoxy)-2,2'-dimethylbiphenyl



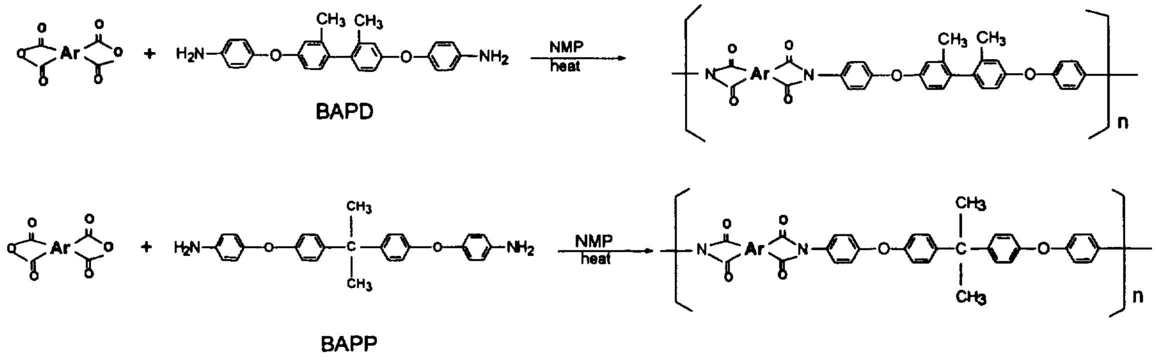


Figure 2 Synthesis of BAPD and BAPP based polyimides

Fig. 3

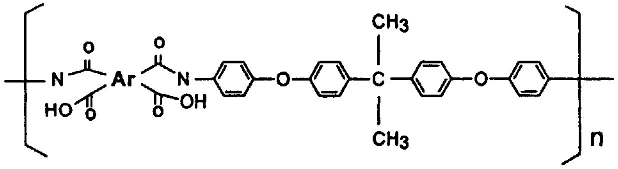
Polyelectrolyte Effect

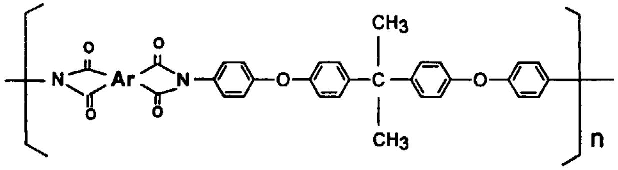
BTDA
+ -------- **Poly(aminc Acids)** ----- **Polyimides**
BAPP

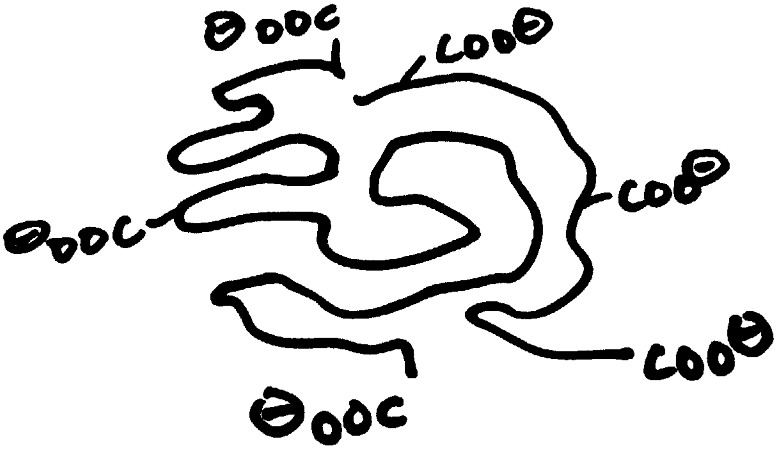
η_{inh} (in situ) = 1.98 dL/g

η_{inh} (ppt) = 1.24 dl/g

η_{inh} (ppt) = 0.28 dL/g







in-situ

ppt

Polyimide (No charge)

Table 1 Viscosity and Solubility of Polyimides Based on BAPD and BAPP Diamines

Property Polyimide	$[\eta]^a$, dL/g	Solubility
BTDA-BAPD	----	Insoluble
BPDA-BAPD	1.26*	m-Cresol
HFDA-BAPD	1.37	NMP
ODPA-BAPD	0.46	NMP
DSDA-BAPD	0.53	NMP
BTDA-BAPP	0.55	NMP
BPDA-BAPP	0.54	NMP
HFDA-BAPP	0.57	NMP
ODPA-BAPP	0.75	NMP
DSDA-BAPP	0.91	NMP

[a] Intrinsic viscosity, $[\eta]$, determined in NMP at 30 °C by extrapolation to infinitely dilute solution from three inherent viscosity measurements.

Table 2 Thermal Properties of BAPD and BAPP Based Polyimides

Properties Polymer	T_g(°C) by TMA[a]	T_g(°C) by DSC[b]	TGA[c]/ N_2(°C) 5% wt loss
BTDA-BAPD	244	243	473
BPDA-BAPD	246	249	511
HFDA-BAPD	256	260	468
ODPA-BAPD	234	231	508
DSDA-BAPD	258	266	438
BTDA-BAPP	239	Tm = 288 virgin T_g=240 quenched[b]	455
BPDA-BAPP	245	245	515
HFDA-BAPP	254	249	477
ODPA-BAPP	218	223	494
DSDA-BAPP	251	252	459

[a] T_g = mid-point of change in the slope on the DSC thermogram with a heating rate of 10 °C/min. DSC analysis were performed on samples compression-molded at 360 °C.

[b] T_g = inflection point in the TMA thermogram with a heating rate of 10 °C/min with 5 gm load. TMA were measure were measured on disks compression-molded at 360 °C.

[c] TGA were obtained with a heating rate of 10 °C/min under a nitrogen flow of 60 cm^3/min.