A New Hyperbranched Poly(arylene-ether-ketone-imide): Synthesis, Chain-End Functionalization, and Blending with a Bis(maleimide)

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ABSTRACT: While aromatic polyimides have found widespread use as high-performance polymers, the present work addressed the need for organosoluble pre-imidized materials through the use of a hyperbranching scheme. The AB₂ monomer, N-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimide, was prepared from 4-fluorosolphthalic anhydride and 3,5-bis(4-hydroxybenzoyl)aniline. The latter was synthesized in three steps starting from commercially available 5-nitrosolphthalic acid. The AB₂ monomer was then polymerized via aromatic fluoride-displacement reaction to afford the corresponding hydroxyl-terminated hyperbranched polymer, HT-PAEKI, which was then functionalized with allyl and propargyl bromides as well as epichlorohydrin to afford allyl-terminated AT-PAEKI, propargyl-terminated PT-PAEKI, and epoxy (glycidyl)-terminated ET-PAEKI, in that order. All hyperbranched poly(ether-ketone-imides) were soluble in common organic solvents. Intrinsic viscosities of HT-, AT-, PT-, and ET-PAEKI in NMP were 0.13, 0.08, 0.08, and 0.08 dL/g, in that order. AT-PAEKI displayed an exotherm due to C1s reformation at 269 °C and allyl-based thermal-cure reaction at 343 °C. PT-PAEKI displayed only a single, strong exotherm at 278 °C. Because of hydrogen bonding, HT-PAEKI displayed T_D of 224 °C while its derivatives exhibited lower T_g values ranging from 122 to 174 °C. Finally, AT-PAEKI was blended with a bisphenol A-based bis(maleimide) (BPA-BMI) in various weight ratios. The results from differential scanning calorimetric study indicated that the presence of AT-PAEKI (up to 32 wt %) significantly affect the glass transition temperatures and cure behavior of BPA-BMI. Dynamic mechanical analysis comparing cured BPA-BMI with the 5 wt % AT-PAEKI blend corroborates this increase in glass transition temperature.

Introduction

Aromatic polyimides (PI’s) are well-known, high-performance materials with widespread applications in the aerospace and electronics industries due to their excellent thermomechanical and dielectric properties. Recently, it was demonstrated that they are also useful as optical materials based on their optical anisotropy when cast in directions parallel (in-plane) and perpendicular (out-of-plane) to the film surface. However, when fully imidized, most aromatic PI’s have limited solubility in common organic solvents, thus restricting the choice in their processing options. Therefore, numerous research efforts have been focused on organosoluble PI’s from the modification of the structure (a) without substantially decreasing rigidity of their backbone, (b) to allow processing polymers with preformed imide units, and (c) to avoid many problems associated with handling poly(amic acid) (PAA) precursors. Furthermore, postpolymerization reactions of soluble aromatic polyimides under homogeneous conditions would also allow better control in the introduction of desirable functional groups.

Another viable alternative to attaining solubility in aromatic PI’s is to change the traditional, linear geometry of the macromolecules to three-dimensional, highly branched (dendritic) architecture. As a subset of dendritic polymers, hyperbranched polymers have several important advantages such as better solubility relative to their linear counterparts, and easier syntheses than their analogous dendrimers, which invariably involve tedious, multistep synthetic schemes. Therefore, larger quantities of hyperbranched polymers can be easily produced from AB(D ≥ 2) monomers containing a preformed aromatic imide as a chemically inert moiety together with A and B functions that can react quantitatively under suitable conditions. This approach is exemplified by the work of Moore et al., who developed a rapid, CsF-mediated synthesis of aromatic hyperbranched poly(ether-imides) from AB₂ monomers containing tert-butyl(dimethyl)silyl ether moieties. Wu and Shu have recently reported similar work. As part of our research program to explore and develop niche applications for aromatic hyperbranched polymers, we describe here the results on (i) the synthesis of a new AB₂ monomer containing a preformed aromatic imide moiety and para-carbonyl functions to
Results and Discussion

Monomer Synthesis. The AB₂ monomer (5) was synthesized according to Scheme 1.

The sequence started with 5-nitroisophthalic acid which was treated with thionyl chloride to afford 5-nitroisophthaloyl dichloride (1). Friedel–Crafts reaction of 1 with anisole in the presence of aluminum chloride yielded 3,5-bis(4-methoxybenzoyl) nitrobenzene (2), which was subsequently demethylated with pyridine hydrochloride to afford 3,5-bis(4-hydroxybenzoyl) nitrobenzene (3). Compound 3 was then reduced to 3,5-bis(4-hydroxybenzoyl) aniline (4). Upon reacting with 4-fluoroisophthalic anhydride with catalytic amount of isoquinoline, 4 was converted to the desired monomer 5, N-[3,5-bis(4-hydroxybenzoyl) benzene]-4-fluoroisophthalimide. The identity and purity of 5 were ascertained by conventional organic characterization prior to polymerization experiments, including FT-IR, NMR, HPLC, elemental analysis, and mass analysis.

Polymerization. The monomer 5 was self-polymerized in an N-methylpyrrolidinone (NMP)/toluene mixture of varying ratio in the presence of potassium carbonate to afford the hydroxyl-terminated hyperbranched poly(arylene–ether–ketone–imide) (HT-PAEKI) after an acidic workup (Scheme 2). We observed that as self-polymerization of 5 was progressing, the polymerization mixture set to a gellike state, most likely due to the large number of phenolate salts at the ends, causing partial insolubility of the growing polymer chains. Therefore, we followed the polymerization kinetics with the aid of gel-permeation (size-exclusion) chromatography (GPC) in terms of the semiquantitative changes in the molecular weights and their distribution.

Thus, samples were withdrawn from the polymerization mixture 10 min after the oil bath temperature had reached the following temperatures: 180, 190, and 202 °C (NMP reflux temperature), in that order. The samples (~1–2 drops each from disposable pipets) were diluted with about 2 mL of tetrahydrofuran (THF) before they were subjected to GPC experiments. As shown in Figure 1, when the polymerization temperature exceeded 180 °C, the left shoulders on GPC curves were growing, suggesting that the high-molecular-weight portion was approaching a limit of approximately 2.2 million Da with reference to polystyrene standards. Although the high-molecular-weight portion could have arisen from (a) the early stage of a cross-linking reaction initiated by the attack of the imide function by the phenolate or (b) the aggregation of the hyperbranched polymer salt in THF/NMP mixture, we rule out possibility (a) because the hyperbranched polymers were completely soluble in NMP after acidic workup. Nevertheless, the peak value of the maximum for each curve remained almost constant at approximately 7000 Da. Thus, to control the molecular weight and polydispersity, the polymerization process was optimized at the reaction temperature of 160 °C and for a duration of 30 min. The resulting hyperbranched polymer, HT-PAEKI (6), was isolated as an off-white product that was quite soluble in most common organic solvents such as polar aprotic solvents (NMP, DMSO, DMF, DMAc, etc.), ether solvents (THF, diethyl ether), and phenolic solvents (m-cresol, phenol), displayed an intrinsic viscosity of 0.13 dL/g (NMP at 0.1 °C), M₀ of 2400 g/mol, Mₕ of 4800 g/mol, and molecular weight distribution (MWD) of 2.0. Its glass transition temperature (Tₕ) was determined to be 224 °C by differential scanning calorimetry (DSC). Although we have not determined the degree of branching (DB) for this hyperbranched polymer, we believe that its DB should be within the range defined by similar hyperbranched ether–imide polymers prepared by Moore et al. (DB ~ 67%)⁹ and by Wu and Shu (DB ~ 50%).¹²

Functionalization of HT-PAEKI. Hyperbranched polymer 6 with hydroxyl end groups was treated with allyl bromide, propargyl bromide, or epichlorohydrin to afford allyl-terminated (AT-PAEKI, 7), propargyl-
terminated (PT-PAEKI, 8), and glycidyl (epoxy)-termin-
tated (ET-PAEKI, 9) poly(arylene
ether-ketone-imides),
in that order (Scheme 2). From their proton NMR (see
Figure 2) and FT-IR spectra, all three conversions were
essentially quantitative as evidenced by the absence of
the signal (δ 10.55–10.84 ppm) characteristic of the
hydroxyl group after the post-polymerization reactions.

Solubility and Solution Properties. All these
functionalized polymers were soluble in polar aprotic
solvents (DMF, DMAc, DMSO, NMP, sulfolane) and an
erth solvent (THF). In general, hyperbranched polymers
have greater solubility than their linear analogues
in a given solvent. The intrinsic viscosity values of AT-
PAEKI, PT-PAEKI, and ET-PAEKI were all found to
be 0.08 dL/g (NMP at 30 °C). These values are
considerably lower than that of their parent hyper-
branched polymer (hydroxyl-terminated). This is most
likely due to the presence of intra- and intermolecular
hydrogen bonding in the latter.

Thermal Properties. The glass-transition tempera-
tures of hyperbranched polymers were determined
using the DSC method. The thermograms were generated
from their powder samples after they had been
previously heated to 200 °C and air-cooled to ambient
temperature. The Tg was defined as the midpoint of the
maximum baseline shift from the second run. As shown
in Table 1 and Figure 3, the HT-PAEKI displayed a Tg
at 225 °C. AT-PAEKI showed a Tg at 122 °C and two
exotherms with peak temperatures at 269 and 343 °C.
The first exotherm stemmed from the Claisen rear-
arrangement reaction, during which o-allylphenols were
formed from the allyl phenyl ether end groups (see
Scheme 3b). The latter exotherm was ascribable to the
thermal reaction cure via the allyl groups. Similar DSC
observation was reported for fluorinated polybenzox-
azoles with allyl ether pendants. PT-PAEKI exhibited
a Tg at 134 °C and an exotherm with the onset
temperature about 200 °C and peak temperature at 278
°C. This exotherm (ΔHexo = 451 J/g) is attributable to

![Scheme 2. Polymerization of AB2 Monomer and Functionalization of the Resulting Hyperbranched Polymer](image-url)
followed by the curing of the latter. ET-PAEKI showed the formation of chromene from the propargyl group.

Figure 3. DSC thermograms of (a) HT-PAEKI; (b) (i) AT-PAEKI, (ii) PT-PAEKI, and (iii) ET-PAEKI.

the formation of chromene from the propargyl group followed by the curing of the latter. ET-PAEKI showed a $T_g$ at 174 °C and an exotherm ($\Delta H_{exo} = 294$ J/g) with onset and peak temperatures at 300 and 350 °C, respectively. This exotherm is likely the result of the ring-opening of the epoxy functions and subsequent reactions as well as descomposition as indicated by some weight loss in its TGA (helium) around 350 °C. It is noteworthy that the sum of heat of reaction ($\Delta H_{exo}$) detected for AT-PAEKI is appreciably smaller than the values for PT-PAEKI and ET-PAEKI. We suspect that the thermal conversion of Claisen rearrangement in AT-PAEKI might not be quantitative and that the loss of some allyl groups might have occurred at such high temperatures.

From the powder samples of HT-PAEKI, AT-PAEKI, PT-PAEKI, and ET-PAEKI, temperatures at which a 5% weight loss was observed were in the range of 330–431 °C in helium and 318–416 °C in air, respectively.

In the case of HT-PAEKI, the lower degradation (weight loss) temperature in helium than that in air was probably due to the presence of a large number of hydroxyl groups at the chain ends, thus making the material hygroscopic and capable to absorb moisture (up to ~2%) between 25 and 100 °C when its TGA experiment was conducted in air. Among the polymer derivatives, the propargyl-terminated one was the most thermally stable and the epoxy-terminated the least (Figure 4).

**AT-PAEKI/BPA-BMI Blends.** BMI resins are attractive in numerous aerospace applications because of their easy processing similar to epoxies but higher use-temperature capability than the latter and relatively low cost. However, their main drawbacks are brittleness and proclivity to microcrack under stresses in cross-ply composites. Therefore, many approaches have been reported in the literature to address these problems: (i) chain extension via Michael addition or cycloaddition reactions (ene and Diels–Alder reactions) with amine-terminated oligomers and thermoplastics, diallyl compounds, or bis(benzocyclobutene) compounds; (ii) reactive liquid rubbers; (iii) thermoplastics powders; (iv) engineering thermoplastics and their derivatives (with reactive pendant or end groups); (v) hyperbranched aliphatic polyester. The challenge of all these approaches is to inhibit microcracking while maintaining high-temperature utility.

In our blend studies, we selected a bisphenol A-based bis(maleimide) (BPA-BMI) as the thermoset component primarily because it has much lower melting temperature (84 °C, DSC) than more commonly used methylenedianiline (MDA)-based BMI (mp 162 °C, DSC). Among the three functionalized hyperbranched polymers synthesized, the allyl-terminated AT-PAEKI was chosen on the basis of the consideration that there is a large number of allyl groups at its chain ends, and the side reaction between diallyl and bis(maleimide) groups is well established. In fact, we found that AT-PAEKI was soluble in molten BPA-BMI. To carry out this study at the lab scale, however, it was more convenient to prepare the intimate mixtures of BPA-BMI and AT-PAEKI in THF.

The DSC scans of virgin BPA-BMI showed a $T_g$ at 70.5 °C, a $T_m$ at 84 °C, and a polymerization exotherm with peak temperature ($T_{exo})$ at 200 °C and 173.5 J/g for the heat of reaction ($\Delta H_{exo}$); see Table 2. No initial $T_g$ was observed for all AT-PAEKI/BPA-BMI blends except the one with AT-PAEKI content of 32 wt %. The latter has a single initial $T_g$ that was 22 °C higher than that of pure AT-PAEKI. This indicates that AT-PAEKI and BPA-BMI form a compatible blend. Furthermore, we suspect that the origin of compatibility goes beyond the presence of imide functions in both components (physical interactions). Since maleimide is a strong

**Table 1. Thermal Properties of Hyperbranched Poly(arylene–ether–ketone–imide) and the Functionalized Derivatives**

<table>
<thead>
<tr>
<th>PAEKI</th>
<th>$\eta_p^a$ (dL/g)</th>
<th>$T_g^b$ (°C)</th>
<th>$T_{exo1}$ (°C)</th>
<th>$\Delta H_1$ (mJ)</th>
<th>$T_{exo2}$ (°C)</th>
<th>$\Delta H_2$ (mJ)</th>
<th>$T_{d5%}^c$ (°C) in helium</th>
<th>char (%) at 850 °C</th>
<th>$T_{d5%}^c$ (°C) in air</th>
<th>char (%) at 850 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-</td>
<td>0.13</td>
<td>225</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>411</td>
<td>55</td>
<td>416</td>
<td>0.6</td>
</tr>
<tr>
<td>AT-</td>
<td>0.08</td>
<td>122</td>
<td>269</td>
<td>98.2</td>
<td>343</td>
<td>114.7</td>
<td>431</td>
<td>58</td>
<td>408</td>
<td>0.1</td>
</tr>
<tr>
<td>PT-</td>
<td>0.08</td>
<td>134</td>
<td>278</td>
<td>450.5</td>
<td>422</td>
<td>50</td>
<td>422</td>
<td>50</td>
<td>412</td>
<td>3.3</td>
</tr>
<tr>
<td>ET-</td>
<td>0.08</td>
<td>174</td>
<td>350</td>
<td>294.2</td>
<td>330</td>
<td>46</td>
<td>318</td>
<td>46</td>
<td>318</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$ Intrinsic viscosity measured in NMP at 30.0 ± 0.1 °C. $^b$ Infection in baseline on DSC thermogram obtained in N2 with a heating rate of 10 °C/min. $^c$ Temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10 °C/min.
dienophile (electron-deficient) and the O-allyl group is a relatively electron-rich olefin, the donor–acceptor interactions are very likely. In addition, it is known that ene reaction (see Scheme 3a) takes place in the temperature range 130–150 °C.21a Hence, in the 32 wt % AT-PAEKI/BPA-BMI blend, a sufficient amount of the adduct must have formed from the ene reaction to allow the detection of initial $T_g$, which is higher than those of both components. One would expect the initial $T_g$ of a physically compatible blend to be somewhere in between those of the components.

As the content of AT-PAEKI increased from 2 to 32 wt %, the exotherm peak shifted proportionally and gradually from 214 to 278 °C, indicating that the hyperbranched polymer was effectively suppressing the homopolymerization of BPA-BMI (see Figure 5). The total heats of reaction ($\Delta H_{exo}$) were in the range 143–157 J/g with a gradual increase as AT-PAEKI content increased. On closer examination of the thermograms, the exotherms of the blends with AT-PAEKI content of 2–16 wt % were bimodal, suggesting the overlap of two or more thermal reactions. In addition, when the sample with largest content of AT-PAEKI (32 wt %) was heated to 400 °C, the characteristic exotherms associated with the thermal reactions, namely, Claisen rearrangement (~269 °C) and allyl radical cure (~343 °C) of allyl ether groups, were not detected. Since the initial $T_g$ of this blend was significantly increased ($\Delta = 73$ °C) in comparison to the neat BPA-BMI, this may have such a delaying effect kinetically on the onsets of both the

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Scheme 3. (a) Ene Reaction between an Allylphenol and a Maleimide; (b) Claisen Rearrangement Reaction of an Allyl Ether; (c) Proposed Thermal Reactions Occurring in BPA-BMI and AT-PAEKI Blends

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$^a$ Temperatures indicated in parentheses are the approximate onset and peak values.
radical homopolymerization of BPA-BMI and the ene reaction that they take place in the same temperature range, resulting in a single exotherm. This explanation is supported by the fact that the magnitude of the shift ($\Delta = 78^\circ C$) between the exotherm peaks for BPA-BMI and the 32 wt % blend is about the same. Thus, we postulate that in the 2–16 wt % BPA-BMI/AT-PAEKI blends the first exotherm can be attributed to the ene reaction of the allyl ether and maleimide groups, followed by radical addition of maleimide to the adduct, and the second exotherm is the result of the residual radical homopolymerization of the excess BMI (see Scheme 3c).

Finally, when BPA-BMI and all the blends were rescanned after previously heating to 400 °C, none of the samples showed any $T_g$ or cure exotherm, indicative of complete cure under DSC conditions.

While DSC analysis on the AT-PAEKI/BPA-BMI blends indicated the absence of either $T_g$ or further cure during a second heating in the instrument, we have employed dynamic mechanical analysis (DMA) to investigate the postcure thermal behavior in a more sensitive manner. Thus, we prepared multiple DMA bars of BPA-BMI and the 5 wt % blend (solvent-blended as for DSC) by melting the materials into a silicone mold at 150 °C and precuring under vacuum for 16 h. This process yielded transparent amber bars of dimension $20 \times 5 \times 2.25$ mm. Such samples were then postcured at 250 °C in a convection oven for 2 h, resulting in dark and rigid bars characteristic of BMI thermostes. Figure 6 shows the temperature dependence of the tensile storage and loss modulus for both BPA-BMI and the 5 wt % AT-PAEKI/BPA-BMI blend. At room temperature, both samples feature a substantial tensile storage modulus of 3.6–3.7 GPa, with the blend showing a slightly larger loss modulus attributed to a weak $\beta$-relaxation centered at 85 °C. At elevated temperatures a clear distinction between the two samples is observed, with the pure BPA-BMI sample undergoing a softening (glass–rubber) transition beginning at 175 °C and featuring a loss modulus maximum at 215 °C, both substantially below the postcure temperature of 250 °C. Continued heating of this sample beyond 300 °C results in an obvious onset of further cure as evidenced by a significant increase in storage modulus with temperature, although samples invariably fracture at this point in the DMA apparatus. In contrast, the 5 wt % AT-PAEKI/BPA-BMI blend maintains a high storage modulus (>2 GPa) until the tests end at 350 °C. An increase in the loss modulus near 325 °C suggests the onset of $T_g$ in these samples, but we note that the exact shape of the loss modulus curve in this temperature region is somewhat variable from sample to sample. This suggests the alternate explanation of prolonged microcracking at high temperature.

**Conclusion**

The results of our thermal studies showed that compatible blends were formed when the allyl-terminated poly(arylene–ether–ketone–imides), AT-PAEKI, was added to a bisphenol A-based bis(maleimide) (BPA-BMI) in various weight percents up to 32 wt %. We believe that the thermodynamic driving force for the compatibility is most likely provided by the combined effect of the similarity in the chemical structures and the chemical interactions of the components. Furthermore, it is possible to modulate the thermal reactions, namely the ene reaction between the O-allyl and maleimide groups to provide covalent bonding between the hyperbranched-polymer additive and the BMI host as well as the radical homopolymerization of BMI, by simply controlling the amount of AT-PAEKI in the blends. The enhancing effect on the fracture toughness of thermoset host via such covalent bonding, similar to the interfacial adhesion between the thermoplastic additives and the host, is expected for our AT-PAEKI/BPA-BMI blend system. To this end, we are currently investigating the cure kinetics, morphology, and mechanical properties of these blends.

**Experimental Section**

**Materials.** 4-Fluorophthalic anhydride was purchased from Matrix Scientific (Columbia, SC). 2,2-Bis[4-(4-maleimidophenoxy)phenyl]propane (BPA-BMI) was obtained via a custom synthesis by University of Dayton Research Institute. All other chemicals were reagent grade and purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified. N-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure over phosphorus pentoxide. Other solvents were used as received.

**Instrumentation.** Proton and carbon nuclear magnetic resonance (1H NMR and 13C NMR) spectra for intermediates, monomer, and polymers were measured at 270 and 50 MHz on a Varian VXR-270 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-2100 Fourier transform spectrophotometer or with Mattson Galaxy Series FTIR 5000 spectrophotometer. Elemental analysis and mass spectral analysis were performed by System Support Branch, Materials Directorate, Air Force Research Lab, Dayton, OH. The melting points (mp) of all compounds were determined on a Mel-Temp.
melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for NMP solution with 1% lithium bromide and polymer concentrations of approximately 0.5–0.1 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) analysis were performed in nitrogen with a heating rate of 10 °C/min using a Perkin-Elmer model 2000 thermal analyzer equipped with differential scanning calorimetry cell. Thermogravimetric analysis (TGA) was conducted in nitrogen (N₂) and air atmospheres at a heating rate of 10 °C/min using a TA Instrument TGA 2950 thermogravimetric analyzer. Gel permeation chromatography (GPC) was carried out on a Waters 150-CV equipped with 254, 280, and 330 nm UV detectors. Tetrahydrofuran (THF) was used as the eluting solvent.

**Table 2. Thermal Properties of AT-PAEKI/BPA-BMI Blends**

<table>
<thead>
<tr>
<th>Composition (wt %)</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>ΔH_f (J/g)</th>
<th>T_ex (°C)</th>
<th>ΔH_ex (J/g)</th>
<th>T_ex2 (°C)</th>
<th>ΔH_ex2 (J/g)</th>
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<tr>
<td>BMI 100 AT-PAEKI 0</td>
<td>70.5</td>
<td>84.0</td>
<td>19.5</td>
<td>200.0</td>
<td>173.5</td>
<td>253.4</td>
<td>33.4</td>
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<tr>
<td>98</td>
<td>214.7</td>
<td>109.4</td>
<td>261.4</td>
<td>63.7</td>
<td>82.5</td>
<td>115.9</td>
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<tr>
<td>96</td>
<td>225.0</td>
<td>87.0</td>
<td>292.6</td>
<td>56.7</td>
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<td>92</td>
<td>233a</td>
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<td>68</td>
<td>32</td>
<td>144.3</td>
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<tr>
<td>0</td>
<td>100</td>
<td>133.5</td>
<td>269.0</td>
<td>98.2</td>
<td>152.6</td>
<td>114.7</td>
<td></td>
</tr>
</tbody>
</table>

*a The first exotherm appears as a shoulder with approximate peak value as indicated.

Figure 5. DSC thermograms of AT-PAEKI/BPA-BMI blends: (i) BPA-BMI, (ii) 2 wt % AT-PAEKI, (iii) 4 wt % AT-PAEKI, (iv) 8 wt % AT-PAEKI, (v) 16 wt % AT-PAEKI, (vi) 32 wt % AT-PAEKI. (a) is the first heating scan, and (b) is the second heating scan.
Hyperbranched Polymer Derived from N-[3,5-Bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimide. Into a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and outlet, and Dean–Stark trap with a condenser, N-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimide (1.5 g, 3.1 mmol), potassium carbonate (1.0 g, 7.2 mmol), and a mixture of NMP (30 mL) and tolulene solvent were placed. The reaction mixture was then heated and maintained at 140–150 °C for 4 h. During this time period, the water formed was removed by toluene azeotropic distillation via a Dean–Stark trap. After complete removal of tolulene by an increased the flow of nitrogen, the orange solution was then heated at 160 °C for 3 h. The solution became brown in color and viscous. Some precipitate was observed 30 min after reaction temperature had reached 160 °C. After being allowed to cool on its own, the mixture was poured into a beaker containing 5% hydrochloric acid (300 mL). The resulting precipitate was collected by suction filtration and air-dried. Off-white powder was dissolved in NMP again and passed through a cake of Celite 545 to remove any insoluble salts. The filtrate was poured in a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure over phosphorus pentoxide at 100 °C for 48 h. The yield was essentially quantitative. \( |y| = 0.13 \text{ g/g; } T_T = 124 \text{ °C. Analy. Calcd for C}_{28}H_{15}FNO_6; C, 72.88\%; O, 3.88\%. Found: C, 72.20\%; O, 4.06\%.\)

Allylation of Hyperbranched Poly(arylene–ether–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–ether–ketone–imide) (0.5 g, 1.08 mmol), potassium carbonate (0.4 g, 2.9 mol%), allyl bromide (0.30 g, 2.48 mmol), and NMP (10 mL) were placed. The reaction mixture was then heated at 160 °C for 3 h. The solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate was poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 4 h. The yield was essentially quantitative. \( |y| = 0.08 \text{ g/g; } T_T = 134 \text{ °C. Analy. Calcd for C}_{31}H_{19}NO_6; C, 74.10\%; N, 4.01\%; O, 19.10\%. Found: C, 73.10\%; H, 4.17\%; N, 2.77\%; O, 17.76\%.\)

Propargylation of Hyperbranched Poly(arylene–ether–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–ether–ketone–imide) (0.5 g, 1.08 mmol), potassium carbonate (0.4 g, 2.9 mmol), propargyl bromide (0.30 g, 2.52 mmol), and NMP (10 mL) were placed. The reaction mixture was then heated and maintained at 80–90 °C for 10 h. During this period, the orange solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate was then poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 4 h. The yield was essentially quantitative. \( |y| = 0.09 \text{ g/g; } T_T = 122 \text{ °C. Analy. Calcd for C}_{43}H_{22}NO_6; C, 74.55\%; H, 3.43\%; O, 19.22\%. Found: C, 73.07\%; H, 3.82\%; N, 2.70\%; O, 17.99\%.\)

Epoxydation of Hyperbranched Poly(arylene–ether–ketone–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–

\[ \text{Figure 6.} \text{ Comparison of the temperature dependence of the storage (upper traces) and loss (lower traces) modulus for BPA-BMI (solid line) and a 5\% BPA-BMI/AT-PAEKI blend.} \]

- The cured samples were tested in three-point bend mode at an oscillation frequency of 1 Hz and a heating rate of 5 °C/min.
- Comparison of the temperature dependence of the storage (upper traces) and loss (lower traces) modulus for BPA-H, 3.64%; N, 3.67%; O, 17.01%. FT-IR (KBr, cm\(^{-1}\)).
- The filtrate was poured in a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure over phosphorus pentoxide at 100 °C for 48 h. The yield was essentially quantitative. \( |y| = 0.13 \text{ g/g; } T_T = 124 \text{ °C. Analy. Calcd for C}_{28}H_{15}FNO_6; C, 72.88\%; O, 3.88\%. Found: C, 72.20\%; O, 4.06\%.\)

Hyperbranched Poly(arylene–ether–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–ether–ketone–imide) (0.5 g, 1.08 mmol), potassium carbonate (0.4 g, 2.9 mol%), allyl bromide (0.30 g, 2.48 mmol), and NMP (10 mL) were placed. The reaction mixture was then heated at 160 °C for 3 h. The solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate was then poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 4 h. The yield was essentially quantitative. \( |y| = 0.08 \text{ g/g; } T_T = 134 \text{ °C. Analy. Calcd for C}_{31}H_{19}NO_6; C, 74.10\%; N, 4.01\%; O, 19.10\%. Found: C, 73.10\%; H, 4.17\%; N, 2.77\%; O, 17.76\%.\)

Propargylation of Hyperbranched Poly(arylene–ether–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–ether–ketone–imide) (0.5 g, 1.08 mmol), potassium carbonate (0.4 g, 2.9 mmol), propargyl bromide (0.30 g, 2.52 mmol), and NMP (10 mL) were placed. The reaction mixture was then heated and maintained at 80–90 °C for 10 h. During this period, the orange solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate was then poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 4 h. The yield was essentially quantitative. \( |y| = 0.09 \text{ g/g; } T_T = 122 \text{ °C. Analy. Calcd for C}_{43}H_{22}NO_6; C, 74.55\%; H, 3.43\%; O, 19.22\%. Found: C, 73.07\%; H, 3.82\%; N, 2.70\%; O, 17.99\%.\)

Epoxidation of Hyperbranched Poly(arylene–ether–ketone–imide). Into a 50 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser, hydroxyl-terminated hyperbranched poly(arylene–
ether–ketone–imide) (0.1 g, 0.22 mmol), potassium carbonate (0.2 g, 14.5 mmol), epichlorohydrin (0.30 g, 2.52 g), and NMP (10 ml) were placed. The reaction mixture was then heated and maintained at 80–90 °C for 10 h. During this time period, the orange solution became light yellow in color and homogeneous. After it had been allowed to cool on its own, the mixture was filtered through a cake of Celite 545 to remove any insoluble salts. The filtrate poured in a beaker containing 5% aqueous. After it had been allowed to cool on its own, the mixture was warmed around 60–70 °C for 2 h. The white powder was collected and dried under the reduced pressure in the presence of phosphorus pentoxide at 50 °C for 48 h. The yield was essentially quantitative. $\eta_t = 0.08$ dL/g; $T_g = 174^\circ$C. Anal. Calcd for C$_{31}$H$_{17}$NO$_6$: C, 74.55%; H, 3.43%; N, 2.80%; O, 19.22%. $1H$ NMR (in ppm): 8.38 (m, 14H, Ar-CH$_2$), 3.95 (s, 2H, O-CH$_2$), and 7.16–8.38 (m, 18H, Ar-H).

**Solution Blending of AT-PAEKI with BPA-BMI.** A stock solution was first prepared by dissolving AT-PAEKI (0.1 g) completely in THF (10 ml). It was then added to the vials containing predetermined amounts of BPA-BMI (0.098–0.068 g) so as to prepare the solutions with AT-PAEKI content ranging from 2 to 32 wt%. Each vial was then diluted with additional THF until the mixture became homogeneous overnight. The solvent was then removed from the blend solutions via rotary evaporation. The resulting solid blends (all formed a coating on the vial walls) were pulverized with a spatula. The power samples were then dried under reduced pressure at 70 °C for 48 h prior to thermal analysis. The DSC thermograms were recorded on the powder samples after they had been heated to 150 °C, cooled to 20 °C (first cycle), heated again to 320 °C, cooled again to 20 °C (second cycle), finally heated to 350 °C and cooled to room temperature (third cycle), all with heating or cooling rate of 10 °C/min. The thermal data are summarized in Table 2. Figure 5a shows the initial scans (after first and second cycles) for BMI–BPA and its blends with AT-PAEKI. No thermal transition was detected for all samples during the third cycle scans (Figure 5b).

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**References and Notes**


(8) (a) Marlene Houtz (University of Dayton Research Institute) for TGA data, and Dr. Kevin Church (Department of Chemistry, University of Dayton) for NMR spectra.