



Branched poly(arylene ether ketone)s with tailored thermal properties: Effects of AB/AB₂ ratio, core (B₃) percentage, and reaction temperature

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ABSTRACT

A series of poly(ether ketone) copolymers were prepared by nucleophilic aromatic polymerization reactions of the AB monomer 4-fluoro-4'-hydroxybenzophenone, **1**, and the AB₂ monomer bis(4-fluorophenyl)-(4-hydroxyphenyl)phosphine oxide, **2**, in the presence of 3 or 5 mol% of a highly reactive core molecule, tris(3,4,5-trifluorophenyl)phosphine oxide (B₃), **4**. All of the copolymers prepared in the presence of a core molecule were sufficiently soluble in *N*-methylpyrrolidinone, NMP, to allow the determination of their molecular weights and polydispersity indices, PDIs. Number-average molecular weights, *M_n*s, of 3200–6800 Da were determined and the PDI values ranged from 1.41 to 4.07. The *M_n* was controlled by the mol% of **4** present in the reaction mixture with higher molar percentages leading to lower *M_n* values. Lower reaction temperatures and lower ratios of AB/AB₂ monomers afforded copolymers with lower PDI values. As expected, the crystallinity of the samples decreased with an increasing AB₂ content or an increase in PDI. The copolymers also exhibited excellent thermo-oxidative stability with a number of samples suffering 5% weight losses at temperatures, in air, well in excess of 450 °C.

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1. Introduction

Incorporating a controlled degree of branching into polymeric systems can provide materials with a balance of tailored mechanical and thermal properties as well as improved processability. Two relatively recent approaches to enhance the physical properties of highly branched polymers are the copolymerization of AB and AB_{*n*}-type monomers and the condensation reactions of oligomeric A₂ species with B₃ components (vide infra). Copolymerization has been widely used with polycondensation reactions to alter or enhance the physical properties and improve the processability of the final polymer. Of particular interest for the current discussion is the copolymerization behavior of AB and AB₂ monomers, as originally described by Flory [1]. There are numerous reports in which an AB monomer has been copolymerized with an AB_{*n*}-type monomer to afford copolymers with varying degree of branching (DB) values. For example, Kricheldorf and Stukenbrock have prepared branched polyesters [2] via this methodology while Moore et al. have prepared poly(ether imide)s [3], Baek and Tan have reported on

poly(ether ketone)s [4], Baek and Harris have synthesized poly(phenyl quinoxaline)s [5], Jikei et al. have generated aromatic amide copolymers [6], and Frey et al. have prepared poly(ester)s [7] and poly(glycerol)s [8]. In a slight variation of the AB/AB₂ approach, Hawker et al. prepared hyperbranched polyesters from AB₂ macromonomers in which the chain length between branch points was controlled via the use of oligomeric poly(ethylene glycol) units [9]. A similar approach was recently described by Jeon et al. for the synthesis of poly(ether ketone)s with flexible spacers [10].

In each instance, as the content of AB monomer increases (increase in average linear segment length) the overall DB for the polymer is lowered and the mechanical properties of the systems are improved accordingly. For example, if poly(arylene ether imide)s, PAEIs, are prepared with a high degree of branching, the materials are brittle and display very poor mechanical stability [3]. However, if the same material is prepared with a low degree of branching, mechanically robust films can easily be prepared. The same type of effect has been observed with the thermal properties of PAEs. Lightly branched poly(ether ketone)s, PEKs, displayed some level of crystallinity, as determined by the presence of a melting temperature, *T_m*, while PEKs with a higher degree of branching, DB, exhibited no *T_m*, indicating that they were completely amorphous [4,11]. All of these systems possessed “random” placement of the branching units and thus, did not provide controlled lengths of linear segments between the branch points.

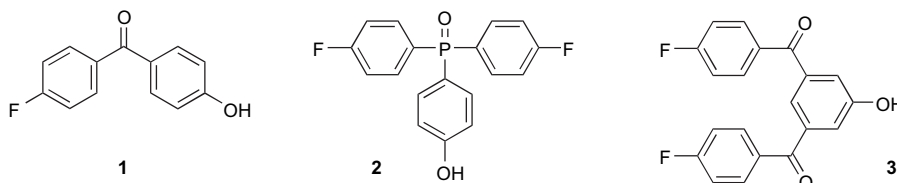
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The research group of Long has thoroughly studied the effects of spacing between branch points in hyperbranched polymers prepared via the $A_2 + B_3$ approach. They prepared a series of hyperbranched (HB) poly(ether ester)s by utilizing a slow addition of hydroxy-terminated poly(ethylene glycol), PEG, to 1,3,5-trimesoyl chloride [12,13]. The length between branch points in the HB poly(ether ester)s is controlled by the MW of the PEG segment. Under relatively dilute conditions (in order to avoid extensive crosslinking), the corresponding soluble HB poly(ester)s have been prepared with weight-average MWs up to 35,000 Da. Unfortunately, as the MW increases, there is a concurrent increase in the polydispersity (PDI) with values as high as 10.0 being observed. As expected, the HB poly(ether ester)s prepared with the longer PEG segments (>2000 Da) show a considerable increase in the crystallinity of the PEG segments, whereas at shorter lengths the materials are completely amorphous. A similar approach has been reported for the synthesis of hyperbranched poly(arylene ether sulfone)s [14].

We have recently reported on the geometrical influence of the AB_n monomer structure on the thermal properties of branched PEKs prepared via the copolymerization reaction of AB and AB_n monomers [11]. It was determined that PEKs prepared by copolymerization of the AB monomer, 4-fluoro-4'-hydroxybenzophenone, **1**, with the AB_2 monomer, bis(4-fluorophenyl)-(4-hydroxyphenyl)phosphine oxide, **2**, possessed a much lower degree of crystallinity than the corresponding polymers prepared with the AB_2 monomer 3,5-bis(4-fluorobenzoyl)phenol, **3**. For example, a copolymer prepared with a ratio of 90/10 of AB/ AB_2 (**1/2**) displayed no T_m , while a copolymer prepared with a ratio of 82.5/17.5 (**1/3**) displayed a T_m of 339.5 °C. This observation was explained based on the tetrahedral geometry of **2** disrupting the crystallization of the material much more efficiently than the more planar **3**.



Unfortunately, very few of the samples prepared in our previous study were soluble in an appropriate solvent, e.g. DMSO or NMP, for size exclusion chromatographic (SEC) analysis, which precluded any determinations of molecular weight and PDI effects. We now wish to report on the synthesis and characterization of soluble, branched copoly(ether ketone)s, with controlled molecular weights and relatively low PDI values, prepared via the copolymerization reactions of **1** and **2** in the presence of a highly reactive core molecule, tris-(3,4,5-trifluorophenyl)phosphine oxide, **4**. The thermal properties of these materials were analyzed to determine the effects of molecular weight, PDI, ratio of AB/ AB_2 , percentage core, and reaction temperature on their morphology.

2. Experimental

2.1. Materials

All reactions were performed under a nitrogen atmosphere and all transfers were done using syringes or cannula as necessary. 4-Fluoro-4'-hydroxybenzophenone was purchased from Aldrich Chemical Co. and recrystallized from ethanol prior to use. Potassium carbonate, K_2CO_3 , was dried in an oven at 120 °C. Toluene was dried over and distilled from sodium/benzophenone prior to use. N-Methylpyrrolidinone, (NMP), was dried over CaH_2 and distilled

prior to use. The AB_2 monomer, bis(4-fluorophenyl)-(4-hydroxyphenyl)phosphine oxide, **2**, [15] and core molecule, tris-(3,4,5-trifluorophenyl)phosphine oxide, **4**, [16] were prepared according to literature procedures.

2.2. Instrumentation

1H and ^{31}P NMR spectra were obtained using a Bruker AVANCE DMX 300 MHz instrument operating at 300 and 121.5 MHz, respectively. Samples were dissolved in $CDCl_3$ or $DMSO-d_6$ as required. Size exclusion chromatography (SEC) analyses were performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70 °C. Polymer Laboratories 5 μm PL gel columns (guard column and two mixed C columns) were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation Model P1000 pump operating at 0.8 mL/min. Molecular weights were calculated from the RI detector signal using polystyrene equivalents. Differential scanning calorimetry (DSC) was performed in nitrogen with a heating rate of 10 °C/min using a Perkin-Elmer DSC 7 thermal analyzer. Thermogravimetric analyses (TGA) were conducted in nitrogen (N_2) and air atmospheres (gas flow rate of 50 mL/min) with a heating rate of 10 °C/min using a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer.

2.3. Typical procedure for the copolymerization of **1** with **2**

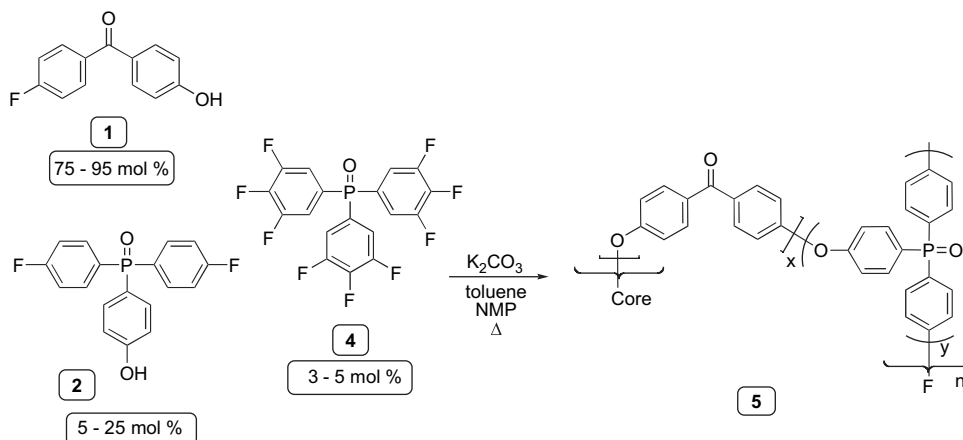
To a 25 mL round-bottomed flask equipped with a magnetic stirrer, a Dean-Stark Trap, a reflux condenser, and a gas inlet, were added 0.5 g (2.31 mmol) of 4-fluoro-4'-hydroxybenzophenone, **1**, 0.0848 g (0.26 mmol) of bis-(4-fluorophenyl)-4-hydroxyphenylphosphine oxide, **2**, 0.0348 g (0.08 mmol) of tris-(3,4,5-trifluorophenyl)phosphine oxide, **4**, 0.533 g (3.86 mmol) of K_2CO_3 ,

5 mL of NMP, and 5 mL of toluene. The Dean-Stark trap was filled with toluene and the reaction mixture was heated to 165 °C for 2 h at which point toluene was removed, and the temperature raised to 180 °C for an additional 3 h. The reaction progress was monitored by the removal of small aliquots at various intervals for analysis via SEC and ^{31}P NMR spectroscopy. The remaining reaction mixture was slowly added into an excess of water to precipitate the polymer as a white powder. The solid was transferred to an extraction thimble and extracted with water, followed by methanol for 24 h each. The off-white solid was subsequently dried in a drying pistol at 115 °C for 8 h before analysis.

3. Results and discussion

3.1. Polymerization reactions

Soluble, branched copoly(ether ketone)s, with varying mol% of **1**, **2**, and **4**, were prepared according to the route shown in Scheme 1. Initial reactions were performed with AB/ AB_2 ratios of 75/25, 90/10, and 95/5 in the presence of 3 mol% of **4**, at a final reaction temperature of 200 °C. The number-average molecular weights, M_n s, and polydispersity indices, PDIs, are listed in Table 1. Subsequent reactions included variations in the reaction temperature, molar ratio of **1** to **2** and the mol% of **4**. The reaction mixtures were



Scheme 1.

azeotropically dried for 2 h at which point toluene was removed and the reaction temperature was increased to 200 °C. Interestingly, all of the polymers were fully soluble in NMP after the precipitation and drying processes had been completed, which is in stark contrast with the low or lack of solubility of the same systems prepared in the absence of a core molecule. Samples prepared in the absence of core molecules remained in solution after the polymerization reactions were complete, however, upon precipitation and drying, most of the samples were insoluble, even in hot NMP. Additionally, the viscosity of the reaction mixtures with core molecules present remained relatively low, presumably due to the presence of lower molecular weight materials. Each of the samples prepared in the presence of a core molecule was sufficiently soluble in NMP to allow SEC analysis for determination of its number-average molecular weight, M_n , and PDI. Even though the samples were soluble in NMP their solubility was insufficient in an appropriate solvent for NMR analysis, which precluded a spectroscopic determination of the ratio of monomers incorporated into the polymer. However, since PEK itself is not soluble in NMP and the samples prepared in this study are, it is highly likely that most, if not all of monomer **2** is present in the polymer.

3.2. Effect of presence and mol% of core

The effect of the presence of a core molecule on the final M_n and PDI values of branched copoly(ether ketone)s is quite dramatic and

Table 1
Molecular weight and polydispersity data for copolymers of **1** and **2** prepared in the presence of core **4** at various reaction temperatures

Sample	Core (%)	1 (mol%)	2 (mol%)	Temp. (°C)	M_n	PDI
5a	3	75	25	200	5420	2.18
5b	3	75	25	180	4560	1.87
5c	3	75	25	170	5240	1.83
5d	3	75	25	150	5220	1.74
5e^a	0	75	25	202	13,000	11.0
5f	3	90	10	200	5370	2.61
5g	3	90	10	180	5650	1.79
5h	3	90	10	170	5070	1.96
5i	3	90	10	150	4940	1.69
5j^a	0	90	10	202	–	–
5k	3	95	5	200	6820	4.07
5l	3	95	5	180	5590	3.50
5m	3	95	5	170	5130	2.06
5n	3	95	5	150	5100	1.79
5o^a	0	95	5	202	–	–
5p	5	95	5	200	4010	1.66
5q	5	95	5	180	3850	1.64
5r	5	95	5	170	3690	1.44
5s	5	95	5	150	3280	1.41

^a Data taken from Ref. [11].

is best illustrated by comparing entries **5a** and **5e** in Table 1. While the M_n value for **5a** is less than half of that for **5e**, the PDI value decreases from 11.0, from a multimodal signal, to 2.18 with a monomodal signal. The expected value of M_n for **5a** is 7450 Da and the experimentally determined value, 5400 Da, is approximately 2/3 of this value, which may, simply, be a result of its compact, branched structure. Of equal importance is the observation of soluble materials prepared with higher ratios of AB/AB₂. At ratios of 90/10 (**5f**) and 95/5 (**5k**) soluble, branched copoly(ether ketone)s with M_n values of 5370 and 6820 Da were observed, respectively. Previous samples with the corresponding ratios of AB/AB₂ were not soluble in NMP, which precluded determining their M_n and PDI values. The expected values of M_n for **5f** and **5k** are 6880 and 6700 Da, respectively. As the degree of branching in the samples decreased the observed M_n values increased accordingly, owing to the less compact structure. As expected, when 5 mol% of core **4** was utilized in the polymerization reaction, **5p–5s**, a corresponding decrease in the M_n value was observed. For example, polymer **5p** had a M_n value of 4010 Da compared with 6820 Da for **5k** which was prepared with 3 mol% core **4**. The theoretical value of M_n for **5p** is 4060 Da and the experimental value (4010 Da) is in very good agreement. Therefore, the ability to control the M_n values of these systems, by altering the mol% of core molecule ($[M]_0/[Core]_0 = DP_n$), has been established, which provides an efficient method to generate materials for a thorough study of structure–property relationships.

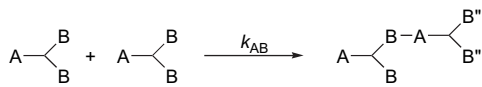
3.3. Effect of AB/AB₂ ratio – number of end groups

At each polymerization temperature, the ratio of AB/AB₂ also has a significant impact on the PDI of the samples. For example, samples **5a**, **5f**, and **5k**, with AB/AB₂ ratios of 75/25, 90/10, and 95/5 possess PDI values of 2.18, 2.61, and 4.07, respectively. The substantial increase in PDI as the ratio of AB/AB₂ increases can be attributed, in part, to the number of end groups present in the growing polymer chains.

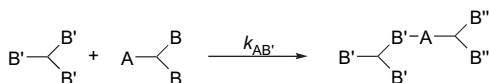
As depicted in Scheme 2, three unique reactions (monomer with monomer, monomer with core, monomer with growing polymer) are possible when an AB₂ monomer is polymerized in the presence of a B'₃-core molecule. The same analysis would apply to copolymerization reactions of AB and AB_n monomers. For the current system in which nucleophilic aromatic substitution, NAS, is the reaction mechanism, each of the reactions is second-order and can be described by a simple second-order rate law, where rate = $k[A][B]$. The ratios of the individual rates and rate constants (α , β , and γ) will determine the outcome of the polymerization reaction.

In order to prepare hyperbranched polymers with controlled MWs and narrow PDIs, all growth of polymers must start at the

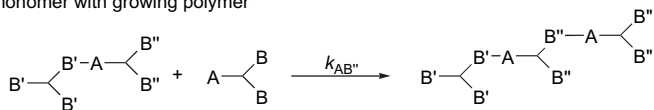
monomer with monomer



monomer with core



monomer with growing polymer



$$\text{rate} = k [A][B(\text{B}' \text{ or } \text{B}'')]]$$

Scheme 2.

core molecules, the polymers must grow at approximately the same rate, and no new polymer species can be formed by the reaction of monomer with another monomer. In terms of the individual rate constants, maximum control over the MW should be achieved when the ratio, α , of the rate constant of monomer addition to core (k_{AB}) to that of the rate constant of monomer addition to another monomer (k_{AB}) is large (all growth start at the cores). In order to prepare polymers with narrow polydispersity indices, the ratio, γ , of the rate constant for addition to the core ($k_{AB'}$) to that of the rate constant for addition to the growing polymer ($k_{AB''}$) must also be $\gg 1$. In addition, the ratio, β , of the rate constant for reaction of monomer with a growing polymer ($k_{AB''}$) to that for the reaction of a monomer with another monomer (k_{AB}) must also be large to prevent the formation of new growing polymer species.

In the current kinetic analysis, the possibility of intramolecular cyclization has been omitted for two reasons. First, while the presence of intramolecular cyclization reactions would lead to a broadening in the PDI values of linear polymers, it has actually been shown to provide hyperbranched polymers with PDI values considerably lower than those predicted by theory [17–20]. Second, the presence of a highly reactive core molecule should eliminate, or at the very least, limit the ability of a system to form macrocyclic species.

We have previously shown that the polymerizations of **2** in the presence of **4** provide hyperbranched poly(arylene ether phosphine oxide)s, HB PAEPOs, with PDI values as low as 1.25 [16]. These results indicated that a highly reactive core molecule such as **4** affords a high value of α and some level of control over the final MW and PDI. It is assumed that a large value for α should also be present in the current AB/AB₂ system. We have also shown that the selectivity for reaction of **2** with **4** over reaction with the growing polymer is quite high and this selectivity should also be present in this case [21].

Some indications of the relative rate constants for these individual reactions can be derived from the ¹³C and ¹⁹F NMR chemical shifts of the *ipso* carbon atoms in the monomers. A number of authors have utilized ¹³C and ¹⁹F NMR chemical shifts to correlate the electron density present at the *ipso* carbon with the relative ability of the fluorine atom to be substituted via nucleophilic aromatic substitution [22–26]. In general, a more downfield signal corresponds to a more reactive electrophilic site. To the best of our knowledge this concept has not yet been applied to AB and AB₂-type monomers. The ¹³C NMR chemical shifts for the *ipso* carbon atoms in **1** and **2** were found to be 164.1 and 164.3 ppm, respectively, while the ¹⁹F chemical shifts for **1** and **2** were –107.8 and –107.7 ppm, respectively. These data indicate that the electrophilic sites in **1** and **2** should possess similar reactivity.

The rate of reaction of a monomer with the growing polymer versus that of the reaction of monomer with another monomer, resulting in the formation of a new chain, will also depend on the concentration of end groups. The more end groups that are present on the polymer chains, the higher the rate of reaction of monomer with polymer will be. This is exemplified by the PDI values observed for **5a**, **5f**, and **5k** (2.18, 2.61, and 4.07, respectively) which increase significantly as the number of end groups is decreased.

3.4. Effect of reaction temperature

Each of the reactions depicted in Scheme 2 has its associated activation energy, E_a . Assuming that the reaction of monomer with core has the lowest E_a and that the reaction of monomer with a growing polymer chain is favored over reaction of two monomers to form a dimeric species, a decrease in the reaction temperature would magnify these effects resulting in lower PDI values. Indeed, a decrease in PDI is observed as the reaction temperature is reduced from 200 to 150 °C. The PDI values follow the same trend with each system, but the effect is more dramatic at higher ratios of AB/AB₂. As shown in Fig. 1, when an AB/AB₂ ratio of 95/5 is utilized in the presence of 3 mol% of **4** at temperatures ranging from 150 to 200 °C, the PDI values increase from 1.79 at 150 °C to 4.07 at 200 °C. The effect of reaction temperature on PDI is not as significant when the polymerization reactions are carried out in the presence of 5 mol% **4**.

The combined effects of AB/AB₂ ratio and reaction temperature are summarized in Fig. 2. At the same reaction temperature, polymers prepared with a higher ratio of AB/AB₂ always possessed a higher PDI value. This observation is most likely a result of the higher number of end groups thus, favoring the reaction of monomer with growing polymer rather than starting a new polymer chain. At lower reaction temperatures, the differences in E_a are magnified and the selectivity for reaction of monomer with growing polymer rather than starting a new polymer chain by reacting with another monomer molecule is, again, higher. For the reactions performed with 5 mol% of **4** the effect of reaction temperature is not as significant as observed at 3 mol%. This observation may be due to the fact that there are simply more polymer chains and thus, the total number of end groups in the system is higher, when a higher mol% of core is utilized.

3.4.1. Thermal analysis – DSC

The thermal properties, glass transition temperature, T_g , crystallization temperature, T_c , and melting temperature, T_m , of the branched copoly(ether ketone)s were evaluated by DSC and the results are summarized in Table 2. What is readily apparent is that most of the branched copoly(ether ketone)s prepared in the presence of a core molecule possess some level of crystallinity which is in stark contrast to our previous work without core molecules in

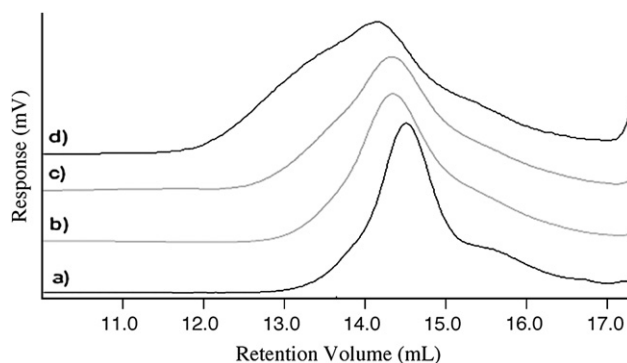


Fig. 1. SEC traces (RI signal) for 95/5 AB/AB₂ with 3 mol% of **4** at (a) 150, (b) 170, (c) 180, and (d) 200 °C.

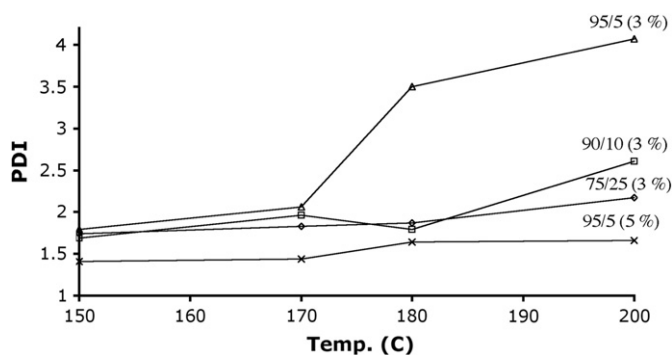


Fig. 2. The combined effects of reaction temperature, the ratio of AB/AB₂, and the mol% of **4** on the final PDI of branched PEK copolymers.

which the vast majority of the samples exhibited no crystallinity [11]. For example, entries **5a** and **5e** correspond to samples prepared under similar reaction conditions (75/25, AB/AB₂), yet **5a**, prepared with 3 mol% of **4** possessed both a T_c (229 °C) and T_m (278 °C) while **5e**, prepared without a core molecule was completely amorphous. Despite the fact that **5a** has a much lower M_n value than **5e** (5400 versus 13,000 Da, respectively) the more homogeneous nature of the sample (PDI 2.18 versus 11.0) allows for better packing into crystalline regions and the observation of a T_m at 205 °C. It may be that the less homogeneous sample, **5e**, is self-plasticizing, thus preventing the formation of crystalline regions. In general, as the PDI of the sample decreased the observed T_m was increased. As expected the lower molecular weight sample, **5a**, possesses a considerably lower T_g than **5e**, 149 versus 184 °C, respectively.

When samples were prepared with a 90/10 ratio of AB/AB₂, most of the materials, with a core molecule present, possessed a T_m , with the exception of the polymer prepared at 200 °C, **5f**, which had a PDI of 2.61. These results indicate that the samples with lower PDI values are more capable of organizing into crystalline regions. Interestingly, even at such a high ratio of the linear component to the branching unit, the sample prepared in the absence of a core molecule did not display a T_m and was not sufficiently soluble to allow for molecular weight determination. The lack of a T_m in this sample is indicative of a broadly disperse system.

Two sets of materials were prepared at the 95/5 ratio of AB/AB₂, one with 3% of core and the other with 5%. Each sample in both sets possessed a T_m , as did the sample prepared in the absence of a core

molecule, which indicates the presence of a significant level of crystallinity. Interestingly, the T_c value for the samples prepared with 3% of core increased substantially as the PDI of the systems decreased. No T_c was observed for the sample prepared in the absence of a core molecule. The T_m values for the 5% core samples were considerably lower than those observed for the 3% core samples, most likely a result of the lower molecular weights for the former. The T_g values for the 3 and 5% core systems showed similar trends to those observed for the T_m values. For example, in the 95/5 systems **5l** (3% core) exhibited a T_g of 139 °C while **5q** (5% core) exhibited a T_g of 120 °C.

3.4.2. Thermal analysis – TGA

In order to determine the effects of the MW and PDI as well as the percentage of the phosphine oxide-based branching unit on the thermal stability, a number of the representative samples were evaluated using TGA in both air and nitrogen (see Fig. 3a and b). The effect of molecular weight can be inferred by comparing the TGA data for the 3 and 5 mol% core samples prepared with a ratio of 95/5 of AB/AB₂, **5n** and **5q**, respectively. The lower molecular weight sample, **5q**, was considerably less stable than **5n**, with 5% weight losses in air occurring at 443 and 464 °C, respectively, indicating that the higher molecular weight systems (see Table 1) possess higher thermo-oxidative stability. An increase in thermo-oxidative stability was also observed when a higher percentage of the

Table 2
Thermal analysis data for branched copoly(ether ketone)s

Sample	AB/AB ₂	Core (%)	Reaction temperature (°C)	PDI	T_g (°C)	T_c (°C)	T_m (°C)
5a	75/25	3	200	2.18	149	–	205
5b	75/25	3	180	1.87	142	–	271
5c	75/25	3	170	1.83	143	–	286
5d	75/25	3	150	1.74	136	229	278
5e	75/25	0	202	11.0	184	–	–
5f	90/10	3	200	2.61	146	–	–
5g	90/10	3	180	1.79	–	223	280, 300
5h	90/10	3	170	1.96	134	212	273, 286
5i	90/10	3	150	1.69	n/d	n/d	n/d
5j	90/10	0	202	–	175	–	–
5k	95/5	3	200	4.07	151	–	291, 299
5l	95/5	3	180	3.50	139	226	281, 300
5m	95/5	3	170	2.06	–	242	285, 302
5n	95/5	3	150	1.79	130	276	289, 305
5o	95/5	0	202	–	167	–	331
5p	95/5	5	200	1.66	120	256	273
5q	95/5	5	180	1.64	120	–	241
5r	95/5	5	170	1.44	106	–	247
5s	95/5	5	150	1.41	n/d	n/d	n/d

n/d = not determined.

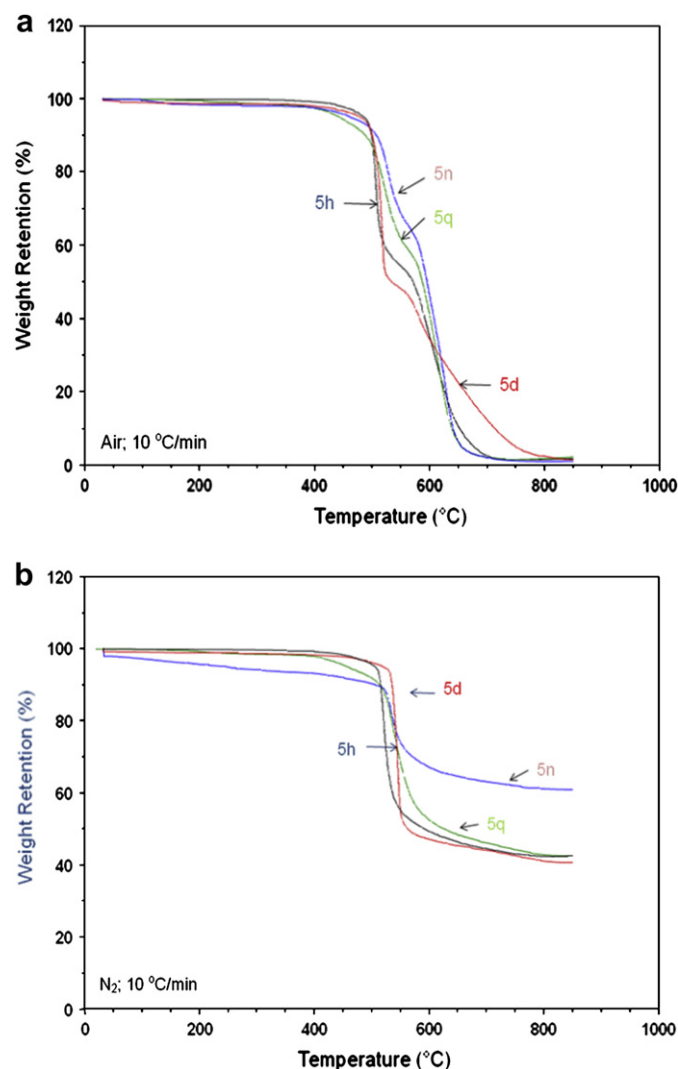


Fig. 3. Thermograms for **5d**, **5h**, **5n**, and **5q** in (a) air and (b) nitrogen atmosphere.

TPO-monomer, **2**, was incorporated into the polymer. For example, **5d** was more stable than **5n**, with 5% weight losses in air occurring at 480 and 464 °C, respectively. These results were not unexpected as the TPO group has been shown to increase the thermo-oxidative stability of many poly(arylene ether)s [15,27–30]. However, it is surprising to note that higher TPO content did not provide higher thermal stability of the respective branched polymers here. We observed that **5n** produced higher char yield (~60%) than **5d**, **5h** and **5q**, (all have higher TPO content than **5n** and gave ~40% char yields) at 800 °C in an inert atmosphere (Fig. 3b). We suspect that the much higher crystallization temperature of **5n** (and possibly has higher heat capacity) than the other samples (Table 2) might have played a role.

4. Conclusions

The effects of AB/AB₂ molar ratio, presence and mol% of core molecule, and reaction temperature on the molecular weight, polydispersity index, and thermal properties of fully soluble, branched copoly(ether ketone)s prepared from 4-fluoro-4'-hydroxybenzophenone, **1**, and bis(4-fluorophenyl)-(4-hydroxyphenyl)phosphine oxide, **2**, have been evaluated. At higher ratios of AB/AB₂, branched copoly(ether ketone)s with higher PDI values were obtained while lower ratios of AB/AB₂ afforded lower PDI values. These observations can be explained by considering the larger number of end groups present when more AB₂ monomer is added to the reaction mixture. The presence of a core molecule results in significantly lower molecular weights when compared to materials prepared without a core molecule. However, the core molecule also leads to substantially lower PDI values (for example, 2.18 versus 11.0 for comparable reactions) and each of the samples prepared in the presence of a core molecule possessed a sufficient level of solubility to allow its molecular weight to be determined via SEC analysis. The final molecular weight could be easily controlled by varying the mol% of core molecule added to the reaction mixture. Systems with lower PDIs possessed higher levels of crystallinity than those with higher PDI as evidenced by the presence of *T_m* values.

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