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

Jong-Beom Baek,[†] Haihu Qin,[‡] Patrick T. Mather,[‡] and Loon-Seng Tan*,[§]

University of Dayton Research Institute, 300 College Park, Dayton, Ohio 45469; University of Connecticut, Institute of Materials Science, 97 N. Eagleville Rd., U-136, Storrs, Connecticut 06269; and Polymer Branch, AFRL/MLBP, Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433-7750

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 AB$_2$ monomer, *N*-[3,5-bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimide, was prepared from 4-fluoroisophthalic anhydride and 3,5-bis(4-hydroxybenzoyl)aniline. The latter was synthesized in three steps starting from commercially available 5-nitroisophthalic acid. The AB$_2$ 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−imide)s 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 Claisen rearrangement 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_g 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.[1] 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.[2] 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,[3,4] (b) to allow processing polymers with preformed imide units, and (c) to avoid many problems associated with handling poly(amic acid) (PAA) precursors.[5,6] 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.[7] 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$_x$ ($x \geq 2$) monomers to facilitate wider evaluation of the materials for their potential applications and commercialization.

In comparison with other classes of wholly aromatic, hyperbranched polymers,[8] there are only few reports on the syntheses of hyperbranched PI's[9−12] and their utilization. The main reason is that amine and anhydride functions are chemically incompatible to be present in the same molecule. However, to circumvent this problem, approaches such as A$_2$ + B$_3$ polymerization[11] and preparation of hyperbranched poly(amic acid methyl ester) followed by intramolecular imidization[10] have been successful. Another approach is to generate an AB$_x$ monomer 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.,[9] who developed a rapid, CsF-mediated synthesis of aromatic hyperbranched poly(ether imide)s from AB$_2$ monomers containing *tert*-butyldimethylsilyl ether moieties. Wu and Shu have recently reported similar work.[12]

As part of our research program to explore and develop niche applications for aromatic hyperbranched polymers,[13] we describe here the results on (i) the synthesis of a new AB$_2$ monomer containing a preformed aromatic imide moiety and para-carbonyl functions to

* Corresponding author. E-mail: Loon-Seng.Tan@wpafb.af.mil.
† University of Dayton Research Institute.
‡ University of Connecticut.
§ Wright-Patterson Air Force Base.

Scheme 1. Synthesis of AB₂ Monomer (5)
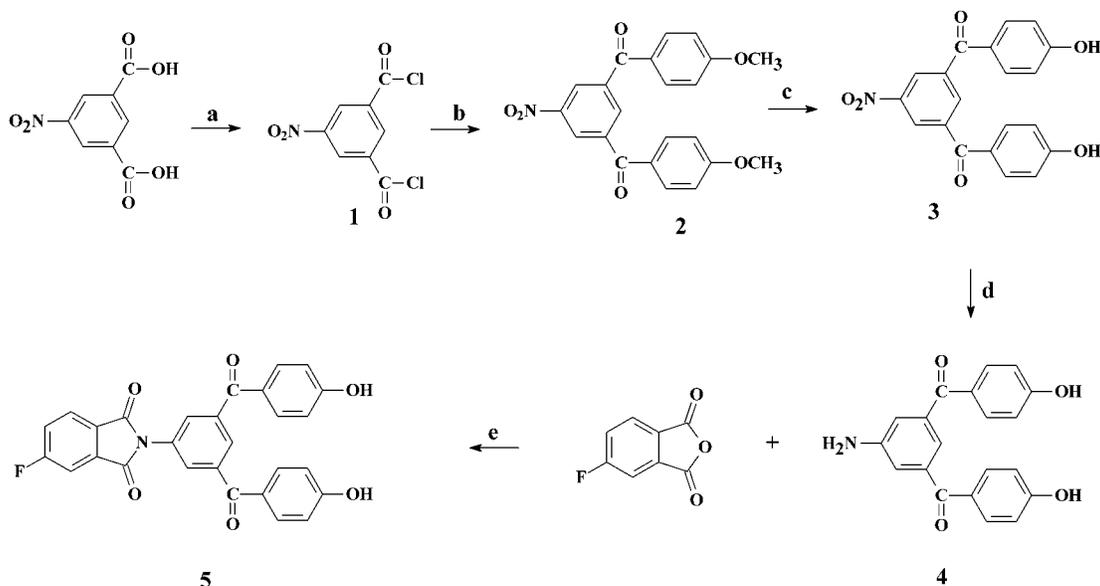
a. SOCl₂, reflux; **b**. AlCl₃, anisole, rt; **c**. Py.HCl, reflux; **d**. H₂ (60−65 psi), EtOH, rt; **e**. isoquinoline, NMP, reflux.

facilitate the formation of phenolate nucleophiles using low-cost potassium carbonate, (ii) functionalization of the resulting hyperbranched poly(ether−ketone−imide) with reactive chain ends, and (iii) a preliminary thermal study of the allyl ether-terminated hyperbranched polymer derivative. The latter effort is to set the stage for further evaluation of such reactive hyperbranched polymer derivatives for uses as toughening additives[14] for high-performance thermosets.

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-PAE-KI) 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 30 ± 0.1 °C), M_n of 2400 g/mol, M_w of 4800 g/mol, and molecular weight distribution (MWD) of 2.0. Its glass transition temperature (T_g) 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-

Scheme 2. Polymerization of AB₂ Monomer and Functionalization of the Resulting Hyperbranched Polymer

6, R = H; HT-PAEKI
7, R = Allyl; AT-PAEKI
8, R = Propargyl; PT-PAEKI
9, R = Epoxy; ET-PAEKI
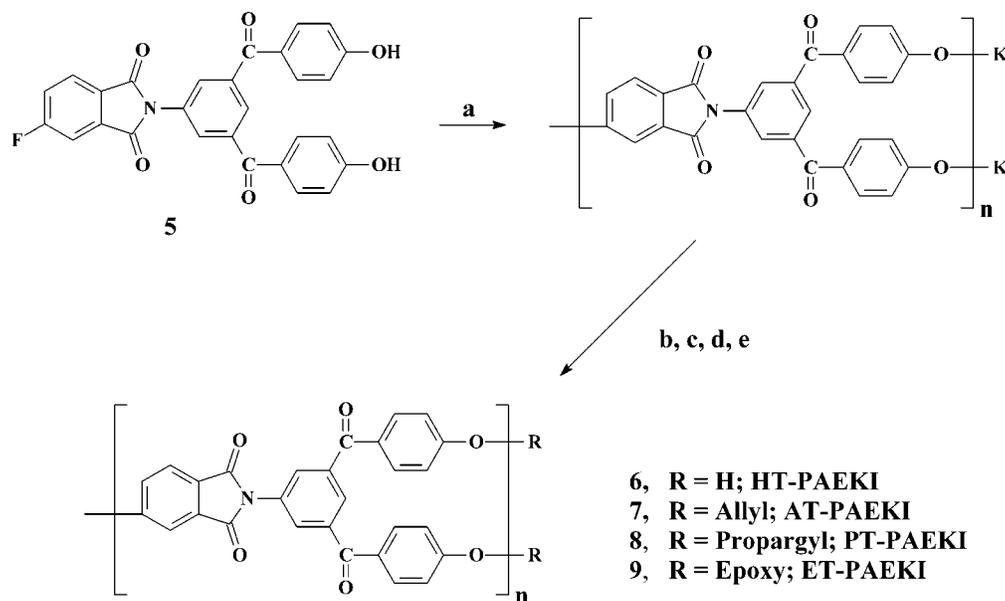
a. K₂CO₃, NMP; **b**. H₃O⁺; **c**. excess allyl bromide, K₂CO₃, NMP, 80−90 °C; **d**. excess propargyl bromide, K₂CO₃, NMP, 80−90 °C; **e**. excess epichlorohydrin, K₂CO₃, NMP, 80−90 °C.
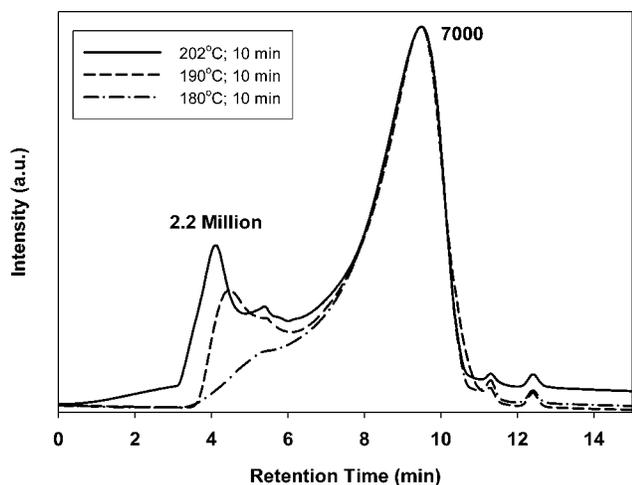

Figure 1. Influence of polymerization temperature of polymer molecular weight and distribution using size-exclusion liquid chromatography, indicating that higher molecular weight portion increases with higher reaction temperature (polystyrene standards were used to estimate the molecular weights).

Figure 2. ¹H NMR (DMSO-d_6) spectra of (1) HT-PAEKI (OH-terminated), (2) AT-PAEKI (allyl-terminated), (3) PT-PAEKI (propargyl-terminated), and (4) ET-PAEKI (epoxy-terminated) (started from bottom). Proton residues from the solvent are denoted by asterisks.

terminated (PT-PAEKI, **8**), and glycidyl (epoxy)-terminated (ET-PAEKI, **9**) poly(aryl−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 ether 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 ± 0.1 °C). These values are considerably lower than that of their parent hyperbranched polymer (hydroxyl-terminated). This is most likely due to the presence of intra- and intermolecular hydrogen bonding in the latter.
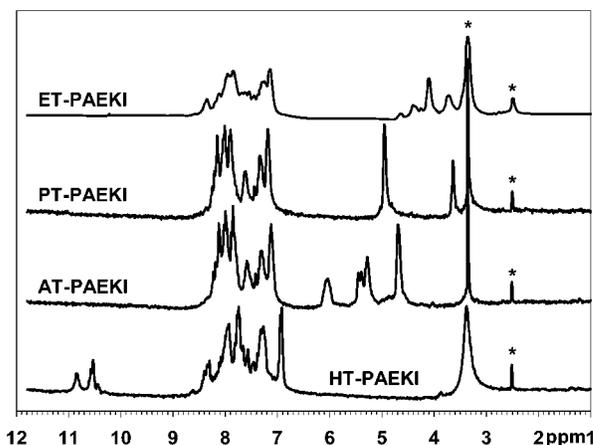
Thermal Properties. The glass-transition temperatures of hyperbranched polymers were determined using the DSC method. The thermograms were generated from their powder samples after they had been previously heated to 200 °C and air-cooled to ambient temperature. The T_g was defined as the midpoint of the maximum baseline shift from the second run. As shown in Table 1 and Figure 3, the HT-PAEKI displayed a T_g at 225 °C. AT-PAEKI showed a T_g at 122 °C and two exotherms with peak temperatures at 269 and 343 °C. The first exotherm stemmed from the Claisen rearrangement reaction,[15] 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 polybenzoxazoles with allyl ether pendants.[16] PT-PAEKI exhibited a T_g at 134 °C and an exotherm with the onset temperature about 200 °C and peak temperature at 278 °C. This exotherm (ΔH_{exo} = 451 J/g) is attributable to

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

							TGA			
							in helium		in air	
PAEKI	$[\eta]^a$ (dL/g)	$T_g{}^b$ (°C)	T_{exo1} (°C)	ΔH_1 (mJ)	T_{exo2} (°C)	ΔH_2 (mJ)	$T_{d5\%}{}^c$ (°C) in	char (%) at 850 °C	$T_{d5\%}{}^c$ (°C) in	char (%) at 850 °C
HT-	0.13	225					411	55	416	0.6
AT-	0.08	122	269	98.2	343	114.7	431	58	408	0.1
PT-	0.08	134			278	450.5	422	50	412	3.3
ET-	0.08	174			350	294.2	330	46	318	1.7

^{a} Intrinsic viscosity measured in NMP at 30.0 ± 0.1 °C. ^{b} Inflection in baseline on DSC thermogram obtained in N_2 with a heating rate of °C/min. ^{c} Temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10 °C/min.
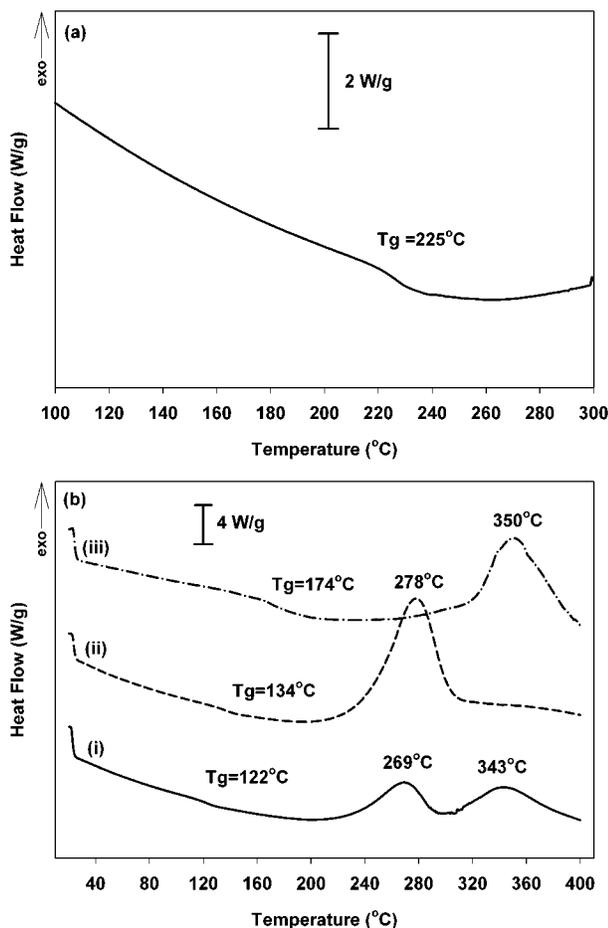

Figure 3. DSC thermograms of (a) HT-PAEKI; (b) (i) AT-PAEKI, (ii) PT-PAEKI, and (iii) ET-PAEKI.

the formation of chromene from the propargyl group followed by the curing of the latter.[17] ET-PAEKI showed a T_g at 174 °C and an exotherm (ΔH_{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 decomposition as indicated by some weight loss in its TGA (helium) around 350 °C. It is noteworthy that the sum of heat of reaction (ΔH_{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[18] 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.[19] 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,[20] diallyl compounds,[21] or bis(benzocyclobutene) compounds;[22] (ii) reactive liquid rubbers;[23−25] (iii) thermoplastics powders;[26] (iv) engineering thermoplastics and their derivatives (with reactive pendants or end groups);[27] (v) hyperbranched aliphatic polyester.[28] The challenge of all of 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)[29] 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 ene reaction between diallyl and bis(maleimide) groups is well established.[21] 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 (ΔH_{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

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[a]
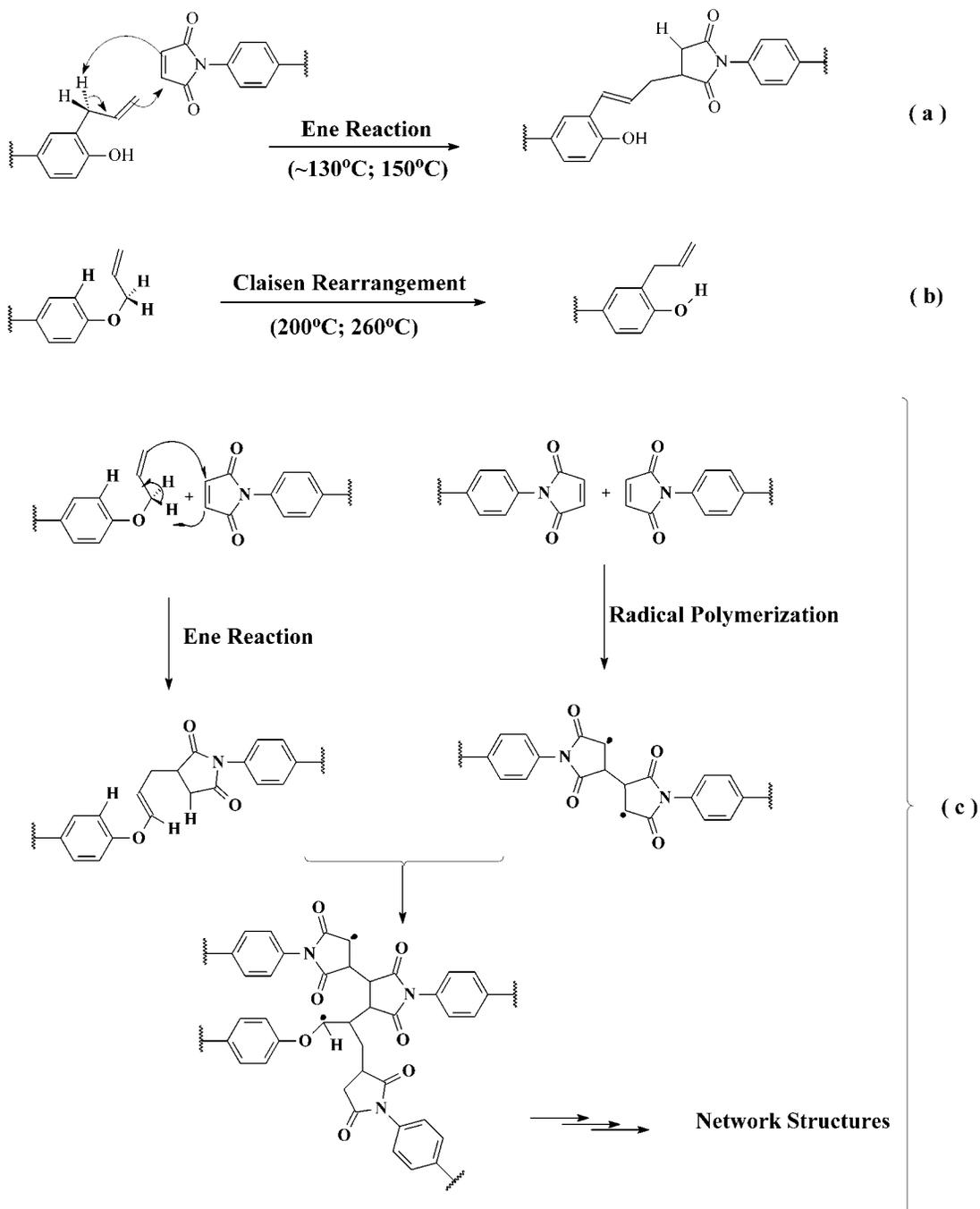
[a] Temperatures indicated in parentheses are the approximate onset and peak values.

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 (ΔH_{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 (Δ = 73 °C) in comparison to the neat BPA-BMI, this may have such a delaying effect kinetically on the onsets of both the
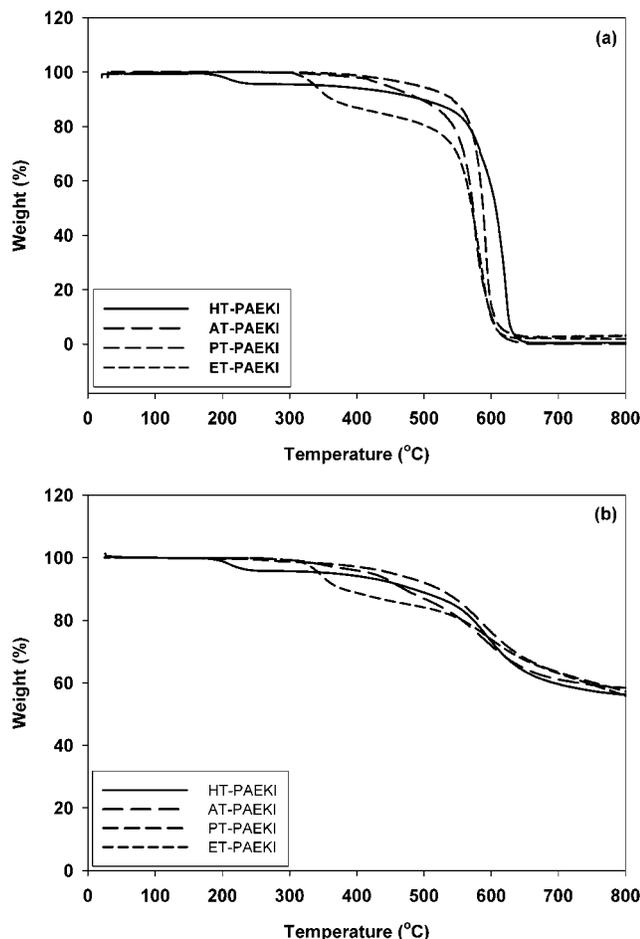
Figure 4. TGA thermograms for the hyperbranched poly-(arylene−ether−ketone−imides): (a) in air, (b) in helium.

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 ($\Delta = 78$ °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** thermosets. 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 β-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−imide), 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[30,31] 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.

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

composition (wt %)		T_g (°C)	T_m (°C)	ΔH_f (J/g)	T_{exo1} (°C)	ΔH_{exo1} (J/g)	T_{exo2} (°C)	ΔH_{exo2} (J/g)
BMI	AT-PAEKI							
100	0	70.5	84.0	19.5	200.0	173.5		
98	2				214.7	109.4	253.4	33.4
96	4				225.0	87.0	261.4	56.7
92	8				~233[a]	~58.1	269.2	82.5
84	16				~237[a]	~32.6	276.4	115.9
68	32	144.3					278.0	152.6
0	100	133.5			269.0	98.2	343.0	114.7

[a] The first exotherm appears as a shoulder with approximate peak value as indicated.
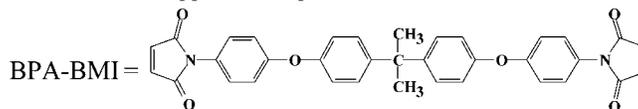
melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for NMP solution with 1% lithium bromide and polymer concentrations of approximately 0.5−0.10 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (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. Themogravimetric analysis (TGA) was conducted in nitrogen (N_2) and air atmospheres at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 themogravimetric 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. Dynamic mechanical analysis was performed using a TA Instruments 2980. The apparatus was run in controlled strain mode and with a three-point bending fixture with a controlled deflection amplitude of 10 μm for our 20 mm span. A heating rate of 5 °C/min was employed, and a purge of N_2 gas was used.

5-Nitroisophthaloyl Dichloride (1). Into a 500 mL one-necked round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet, 5-nitroisophthalic acid (25.0 g, 0.12 mol) was dissolved freshly distilled thionyl chloride (80 mL) containing DMF (3 drops). The mixture was stirred at room temperature for 2 h and gently heated under reflux for 6 h. Excess amount of thionyl chloride was distilled off, and the mixture was then chilled in an ice-and-salt bath. Freshly distilled hexane was added into the light yellow residue with vigorous stirring. The resulting white needles are collected by suction filtration and dried under reduced pressure to give 29.1 g (99.1% yield) of white needles; mp 59−61.5 °C. FT-IR (KBr, cm^{-1}): 1536, 1349 (Ar−NO$_2$), 1757 (carbonyl). Mass spectrum (m/e): 248 (M$^+$, 100% relative abundance). ^{1}H NMR (CDCl$_3$, δ in ppm): 8.96 (s, 2H, Ar), 9.12 (s, 1H, Ar). ^{13}C NMR (CDCl$_3$, δ in ppm): 127.89, 133.33, 136.12, 148.25, 165.35.

3,5-Bis(4-methoxylbenzoyl)nitrobenzene (2). Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and dropping funnel, aluminum chloride (25.4 g, 0.19 mol) and anhydrous anisole (60 mL) were introduced. After the mixture was cooled to 15 °C in an ice−water bath, a solution of 5-nitroisophthaloyl dichloride (15.0 g, 60 mmol) in anhydrous anisole was then added dropwise for 20 min. The mixture was allowed to warm to room temperature. After 8 h of stirring, the mixture was poured into 5% hydrochloric acid. The organic layer was diluted with methylene chloride, separated with the aid of a separatory funnel, and rotavapped to dryness. The resulting off-white solid residue was dissolved in hot ethanol and allowed to cool to room temperature to give 11.2 g (47.7% yield) of off-white solids; mp 181−182 °C. Anal. Calcd for C$_{22}$H$_{17}$NO$_6$: C, 67.52%; H, 4.38%; N, 3.58%; O, 24.53%. Found: C, 67.56%; H, 4.35%; N, 3.45%; O, 24.76%. FT-IR (KBr, cm^{-1}): 1538 (Ar−NO$_2$), 1262, 1325 (ether), 1598, 1655 (carbonyl). Mass spectrum (m/e): 391 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6; δ in ppm): 3.89 (s, 6H, OCH$_3$), 7.12−7.15 (d, 2H, Ar), 7.85−7.88
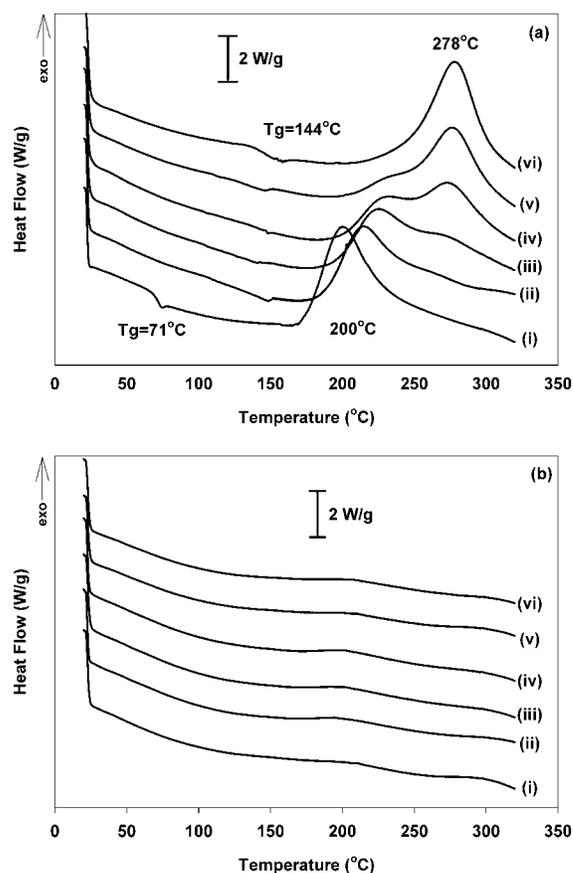

Figure 5. DSC thermograms of AT-PAEKI/BPA-BMI blends: (i) BPA-BMI, (ii) 2 wt % AT-PAEKI, (iii) 4 wt % AT-PAEKI, (iv) 8 wt % AT-PAEKI, (v) 16% AT-PAEKI, (vi) 32 wt % AT-PAEKI 32. (a) is the first heating scan, and (b) is the second heating scan.

(d, 2H, Ar), 8.26 (t, 1H, Ar), 8.61 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6; δ in ppm): 55.61, 114.15, 126.27, 128.09, 132.47, 135.00, 139.18, 147.67, 163.57, 191.53.

3,5-Bis(4-hydroxybenzoyl)nitrobenzene (3). Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, a condenser, and nitrogen inlet, 3,5-bis(4-methoxyphenylcarbonyl)nitrobenzene (6.2 g, 15.8 mmol) and freshly prepared pyridine hydrochloride (100 g) were placed. The mixture was heated under reflux until the solution became homogeneous. It took about 4 h. After being cooled to 120 °C, the mixture was poured into water. The resulting precipitate was collected and dried. The yellow solid was slurred in boiling toluene and collected by suction filtration to give 5.5 g (96% yield); mp 230−231.8 °C. Anal. Calcd for C$_{20}$H$_{13}$NO$_6$: C, 66.12%; H, 3.61%; N, 3.86%; O, 26.42%. Found: C, 66.07%;
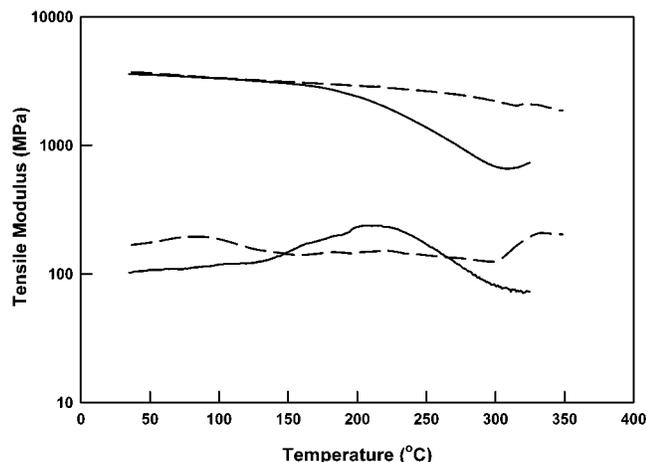
Figure 6. Comparison of the temperature dependence of the storage (upper traces) and loss (lower traces) modulus for BPA-BMI (solid line) and a 5% BPA-BMI/AT-PAEKI blend. The cured samples were tested in three-point bend mode at an oscillation frequency of 1 Hz and a heating rate of 5 °C/min.

H, 3.64%; N, 3.67%; O, 17.01%. FT-IR (KBr, cm^{-1}): 1321, 1538 (Ar–NO$_2$), 1602, 1648 (carbonyl), 3420 (Ar–OH). Mass spectrum (*m/e*): 363 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 6.93–6.96 (d, 4H, Ar), 7.76–7.79 (d, 4H, Ar), 8.23 (s, 1H, Ar), 8.58 (s, 2H, Ar), 10.66 (s, 2H, OH). ^{13}C NMR (DMSO-d_6, δ in ppm): 115.48, 126.02, 126.65, 132.84, 134.83, 139.44, 147.61, 156.80, 162.70, 191.36.

3,5-Bis(4-hydroxybenzoyl)aminobenzene (4). Into a 500 mL high-pressure bottle, 5-nitroisophthalic acid (4.8 g, 13 mmol), palladium on activated carbon (10%, 0.5 g), and ethanol (100 mL) were charged. The bottle was placed on the hydrogenation vessel. Hydrogen was charged and discharged five times and agitated at 60–65 psi for 24 h. After the reaction mixture had been filtered through a cake of Celite 545 to remove catalyst, the solvent of the filtrate was removed on a rotary evaporator. The light yellow solid was recrystallized from deoxygenated 20% ethanol to give 4.4 g (>99% yield) of yellow powder; mp 249.5–250.5 °C. Anal. Calcd for C$_{20}$H$_{15}$-NO$_4$: C, 72.06%; H, 4.54%; N, 4.20%; O, 19.20%. Found: C, 72.04%; H, 4.89%; N, 3.91%; O, 18.60%. FT-IR (KBr, cm^{-1}): 763 (Ar–NH$_2$), 1598 1634 (carbonyl), 3378 (Ar–NH$_2$). Mass spectrum (*m/e*): 333 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 5.71 (s, 2H, NH$_2$), 6.90–6.93 (d, 4H, Ar), 6.70 (s, 1H, Ar), 7.14 (s, 2H, Ar), 7.70–7.71 (d, 4H, Ar), 10.44 (s, 1H, OH). ^{13}C NMR (DMSO-d_6; δ in ppm): 115.10, 117.09, 117.55, 127.95, 132.35, 138.57, 148.91, 161.87, 194.21.

N-[3,5-Bis(4-hydroxybenzoyl)benzene]-4-fluorophthalimide (5). Into a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet and outlet, 3,5-bis(4-hydroxyphenylcarbonyl)aminobenzene (4.3 g, 13 mmol) was completely dissolved in NMP (50 mL). 4-Fluorophthalic anhydride (2.1 g, 12 mmol) was then added. The mixture was then heated, and when temperature was approaching 170–180 °C, isoquinoline (5 drops) was added. The mixture was heated at 200 °C with stirring for 18 h. After cooled to room temperature, the mixture was poured into 5% hydrochloric acid, and the resulting precipitate was collected by suction filtration and dried under the reduced pressure. The off-white solid was dissolved in hot toluene and allowed to cool to room temperature to give 4.3 g (72% yield) of off-white solid; mp 274–276 °C. Anal. Calcd for C$_{28}$H$_{16}$FNO$_6$: C, 69.86%; H, 3.35%; N, 2.91%. Found: C, 69.90%; H, 3.90%; N, 2.66%. FT-IR (KBr, cm^{-1}): 1644, 1601 (imide), 1724 (carbonyl) 3413 (Ar–OH). Mass spectrum (*m/e*): 481 (M$^+$, 100% relative abundance). ^{1}H NMR (DMSO-d_6, δ in ppm): 6.93–6.96 (d, 4H, Ar), 7.71–7.75 (d, 1H, Ar), 7.78–7.82 (d, 4H, Ar), 7.89–7.93 (dd, 1H, Ar), 7.96–7.97 (t, 1H, Ar), 8.05–8.07 (d, 1H, Ar), 8.09–8.10 (d, 2H, Ar), 10.58 (s, 2H, OH). ^{13}C NMR (DMSO-d_6, δ in ppm): 111.44, 115.36, 121.38, 126.30, 127.11, 127.71, 128.95, 130.45, 132.70, 134.65, 138.43, 162.36, 163.97, 165.47, 165.73, 167.71, 192.45.

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 toluene 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 toluene 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 warmed to 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. [η] = 0.13 dL/g; T_g = 224 °C. Anal. Calcd for C$_{28}$H$_{15}$NO$_6$: C, 72.88%; H, 3.28%; N, 3.06%. Found: C, 68.55%; H, 3.93%; N, 3.01%. ^{1}H NMR (DMSO-d_6; δ in ppm): 6.89–8.39 (Ar–**H**) and 10.55–10.84 (Ar–**OH**).

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 mmol), allyl bromide (0.30 g, 2.48 mmol), 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 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 48 h. The yield was essentially quantitative. [η] = 0.08 dL/g; T_g = 134 °C. Anal. Calcd for C$_{31}$H$_{19}$NO$_6$: C, 74.10%; H, 4.01%; N, 2.79%; O, 19.10%. Found: C, 73.10%; H, 4.17%; N, 2.77%, O, 17.76%. ^{1}H NMR (DMSO-d_6, δ in ppm): 4.71 (–**CH$_2$**–CH=CH$_2$), 5.24–5.43 (–CH$_2$–CH=**CH$_2$**), 6.01 (–CH$_2$–**CH**=CH$_2$), and 7.11–8.21 (Ar–**H**).

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 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 was then poured into a beaker containing 5% hydrochloric acid (300 mL), and the mixture was warmed to 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. [η] = 0.08 dL/g; T_g = 122. Anal. Calcd for C$_{31}$H$_{17}$NO$_6$: C, 74.55%; H, 3.43%; N, 2.80%; O, 19.22%. Found: C, 73.07%; H, 3.82%; N, 2.70%; O, 17.99%. ^{1}H NMR (DMSO-d_6, δ in ppm): 3.64 (–CH$_2$–C≡C**H**), 4.96 (–**CH$_2$**–C≡CH), and 7.11–8.21 (Ar–**H**).

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), 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% 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 48 h. The yield was essentially quantitative. $[\eta] = 0.08$ dL/g; $T_g = 174$ °C. Anal. Calcd for $C_{31}H_{17}NO_6$: C, 74.55%; H, 3.43%; N, 2.80%; O, 19.22%. Found: C, 73.07%; H, 3.82%; N, 2.70%; O, 17.99%. ^{1}H NMR (DMSO-d_6, δ in ppm): 3.33 (s, 2H, $-CH_2-CH(O)CH_2$), 3.70 (s, 1H, $-CH_2-CH(O)CH_2$), 3.95 (s, 2H, $-CH_2-CH(O)CH_2$), and 7.16−8.38 (m, 14H, 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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