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## SOLUBLE POLY(AMIDE-IMIDE)S FROM BIS-[(4'-AMINOBENZYL)-4-BENZAMIDE] ETHER - SYNTHESIS AND CHARACTERIZATION



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### ABSTRACT:

A novel aromatic diamine, bis-[(4'-aminobenzyl)-4-benzamide] ether (BABE) containing preformed amide, ether and methylene groups was synthesized and characterized by FT-IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT  $^{13}\text{C}$ ) and Mass spectrometry. A series of novel aromatic poly(amide-imide)s was prepared from BABE and different aromatic dianhydrides using two-step low temperature solution polycondensation method. All the poly(amide-imide)s were obtained in very good yields and were characterized by FT-IR Spectroscopy, viscosity measurements, solubility tests, differential scanning Calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The inherent viscosities ( $\eta_{\text{inh}}$ ) of these poly(amide-imide)s were in the range 0.57-0.87 dL/g in DMAc at  $30 \pm 0.1$  °C; indicating moderate to high molecular weight buildup. The poly(amide-imide)s showed solubility in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO) and N,N-dimethylformamide (DMF) containing LiCl. The XRD results showed that the poly(amide-imide)s were partly crystalline. The glass transition temperature ( $T_g$ ) of these poly(amide-imide)s were in the range 251 to 274 °C. The thermogravimetric analysis of all polymers showed no weight loss below 322°C whereas the char yields at 900 °C were in the range 21 to 58 % indicating high thermal stabilities of these polymers. Thus these polymers meet high temperature resistant requirements and could find applications as special materials in aerospace, military and microelectronics industries. The structure–property correlation among these poly(amide-imide)s is discussed.

**Keywords:** Bis-[(4'-aminobenzyl)-4-benzamide] ether, inherent viscosity, XRD, thermal stability.

### INTRODUCTION:

Aromatic polyimides are widely used in the aerospace and microelectronics industries because of their unique combined properties like excellent thermal stability, electrical insulation properties and chemical resistance<sup>1</sup>. However, they are usually difficult to process in their imidized form because of high softening temperature and limited solubility in most organic solvents. These problems are caused by the rigid polymer backbones and strong interchain interactions. Many attempts have been made to improve the solubility and processability<sup>2,3</sup> of polyimides such as incorporation of flexible or bridging functional groups<sup>4,5</sup>, bulky pendant groups<sup>6,7</sup>, or cardo groups<sup>8</sup>, copolymerization<sup>9</sup> etc.

In the present investigation, we report the synthesis of new aromatic-aliphatic diamine, bis-[(4'-aminobenzyl)-4-benzamide] ether (BABE), containing preformed amide linkage, flexible ether and methylene linkages, its characterization by IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT  $^{13}\text{C}$ ) and mass spectroscopy and preparation of a series of poly(amide-imides) from BABE with five commercially available aromatic dianhydrides using a standard two stage polycondensation process. The resulting poly(amide-imide)s were characterized by measurement of IR spectroscopy, inherent viscosity, solubility, thermal analysis and XRD analysis to correlate the structure property relations. The effect of introduction of preformed amide, flexible ether and methylene linkage in to the polymer backbone on properties of these polymers has been studied.

## EXPERIMENTAL:

### Synthesis of Monomer:

Bis-[(4'-aminobenzyl)-4-benzamide] ether (BABE) was synthesized by the procedure reported by us earlier<sup>10</sup>.

### Synthesis of Polyimides:

The novel aromatic diamine BABE was used to synthesize poly(amide-imide)s from five commercially available aromatic dianhydrides using a standard two stage process with thermal imidization of intermediate poly(amic-acid)s. The synthesis of the poly(amide-imide), API-1, as an example, is given below.

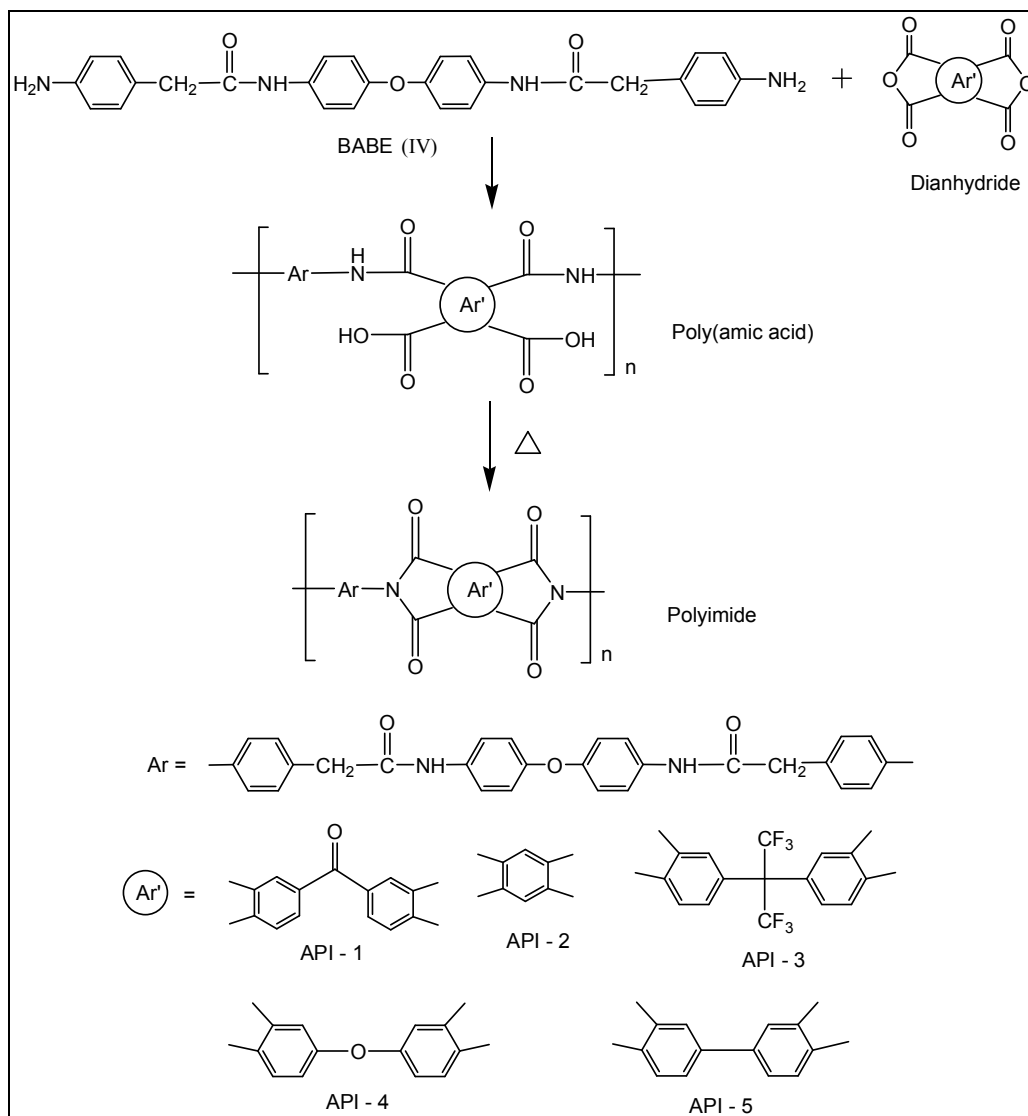
To a 100 mL flame dried three-necked, round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube, the diamine, BABE (0.466 g, 1 mmol) and NMP (3 mL) were added, stirred to form homogenous solution and cooled to 0 °C in ice bath. To this cold solution, BTDA (0.322 g, 1 mmol) was added in small quantity lots over a period of 1 h. The stirring was continued for additional 2 h at 0 °C and then at room temperature for 12 h under nitrogen atmosphere to afford a highly viscous poly(amic acid) solution.

A part of viscous solution was poured into methanol with rapid stirring to precipitate poly(amic acid). The precipitated polymer was filtered, washed with methanol and dried under reduced pressure at 25 °C for 6 h. The poly(amic acid) was characterized by IR spectroscopy and inherent viscosity;  $\eta_{\text{inh}}$  0.87 dL/g. The remaining poly(amic-acid) solution was cast onto a clean glass plate uniformly and heated (100 °C/1 h, 150 °C/1 h, 200 °C/2 h and finally 250 °C/30 min) to produce a fully imidized poly(amide-imide) film. Other poly(amide-imide)s, API-2 to API-5 were synthesized by similar procedure using different dianhydrides.

## RESULTS AND DISCUSSION:

New aromatic diamine, bis-[(4'-aminobenzyl)-4-benzamide] ether (BABE) containing preformed amide, ether linkage and methylene group was synthesized and characterized by IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT  $^{13}\text{C}$ ) and mass spectrometry<sup>10</sup>.

Aromatic poly(amide-imide)s were synthesized by the reaction of stoichiometric quantities of BABE and aromatic dianhydrides such as BTDA, PMDA, 6-FDA, ODPDA and BPDA using a standard two step process with thermal imidization of the intermediate poly(amic-acid)s (**Scheme I**).



**Scheme I: Synthesis of Poly(amide-imide)s from BABE and various dianhydrides**

All the polymers were obtained in good yields (97-98 %) and their inherent viscosities were in the range 0.57 to 0.87 dL/g (**Table 1**), indicating reasonably high molecular weights. The polymers were characterized by IR spectroscopy. The intermediate poly(amic acids) of all polyimides showed absorption at 1632 and 1540 (amide I and II) and 3437  $\text{cm}^{-1}$  (broad, -OH). All polyimides exhibited characteristic absorption bands for the imide ring at 1776 and 1723 (asymmetrical and symmetrical C=O stretching vibrations), 1370-1379 (C-N stretching), 3370-3410 (N-H stretching vibrations), 1094 and 725 (imide ring deformation) and 1240 and 1012  $\text{cm}^{-1}$  (ether linkage).

The solubility behavior of the resulting polyimides was tested qualitatively in various solvents. Polymers showed the solubility in aprotic solvents such as NMP, DMAc, and DMF containing LiCl.

**Table 1: Yield, inherent viscosity of Poly(amide-imide)s<sup>a</sup> from BABE<sup>b</sup> and different aromatic dianhydrides**

Serial No.	Polymer Code	Dianhydrides	Yield (%)	Inherent Viscosity <sup>c</sup> $\eta_{inh}$ , (dL/g)
1.	API-1	BTDA	97.4	0.87
2.	API-2	PMDA	98.1	0.65
3.	API-3	6-FDA	97.7	0.57
4.	API-4	OPDA	98.3	0.64
5.	API-5	BPDA	98.5	0.69

- a) Polymerization was carried out with 1 mmole each of BABE and dianhydride.  
 b) BABE, bis-[(4'-aminobenzyl) - 4-benzamide] ether.  
 c) Inherent viscosity of the poly(amic acid) precursor measured with a 0.5 % (w/v) polymer solution in DMAc at 30 ± 0.1 °C.

The thermal properties of these polymers were evaluated by differential scanning calorimetry (at heating rate 20°C/min) and thermogravimetric analysis in nitrogen at heating rate 10°C/min. The thermal characteristics such as initial decomposition temperature ( $T_i$ ), 10 % weight loss temperature ( $T_{10}$ ), temperature of maximum rate of decomposition ( $T_{max}$ ), residual weight (char yield) at 900 °C and glass transition temperature ( $T_g$ ) are summarized in **Table 2**.  $T_g$  values of polyimides increased in the order of 6-FDA > OPDA > BTDA > BPDA > PMDA in the range 251 to 274 °C.

**Table 2: Thermal properties<sup>a</sup> of Poly(amide-imide)s**

Polymer code	<sup>b</sup> $T_i$ (°C)	<sup>c</sup> $T_{10}$ (°C)	<sup>d</sup> $T_{max}$ (°C)	Residual Wt. (%) at 900 °C	<sup>e</sup> $T_g$ (°C)
API-1	343	405	520	46	260
API-2	369	435	516	58	274
API-3	354	443	627	21	251
API-4	322	433	625	51	256
API-5	341	426	557	53	268

- a) Thermogravimetric analyses were conducted at a heating rate of 10 °C / min under nitrogen.  
 b) Temperature at which weight loss initiated.  
 c) Temperature at which 10% weight loss was observed.  
 d) Temperature at which maximum rate of weight loss was observed.  
 e) Determined by DSC measured at a heating rate 20 °C/min

TG curves of all the poly(amide-imide)s showed more or less similar pattern of decomposition with no weight loss below 322 °C. The  $T_i$  and  $T_{10}$  of these polyimides varied in the range 322 to 369 and 405 to 443 °C respectively whereas  $T_{max}$  values were between 516 to 627 °C. The char yields at 900 °C were in the range 46 to 58 % except for API-3. This shows, these poly(amide-imide)s exhibited good thermal stability. API-3, based on 6-FDA had lower char yield at 900 °C suggesting the lower stability in the final degradation step. This can be attributed to the presence of unstable  $CF_3$  groups in hexafluoro isopropylidene moiety in API-3 polymer.

In order to study the morphology of the polyimides, WAXD measurements at room temperature in the region  $2\theta = 5$  to  $50^\circ$  were performed. WAXD analysis of polyimides revealed the partly crystalline pattern, showing peaks in the region  $2\theta = 15$  to  $30^\circ$ .

## CONCLUSION:

A new aromatic diamine monomer BABE, containing ether and methylene linkage as flexible units and preformed aromatic-aliphatic amide linkage was successfully prepared and used to

synthesize a series of aromatic poly(amide-imide)s with various aromatic dianhydrides by a two step thermal imidization process. These poly(amide-imide)s exhibited good solubility in various aprotic solvents containing LiCl and polymer films could be obtained by casting their DMAc solutions. The poly(amide-imide)s were semi crystalline and showed high thermal stability. These poly(amide-imide)s could be considered as a new processable high performance polymeric materials.

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