Self-Controlled Synthesis of Hyperbranched Poly(ether ketone)s from $A_3 + B_2$ Approach via Different Solubilities of Monomers in the Reaction Medium

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ABSTRACT: Hyperbranched poly(ether ketone)s (PEK's) were synthesized via $A_3 + B_2$ polymerization approach without forming cross-linked products, because the polymer-forming process based on Friedel−Crafts reaction was kinetically controlled by the solubility difference of monomers in the viscous hydrophilic reaction medium, poly(phosphoric acid) (PPA)/phosphorus pentoxide (P_2O_5). The hydrophilic trimesic acid as an A_3 monomer is soluble in the reaction medium, while hydrophobic diphenyl ether and 1,4-diphenoxybenzene as B_2 monomers are marginally soluble. It is hypothesized that the gelation was avoided because of the following two factors: (i) self-regulated feeding of the arylether monomers into the system driven by their poor solubility and phase separation from PPA/P_2O_5 medium; (ii) reaction-medium-induced isolation of growing macromolecules promoted by the high bulk viscosity. Both polymerization experiments based on equimolar or equifunctional stoichiometry (A_3:B_2) resulted in completely soluble hyperbranched PEK's in polar aprotic solvents when these polymers contained a little amount of solvent residues and only in strong acids if they were rigorously dried. The structural analysis by using MALDI−TOF mass spectroscopy in the low molar mass region provided further confirmation that there was no trace of networks; various sizes of cyclics were detected instead.

Introduction

Hyperbranched polymers (HBP's) are an important class of dendritic macromolecules, which could be synthesized by one-pot polymerization processes. Unlike the dendrimers that have precisely controlled structures and unique properties, HBP's are polydisperse and randomly branched. However, their attractive properties, such as low viscosity, good solubility, and multifunctionality, combined with the ease of their preparations, make them ideally suitable for specific industrial applications.[1,2] On the other hand, a drawback from the viewpoint of raw material cost is that most hyperbranched polymers have been produced from specially designed AB_x ($x \geq 2$) monomers, whose synthetic sequences generally involve multiple steps, albeit a few were prepared from commercial AB_x monomers.[3] From this perspective, HBP's generated from commercially available A_3 and B_2 or A_2 and B_3 would be more likely to be considered in the material selection processes for commercial and military applications. The key issue, nevertheless, in this alternative approach to HBP's is how to avoid gelation during polymerization processes. Although various HBP's have been synthesized from A_3 and B_2 monomers,[4] this approach has an inherent difficulty in controlling the polycondensation reaction with respect to the premature gelation as predicted in Carother's and statistical mechanics equations,[5] but several techniques to circumvent this problem have been described. The easiest way is to design stoichiometrically off-balanced systems that are set for the conversion not to approach theoretical limit using diluted reaction mixtures.[6] However, insoluble gels were still produced in some cases, depending upon the concentration used and monomer structures. Another way is the slow addition of a diluted monomer solution to the reaction mixture containing the co-monomer at relatively lower concentration and reaction temperature.[7] At higher reaction temperatures, when simultaneous addition of monomers, and higher monomers concentration were applied, the polymerization often resulted in gelation. The $A_2 + BB'_2$ polymerization is an interesting but viable modification to the alternative approach. The rapid reaction between A and B leads to the in situ formation of AB'_2-type monomer before the addition of suitable polymerization promotor/catalyst.[8] In this case, no gelation is observed during the polymerization, but the availability of either monomer is limited.

In this paper, we describe the discovery of a new self-controlled polycondensation methodology to prepare ether−ketone-based HBP's directly from commercially available A_3 and B_2 monomers without the problem of gelation. In such system, one monomer is soluble well in the medium while the other monomer is poorly soluble, reacting very slowly in the polymer-forming process. The critical component of this system is a special reaction medium that would promote complete phase separation of the co-monomers. One such reaction medium, optimized PPA/P_2O_5 mixture, has been established for the electrophilic substitution reaction to yield high molecular weight linear poly(ether ketone)s (PEK's).[9] It was even applicable in the arylcarbonylation of electron deficient substrates such as C_{60}, multiwalled carbon nanotubes (MWNT's) and vapor-grown carbon nanofibers (VGCNF's).[10]

Our technique is pictorially depicted in Figure 1a with trimesic acid (A_3) and diphenyl ether (B_2) as the co-monomers. The polymerization process is kinetically controlled by a slow feeding of the arylether monomer, automated by its poor solubility, into the PPA/P_2O_5 reaction medium that contains

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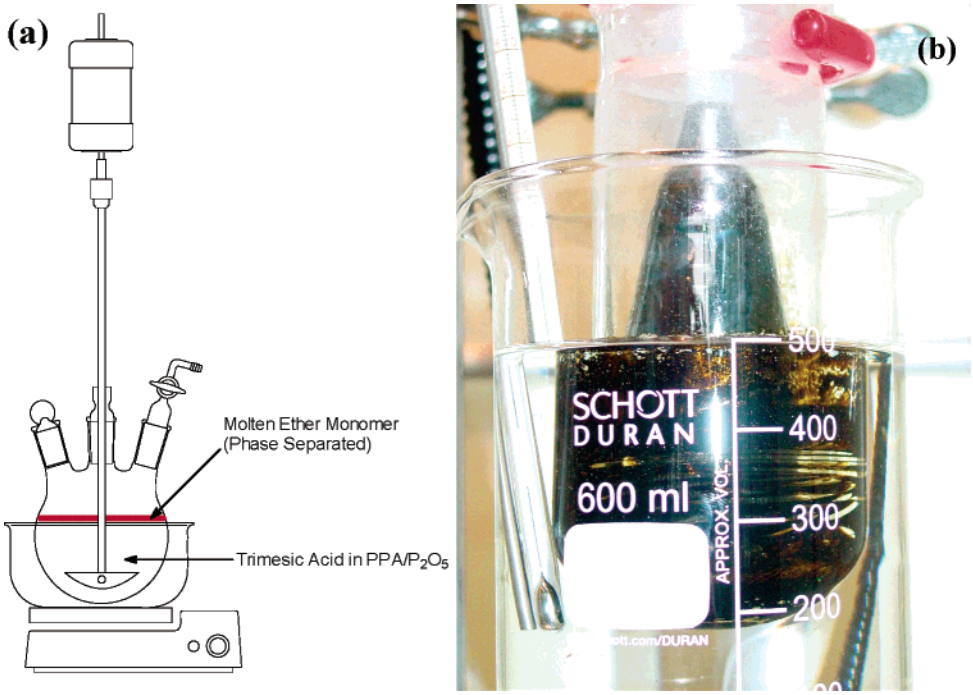


Figure 1. (a) Schematic representation of different solubility of monomers at reaction temperature: trimesic acid as a hydrophilic monomer was blended in the hydrophilic reaction medium and diphenyl ethers as hydrophobic monomers were isolated from the medium. (b) Digital photograph of hyperbranched PEK **1b** obtained after full conversion. Ether monomer was completely digested and the mixture was homogeneous and highly viscous.

trimesic acid and the growing macromolecules. It has resulted in soluble HBP at high conversion and without forming any insoluble gels. Potentially, this technique can be a unique way to silmutaneously control molecular weight and prevent gelation.

Experimental Section

Materials. Trimesic acid, 1,4-diphenoxybenzene, diphenyl ether, polyphosphoric acid (PPA, ~83%), and phosphorus pentoxide were purchased from Aldrich Co., Ltd. Trimesic acid was recrystallized from water to give white crystals (mp > 350 °C) and 1,4-diphenoxybenzene was recrystallized from heptane to give white flakes (mp 72.3−74.2 °C). All electrophilic substitution syntheses of hyperbranched PEK's were performed in PPA/P_2O_5 as reported.[8]

Instrumentation. Infrared (IR) spectra were recorded on Jasco FT−IR 480 Plus spectrophotometer. Solid samples were imbedded in KBr disks. Elemental analyses were performed by system support at CBNU with a CE Instruments EA1110. Melting points (mp) were measured using a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon Ubbelohde No. 200 viscometers. The solutions were filtered through a 0.45 μm syringe filter prior to the measurement. Flow times were recorded for methanesulfonic acid (MSA) solutions with polymer concentrations of approximately 0.5−0.25 g/dL at 30.0 ± 0.1 °C. Differential scanning calorimetry (DSC) was performed under the nitrogen atmosphere with ramping rate of 10 °C/min using a TA Instruments model MDSC2910. The thermograms were obtained on powder samples after they had been heated to 300 °C and air-cooled to ambient temperature. Glass transition temperatures (T_g's) were taken as the mid of the baseline shift. Thermogravimetric analysis (TGA) was conducted in nitrogen and air atmospheres with a heating rate of 10 °C/min using a TA Instruments SDT 2960 thermogravimetric analyzer. The field emission scanning electron microscopy (FESEM) used in this work was LEO 1530FE. A Shimadzu MALDI time-of-fight (TOF) mass spectrometer was employed to determine masses using a linear mode. Dithranol (1,8,9-trihydroxyanthracene) and silver trifluoroacetate were used as the UV-absorbing matrix and cationizing salt, respectively.

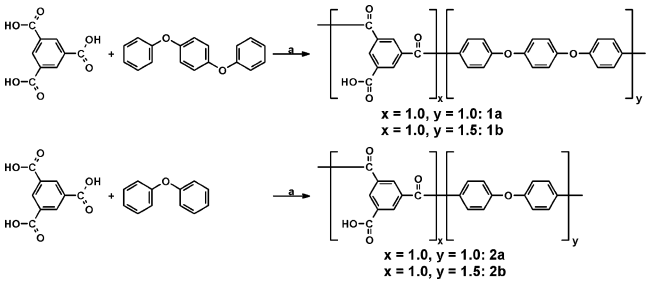
Polymerization of Trimesic Acid (A_3) + 1,4-Diphenoxybenzene (B_2) (1a and 1b). Into a 250 mL resin flask equipped with a high torque mechanical stirrer and nitrogen inlet and outlet, and a side opening for additions was charged poly(phosphoric acid) (PPA, 60 g). Then a mixture of the monomers, trimesic acid (2.10 g, 10 mmol) and 1,4-diphenoxybenzene (2.62 g, 10 mmol), was placed in the flask. The mixture was stirred at 70 °C for 12 h to assess the solubility of monomers. While some undissolved crystals of trimesic acid were still visible in the PPA, 1,4-diphenoxybenzene had melted, phase-separated, and was floating on top of the reaction mixture. Then, P_2O_5 (15 g) was added in one portion, well mixed, and heated to 130 °C. After 24 h, the mixture became homogeneous and stuck to the stirring rod. After a cooldown period, water was added to the reaction mixture, which was then warmed up and kept at 60−70 °C overnight under a nitrogen atmosphere. The resulting pink solids were isolated, collected by suction filtration, and washed with 5% hydrochloric acid and a large amount of water. The isolated polymer was further Soxhlet-extracted with water for 2 days, methanol for 2 days, and finally dried under reduced pressure (0.05 mmHg) at 100 °C for 150 h to give 3.30 g (76% yield) of pink powder (**1a**): $[\eta] = 0.36$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Anal. Calcd for $C_{27}H_{16}O_6$ C, 74.31; H, 3.70; O, 22.00. Found: C, 74.19; H, 4.25; O, 20.04.

The same polymerization experiment was also performed with stoichiometric balance of functional groups. Thus, trimesic acid (2.10 g, 10 mmol) and 1,4-diphenoxybenzene (3.93 g, 15 mmol) were reacted, and the same workup procedure for **1a** was carefully followed to give 2.6 g (88% yield) of pink powder (**1b**): $[\eta] = 0.38$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Anal. Calcd for $C_{28.8}H_{17.6}O_{5.6}$ C, 76.32; H, 3.91; O, 19.77. Found: C, 74.70; H, 4.15; O, 19.90.

Polymerization of Trimesic Acid (A_3) + Diphenyl Ether (B_2) (2a and 2b). The polymerizations were performed following the same procedure as described for **1a** and **1b**, respectively. The resultant polymer was Soxhlet-extracted with water for 2 days, methanol for 2 days, and finally dried under reduced pressure (0.05 mmHg) at 100 °C for 150 h to give 5.30 g (77% yield) of pink powder (**2a**): $[\eta] = 0.51$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Anal. Calcd for $C_{21}H_{12}O_3$ C, 73.25; H, 3.51; O, 23.23. Found: C, 76.61; H, 4.36; O, 17.94.

Following the same procedure, the polymerization was also carried out with stoichiometric balance of functional groups. Thus,

Scheme 1. Polymerizations of PEK's[a]



[a] PPA/P_2O_5, 130 °C.

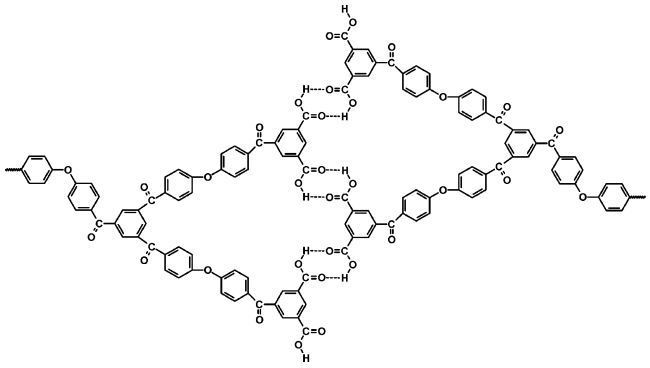
trimesic acid (2.10 g, 10 mmol) and diphenyl ether (2.55 g, 15 mmol) were reacted, followed by the workup using same procedure as described for **1a** to give 1.85 g (83% yield) of pink powder (**2b**): $[\eta] = 0.20$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Anal. Calcd for $C_{21.6}H_{12.8}O_{4.4}$ C, 75.70; H, 3.76; O, 20.54. Found: C, 78.19; H, 4.19; O, 17.21.

Results and Discussion

Polymerizations. Friedel−Crafts acylation reaction for the polycondensation of A_3 and B_2 monomers were carried out following the reported optimized procedure.[8] All reactions between trimesic acid (A_3) and corresponding ether (B_2) monomers were conducted at 130 °C in commercial PPA (83% assay) with 25 wt % of P_2O_5 relative amount to the PPA. Corresponding sets of hyperbranched PEK's **1a** and **1b**, **2a** and **2b** were prepared in fixed concentration of ∼6 wt % of total monomer content, which are relative to the amount of PPA used (see Scheme 1).[8] The HBP's **1a** and **2a** were prepared from the stoichiometric balance (equimolar ratio) of monomers. The HBP's **1b** and **2b** were prepared from the stoichiometric balance (equifunctional ratio) of functional groups. As reaction proceeded, interesting color and phase changes were monitored with respect to reaction time and temperature for all systems. When the reaction temperature was below 70 °C, the color of mixture was gray and its texture was heterogeneous. When it was approaching 130 °C, the color of mixture turned to pink indicating that the acylium ion (−C^+═O) was being generated to promote a Friedel−Crafts reaction, but the mixture was still heterogeneous at this early stage. Because of the hydrophilic nature of trimesic acid, it was gradually blended into the hydrophilic PPA medium at 130 °C. The bulk (bottom part) of reaction mixture, where trimesic acid had dissolved in PPA, became homogeneous after 2 h, while the molten phenyl ether monomer was phase-separated from the rest of the reaction mixture as depicted in Figure 1a. The clear liquid floated on the top surface of the reaction mixture because of the hydrophobicity and lower density of ether monomer compared to the reaction mixture. For both **1a** and **1b**, the color of the reaction mixture became red after 6 h at 130 °C. After stirring for 24 h at 130 °C, the color of reaction mixture changed to deep red and the immiscible upper phase was almost digested and the reaction mixture became completely homogeneous with drastic increase in the bulk viscosity (Figure 1b). As a result, the entire polymerization dope became stuck to the stirring rod. To sum up, our observation clearly indicated that the phenyl ether monomer was slowly mixing into the reaction mixture and engaged in the polymer-forming process via Friedel−Crafts acylation in the bulk of PPA/P_2O_5 medium.

For the **2a** and **2b**, the color of the mixture became red after 3 h at 130 °C. The color changed to deep red, and the two initially immiscible phases collapsed into a single phase after 12 h with rapid increase in mixture viscosity resulting in the whole dope also stuck to the stirring rod. All isolated polymer samples were subjected to elemental analysis to confirm the compositions of hyperbranched PEK's. Samples **1b** and **2b** obtained from equifunctional stoichiometric balance had higher yields than **1a** and **2a** after the similar workup procedure, which involved Soxhlet extraction with water for 2 days and methanol for 2 days to get rid of residual PPA, trimesic acid, ether monomers, low molecular weight oligomers, etc. The higher yields from sample **1b** and **2b** are most probably due to the higher conversion driven by the stoichiometric balance of functional groups.

Scheme 2. Schematic Representation of Hydrogen Bonding



Solution Properties. The resulting polymers were soluble in most of polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), methyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidinone (NMP) when they were not rigorously dried. For example, when residual water content was more than 5 wt % by TGA, the polymers were soluble and there were no insoluble gels in the solutions. All samples were also partially soluble in acetone when they were containing a little amount of residual water. Once the samples had been subjected to rigorous drying, all samples became much less soluble in common polar aprotic solvents, but they were still soluble well in strong acids such as trifluoroacetic acid (TFAA), sulfuric acid, methanesulfonic acid (MSA), and trifluoromethanesulfonic acid (TFMSA). The reason why the samples display limited solubility in common polar aprotic solvents upon complete dryness while still showing good solubility in strong acids is due to the formation of strong intramolecular and intermolecular hydrogen bonding originated from a large number of periphery carboxylic acid groups as shown in Scheme 2. Similar solubility/solution behavior was also reported for hydroxyl-terminated hyperbranched polyphenylquinoxaline.[11] It is also noteworthy that the polyelectrolyte behaviors of polar group terminated HBP's as a function of their concentrations in MSA was monitored during viscosity measurements. All solutions displayed polyelectrolyte effects. As the concentration decreased, both reduced and inherent viscosities increased drastically (see Figure 2 for a representative result). We expect that in a strong acid such as MSA, all carboxylic acid terminated PEK's become polyelectrolytes due to the protonation of the relatively less acidic carboxylic acid groups, which act as conjugate bases to MSA (Scheme 3). Upon further dilution, these hyperbranched polyelectrolyte macromolecules stretch out and expand their hydrodynamic volumes, resulting in the observed viscosity increase. Because of the polyelectrolyte effect, it was difficult to determine intrinsic viscosity via multipoints (five points) measurement. The values presented in Table 1 were obtained by initial two-point extrapolation to the origin. It should be noted that this extrapolation might have overestimated the values for these hyperbranched PEK's.

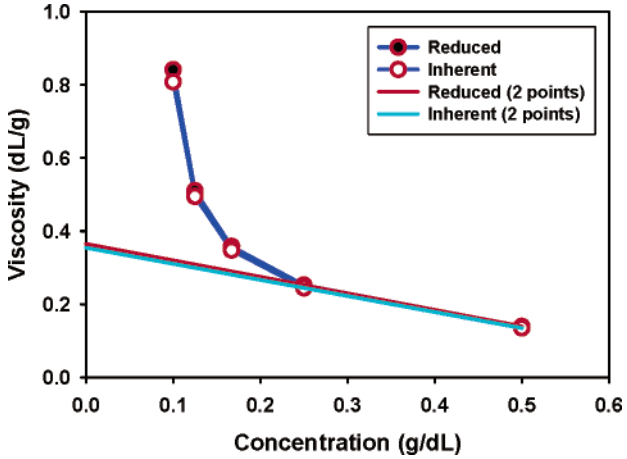


Figure 2. Viscosity vs concentration curves for **1a**. Due to the polyelectrolyte effect in strong acid MSA solution, solution viscosity increased as the concentration decreased.

Scheme 3. Polyelectrolyte Behavior of Hyperbranched PEK

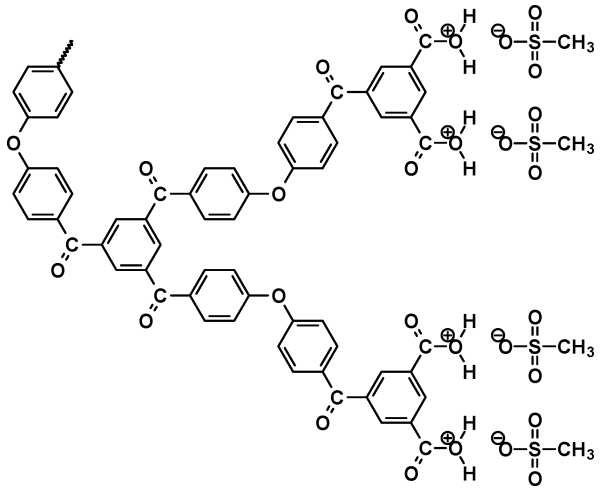


Table 1. Molar Feed Ratio of Monomers, Intrinsic Viscosities, and Elemental Analysis Obtained from Resultant HBP's

				elemental analysis			
sample	A_3 (mol)	B_2 (mol)	$[\eta]^a$ (dL/g)		C (%)	H (%)	O (%)
1a	1	1	0.36	calcd	74.31	3.70	22.00
				found	75.83	4.05	18.20
1b	1	1.5	0.38	calcd	73.25	3.51	23.23
				found	76.59	4.03	17.82
2a	1	1	0.51	calcd	76.32	3.91	19.73
				found	74.70	4.15	19.90
2b	1	1.5	0.20	calcd	75.70	3.76	20.54
				found	78.19	4.19	17.21

[a] Intrinsic viscosity (MSA at 30 ± 0.1 °C) determined by the extrapolation of two concentration points at 0.25 and 0.5 g/dL.

Furthermore, **1a** and **2a** seemed to have greater differences between the true and extrapolated values for **1a** and **2a** because of more extensive hydrogen bonding with their greater numbers of terminal carboxylic groups than **1b** and **2b**. This point will be further discussed in conjunction with thermal analysis data below.

Thermal Properties. The DSC samples in powder form were subjected to two cycles of heating from room temperature to 360 °C and then cooling to 20 °C with the same ramping rate of 10 °C/min. The T_g value was taken as the midpoint of the maximum baseline shift from each run. The hyperbranched PEK sample **1a** ($[\eta] = 0.36$ dL/g) exhibited T_g at 279 °C (Figure 3).

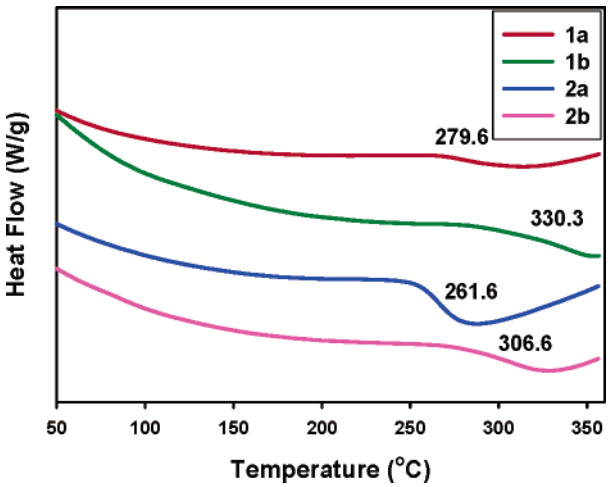


Figure 3. DSC thermograms for hyperbranched PEK's with heating and cooling rates of 10 °C/min.

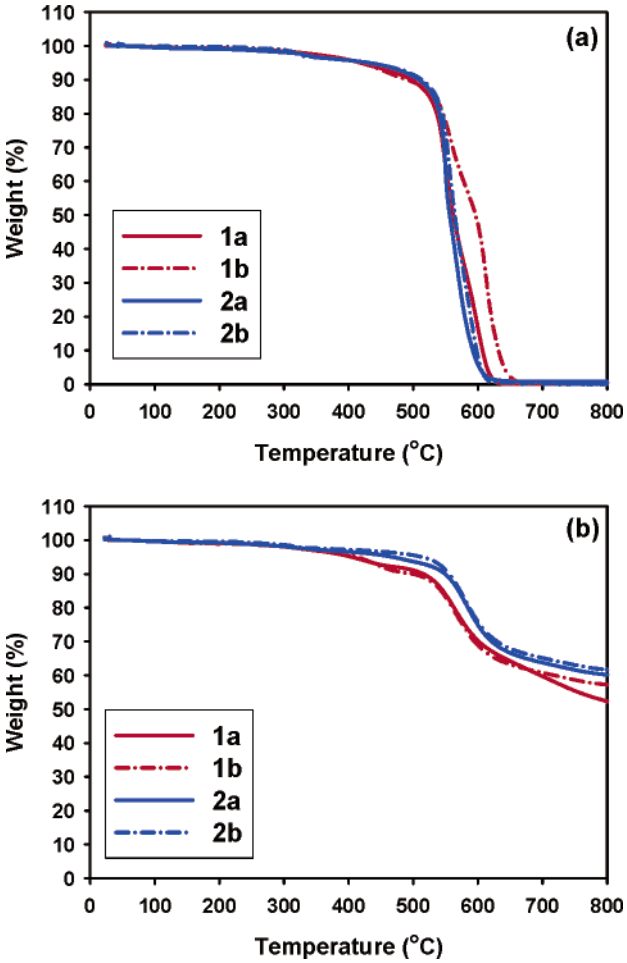


Figure 4. TGA thermograms for hyperbranched PEK's with heating rate of 10 °C/min.

The T_g of hyperbranched PEK **1b** ($[\eta] = 0.38$ dL/g), which has the similar inner structural unit as **1a** but with different composition of the periphery groups, was shifted higher to 330 °C. The hyperbranched PEK sample **2a** ($[\eta] = 0.51$ dL/g) exhibited T_g at 262 °C (Figure 3). The T_g of hyperbranched PEK **2b** ($[\eta] = 0.20$ dL/g), which also has the similar interior structural unit as **2a** but with different composition, was also shifted to 307 °C. The systems displayed two unexpected thermal behaviors. One is that T_g's of **1a** and **1b** were expected to be lower than those of **2a** and **2b**, since the formers have additional flexible ether

Table 2. Thermal Analysis Data for Hyperbranched PEK's

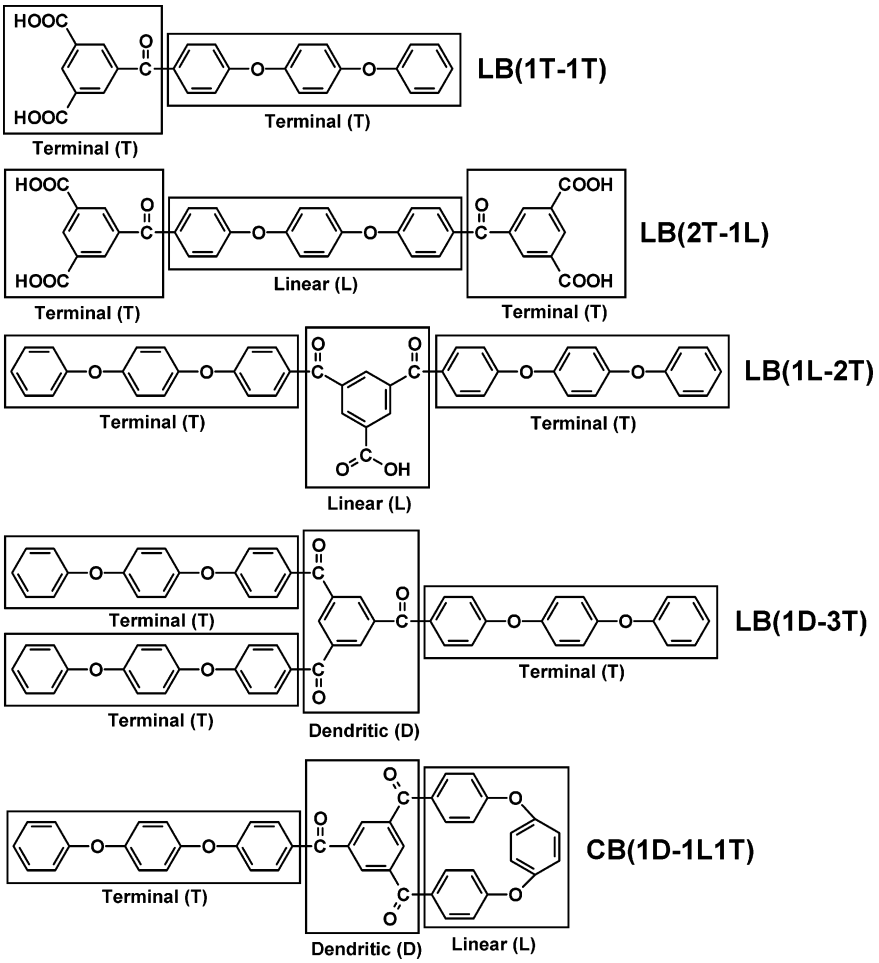
		TGA			
		in air		in nitrogen	
sample	T_g[a] (°C)	$T_{d5\%}$[b] (°C)	char at 800 °C (%)	$T_{d5\%}$[b] (°C)	char at 800 °C (%)
1a	279	419	0.2	405	52
1b	330	419	0.2	412	57
2a	262	432	0.8	468	60
2b	307	432	0.4	513	62

[a] Glass transition temperature (T_g) determined by DSC with a ramping rate of 10 °C/min. [b] Temperature at which 5% weight loss occurred on TGA thermogram obtained with a ramping rate of 10 °C/min.

linkage. Possible explanation would be due to the flexibility of molecule that provided the mobility for better formation of hydrogen bonding. Additional flexibility in the structural unit of the **1a** and **1b** could be the origin of stronger molecular packing driven by intra- and intermolecular hydrogen bonding formed by the large number of periphery carboxylic acids. Furthermore, the more flexible B_2 monomer used in these reactions could have led to more cyclic structures formed within the polymer, resulting in higher degree of overall rigidity, and in turn, a higher T_g. Another explanation is that the T_g's of **1a** and **2a** were also expected to be lower than those of **1b** and **2b**, since the former hyperbranched PEK's have statistically larger number of terminal carboxylic acids. The molecular weights of **1b** and **2b** were expected to be higher than those of **1a** and **2a**, because they were prepared from equifunctional balance of A_3 and B_2 monomers. Although the viscosity data do not agree with the expected molecular weights of **1b** and **2b,** we believe that their T_g could still be largely determined by their molecular weights. With respect to the solution properties of samples, the viscosity values were taken from the two-point method in MSA solutions that displayed the polyelectrolyte behaviors of all samples, and thus, the values might not correspond to the true values of molecular weights of samples. The viscosity values of the samples would be greatly depending upon the number of carboxylic acids at the periphery of hyperbranched macromolecules, because the hydrodynamic volumes of samples **1a** and **2a** in MSA solutions would be larger than those of **1b** and **2b**. Theoretically, the higher number of carboxylic acids should present in the samples **1a** and **2a**. As a result, the larger number of intermolecular hydrogen bonds would be formed in MSA solutions resulting in more extended molecules and thus, higher viscosity.

The thermooxidative thermal stabilities of the hyperbranched PEK's were determined by thermogravimetric analysis (TGA) on the powder samples in air and in nitrogen, respectively. The results are depicted in Figure 4. In general, these hyperbranched PEK's are thermally stable as indicated by the fact that the temperatures at which a 5% weight loss occurred are in the range of 419−432 °C in air and 405−513 °C in nitrogen (see Table 2). Additionally, it is noteworthy that the samples **1a** and **1b** as well as **2a** and **2b** displayed identical 5% weight loss temperatures in air at 419 and 432 °C, respectively. Although the number of the periphery groups such as carboxylic acid and phenyl could be varied depending upon the monomer feed ratio for each set of samples, the inner structural units would be very similar for each set. As a result, the degradation starts almost

Scheme 4. Proposed Basic Structures of Hyperbranched PEK 1a



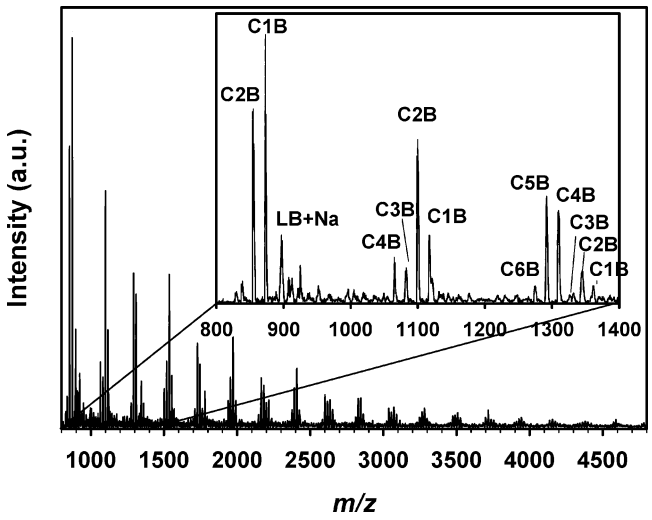


Figure 5. MALDI−TOF mass spectrum of the hyperbranched PEK **1b** prepared from equifunctional monomers feed. The detailed peak assignments are summarized in Table 3.

at the same temperature. The 5%-weight-loss temperatures in nitrogen also followed the same trend. For the samples **1a** and **1b**, it occurred at 405 and 412 °C with char yields of 52 and 57% at 800 °C, respectively. The samples **2a** and **2b** had it at 468 and 513 °C with char yields of 60 and 62% at 800 °C. Although the difference in the degradation temperatures between **1b** and **2b,** which were prepared with equifunctional monomer feed ratios, was only 13 °C in air, it was as high as 101 °C in nitrogen. This is rather surprising, although the disparity could suggest that the stability of carboxylic acids in **2b** is somewhat better than those in **1b**.

Matrix-Assisted Laser Desorption Ionization-Time-of-Flight (MALDI—TOF) Study. The hyperbranched polymers are structurally composed of dendritic (D), linear (L), and terminal (T) units.[12] Here, MALDI−TOF mass spectroscopy was employed to characterize the compositions and structures of the low molecular weight hyperbranched PEK (<4000 Da oligomers) produced by the PPA-promoted electrophilic substitution reaction of A_3 and B_2 monomers. Careful study on MALDI−TOF analysis would potentially provide useful information to trace mechanistic pathway of hyperbranched polymer formation via $A_3 + B_2$ approach. The MALDI−TOF mass spectrum of the hyperbranched polymer **1a**, which was prepared from equimolar monomer feed ratio (50 mol % excess of A functionality), and thus carboxylic acids are considered to be major surface groups, containing a series of equidistant peaks (Figure 5). For the easy understanding of peak assignment, various peaks are grouped into two basic structures. The one is a family of linear branched (LB) structures and the other is that of cyclic branched (C*N*B) structures. The letter "*N*" is the number of cycle(s). Combining these basic two structural families with the three symbols of dendritic (D), linear (L), and terminal (T) units and the number of monomer units incorporated into the structures, detailed peak assignment from MALDI−TOF spectrum would be possible. In the case of two monomers $A_3 + B_2$ polymerized, a few basic polymer structures are postulated in Scheme 4, and the structural assignments from MALDI spectrum and the combination values are summarized in Table 3. In the symbol "LB(1D-3T)" in Scheme 4, 1D indicates one trimesic acid (A_3) as a dendritic unit (1D, all three A-functional groups react) and three 1,4-diphenoxybenzenes (B_2) as terminal units (3T, only one end-functional group is reacted) are incorporated into the LB structure. The symbol "C*1*B(1D-1L1T)" stands for one A_3 monomer as dendritic unit (1D) plus one B_2 monomer as terminal (1T) and another B_2 monomer as linear unit (1L, two functional groups are reacted) are involved in the C*1*B structure. Here, the number 1 is a cycle in the structure indicating an intramolecular condensation occurred with loss of a water molecule as a byproduct.

Table 3. MALDI−TOF Analysis for Hyperbranched PEK 1a

entry	*x*	*y*	calcd (m/z)	found (m/z)
LB	1T	1T	454.4	ND[a]
LB	2T	1L	646.6	ND
LB	1L	2T	698.7	ND
C3B	2D	2L1L″ or 1L2L′	839.0	838.9
C2B	1D1L	1L1L′	856.0	855.4
C1B	1D1T	2L	873.0	873.4
LB	1L1T	1L1T	890.9	ND
LB	1D1T + Na	2L	896.9	897.4
LB	1D	3T	943.0	ND
C4B	2D	2L1L″	1066.2	1065.7
C3B	2D	1L1L′	1083.2	1082.9
C2B	2D	3L	1100.2	1100.2
C1B	1D1L	2L1T	1117.2	1117.8
LB	1D1T	1L2T	1135.2	ND
C6B	2D	2L2L′	1275.4	1275.2
C5B	2D	3L1L″	1292.4	1292.3
C4B	2D	3L1L′	1310.4	1310.1
C3B	2D	4L	1328.4	1328.5
C2B	2D	3L1T	1345.4	1345.1
C1B	1D1L	2L2T	1362.4	1362.1
LB	1D1L	1L3T	1379.4	ND
C7B	2D	3L2L′	1502.7	1502.4
C6B	2D	4L1L″	1519.7	1519.2
C5B	2D	4L1L′	1536.7	1536.7
C4B	2D	5L	1554.7	1554.4
C3B	2D	4L1T	1569.7	1569.6
C2B	2D	3L2T	1587.7	ND
C1B	2D	2L3T	1605.7	ND
LB	2D	1L4T	1623.7	ND
C6B	3D	3L2L′	1711.9	1712.0
C5B	3D	4L1L″	1728.9	1729.0
C4B	3D	4L1L′	1746.9	1746.7
C3B	3D	5L	1762.9	1763.0
C2B	3D	4L1T	1780.9	1781.0
C1B	2D1T	3L2T	1797.9	ND
LB	2D1T	2L3T	1815.9	ND
C4B	4D	4L1L″	1939.0	1939.1
C3B	3D1L	4L1L′	1956.0	1955.6
C2B	2D2L	5L	1973.0	1973.1
C1B	2D1L1T	4L1T	1991.0	1991.2
LB	2D2T	3L2T	2008.0	ND

[a] ND = not detected.

From Figure 5 and Table 3, it is noteworthy that there is no LB polymer detected up to *m*/*z* 2200 for LB(2D3T−4L1T). Low molar mass molecules less than *m*/*z* 2200 consist of all C*N*B structures. The structures in the first group of peak series are the highest peak intensity at *m*/*z* 873, 855, 839, and 897 corresponding to C*1*B(1D1T−2L), C*2*B(1D1L−1L1L′), C*3*B-(2D−lL′1L′) or C*3*B(2D−1L1L″), and sodium-containing LB-(1L1T−lL1T) + Na in that order. We could draw two important points from the MALDI−TOF result. First, the hydrophobic ether monomer (B_2) is indeed very slowly fed into the reaction medium and reacts with trimesic acid (A_3) monomer. With time passed and during the confinement by the viscous PPA solvent molecules, the large excess of A-functional groups attacks the B-functional (focal) group to form the cyclic structure, C*1*B-(1D1T−2L). Some of existing A-functional groups in the C*1*B-(1D1T−2L) molecule are further attacked by any of the available reactive B′-functional sites such as ortho positions to the ether linkage forming C*2*B(1D1L−1L1L′) and C*3*B(2D−

lL′1L′) or C*3*B(2D−1L1L″). The second point is that the high degree of intramolecular cyclizations (C*1*B, C*2*B, C*3*B, etc.) at low molecular weight regions (there is no LB detected by *m*/*z* 2200) could be originated from the relatively high viscosity of the polymeric reaction medium, PPA/P_2O_5 as well as low monomer content (∼6 wt % relative to the PPA). The growing molecules are trapped in the viscous medium resulting in higher probability of intramolecular reaction. Furthermore, relatively low monomer concentration can also be conducive to the formation of intramolecular cyclization. On the basis of these observations, the gelation from $A_3 + B_2$ approach could be controlled and thus prevented by the two important factors mentioned above. A detailed analysis of the MALDI−TOF spectra from all samples **1a**, **1b**, **2a**, and **2b** is underway. The correlations of MALDI−TOF peaks to the corresponding structures will be reported elsewhere.

In summary, intramolecular ring closure was the dominant process in hydrophilic (leading to slow hydrophobic monomer feed to reaction mixture) viscous (leading to isolation of growing hyperbranched molecules) reaction medium and it drives the polycondensation to full conversion and only to the cyclic hyperbranched structures without forming network gels.

Conclusion

Hyperbranched PEK's from commercially available hydrophilic A_3 and hydrophobic B_2 monomers in a hydrophilic reaction medium, PPA/P_2O_5, were successfully synthesized by relying on the large solubility difference of corresponding monomers. This represents arguably an important progress in hyperbranched polymer synthesis from the standpoints of providing an easy way in preventing gelation in $A_3 + B_2$ polymerization under the conditions described in this work, and possibly extending the $A_3 + B_2$ (or $A_2 + B_3$) methodology to other interfacial conditions. Furthermore, the reaction mechanism to afford hyperbranched polymers instead of cross-linked networks was investigated with MALDI−TOF mass analysis. It supported our claim that the gelation was indeed prevented by automatic and slow feeding of the hydrophobic monomer into the hydrophilic and viscous reaction medium, which could also confine the growing macromolecules to form hyperbranched cyclic structures instead of cross-linked networks.

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