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# Linear-hyperbranched copolymerization as a tool to modulate thermal properties and crystallinity of a *para*-poly(ether-ketone)

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**Abstract**

The $AB_2$ monomer, 3,5-bis(4-fluorobenzoyl)phenol was synthesized via an improved four-step scheme. It was polymerized to form the corresponding fluoride-terminated hyperbranched polymer with higher molecular weight than previously reported, as evidenced by higher glass-transition temperature ($T_g$ = 159 °C vs. 140–143 °C). The homopolymerization showed a bimodal molecular weight distribution that was also observed for other related linear-hyperbranched systems. The $AB_2$ monomer was then copolymerized with 4-fluoro-4′-hydroxybenzophenone (AB monomer), in weight ratios of 1:3, 1:1 and 3:1 to afford the respective hyperbranched poly(ether-ketones) with variable degrees of branching. The 1:1 copolymer had $T_g$ value (212 °C) that was significantly (35 °C) higher than both linear and hyperbranched homopolymers. Only the 1:3 copolymer was semi-crystalline, displaying melting at 340 °C and its wide angle X-ray scattering (WAXS) pattern indicated that its crystal structure is exactly the same as that of the linear homopolymer. The WAXS results of the copolymers correlated well with differential scanning calorimetry and themogravimetric analysis results.
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## 1. Introduction

Crystallinity in polymers can improve tensile properties, increase thermal transition temperatures, and provide resistance to corrosive chemicals and thermo-oxidative degradation. Conversely, it can also destroy transparency, diminish toughness, and limit the processing options because of insolubility problem or melting temperatures too close to the degradation temperatures. Poly(arylene ether ketones) are a class of engineering thermoplastics that embody such property-processing trade-off. In comparison with the related poly(ether-ketone-ketones), PEKK or poly(ether ether ketone), PEEK (Victrex®) that finds wider acceptance as a general-purpose molding and extruding thermoplastic for high-performance applications in aerospace, automotive and construction sectors [1], *para*-PEK (Kadel®) has an exceedingly high melting point (>360 °C) in addition to the limited solubility due to its semi-crystallinity. To improve the processability of *para*-PEK, Teasley and Hsiao conducted a systematic study in the co-polymerization of the *para*-PEK monomer, i.e. 4-fluoro-4′-hydroxybenzophenone and its structurally more flexible *meta*-isomer and found that the copolymer with *meta* content of 35 mol% had the best balance of thermo-mechanical properties and melt-processability [2]. Another approach would involve the design of an AB monomer containing a removable bulky pendant, e.g. *t*-butyl group, and was successfully used to prepare organo-soluble PEEK-type polymers and copolymers [3]. A third approach, similar to the one initially demonstrated by Kricheldorf et al. [4], would be to introduce controllable degrees of branching via incorporating an appropriate $AB_2$ monomer into the linear *para*-PEK polymer chain. As part of our research effort [5] to explore and develop niche applications for aromatic hyperbranched polymers [6], we describe herein the results on the synthesis and characterization of a series of linear-hyperbranched poly(ether-ketones) derived from the $AB_2$ monomer, 3,5-bis(4-fluorobenzoyl)phenol and the AB monomer, 4-fluoro-4′-hydroxybenzophenone. The objective

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of this work is to investigate the use of one-step, linear-hyperbranched copolymerization as a practical method to control the thermal properties and the crystallinity of the *para*-PEK co-polymers. Although the $AB_2$ monomer, 3,5-bis(4-fluorobenzoyl)phenol, is known in the literature [7,8], its utilization for such purpose has not been reported.

## 2. Experimental

### 2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise specified. *N*-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure over phosphorous pentoxide. 4-Fluoro-4′-hydroxybenzophenone was recrystallized from 90% aqueous ethanol (mp 169–171 °C).

### 2.2. Instrumentations

Proton and carbon nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) spectra for the intermediates and monomer were obtained at 270 and 50 MHz on a Jeol-270 spectrometer. Infrared (IR) spectra were run on a Bruker IFS28 Fourier transform spectrophotometer. Elemental analysis and mass analysis were performed by System Supports Branch, Materials Directorate, Air Force Research Laboratory, Dayton, OH. All melting points (mp) were determined on a Mel-Temp melting point apparatus and the values are uncorrected. Intrinsic viscosities were determined with a Cannon-Ubbelohde No. 150 viscometer. Flow times were recorded for methanesulfonic acid (MSA) solutions with polymer concentrations of 0.5–0.1 g/dl at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) was performed in nitrogen with a heating rate of 10 °C/min using a Perkin–Elmer DSC-7 thermal analyzer. The $T_g$s were determined from maximum inflection in baseline on DSC thermograms. Themogravimetric analysis (TGA) was conducted in helium and air atmospheres with a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 themogravimetric analyzer. Thermomechamical analysis (TMA; TA model 2940) was conducted in nitrogen with heating rate of 4 °C/min in nitrogen. The TMA samples were compression-molded at 260–300 °C, and their $T_g$s were determined from maximum inflection in baseline on TMA thermograms. Wide-angle X-ray diffraction (WAXS) powder patterns were recorded with a Rigaku RU-200 diffractometer using Ni-filtered Cu Kα radiation (40 kV, 100 mA, $\lambda = 0.15418$ nm). Gel permeation chromatography (GPC) was carried out on a Waters 150-CV equipped with UV detector. Tetrahydrofuran (THF) was used as the eluting solvent.

### 2.3. 5-Acetoxyisophthalic acid (1)

Into a 100 ml single-necked, round-bottomed flask equipped with a magnetic stirrer and a nitrogen inlet, 5-hydroxyisophthalic acid (10.0 g, 54.9 mmol) was dissolved in freshly distilled acetic anhydride (50 ml) containing a catalytic amount of fuming sulfuric acid (three drops). The reaction mixture was then heated at 60 °C with stirring for 24 h. It was poured into ice water and the resulting precipitate was collected by suction filtration and air-dried overnight. The white solid crude product was then dissolved in a mixture of hot ethanol and water (1:1 v/v), and the filtrate was allowed to cool to room temperature to give 12.0 g (97.6% yield) of white solid, mp 255–256 °C. Anal. calcd for $C_{10}H_8O_6$: C, 55.38%; H, 3.60%; O, 42.82%. Found: C, 54.19%; H, 3.23%; O, 42.02%. FT-IR (KBr, $cm^{-1}$): 1703, 1774, 2880. Mass spectrum (*m*/*e*) : 224 ($M^+$, 100% relative abundance). $^1$H NMR (DMSO-$d_6$, $\delta$ in ppm): 2.32 (s, 3H, $CH_3$), 7.92 (s, 2H, Ar), 8.37 (s, 1H, Ar). $^{13}$C NMR (DMSO-$d_6$, $\delta$ in ppm): 20.76, 126.76, 127.11, 132.64, 150.61, 165.76, 169.07.

### 2.4. 5-Acetyloxyisophthaloyl diacid chloride (2)

Into a 500 ml three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and a condensor, 5-acetyloxyisophthaloic acid (10.0 g, 44.6 mmol), thionyl chloride (40 ml), and five drops of DMF was placed. The flask was stirred at room temperature for 30 min and then gently heated up to 60 °C for 8 h. Excess amount of thionyl chloride was then distilled off. After cooling down, freshly distilled hexane (300 ml) was added into the flask while it was chilled in ice-salt bath with vigorous stirring. The resulting white needles were collected by quick filtration and dried under reduced pressure to afford 9.10 g (90.1% yield): mp 47.0–48.5 °C. Anal. calcd for $C_{10}H_6Cl_2O_4$: C, 46.01%; H, 2.32%; Cl, 27.16%; O, 24.51%. Found: C, 46.82%; H, 2.43%; Cl, 27.89%; O, 24.84%. FT-IR (KBr, $cm^{-1}$): 1773. Mass spectrum (*m*/*e*) : 260, 262 ($M^+$, 100% relative abundance). $^1$H NMR ($CDCl_3$, ppm) $\delta$ 2.34 (s, 3H, $CH_3$), 7.92–7.93 (d, 2H, Ar), 8.56–8.57 (t, 1H, Ar). $^{13}$C NMR ($CDCl_3$, ppm) $\delta$ 20.94, 126.94, 128.26, 132.78, 150.47, 166.56, 168.92.

### 2.5. 3,5-Bis(4-fluorobenzoyl)phenol (4)

Into a 250 ml three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and a dropping funnel, aluminum chloride (10.85 g, 81.4 mmol) and fluorobenzene (80 ml) were introduced. The flask was then placed in an ice-water bath with its temperature maintained between 15 and 20 °C. The solution of 5-acetyloxyisophthaloyl dichloride (8.5 g, 32.5 mmol) in fluorobenzene (20 ml) was then added dropwise for 20 min. The reaction mixture was then allowed to warm up to room temperature and stand with stirring at room

temperature for 12 h. The resulting light brown solution was poured into ice-water (500 ml) containing hydrochloric acid (50 ml). Methylene chloride (50 ml) was then added to the mixture and the organic layer was separated with the aid of a separatory funnel. The solvent of the organic extract was then removed on a rotary evaporator. The resulting yellow jelly-like residue was further dried under the reduced pressure to give 11.8 g of 1-acetoxy-3,5-bis(benzoyl)benzene (**3**, 95.5% crude yield). The 1-acetoxy-3,5-bis(benzoyl)benzene was then dissolved in ethanol (130 ml), followed by the addition of a solution of potassium hydroxide (10.0 g, 178 mmol) in water (20 ml). The resulting mixture was subsequently heated under the reflux for 1.5 h. After it had been allowed to cool to near room temperature, the solution was poured into ice-water (500 ml) containing hydrochloric acid (50 ml). The precipitates were collected by suction filtration, air-dried overnight and finally recrystallized from toluene to afford 9.9 g (90% overall yield) of 3,5-bis(4-fluorobenzoyl)phenol as white crystals, mp 133.5–134 °C. Anal. calcd for $C_{20}H_{12}F_2O_3$: C, 71.01%; H, 3.58%; O, 14.19%. Found: C, 70.79%; H, 3.98%; O, 14.51%. FT-IR (KBr, $cm^{-1}$): 1596, 1657, 3298. Mass spectrum (*m*/*e*) : 338 ($M^+$, 100% relative abundance). $^1H$ NMR ($CDCl_3$, $\delta$ in ppm): 7.13–7.19 (d, 4H, Ar), 7.48–7.49 (d, 2H, Ar), 7.53–7.54 (d, 1H, Ar), 7.84–7.89 (dd, 4H, Ar). $^{13}C$ NMR ($CDCl_3$, $\delta$ in ppm): 115.71, 120.52, 121.96, 132.73, 133.36, 138.83, 157.69, 167.34, 194.32.

### 2.6. Homopolymerization of 3,5-bis(4-fluorobenzoyl)phenol

Into a 100 ml three-necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet, and Dean–Stark trap with a condenser, 3,5-bis(4-fluorobenzoyl)phenol (2.0 g, 5.91 mmol), potassium carbonate (2.0 g, 14.5 mmol), and a mixture of NMP (20 ml) and toluene (60 ml) were introduced. The reaction mixture was then heated and maintained at 140–150 °C for 4 h. During this time, the water formed was removed by toluene azeotropic distillation. After complete removal of toluene, the orange solution was then heated at 180 °C for 1 h and 202 °C until the mixture completely stuck to stirring rod to render further stirring ineffective. The polymerization process took about 40 min at 202 °C. The mixture was diluted with NMP (50 ml) and filtered through glass filter while the mixture was still hot (130–150 °C). The filtrate was poured into distilled water containing 5% hydrochloric acid. The resulting white precipitates was collected by suction filtration and air-dried. Off-white powder was dissolved in NMP again and passed through Celite 545 to remove any insoluble salts. The filtrate poured in 5% hydrochloric acid and warmed up around 60–70 °C for 24 h and Soxhlet extracted with water for 3 days and with methanol for 3 days. The white powder was collected and dried under reduced pressure (1 mm Hg) at 150 °C over phosphorous pentoxide. The yield was essentially quantitative. $[\eta] = 0.94$ dl/g (in MSA, at 30.0 ± 0.1 °C). $T_g = 159$ °C. Anal. calcd for $C_{20}H_{11}FO_3$: C, 75.47%; H, 3.48%. Found: C, 75.32%; H, 4.26%.

### 2.7. Homopolymerization of 4-fluoro-4′-hydroxybenzophenone

Into a 100 ml three-necked, round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet and outlet, and a Dean–Stark trap with a condenser, 4-fluoro-4′-hydroxybenzophenone (3.0 g, 13.88 mmol), potassium carbonate (3.0 g, 21.7 mmol), and a mixture of NMP (30 ml) and toluene (60 ml) was placed. The reaction mixture was then heated and maintained at 140–150 °C for 4 h. During this time, the water formed was removed by azeotropic distillation with toluene. After the complete removal of toluene by drastic nitrogen purging, the orange solution was then heated at 180 °C for 1 h. The mixture was then heated to 202 °C. After 30 min, the mixture became heterogeneous. The mixture was stirred for additional 6 h, allowed to cool to room temperature, and poured into distilled water containing 5% hydrochloric acid. The resulting white precipitate was collected by suction filtration and Soxhlet-extracted with water for 3 days, and then with methanol for another 3 days. The pale white powder was collected and dried under reduced pressure (1 mm Hg) at 150 °C over phosphorous pentoxide. The yield was essentially quantitative. $[\eta] = 0.85$ dl/g (in methanesulfonic acid (MSA), at 30.0 ± 0.1 °C). $T_m = 360.5$ °C (DSC). Anal. calcd for $C_{20}H_{11}FO_3$: C, 79.58%; H, 4.11%; O, 16.31%. Found: C, 77.34%; H, 4.52%; O, 15.35%.

### 2.8. Copolymerization of $AB_2$ and AB monomers

Into a 100 ml three-necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet, and Dean–Stark trap with a condenser, 3,5-bis(4-fluorobenzoyl)phenol (1.5, 1.0, 0.5 g, 4.43, 2.96, 1.48 mmol, respectively), 4-fluoro-4′-hydroxybenzophenone (0.5, 1.0, 1.5 g, 2.31, 4.63, 6.94 mmol, respectively), potassium carbonate (2.0 g, 14.5 mmol), and a mixture of NMP (20 ml) and toluene (60 ml) was placed. Following the same procedure for the homopolymerization of $AB_2$ monomer, the mixture was heated under reflux. The time of polymerization process was varied depending on the amount of $AB_2$ monomer content. The more $AB_2$ content, it took the shorter reaction time from 70 min to 2 h. The reaction mixture was poured into distilled water containing 5% hydrochloric acid. The resulting white precipitate was collected by suction filtration and Soxhlet extracted with water for 3 days and with methanol for 3 days. The pale white powders were collected and dried under reduced pressure (1 mm Hg) at 150 °C over phosphorous pentoxide. The yields were essentially quantitative in all three cases. The following data are arranged in the order of HB-PEK **8**, HB-PEK **9** and HB-PEK **10**: $[\eta] = 0.61$, 0.66, and 0.60 dl/g (in MSA, at 30.0 ± 0.1 °C; $T_g = 164$, 213 °C, and

$T_m = 340\,°C$. Anal. calcd. for $C_{17.55}H_{9.95}F_{0.65}O_{2.65}$: C, 77.50%; H, 3.52%. Found: C, 76.22%; H, 4.32%. $C_{15.73}H_{9.17}F_{0.39}O_{2.39}$: C, 78.35%; H, 3.76%. Found: C, 76.95%; H, 4.33%. $C_{16.19}H_{9.61}F_{0.27}O_{2.47}$: C, 78.99%; H, 3.94%; O, 17.06. Found: C, 77.83%; H, 4.56%; O, 15.45%.

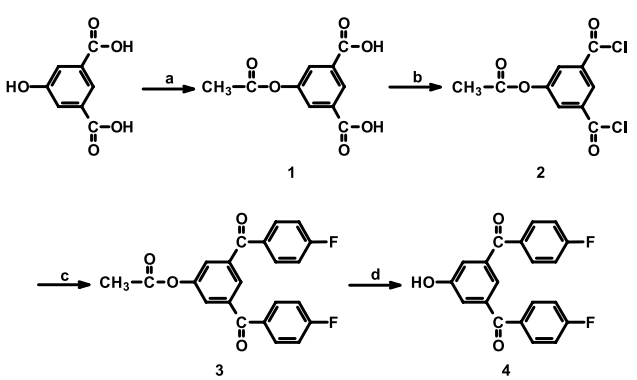
## 3. Results and discussion

### 3.1. Monomer synthesis

The previously reported $AB_2$ monomer (**4**) [7,8] was synthesized via a slightly different route as shown in Scheme 1. The key difference in our synthesis from a previous one with detailed procedures [8] rests on the use of an acetyl group as the protecting group for the hydroxyl function instead of a methyl group. We found that the former is easily to add on with less hazardous reagent and remove under milder conditions than the latter (acetic anhydride vs. dimethylsulfate). Thus, the sequence began with 5-hydroxyisophthalic acid being treated with acetic anhydride to afford 5-acetoxyisophthalic acid (**1**). The intermediate **1** was then treated with thionyl chloride to give 5-acetoxyisophthaloyl dichloride (**2**), which reacted with fluorobenzene in the presence of aluminum chloride to form 3,5-bis(4-fluorobenzoyl)phenyloxyacetate (**3**). Finally, the alkaline hydrolysis of the precursor **3** led to the desired $AB_2$ monomer, 3,5-bis(4-fluorobenzoyl)phenol (**4**) with over 99.99% purity based on liquid chromatographic determination.

### 3.2. Polymerization

Previously, Miller et al. [7] reported the polymerization of the same $AB_2$ monomer (**4**) in dimethylacetamide (DMAc) at 100–180 °C for 0.5–2 h after it had been first converted to the corresponding phenolate form with NaH in terahydrofuran (THF), followed by filtration to remove excess NaH, the removal of THF in vacuum, and addition of DMAc. However, we found that the polymerization of **4** in an NMP/toluene mixture in the presence of potassium carbonate was more operationally convenient and perhaps more effective [9] when conducted at higher temperature. An idealized structure for the fluoride-terminated hyperbranched poly(ether-ketone), HB-PEK **5** is depicted in Scheme 2. After the water of reaction had been completely removed via a Dean–Stark trap, the subsequent stage of the polymerization process was monitored with gel-permeation (size-exclusion) chromatography (GPC) with respect to the changes in the molecular weights and molecular weight distribution (MWD) against the polystyrene standards. Thus, the reaction mixture was sampled at specific intervals over a period of 40 min, immediately after the temperature had reached 200 °C at which point NMP was refluxing. The aliquots were diluted with THF before the injection into a GPC instrument. It is apparent from Table 1 and Fig. 1 that as soon as the temperature had reached 200 °C, the number average molecular weight ($M_n$) and weight-averaged molecular weight ($M_w$) had already exceeded 9500 and 23,000 Da, respectively. In addition, there was a small shoulder in the higher molecular weight region on the GPC curve. The size of this shoulder increased with an increase in reaction time at 200 °C. After 40 min of reaction time had elapsed, the polymerization was terminated. The final GPC curve was clearly bimodal. The peak value in the lower number-average molecular weight region remained relatively constant around 9900 Da, but the higher number average molecular weight region was approaching 360,000 Da. Although Miller et al. had noted that the molecular weights ($M_w = 11,300–66,600$ Da and $M_n = 7410–16,200$ Da vs. polystyrene standards) and polydispersity (1.53–4.11) of hyperbranched polymer **5** increased with an increase in monomer concentration (0.19–2.2 M), no mention of the bimodal MWD was made [7]. As similar GPC results have been encountered for the polymerization processes for other related hyperbranched systems derived from the $AB_2$ monomers **6** [10], and **7** [11] (Scheme 3), a pattern seems to have emerged. We suspect that such bimodal MWD may be a rather common feature among hyperbranched polymers; in our hand, those prepared via aromatic nucleophilic substitution reaction as indicated by our data. It is very likely that similar observations had been made by other researchers in the field but were not reported. Although we are not clear at this

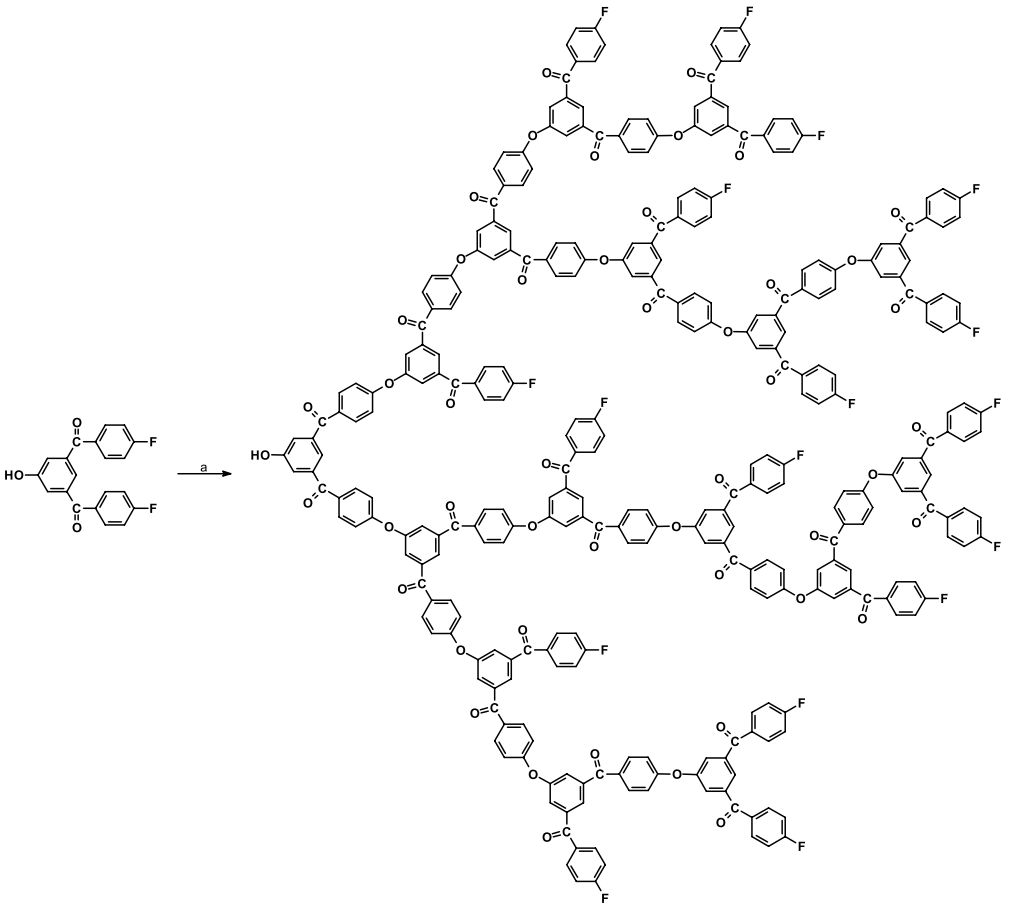



Scheme 1. Synthesis of $AB_2$ monomer. (a) $Ac_2O$, $H_2SO_4$, 60 °C. (b) $SOCl_2$, reflux. (c) $AlCl_3$, anisole, 60 °C. (d) KOH, aq. EtOH, reflux.

Table 1
Molecular weight and MWD of HB-PEK **5** as function of reaction time at NMP boiling temperature

| Rxn time[a] (min) | $M_{n_1}$ (g/mol) | $M_{w_1}$ (g/mol) | $MWD_1$ | $M_{n_2}$ (g/mol) | $M_{w_2}$ (g/mol) | $MWD_2$ |
|---|---|---|---|---|---|---|
| 0 | 9600 | 23,900 | 2.50 | – | – | – |
| 5 | 10,200 | 30,300 | 2.96 | – | – | – |
| 10 | 10,700 | 34,300 | 3.20 | – | – | – |
| 20 | 11,900 | 49,800 | 4.19 | – | – | – |
| 40 | 9900 | 26,000 | 2.64 | 360,100 | 374,500 | 1.04 |

[a] At NMP boiling temperature.



**5**

Scheme 2. Synthesis of hyperbranched polymer **5** via homopolymerization of $AB_2$ monomer: (a) $K_2CO_3$, NMP/toluene, 150–180–202 °C.

point about the true origin from which the smaller band at shorter elution time arose and grew after the main band had remained constant, there are possibilities for occurrence such as (i) intermolecular reaction between the focal functional group (A) of one dendritic macromolecule and the peripheral group (B) of a second macromolecule; (ii) intramolecular reaction between A and B leading to such intramolecular cyclization that a significant increase in the hydrodynamic volume results from a more open macromolecular structure.

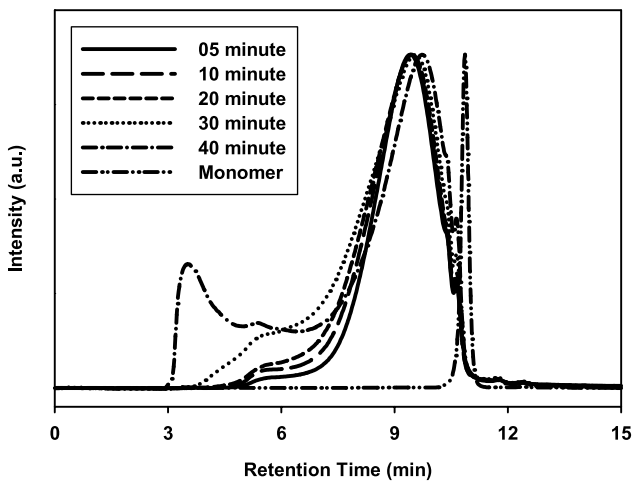
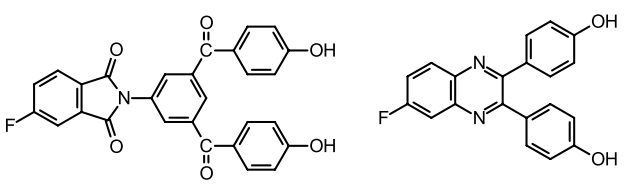



Fig. 1. GPC traces showing MW build-up of HB-PEK-5 during polymerization as a function of time at ~200 °C.

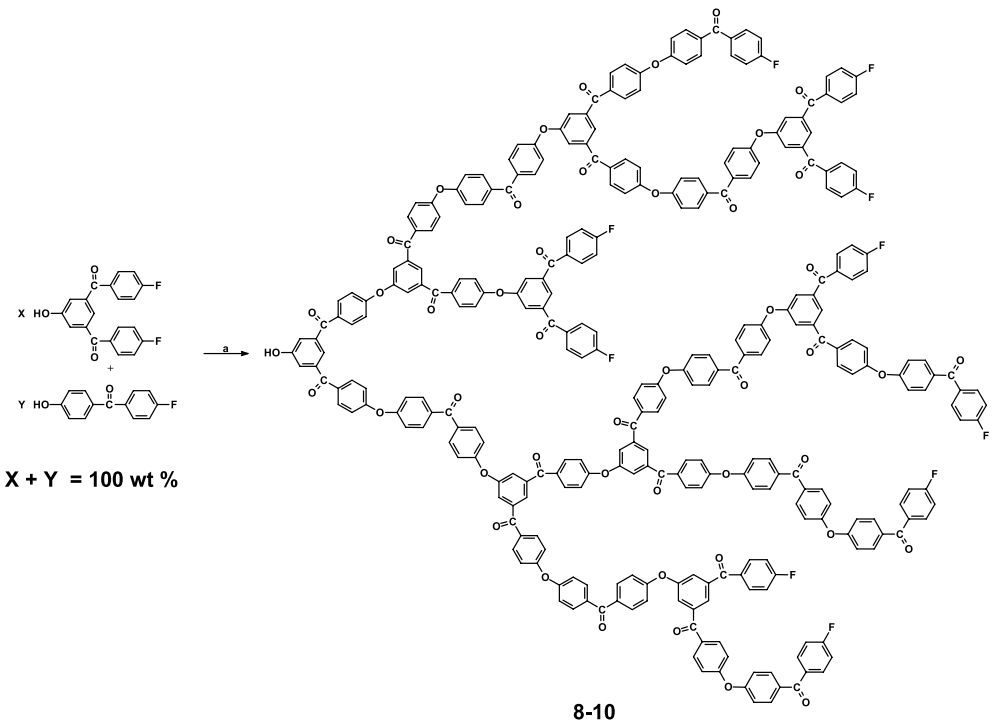
### 3.3. Random co-polymerization

The $AB_2$ monomer (**4**) was co-polymerized with the commercially available AB monomer, 4-fluoro-4′-hydroxybenzophenone, following the similar procedure to prepare HB-PEK **5** to afford the hyperbranched co-polymers HB-PEKs **8**–**10** (Scheme 4). In the synthesis of linear-hyperbranched copolyamides, Kakimoto et al. reported that the resultant macromolecular structures depended on how the polymerization process was conducted. One-pot



**6** **7**

Scheme 3. Structure of $AB_2$ monomers.

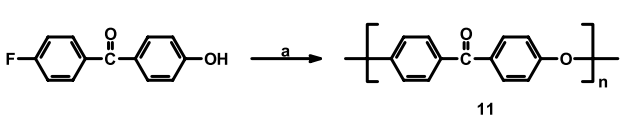



Scheme 4. Synthesis of HB-PEK **8**–**10** via copolymerizations of $AB_2$ and AB monomers. (a) $K_2CO_3$, NMP/toluene, 150–180–202 °C.

copolymerization of the $AB_2$ and AB comonomers in various feed ratios led to the copolymer structures consistent with the statistical distribution of the repeat units derived from both monomers [12]. However, when $AB_2$ + AB copolymerization was conducted in several permutations of (a) stepwise addition of the comonomers and (b) reaction times, the physical properties such as solution viscosity and solubility were distinctly different from the random linear-hyperbranched copolymers obtained from one-pot operation [12b]. In our case, since the step-growth process was conducted in a one-pot fashion, it is expected that the copolymerization should be statistical. Unfortunately, the insolubility of the copolymers in common solvents precluded the effective use of NMR technique to determine the degree of branching as well as the distribution of the linear, dendritic and terminal units. For comparison purposes, the linear PEK **11** was synthesized under similar conditions from the AB monomer (Scheme 5). As expected, PEK **11** precipitated out of the polymerization mixture because of its relatively high crystallinity, and it could not be re-dissolved in all polar aprotic solvents tested.

### 3.4. Thermal properties

The glass-transition temperatures ($T_g$s) of the linear and hyperbranched PEK polymers were determined by DSC. The DSC scans were run on the powder samples after they had been heated to 200 °C in the DSC chamber and allowed to cool to ambient temperature under a nitrogen purge. The $T_g$ was taken as the mid-point of the maximum baseline shift from the second run. The DSC results are shown in Fig. 2 and Table 2. HB-PEK **5** displayed a $T_g$ at 159 °C, which is 15 °C higher than previously reported [7] but slightly lower (3 °C) than a similar fluoride-terminated hyperbranched PEK [13] derived from 3,5-difluoro-4′-hydroxybenzophenone. Also, Morikawa elegantly demonstrated that the $T_g$ value of HB-PEK **5** could be increased up to about 240 °C by the incremental insertion of *para*-phenylene units (1–4) between the hydroxyl group and the 1,3,5-substituted phenyl moiety, i.e. an elevation of ~20 °C per *para*-phenylene unit [14].




Scheme 5. Synthesis of linear PEK **11** via homopolymerization of AB monomer. (a) $K_2CO_3$, NMP/toluene, 150–180–202 °C.

In the case of the linear-hyperbranched PEK copolymers, the DSC results revealed that the $T_g$s were increased to 164 and 213 °C when the AB contents are 25 and 50 wt%, respectively, during the heating scan from room temperature to 400 °C. The copolymer with AB content of 75 wt% showed no $T_g$ and instead a small but well-defined melting endotherm centered at 340 °C. During the cooling scan, the glass transitions for all the hyperbranched PEK, linear-hyperbranched PEK copolymers and linear PEK were detected. In addition, both the linear PEK and the copolymer with AB content of 25 wt% exhibited crystallization exotherms centered at 272 and 241 °C, respectively. Noteworthy is HB-PEK **9** (50 wt% AB) whose $T_g$ at 210 °C, as detected during the cooling scan, is significantly higher than both the linear PEK (175 °C) and the parent

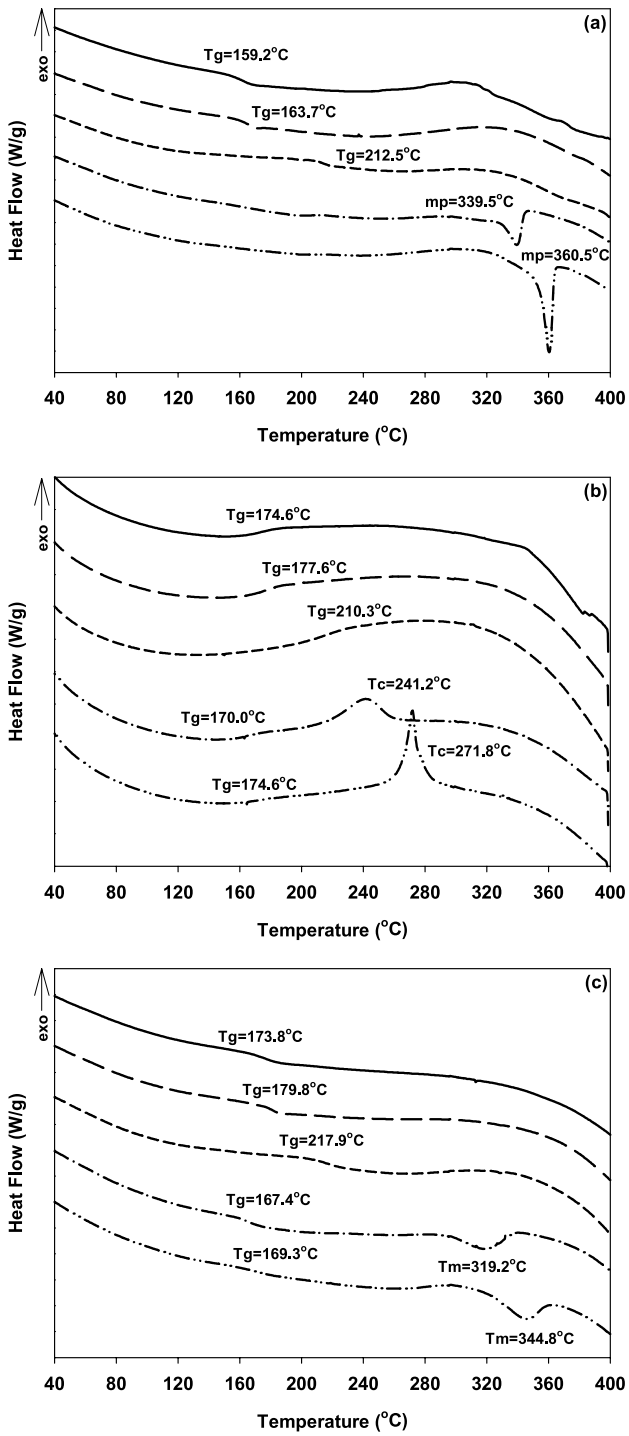



Fig. 2. DSC thermograms for linear and hyperbranched PEKs with heating rate of 10 °C/min: (a) first heating scan. (b) First cooling scan. (c) Second heating scan; $AB_2$ 100 wt% (solid line), $AB_2$ 75 wt% (long dash), $AB_2$ 50 wt% (short dash), $AB_2$ 25 wt% (dash-dot), and linear (dash-dot-dot).

hyperbranched PEK (175 °C). This is rather surprising because it is in contrast to the observations documented for other linear-hyperbranched systems: (i) Kricheldorf and Stukenbrock [15] showed that the $T_g$-composition relationship of the linear-hyperbranched copolyesters derived from β-(4-hydoxyphenyl)propionic acid (AB) and 3,5-dihydroxybenzoic acid ($AB_2$) followed closely that predicted by Fox equation [16]; (ii) Moore et al. reported on the amorphous linear-hyperbranched poly(ether-imides) which showed an increasing trend in $T_g$ values as the linear content increased [17] and (iii) Kricheldorf et al. [4,18] and Kakimoto et al. [12a] separately described the presence of minimal $T_g$ values in the respective series of linear-hyperbranched aromatic copolyesters and copolyamides. In all cases, the observed $T_g$ value for any copolymer was never higher than both homopolymers. HB-PEK **9** appears to be the first such example. To render support to the DSC observations, the more reliable thermomechanical analysis (TMA) was performed to determine the $T_g$ values for the samples with $AB_2$ content ranging from 50 to 100 wt%. The TMA values obtained were almost identical to the DSC values (see Fig. 3 and Table 2). Thus, it is apparent that the glass-transition behaviors of linear-hyperbranched systems are more complicated than the analogous linear copolymers.

When the $AB_2$ content was 25%, the resulting hyperbranched co-polymer became semi-crystalline, displaying a melting temperature at 340 °C and crystallization temperature at 241 °C. The linear PEK has a melting temperature at 361 °C and its crystallization was observed at 272 °C.

The short-term thermo-oxidative and thermal stabilities of the linear-hyperbranched copolymers and linear PEK were determined by thermogravimetric analysis (TGA) on the powder samples in air and helium, respectively. The results are shown in Fig. 4. In general, the homo-and copolymers are thermally stable as indicated by the fact that the temperatures at which a 5 wt% loss occurred are in the range of 409–461 °C in air and 418–463 °C in helium (see Table 2). Additionally, it is clear from the composite TGA thermograms that the linear-hyperbranched copolymer with an $AB_2$ content of 25 wt% has the onset for the catastrophic degradation of linear at the temperature range comparable to the linear PEK whereas for the other copolymers with higher $AB_2$ content, the onset temperatures practically

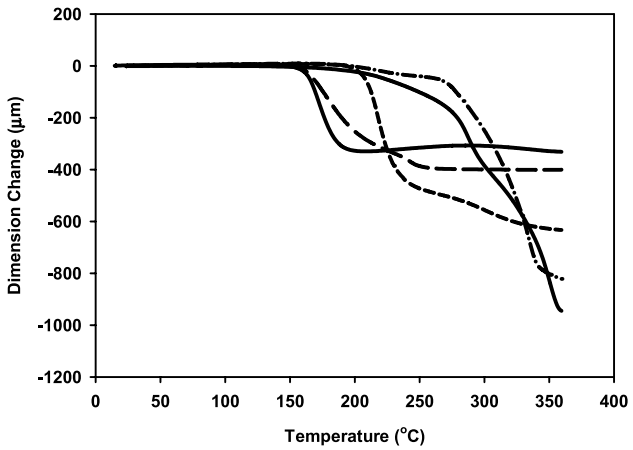



Fig. 3. TMA thermograms for hyperbranched PEKs with heating rate of 4 °C/min in nitrogen: $AB_2$ 100 wt% (solid line), $AB_2$ 75 wt% (long dash), $AB_2$ 50 wt% (short dash), $AB_2$ 25 wt% (dash-dot), and linear PEK (dash-dot-dot).

Table 2
Thermal properties of linear and hyperbranched PEKs

| $AB_2$ (wt%) | AB (wt%) | $[\eta]$[a] (dl/g) | DSC | | | TMA | $T_m$[b] (°C) | $\Delta H_f$ (J/g) | $T_c$[c] (°C) | $\Delta H_c$ (J/g) | TGA[d] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | In air at 900 °C | | In helium at 900 °C | |
| | | | $T_{gh1}$[b] (°C) | $T_{gc1}$[c] (°C) | $T_{gh2}$[b] (°C) | $T_g$[e] (°C) | | | | | $T_{d5\%}$ (°C) | Char (%) | $T_{d5\%}$ (°C) | Char (%) |
| 100 | 0 | 0.94 | 159.2 | 174.6 | 173.8 | 172.4 | – | – | – | – | 409 (485) | 3.5 | 418 (553) | 27.7 |
| 75 | 25 | 0.61 | 163.7 | 177.6 | 179.8 | 179.8 | – | – | – | – | 401 (532) | 5.8 | 410 (565) | 8.7 |
| 50 | 50 | 0.66 | 212.5 | 210.3 | 217.9 | 218.7 | – | – | – | – | 411 (542) | 1.2 | 432 (574) | 4.0 |
| 25 | 75 | 0.60 | – | 170.0 | 167.4 | – | 339.5 (319.2) | 19.7 | 241 | 18.1 | 426 (553) | 0.1 | 462 (557) | 31.7 |
| 0 | 100 | 0.85 | – | 174.6 | 169.3 | – | 360.5 (344.8) | 36.9 | 272 | 34.6 | 461 (560) | 0.1 | 463 (552) | 37.6 |

[a] Intrinsic viscosity determined in methanesulfonic acid at 30 ± 0.1 °C.
[b] Glass transition temperature ($T_{gh}$) and melting temperature ($T_m$) determined by DSC with heating rate of 10 °C/min. The number in the parentheses are melting temperature ($T_m$) determined from the second heating run with heating rate of 10 °C/min.
[c] Glass transition temperature ($T_{gc}$) and crystallization temperature ($T_c$) determined by DSC with cooling rate of 10 °C/min.
[d] The temperature at which 5 wt% loss occurred on TGA thermogram obtained with heating rate of 10 °C/min. The number in the parentheses are maximum degradation temperatures.
[e] Glass transition temperature ($T_g$) determined by TMA with heating rate of 4 °C/min.

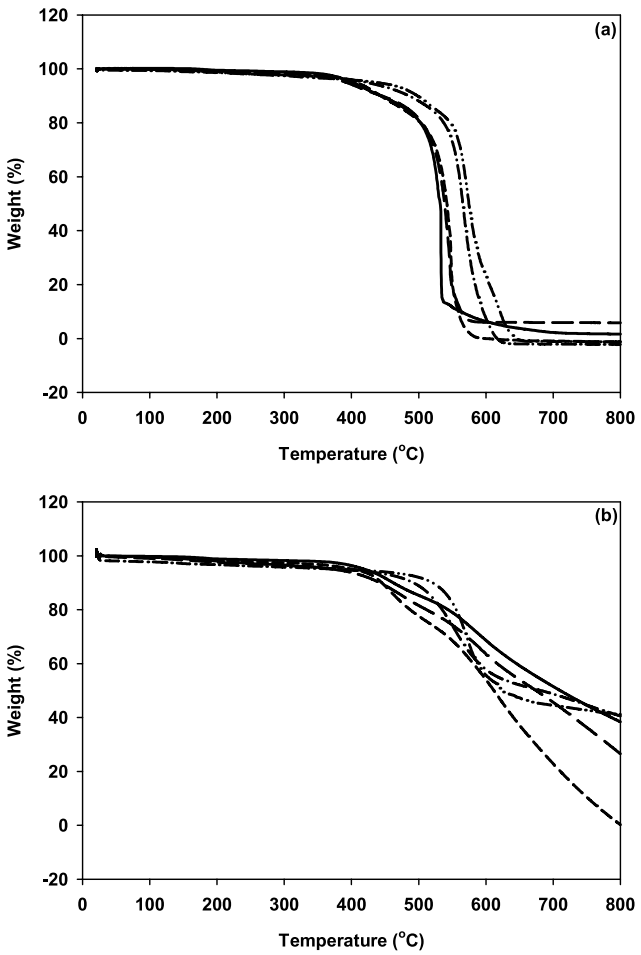



Fig. 4. TGA thermograms for linear and hyperbranched PEKs with heating rate of 10 °C/min: (a) In air. (b) In helium. $AB_2$ 100 wt% (solid line), $AB_2$ 75 wt% (long dash), $AB_2$ 50 wt% (short dash), $AB_2$ 25 wt% (dash-dot), and linear PEK (dash-dot-dot).

coincide with that of the hyperbranched PEK (Fig. 4 and Table 2). The difference in temperature is as high as 52 °C in air. Similar behaviors were observed in the inert atmosphere with respect to the onset temperatures, albeit at higher values. However, the char yield at 900 °C in helium for the hyperbranched PEK was unexpectedly high in comparison with the linear-hyperbranched copolymers.

### 3.5. Wide angle X-ray diffraction

To correlate with the thermal analysis data, all samples were characterized with an X-ray diffraction technique to determine their degrees of crystallinity (Fig. 5). Among the four linear and linear-hyperbranched PEK samples (**5**, **8**–**10**), the linear-hyperbranched co-polymers with 50 wt% or more $AB_2$ content were all amorphous. HB-PEK **10** with

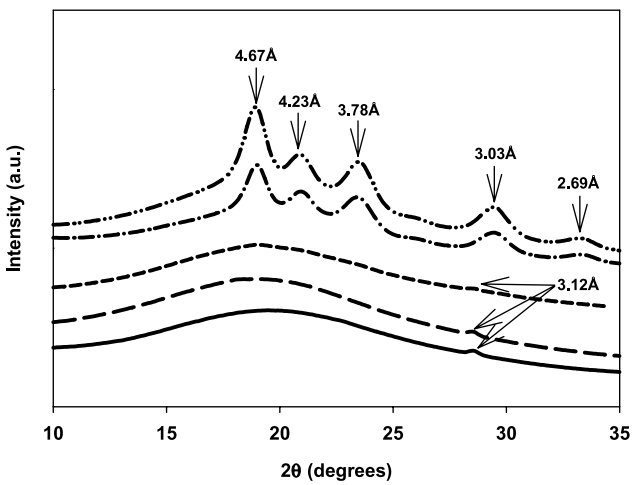



Fig. 5. WAXS diffraction curves for linear and hyperbranched PEKs: $AB_2$ 100 wt% (solid line), $AB_2$ 75 wt% (long dash), $AB_2$ 50 wt% (short dash), $AB_2$ 25 wt% (dash-dot), and linear PEK (dash-dot-dot).

25 wt% of $AB_2$ monomer content displayed peaks at 2.69, 3.03, 3.78, 4.23, 4.67 Å which are identical to the peak positions observed for the linear PEK, but at lower intensities. As expected, this reflects lower degree of crystallinity in **10**. These results are in excellent agreement with their thermal properties determined by DSC and TGA. In addition, with 25 wt% of $AB_2$ content, the melting temperature of **10** was lowered to 340 °C comparable to that of PEEK ($T_m = 343$ °C).

## 4. Conclusion

An improved preparation of $AB_2$ monomer, 3,5-bis(4-fluorobenzoyl)phenol was developed. The combination of monomer purity and optimal polymerization conditions resulted in the corresponding fluorine-terminated hyperbranched polymer with higher molecular weight, as evidenced by significantly higher $T_g$ values than previously reported. However, the polymerization process showed a bimodal MWD that were observed for other aromatic hyperbranched polymers generated from similar nucleophilc displacement reactions. The $T_g$ detected from the cooling scan for the linear-hyperbranched copolymers with $AB_2$ content of 50 wt% was 35 °C higher than the $T_g$ for both parent polymers. This is very unusual, and to our knowledge, not observed before for the aromatic linear-hyperbranched copolymers reported. At 25 wt% $AB_2$ content, the branched polymer become semi-crystalline, displaying melting at 340 °C, which is comparable to the $T_m$ of the most commonly used poly(ether ether ketone), PEEK, but higher than the related linear–linear 35/65 copolymer ($T_m = 296$ °C) [2]. Finally, the observed changes in the thermal oxidative and thermal stabilities and degree of crystallinity in PEK are quite systematic and consistent with the amount of $AB_2$ monomer added.

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[9] For instance, under our polymerization conditions, [**4**] = 0.30 M, 200 °C, 5 min, we obtained higher molecular weights for the hyperbranched PEK, **5**, $M_n = 10,200$ and $M_w = 30,300$ versus under the conditions of Miller et al. [4] = 0.75 M, 100–180 °C, 0.5–2 h, the values are $M_n = 9040$ and $M_w = 19,100$. Also, glass transition temperature is 16–19 °C higher for **5** obtained under our conditions.
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