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Synthesis and characterization of hyperbranched polyether imides based on 1,3,5-tris[4-(4'-aminophenoxy)phenoxy]benzene

M. Fathima Rigana, P. Thirukumaran, K. Shanthi, M. Sarojadevi*

A new triamine monomer 1,3,5-tris[4-(4'-aminophenoxy)phenoxy]benzene, was synthesized by a three step process using hydroquinone, 1-chloro-4-nitrobenzene and 1,3,5-trichlorobenzene. It was successfully polymerized with commercially available dianhydrides [3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA)] into hyperbranched polymides (HBPIs) by A2+B3 method. Different monomer addition methods and different monomer molar ratios resulted in hyperbranched polymides with amino and anhydride end groups. The structure of the resulting hyperbranched polymides were characterized by FT-IR, 1H-NMR, 13C-NMR and mass spectral analysis. All the synthesized HBPIs were soluble in most of the common organic solvents. They also exhibit good thermal stability. The dielectric constant of the synthesized HBPIs is in the range of 3.08–3.29 at 1 MHz and dielectric loss is in the range of 0.65–0.82 at 1 MHz.

**Keywords:** Hyperbranched poly (etherimides), condensation polymerization, A2+B3 solubility, thermal and electrical properties.

Introduction

Aromatic polyimides are recognized as an important class of high performance materials which are used in a wide variety of applications such as membrane separation, photoresist, adhesives, matrix materials for composites and Langmuir-applications such as membrane separation, photoresist, etc. These are mainly classified as dendrimers with well-defined branched structures, which are synthesized by step wise reactions requiring time consuming purifications, and as hyperbranched polymers with imperfectly branched structure which can be simply prepared through one-step polymerization. Hyperbranched polymers are thought to have physical properties similar to those of dendrimers and can be used as an alternative for dendrimers in various industrial applications.[10-41]

Generally hyperbranched polyimides are synthesized by the self-condensation of AB2 (A & B represent two kinds of functional groups) type monomers. Monomer containing one amine and two anhydride groups or vice-versa seems unavailable because the reactivity between the functional groups is too high, and they cannot exist in stable form within a molecule.[21, 29, 42-44]. To overcome this problem, hyperbranched polymides can be synthesized using A2 + B3 polymerization technique whereas A2 represents a difunctional monomer (dianhydride) and B3 represents a trifunctional monomer (triamine). This type of polymerization reactions leads to soluble hyperbranched polymers.

Most of the research works are based on A2 + B3 type of polymerization. Fang et al. first reported the preparation of HBPIs by the condensation of a triamine (B3), tris(4-aminophenyl)amine, and conventional dianhydrides (A2). Unfortunately, except for 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)-based polymers, the HBPIs were insoluble. Chen et al. reported the synthesis of HBPIs from TAPOB (B3) and commercially available dianhydrides (A2). Recently, Shen et al. reported HBPIs with prolonged chain segments and other linkages. The synthesized polymers were soluble in most of the common solvents.
organic solvents. Still, it exhibits low solubility in THF, CHCl₃ and methanol.

In the present study, a new triamine 1,3,5-tris[4-(4-aminophenoxy)phenoxy]benzene (TAPPOPOB) containing flexible ether linkages was synthesized. This triamine was used for the preparation of hyperbranched polyimides by reacting with commercially available dianhydrides BTDA (3,3',4,4'-benzophenonetetracarboxylic dianhydride) and PMDA (pyromellitic dianhydride) using A₂ + B₃ method. The synthesized polymers were expected to have good solubility in most of the organic solvents without lacking its thermal properties. The structure of the synthesized triamine and polyimides were characterized by FT-IR and NMR analysis. The thermal and dielectric properties of the polyimides were analyzed by DSC, TGA and Impedence analyzer.

**Experimental**

**Materials**

Hydroquinone was purchased from Fisher Scientific (a part of Thermo Fisher Scientific, India Pvt. Ltd.); p-Chloronitrobenzene (98%) and 10% Pd/C were purchased from Sisco Research Laboratories, Pvt. Ltd., India. 1,3,5-Trichlorobenzene was purchased from Alfa Aesar (India), N,N-dimethylformamide (DMF) and phthalic anhydride were purchased from E-Merck India. Analytical-grade Potassium carbonate, N, N-dimethylacetamide (DMAC), triethyamine, methanol and ethanol were purchased from Spectrochem, India. BTDA and PMDA were purchased from Sigma Aldrich, U.S.A. Both were recrystallized from acetic anhydride and dried in a vacuum oven at 150 °C overnight prior to use. DMF was purified by stirring with sodium hydroxide, followed by distillation from phosphorus pentoxide under reduced pressure. Potassium carbonate was dried in a vacuum oven at 120 °C for an hour. Then, hydroquinone (15 g, 0.14 mol) dissolved in DMF was added dropwise to the solution. After complete addition, the mixture was refluxed for 12 h, cooled to room temperature and poured into a beaker containing 1 L of ice cold water. The yellow precipitate of 4-(4-nitrophenoxy) phenol thus obtained was collected by filtration and dried in an air oven. The crude product was recrystallized from ethanol/water (1/1 v/v) to give yellow powder. Yield: 93.5%

FT-IR (KBr, cm⁻¹): 3441 (stretching vibrations of the –OH group), 1345 (stretching vibrations of the -NO₂ group), and 1234 (stretching vibrations of the C-O-C group).

**Characterization methods**

Fourier transform infrared (FT-IR) spectra of the samples were obtained using an ABB Bomen (Model MB 3000) spectrometer. The samples were ground with spectroscopy grade KBr and made into pellets. ¹H (500 MHz) and ¹³C (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Jeol spectrometer with tetramethylsilane (TMS) as the internal standard. Solutions were prepared in DMSO-d₆. The molecular weight of the triamine was analyzed using Agilent 6330 Ion Trap Mass spectrometer (ESI-MS). Molecular weight of the polymers was determined by gel permeation chromatography (GPC) on a Shimadzu, Lab solution, LC solution version 1.25 spz. Analysis was performed at 30 °C using THF as eluent at a flow rate of 1 mL/min. Differential scanning calorimetry analysis of the polymers was performed in a TA instrument Q10 model using 5–10 mg of the sample at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed using a TA Q 600 thermal analyzer at a heating rate of 20 °C min⁻¹ in N₂ atmosphere up to a maximum temperature of 800 °C. Dielectric constant and dielectric loss measurements were carried out with the help of an impedance analyzer (Solatron 1260 Impedance/Gain-phase Analyzer, UK) at room temperature. The polymer samples were made in the form of pellets (1 mm thickness x 12 mm diameter) using a platinum electrode sandwich model in the frequency range of 1 kHz–1 MHz at room temperature. The dielectric constant and dielectric loss of the samples were determined using e’ and e” as the standard relations. The inherent viscosities of all polyimides were measured using a 0.5 g dl⁻¹ Ubbelohde viscometer. Solubility of the polymers was determined at a concentration of 5% (w/v) in various organic solvents. The polymer solvent mixture was kept aside for 24 h with occasional shaking. If the mixture was insoluble at ambient temperature, then it was heated and cooled.

**Synthesis of 4-(4-nitrophenoxy) phenol [NPOP]**

In a 500 mL three necked round bottomed flask fitted with a reflux condenser, p-chloronitrobenzene (22.1 g, 0.14 mol) dissolved in 40 mL of DMF was taken. The solution was magnetically stirred under nitrogen atmosphere. Potassium carbonate (20 g, 0.14 mol) was added subsequently to the solution, while stirring and heated at 70 °C for an hour. Then, hydroquinone (15 g, 0.14 mol) dissolved in DMF was added dropwise to the solution. After complete addition, the mixture was refluxed for 12 h, cooled to room temperature and poured into a beaker containing 1 L of ice cold water. The yellow precipitate of 4-(4-nitrophenoxy) phenol thus obtained was collected by filtration and dried in an air oven. The crude product was recrystallized from ethanol/water (1/1 v/v) to give yellow powder. Yield: 93.5%.

FT-IR (KBr, cm⁻¹): 3441 (stretching vibrations of the –OH group), 1345 (stretching vibrations of the -NO₂ group), and 1234 (stretching vibrations of the C-O-C group).

**Synthesis of 1,3,5-tris[4-(4-nitrophenoxy)phenoxy]benzene [TNPOPOB]**

In a 100 mL three necked round bottomed flask fitted with a reflux condenser, NPOP (23 g, 0.09 mol) dissolved in 10 mL of DMF was taken and the solution was magnetically stirred under nitrogen atmosphere. Potassium carbonate (14 g, 0.09 mol) was added subsequently to the solution, while stirring and heated at 80 °C for 2 h. After that, 1,3,5-trichlorobenzene (6 g, 0.03 mol) dissolved in 10 mL of DMF was added dropwise. After complete addition, the mixture was refluxed for 12 h, cooled to room temperature and poured into a beaker containing 1 L of ice cold water. The brown precipitate of TNPOPOB thus obtained was collected by filtration and dried in an air oven for...
12 h. The crude product was recrystallized from ethanol/water (1/1 v/v) to give brown powder. Yield: 92.8%, Melting Point: 96 °C.

FT-IR (KBr, cm⁻¹): 1535, 1342 (asymmetric and symmetric stretching vibrations of the -NO₂ group), 1234 (stretching vibrations of the C-O-C group).

Synthesis of 1,3,5-tris[4-(4-aminophenoxy)phenoxy]benzene [TAPOPOB]

In a 250 mL three necked round bottomed flask fitted with a reflux condenser, TNPOPOB (15 g, 0.02 mol) dissolved in 25 mL of ethanol was taken. The mixture was stirred well and to it 1.5 g of Pd/C was added portionwise. Then, hydrazine hydrate (20 mL) was added dropwise over a period of 30 minutes. After complete addition, the mixture was heated at 80 °C for 12 h. The hot solution was then filtered to remove the catalysts, cooled to room temperature to obtain the white crystals of TAPOPOB. The product was filtered and dried in an air oven at 60 °C for 12 h. The crude product was recrystallized from ethanol to give white powder. Yield: 92.5%, Melting Point: 96°C.

FT-IR (KBr, cm⁻¹): 3379, 3301 (asymmetric and symmetric stretching vibrations of the N-H group), 3062, 3039 (asymmetric and symmetric stretching vibrations of the aromatic C-H group), 1681 (bending vibrations of the C-N group), 1594, 1451, 1331, 1216, 1153, 1088, 1012, 984, 835, 754, 681 (stretching vibrations of the C-O-C group).

Synthesis of Model compounds

Preparation of Model compounds

Synthesis of Model compound 1 (M1 - Terminal)

TAPOPOB (0.34 g, 0.5 mmol) dissolved in 10 mL of DMAC was taken in a 3-necked round bottomed flask and stirred under nitrogen atmosphere. While stirring, a solution of phthalic anhydride (0.07 g, 0.5 mmol) in 5 mL of DMAC was added dropwise to the mixture through a syringe over 30 minutes. The molar ratio between triamine and phthalic anhydride was kept at 1:3. The reaction was further continued for 12 h at 40 °C. Then, 30 mL of xylene was added, and the mixture was heated to reflux with a Dean-Stark apparatus for 5 h. After cooling to room temperature, the mixture was poured into ice cold water and the formed brown precipitate was filtered and washed with methanol and dried in an air oven at 70 °C for 24 h [21, 45].

Synthesis of Model compound 2 (M2 - Linear)

TAPOPOB (0.34 g, 0.5 mmol) dissolved in 10 mL of DMAC was taken in a 3-necked round bottomed flask and stirred under nitrogen atmosphere. While stirring, a solution of phthalic anhydride (0.14 g, 1 mmol) in 5 mL of DMAC was added dropwise to the mixture through a syringe over 30 minutes. The molar ratio between triamine and phthalic anhydride was kept at 1:2. The reaction was further continued for 12 h at 40 °C. Then, 30 mL of xylene was added, and the mixture was heated to reflux with a Dean-Stark apparatus for 5 h. After cooling to room temperature, the mixture was poured into ice cold water and the formed brown precipitate was filtered and washed with methanol and dried in an air oven at 70 °C for 24 h [21, 45].

Synthesis of Model compound 3 (M3 - Dendritic)

TAPOPOB (0.34 g, 0.5 mmol) dissolved in 10 mL of DMAC was taken in a 3-necked round bottomed flask and stirred under nitrogen atmosphere. While stirring, a solution of phthalic anhydride (0.22 g, 1.5 mmol) in 5 mL of DMAC was added dropwise to the mixture through a syringe over 30 minutes. The molar ratio between triamine and phthalic anhydride was kept at 1:3. The reaction was further continued for 12 h at 40 °C. Subsequently, a mixture of 1 g of triethylamine and 3 g of acetic anhydride into the solution. The solution was kept at 70 °C for 6 h under stirring. After cooling to room temperature, the mixture was poured into methanol. The gray precipitate...
formed was collected by filtration and dried in a vacuum oven at 70 °C for 24 h.\textsuperscript{[21, 45]}

**Synthesis of anhydride-terminated HBPIs**

To a solution of dianhydride (0.64 g, 2.0 mmol) in 20 mL of DMAc in a 100 mL round bottomed flask, TAPOPOB (0.68 g, 1 mmol) in 10 mL of DMAc was added dropwise over a period of 1 h. The mixture was stirred for 24 h at 40 °C. The chemical imidization was carried out by adding a mixture of 1 g of triethylamine and 3 g of acetic anhydride into the polyamic acid solution. The solution was kept at 70 °C for 6 h under stirring. After cooling to room temperature, the mixture was poured into methanol. The precipitate formed was collected by filtration and dried in a vacuum oven for 12 h. The anhydride-terminated HBPIs obtained from BTDA and PMDA will be referred to as HBPI-BTDA-AD-1 and HBPI-PMDA-AD-2 respectively\textsuperscript{[21, 45]}.

**Synthesis of amino-terminated HBPIs**

TAPOPOB (0.68 g, 1 mmol) was dissolved in 10 mL of DMAc in a 100 mL, three-necked round bottomed flask under nitrogen atmosphere, and the solution was stirred. A solution of dianhydride (0.32 g, 1 mmol) in DMAc was added dropwise to the mixture through a syringe over a period of 1 h under stirring at 35 °C. The reaction mixture was further stirred for 24 h. Then, 10 mL of m-xylene was added, and the mixture was heated to reflux with a Dean-Stark apparatus for 5 h. After cooling to room temperature, the mixture was precipitated from methanol. The precipitate was collected by filtration and dried in a vacuum oven for 24 h. The amino-terminated HBPIs obtained from BTDA and PMDA will be referred to as HBPI-BTDA-AM-1 and HBPI-PMDA-AM-2 respectively\textsuperscript{[21, 45]}.
RESULTS AND DISCUSSION

Structural characterization of the triamine (TAPOPOB)

A new triamine (TAPOPOB) containing flexible ether linkage was synthesized by a three-step procedure. In the first step, the nucleophilic substitution reaction of hydroquinone with p-chloronitrobenzene in the presence of potassium carbonate yielded the intermediate compound NPOP. In the second step, synthesized NPOP was reacted with 1,3,5-trichlorobenzene in the presence of potassium carbonate, to obtain the trinitro compound (TNPOPOB). Finally, the triamine monomer TAPOPOB was synthesized by the reduction of TNPOPOB using hydrazine hydrate catalyzed by Pd/C. The structure of the triamine monomer was characterized by FT-IR, NMR spectroscopy and confirmed by mass spectral analysis. Figures 1a and 1b show the FT-IR spectra of the TNPOPOB and TAPOPOB. Figure 1a shows the characteristic absorptions at 1535 and 1342 cm\(^{-1}\) due to the asymmetric and symmetric stretching vibrations of the -NO\(_2\) group. The absorptions observed at 3062 and 1234 cm\(^{-1}\) are due to the stretching vibrations of the aromatic C-H and C-O-C groups respectively. Figure 1b shows the characteristic absorptions at 3371 and 3301 cm\(^{-1}\) corresponding to the stretching vibrations of the amino group. Moreover, the absorptions of the nitro group were not found in figure 1b, thus confirming that all the nitro groups in TNPOPOB were completely reduced to the amino group. Figure 2 shows the \(^1\)H-NMR spectrum of the triamine. The singlet peak at 3.5 ppm corresponds to the –NH\(_2\) protons. The peaks between 6.5 ppm and 6.8 ppm are assigned to the aromatic protons. Figure 3 shows the \(^{13}\)C-NMR spectrum of the triamine. The peaks between 113.1 ppm and 153.8 ppm are assigned to characteristic carbon resonances of the aromatic ring present in the triamine. The mass spectrum of the triamine is shown in figure 4, which shows the molecular ion peak at 674.5 for the triamine. The FT-IR, \(^1\)H-NMR, \(^{13}\)C-NMR and mass spectral analysis confirm the proposed structure of the triamine.

Synthesis of HBPIs

Hyperbranched polyimides were prepared by A\(_2\) + B\(_3\) polymerization technique, using the commercially available dianhydrides, BTDA and PMDA as A\(_2\) monomer and the newly synthesized triamine (TAPOPOB) as B\(_3\) monomer. By varying the mole ratio of the triamine and dianhydrides, different types of hyperbranched polyimides were formed. The addition of dianhydride into triamine (TAPPOB) with a monomer molar ratio of 1:1 (the molar ratio between the
amine and anhydride groups in the monomer was 3:2) yielded the amine terminated hyperbranched polyimides. While the addition of triamine into dianhydride with a monomer molar ratio of 1:2 (the molar ratio between the amine and anhydride groups in the monomer was 3:4) yielded the anhydride terminated hyperbranched polyimides [20]. In both cases, the monomer was added dropwise to avoid any high local concentration.

To protect the terminal functional groups different imidaziation procedures were employed. The amino-terminated hyperbranched polyamic acid solutions were thermally imidized at 160 °C for 24 h. The anhydride-terminated polyamic acid solutions were chemically converted into HBPIs in the presence of acetic anhydride and triethylamine at 70 °C [20-22, 30].

Characterization of the HBPIs

The formation of HBPIs was confirmed by FT-IR spectroscopy. Figure 5 shows the FT-IR spectra of the amino- and anhydride-terminated HBPIs based on BTDA (HBPI-BTDA-AM1 and HBPI-BTDA-AD1). The bands at 1784 cm⁻¹ (asymmetric stretching vibrations of the imide >C=O group), 1728 cm⁻¹ (symmetric stretching vibrations of the imide >C=O group), 1380 cm⁻¹ (stretching vibrations of the imide C-N group), and 725 cm⁻¹ (bending vibrations of the imide C-N group) are the characteristic absorption bands of the HBPIs. The characteristic band of the polyamic acid at 1680 cm⁻¹ is not found in the FT-IR spectra. The band between 3384 and 3312 cm⁻¹ represents the N-H stretching vibrations of the terminal amino groups present in the amino-terminated HBPIs, while the band around 1859 cm⁻¹ represents the >C=O stretching vibrations of the terminal anhydride groups in anhydride-terminated HBPIs. Similar characteristic bands were observed in the FT-IR spectra of HBPI-PMDA-AM1 and HBPI-PMDA-AD2 (based on PMDA). From these results, it can be concluded that the prepared HBPIs were completely imidized.

The structural perfection of hyperbranched polymers is generally characterized by the degree of branching (DB), which was defined by Hawker and Frenchet [46] in 1991 as follows,

$$\text{DB} = \frac{(D+T)}{(D+T+L)}$$

where D, T, L refer to the number of dendritic, terminal, and linear units in the hyperbranched polymer, respectively. DB is usually determined from the ¹H-NMR spectra by comparing the integration of the peaks for the respective units in the hyperbranched polymers with the help of model compounds prepared using synthesized triamine and phthalic anhydride. To determine the DB of amino-terminated HBPIs, three model compounds were synthesized.

To determine the DB of the HBPIs three model compounds M-1 (terminal); M-2 (linear); M-3 (dendritic) were synthesized. Figure 6 shows the ¹H-NMR spectra of the three model compounds, amino-terminated HBPI and anhydride-terminated HBPI. The peak at 3.5 ppm due to the amino proton has the highest intensity for M-1 (terminal) which has 2 unreacted amino groups. The same peak has moderate intensity for M-2 (linear) as it has only one unreacted amino group. The same peak has moderate intensity for M-2 (linear) as it has only one unreacted amino group. For M-3 (dendritic) with no unreacted amino groups, there is no peak at 3.5 ppm. For the hydrogens in the phenyl rings of TAPOPOB residues, terminal model compound 1 has 6
peaks at 6.5 (H_a), 7.1 (H_b), 6.9 (H_c), 6.7 (H_d), 7.6 (H_e), 7.7 (H_f) ppm; linear model compound 2 also has 6 peaks at 6.4 (H_a), 7.1 (H_b), 6.8 (H_c), 6.7(H_d), 7.5 (H_e), 7.8 (H_f) ppm and model compound 3 has 4 peaks at 6.9 (H_a), 7.1 (H_b), 7.6 (H_c), 7.7 (H_d) ppm.

Solubility of HBPIs

The synthesized HBPIs show excellent solubility in most of the common organic solvents. The solubility test was done by dissolving 0.5 g of the HBPIs in 1 mL of the solvent at room temperature, and the results are shown in table 1. All the synthesized HBPIs (based on BTDA and PMDA) dissolved completely in polar aprotic solvents such as NMP, DMF, DMAc, m-cresol, and DMSO. They also exhibit good solubility in chloroform, THF, acetone, ethanol and methanol. The excellent solubility is due to the presence of flexible ether linkages in the backbone of the HBPIs. These linkages will hinder intermolecular packing and increase the free volume, hence solubility improved [20]. In all cases, chemically imidized anhydride–terminated HBPIs show good solubility when compared with thermally imidized amino-terminated HBPIs which is due to cross-linking of polyimide during imidization at high temperature [47].

Inherent Viscosity

The inherent viscosity of the synthesized HBPIs was determined using a Ubbelohde viscometer at a concentration of 0.5g/dL in NMP at 30 °C. The inherent viscosity values were found to be in the range of 0.76 to 1.21 dl g⁻¹. Synthesized HBPIs exhibit moderate viscosity and better solubility, which is due to the branching nature and presence of terminal functional groups [48]. Inherent viscosity of the anhydride-terminated HBPIs is higher than the amine-terminated HBPIs [30]. These results indicate that the anhydride-terminated HBPIs show high molecular weight when compared to the amine-terminated HBPIs. PMDA-HBPIs show better viscosity than the BTDA-HBPIs is due to the presence of rigid backbone. The results are shown in table 2.

Molecular weight

Molecular weight of the synthesized HBPIs was determined by GPC. Weight average molecular weight (M_w), number average molecular weight (M_n), Polydispersity index (PDI) values are shown in table 2. M_w, M_n values of the HBPIs are in the range
Table 1: Solubility of HBPIs

<table>
<thead>
<tr>
<th>Synthesized HBPIs</th>
<th>Solvents</th>
<th>DMF</th>
<th>NMP</th>
<th>DMSO</th>
<th>DMAc</th>
<th>m-cresol</th>
<th>CHCl₃</th>
<th>THF</th>
<th>Methanol</th>
<th>Acetone</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBPI-BTDA-AM1</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HBPI-PMDA-AM2</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
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<tr>
<td>HBPI-BTDA-AD1</td>
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<tr>
<td>HBPI-PMDA-AD2</td>
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<td>+</td>
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</tr>
</tbody>
</table>

++ - soluble; + - partially soluble; -- - insoluble

Table 2: Inherent viscosity and molecular weight of HBPIs

<table>
<thead>
<tr>
<th>Synthesized HBPIs</th>
<th>Inherent Viscosity dl g⁻¹</th>
<th>M_w (g mol⁻¹)</th>
<th>M_n (g mol⁻¹)</th>
<th>PDI (M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBPI-BTDA-AM1</td>
<td>0.76</td>
<td>66120</td>
<td>42518</td>
<td>1.55</td>
</tr>
<tr>
<td>HBPI-PMDA-AM2</td>
<td>0.87</td>
<td>165194</td>
<td>55382</td>
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<tr>
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<td>1.01</td>
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<td>170916</td>
<td>1.44</td>
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<tr>
<td>HBPI-PMDA-AD2</td>
<td>1.21</td>
<td>329172</td>
<td>263289</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 2: Inherent viscosity and molecular weight of HBPIs

Thermal analysis

Thermal stability of the HBPIs was characterized by TGA at a heating rate of 20 °C min⁻¹ from room temperature to 800 °C under N₂ atmosphere. As shown in figure 7, all the synthesized HBPIs exhibit good thermal stability with a 10% weight loss temperature (T₁₀) above 450 °C (Table 3). In figure 7, a, b, c, d represents HBPI-PMDA-AM2, HBPI-BTDA-AM1, HBPI-PMDA-AD2, HBPI-BTDA-AD1 respectively. Amino-terminated HBPIs (HBPI-BTDA-AM1 and HBPI-PMDA-AM2) show better thermal stability than anhydride-terminated HBPIs. This is due to the free terminal functional groups present in amino-terminated HBPIs [21].

Flame Retardancy of the Polymers

The limiting oxygen index (LOI) value indicates the flame retardant property of the polymers which is shown in table 2. The LOI values were calculated from the char yield obtained from TGA analysis by using Van Krevelan and Hofytzer equation [49], as shown below,

\[
\text{LOI} = 17.5 + (0.4) \times \text{CY}
\]

where, LOI – limiting oxygen index, CY – char yield

The LOI values of the synthesized HBPIs are in the range of 35-39% indicating high flame retardancy. In general, the LOI value of the polymer should be above the threshold value of 26, to render them self-extinguishing property and to qualify their requirement in many applications requiring good flame resistance [50]. The synthesized HBPIs show LOI values greater than 26, hence exhibit good flame retardant properties [51].
Dielectric Properties

The dielectric constant and dielectric loss were measured, and the results are summarized in table 2. The dielectric constant of the synthesized HBPIs is in the range of 3.08–3.29 at 1 MHz and dielectric loss is in the range of 0.65–0.82 at 1 MHz which is shown in figures 9 and 10. These values are comparatively low when compared with that of the fluorinated polyimides \(^{[4]}\). The dielectric constant and dielectric loss of the materials are directly related to the polarizability and porosity of the materials and are strongly dependent on their chemical structure \(^{[52]}\). Low dielectric constant of the HBPIs are due to the introduction of the flexible ether linkages, and increased free volume due to the highly branched structure of the HBPIs which loosened polymer packing, leading to reduced dielectric constant \(^{[53]}\).
Conclusions

A series of hyperbranched polyimides (HBPIs) were successfully synthesized using a new triamine and commercially available dihydrides. The structure of the triamine and synthesized HBPIs were characterized by FT-IR and $^1$H-NMR techniques. The introduction of flexible ether linkages in the backbone of the polymers increases its solubility in most of the common organic solvents. Synthesized HBPIs exhibit moderate inherent viscosity ($0.76-1.21 \text{ dL g}^{-1}$) and high molecular weight (Mw). All the HBPIs show good thermal stability ($234-254 ^\circ \text{C}$) and flame retardancy as indicated by their $T_{10}$ values (above $450 ^\circ \text{C}$) and LOI values (36-38). The dielectric constant of the synthesized HBPIs is in the range of 3.08–3.29 at 1 MHz and dielectric loss is in the range of 0.65–0.82 at 1 MHz. The synthesized HBPIs exhibit good solubility, good thermal and dielectric properties, hence can be used in various industrial applications.

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