Self-Controlled Synthesis of Hyperbranched Poly(ether-ketone)s from A₂ + B₃ Approach in Poly(phosphoric acid)

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ABSTRACT: Self-controlled synthesis of hyperbranched poly(ether-ketone)s (HPEKs) were prepared from “A₂ + B₃” approach by using different monomer solubility in reaction medium. 1,3,5-Triphenoxybenzene as a hydrophobic B₃ monomer was reacted with commercially available terephthalic acid or 4,4'-oxybis(benzoic acid) as a hydrophilic A₂ monomer in a hydrophilic reaction medium, polyphosphoric acid (PPA)/phosphorous pentoxide (P₂O₅). The resultant HPEKs were soluble in various common organic solvents and had the weight-average molecular weight in the range of 3900–13,400 g/mol. The results implied that HPEKs were branched structures instead of crosslinked polymers. The molecular sizes and shapes of HPEKs were further assured by morphological investigation with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hence, the applied polymerization condition was indeed strong enough to efficiently facilitate polycondensation via “direct” Friedel-Crafts reaction without gelation. It could be concluded that the polymer forming reaction was kinetically controlled by automatic and slow feeding of the hydrophobic B₃ monomer into the hydrophilic reaction mixture containing hydrophilic comonomer. As a result, hyperbranched structures were formed instead of crosslinked polymers even at full conversion (equifunctional monomer feed ratio). © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 3326–3336, 2009

Keywords: Friedel-Crafts acylation; high performance polymer; hyperbranched polymer; poly(ether-ketone)s; poly(phosphoric acid)

INTRODUCTION

Dendritic macromolecules such as dendrimers and hyperbranched polymers (HBPs) are important and relatively new class of macromolecules.¹ Dendrimers are generally prepared by reaction-purification sequences to have precisely controlled structures and unique properties.² As a result, their tedious preparative procedure hampers dendrimers to be used as bulk materials. They are useful only for specific demands such as electro-optical³ and medical⁴ applications, where precisely controlled microstructure is needed. On the other hand, HBPs are prepared in a one-pot process, which allows a simple cost-effective manufacturing. Although the resultant HBPs have polydisperse and randomly branched structures, the general properties of HBPs resemble those of
Self-controlled synthesis of hyperbranched poly(ether-ketone)s (HPEKs) were prepared from A2 + B3 Approach in Poly(phosphoric acid). 1,3,5-Triphenoxybenzene as a hydrophobic B3 monomer was reacted with commercially available terephthalic acid or 4,4'-oxybis(benzoic acid) as a hydrophilic A2 monomer in a hydrophilic reaction medium, polyphosphoric acid (PPA)/phosphorous pentoxide (P2O5). The resultant HPEKs were soluble in various common organic solvents and had the weight-average molecular weight in the range of 3900-13,400 g/mol. The results implied that HPEKs were branched structures instead of crosslinked polymers. The molecular sizes and shapes of HPEKs were further assured by morphological investigation with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hence, the applied polymerization condition was indeed strong enough to efficiently facilitate polycondensation via direct Friedel-Crafts reaction without gelation. It could be concluded that the polymer forming reaction was kinetically controlled by automatic and slow feeding of the hydrophobic B3 monomer into the hydrophilic reaction mixture containing hydrophilic comonomer. As a result, hyperbranched structures were formed instead of crosslinked polymers even at full conversion (equifunctional monomer feed ratio). VVC
dendrimers. For example, HBPs display enhanced solubility and low viscosity because of pseudo three-dimensional architecture. They also have multifunctionality, which largely affects physical properties. Thus, desired properties could be obtained by simple surface modification, since the properties such as solubility, compatibility, reactivity, adhesion, and so on are significantly dependent on the number and type of functional groups on HBPs. In addition, they have highly branched architecture and thus exhibit enhanced compatibility with other polymers by chemical affinity as well as mechanical interlocking. Their mechanical properties such as initial modulus, tensile strength, and compressive modulus reflect the highly branched and compact features of these relatively new polymer architectures.

The synthesis of HBPs can be divided into three main strategies: (i) step-growth polycondensation of AB, and A2 + B3 monomers, (ii) self-condensing vinyl polymerization of AB* monomers, and (iii) multibranching ring-opening polymerization of latent AB2 monomers. The most common approach is HBPs from specially designed AB, (x ≥ 2) monomers. Although a few HBPs were prepared from commercially available AB, monomers, the synthesis of AB2 monomers generally involves multistep reaction sequences. Most approaches for HBPs synthesis suffer from drawbacks such as expensive monomers, limited monomer availability, gelation, or undesirable side reactions during the polymerization. Possible alternatives for mass production are “A2 + B2” or “A2 + B3” polymerization, which requires tedious reaction control to prevent gelation as predicted in Carother’s and Flory’s equations. There are many reports to address the gelation problem. Hitherto, the commonly used approaches are stoichiometrically unbalanced systems and the slow addition of a dilute monomer solution into the reaction mixture containing the comonomer at relatively lower concentration and reaction temperature. However, both approaches often resulted in gelation. Thus, as an alternative to AB, monomer approach, AB′ monomer has been in situ generated from A2 + BB2 and polymerized to HBPs. Although the gelation can be prevented, the availability of the BB2 monomer is still limited.

We have previously described the discovery of a new “self-controlled” polycondensation methodology through different solubility of monomers in the reaction medium, poly(phosphoric acid) (PPA)/phosphorous pentoxide (P2O5), to prepare hyper-branched poly(ether-ketone)s (HPEK’s) directly from commercially available A3 and B2 monomers without any problem of gelation.

In this article, we would like to report our continued effort on the preparation of HPEKs via “A2 + B3” monomers system, which is a “reverse” system to previously reported “A3 + B2” monomers system. The A-functionality and B-functionality are hydrophilic carboxylic acid group and hydrophobic ether-activated phenyl group, respectively. With this system, we would like to further demonstrate the universality and feasibility of the “self-controlled” concept for preventing gelation. Thus, 1,3,5-tri phenox ybenzene (TPB) as a hydrophobic B2 monomer was synthesized with 1,3,5-tri bromo benzene and phenol. Commercially available terephthalic acid (TA) or 4,4′-oxybis(benzoic acid) (OBA) as a hydrophilic A2 monomer was reacted with TPB in hydrophilic reaction medium PPA/P2O5 as a “direct” Friedel-Crafts acylation condition. The resultant HPEKs were expected to have highly branched structure instead of cross-linked network and thus, to be soluble in common organic solvents for applications.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from Aldrich Chemical Inc. or Lancaster Synthesis Ltd. and used as received, unless otherwise specified. Terephthalic acid and 4,4′-oxybis(benzoic acid) were recrystallized from water to give white crystals (HPLC purity > 99.99%, mp > 300 °C) and light yellow power (HPLC purity > 99.99%, mp = 330–331 °C), respectively.

Instrumentation

Infrared (FT-IR) spectra were recorded on a Jasco Fourier-transform spectrophotometer model 480 Plus. Elemental analysis was performed with a CE Instruments EA1110. Melting points (mp) were measured using a digital melting point apparatus model Electrothermal 1A 8104 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 concentration of ~0.5–0.1 g/dL at 30.0 ± 0.1 °C. High-performance liquid chromatography (HPLC) analysis was performed on a
Shimadzu LC-600 liquid chromatographt with Shimadzu SPD-6A UV spectrophotometric detector, a Shimadzu CD 501 Chromatopac, and a YMC, Inc., HPLC reverse-phase column. HPLC samples were run with a 7/3 (v/v) acetonitrile/water mixture solvent system. Size exclusion chromatography was performed with Jasco LC-NET (LC-NET II/ADC) equipped with columns (Jordi Gel DBV 10000A, Jordi 1000A, Jordi Gel Mixed Bed). Jasco column oven (CO-2065), Jasco Intelligent RI detector (RI-2031 plus) and Jasco HPLC pump (PU-2080 plus). The molecular weights and polydispersity index were determined with Jasco system control program (HSS-2000). Polymers were dissolved in Tetrahydrofuran (THF) at a concentration of 5 mg/mL. THF was used as an eluent at 23 °C. Proton and carbon nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) spectra were obtained on a Bruker Avance 500 MHz spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done using a Perkin-Elmer DSC7 and a Perkin–Elmer TGA7, respectively, equipped with TAC7 controller. The ramping rate of DSC and TGA was 10 °C/ min. The field emission scanning electron microscopy (FE-SEM) was LEO 1530FE. Samples were gold coated and accelerating voltage was 20 kV. The images of atomic force microscope (AFM) were obtained from Veeco Nanoman. Samples for AFM analysis were prepared by dilute solution casting at ambient temperature by spin-coating on silicon substrates starting from deposits of THF solutions. The samples were analyzed after complete evaporation of the solvent under reduced pressure. AFM images were recorded with the commercially available silicon probe in tapping mode.

**Synthesis of 1,3,5-Triphenoxybenzene**

Into a 500-mL, three-necked, round-bottom flask equipped with a magnetic stirrer, a reflux condenser, a Dean–Stark trap and a nitrogen inlet, 1,3,5-tribromo benzene (40.0 g, 0.127 mol), phenol (40.0g, 0.425 mol), sodium carbonate (50.0 g, 0.75 mol), copper(I) iodide (4.0g, 0.02 mol), sodium acetate (40.0 g, 0.22 mol), and toluene (250 mL) were then carefully poured in the flask. The mixture was then heated to 160 °C for 12 h. The reaction mixture was heated at 130 °C for 9 h.

**Polymerization of Terephthalic Acid (A₂) + 1,3,5-Triphenoxybenzene (B₃) (1a and 1b)**

Into a 250-mL resin flask equipped with a high torque mechanical stirrer, and nitrogen inlet and outlet, terephthalic acid (0.47g, 4.2 mmol), 1,3,5-triphenoxoxygenzene (1.0 g, 2.8 mmol), PPA (83% assay, 30g), and P 2O 5 (7.5g) were placed and stirred with dried nitrogen purging at 70 °C for 12 h. The reaction mixture was heated at 130 °C for 9 h. As time goes by, molecular weight of reaction mixture was slowly increased as judged visually by the increment in bulk viscosity. During reaction progress, the colors of the reaction mixture were changed from light red, deep red, dark red, and finally dark-brown. After cooling down to room temperature, water was added. The resultant powder precipitates were collected by suction filtration and washed with water. The solid product was transferred to an extraction glass thimble and Soxhlet extracted with water for three days and methanol for three days, and finally freeze dried for 48 h to give 1.37 g (99.3% yield) of light orange powder ($\text{1a}$): $[\eta] = 0.20 \text{ dL/g (0.5% solution in MSA at 30.0 } \pm 0.1 \text{ °C). Calcd. for C 32H 20O 5: C, 79.33%; H, 4.16%. Found: C, 75.33%; H, 4.89%.$

The same polymerization experiment was also performed with a stoichiometric balance of functional groups (equifunctional stoichiometry). Thus, terephthalic acid (0.70 g, 4.2 mmol) and 1,3,5-triphenoxoxygenzene (1.0 g, 2.8 mmol) were reacted, and the same workup procedure for 1a was carefully followed to give 1.47 g (95.5% yield) of light orange powder ($\text{1b}$): $[\eta] = 0.22 \text{ dL/g (0.5% solution in MSA at 30.0 } \pm 0.1 \text{ °C). Calcd. for C 36H 21O 6: C, 78.68%; H, 3.85%. Found: C, 77.05%; H, 4.36%.$

Polymerization of 4,4′-Oxybis(benzoic acid) (A2) + 1,3,5-Triphenoxybenzene (B3) (2a and 2b)

The polymerizations were performed following the same procedure as described for 1a. The equimolar stoichiometric amounts of 4,4′-oxybis(benzoic acid) (0.73 g, 2.8 mmol) and 1,3,5-triphenoxybenzene (1.0 g, 2.8 mmol) were reacted, and the same workup procedure for 1a was carefully followed to give 1.56 g (96.9% yield) of cherry red powder (2a): \( [\eta] = 0.16 \text{ dL/g (0.5% solution in MSA at 30.0 °C).} \) Calcd. for C\(_{38}\)H\(_{24}\)O\(_6\): C, 79.16%; H, 4.20%. Found: C, 75.87%; H, 4.15%.

Following the same procedure, equifunctional amounts of 4,4′-oxybis(benzoic acid) (1.09 g, 4.2 mmol) and 1,3,5-triphenoxybenzene (1.0 g, 2.8 mmol) were reacted, and the same workup procedure for 1a was carefully followed to give 1.87 g (96.9% yield) of cherry red powder (2b): \( [\eta] = 0.21 \text{ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C).} \) Calcd. for C\(_{45}\)H\(_{27}\)O\(_{7.5}\): C, 78.59%; H, 3.96%. Found: C, 75.61%; H, 4.02%.

**RESULTS AND DISCUSSION**

**B\(_3\) Monomer Synthesis and Polymerization**

As described in the Ullmann ether condensation procedure as shown in Scheme 1,\(^{15} \) 1,3,5-triphenoxybenzene (TPB) was synthesized by the reaction between 1,3,5-tribromobenzene and excess amount of phenol in the presence of K\(_2\)CO\(_3\) and CuI in a DMAc/toluene mixture. The purified yield of TPB was ≈63%. The structure was ascertained by \(^1\)H and \(^{13}\)C NMR spectra (Fig. 1).

The polycondensations between TPB and TA or OBA were carried out in PPA with additional 25 wt % of P\(_2\)O\(_5\) as an alternative reaction medium for “direct” Friedel-Crafts acylation, which we previously optimized.\(^{14} \) For all cases, the monomer concentration to the PPA was fixed at 5 wt % and the reaction temperature was maintained at 130 °C as described in Scheme 2. The reaction mixtures were heterogeneous in the beginning of the reaction, since the hydrophobic TPA as a B\(_3\) monomer had melted and its liquid phase stayed separated on top of the reaction mixture (Fig. 2, arrow). TPB slowly mixed into the reaction mixture and disappeared at the end of reaction. The reaction mixture became completely homogeneous. The homogeneity of the reaction mixture was a strong indication that gelation had not occurred. The formation for highly branched structure instead of crosslinked one can be explained by following scenario. The hydrophobic B\(_3\) monomer is marginally soluble into hydrophobic reaction medium containing hydrophilic A\(_2\) monomer. Thus, the Friedel-Crafts reaction could occur at the interface of hydrophobic B\(_3\) monomer melt and hydrophilic A\(_2\) monomer in reaction medium. Because of the poor solubility, the B\(_3\) monomer should very slowly mix into the reaction medium, which leads to kinetically controlled polymerization. However, the slow addition of B\(_3\) monomer into reaction medium containing A\(_2\) monomer tends to form highly branched structure in the beginning of the reaction,\(^{16} \) since A\(_2\) is in excess. In some cases, highly crosslinked polymers could form even at very slow B\(_3\) monomer addition.\(^{16} \) Forming no network structures in this work is unusual and could be explained by two possible contributions. The one should be...
relatively low solid content (5 wt% to PPA) and the other could be because of viscous polymeric medium PPA, in which reactive species must be quite isolated not to crosslink but to intramolecularly cyclize. As a result, the molecular weights are not such high even after full conversion (See Table 1). Although the system is not the same, our previous report on in situ grafting of AB₂ monomer onto the surface of multiwalled carbon nanofiber (CNF) is able to support the speculations.¹⁷ The final hyperbranched PEK-grafted CNF (HPWK-g-CNФ) was expected to be crosslinked network structure, but it was soluble in organic solvent. Thus, we believe that not only relatively low solid content, but viscous PPA play together to prevent gelation.

The color of each reaction mixture became dark-brown at the end of reaction. The final products were completely worked-up in the Soxhlet extraction in water for three days to remove any residual PPA/P₂O₅ and in methanol for three days to get rid of low molecular-weight impurities. The worked-up yields were almost quantitative in all four cases (1a and 1b, 2a and 2b). The discrepancy between the theoretical and experimental carbon contents in the elemental analysis (see Experimental) could be originated from hygroscopic nature of resultant HPEKs. Entrapped carboxylic acids groups at inner core of HPEKs could be responsible for bounded water, which is difficult to be completely removed.

**FT-IR Study**

The aromatic carbonyl (C=O) bands at 1656 cm⁻¹ from 1a and 1b samples could be an evidence of carbonyl bond formation due to the “direct” Friedel-Crafts acylation forming HPEKs (Fig. 3). Similarly, the carbonyl bands at 1649 cm⁻¹ of 2a and 2b samples further confirm that electrophilic substitution reaction is the polymer-forming reaction. The minor aromatic keto-band arised from carboxylic acids, which could be part of terminal groups of HPEKs, ranged from 1708 to 1719 cm⁻¹. The carbonyl bands from carboxylic acids of A₂ monomers, TA or OBA, appeared at 1691, 1684 cm⁻¹ (not shown), respectively. However, after polycondensation process, they were shifted to higher frequency, because of the electron-withdrawing effect and weakened hydrogen bonding. Therefore, we could suppose that the minor portion of HPEKs were terminated with carboxylic acid groups and the majority of those were terminated with phenoxyl groups. That explained how hydrophilic A₂ monomers have higher chance to react than hydrophobic B₃ monomer due to vastly different solubility between them in the hydrophilic reaction medium. Although the polymerization was carried out with equimolar (50% excess phenoxy groups) and equifunctional stoichiometric balances, a portion of HPEKs were still terminated with carboxylic acid groups, which contributed to the observed high moisture uptake and polyelectrolyte behavior in acidic solvent.

**Solution Properties**

HPEKs homopolymers were well soluble in trifluoroacetic acid, dichloromethane, phenol, THF, and polar aprotic solvents such as N-methyl-2-pyrrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and so forth (Fig. 4). The solutions of homopolymers showed the various color such as yellow, orange, dark red, and so forth. The colors could be originated from the amount and kinds of charged complex in different solvent. The solubility of HPEKs could be direct visual evidence that the reaction condition had
indeed worked well for the synthesis of HPEKs without gelation.

The number and weight average molecular weights of HPEKs were in the range of 2800–7500 g/mol and 3900–13,400 g/mol, respectively, (Fig. 5 and Table 1). Although HBP generally displayed broad molecular weight distribution (MWD), HPEKs showed narrow in the range of 1.4–1.8 [Fig. 5(a)]. The narrow MWD in this system could be related to the viscosity of reaction medium and monomer concentration. PPA is viscous polymeric acid, which could sequester molecules with reactive chain ends at lower concentration (5.0 wt % in this work). Thus, the probability of intramolecular cyclization should be increased. Indeed, SEC chromatogram shows cyclic oligomer peaks [Fig. 5(b)]. In addition, the sample 1a and 2a displayed relatively low molecular weights compared with the corresponding 1b and 2b. It should be because 1a and 2a were prepared from equimolar feed ratio of monomers, which result in an excess (50% excess phenoxy groups) of B-functional groups, while 1b and 2b were prepared from equifunctional ratio of monomers.

Samples displayed characteristic solution behaviors. For example, relatively rigid HPEK 1a, which was terminated by phenoxy termini, displayed a weak “inverse” polyelectrolyte behavior [Fig. 6(a)]. Both reduced and inherent viscosities were slightly lower than linear 2-point reference lines. Conversely, the HPEK 1b displayed a strong polyelectrolyte effect [Fig. 6(b)]. Polyelectrolyte effect occurs when the hydrodynamic volume of molecule is increased as the solution concentration was lowered. This is because of expanded molecular conformation driven by charge repulsion resulting in drastic viscosity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intrinsic Viscosities (η) (dL/g)</th>
<th>Number Average MW (g/mol)</th>
<th>Weight Average MW (g/mol)</th>
<th>Molecular Weight Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.20</td>
<td>2,800</td>
<td>3,900</td>
<td>1.4</td>
</tr>
<tr>
<td>1b</td>
<td>0.24</td>
<td>6,500</td>
<td>11,300</td>
<td>1.7</td>
</tr>
<tr>
<td>2a</td>
<td>0.16</td>
<td>5,100</td>
<td>8,100</td>
<td>1.6</td>
</tr>
<tr>
<td>2b</td>
<td>0.21</td>
<td>7,500</td>
<td>13,400</td>
<td>1.8</td>
</tr>
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*a Intrinsic viscosities (MSA, 30 ± 0.1 °C) determined by the extrapolation of two concentration points at 0.25 and 0.50 g/dL.
increase. In the case of “inverse” polyelectrolyte, molecular conformation is shrunken as concentration decreased. Similar to HPEK 1a, HPEK 2a and 2b also showed strong “inverse” polyelectrolyte effect [Fig. 6(c) and 6 days], which is in contrast to our previous report on carboxylic acid-terminated HPEK.\(^\text{19}\) The hydrodynamic volume changes of 1a, 2a, and 2b with respect to concentration must be different with that of 1b. Hence, it was difficult to determine intrinsic viscosity via multipoint (five points) measurements. The values taken and presented in Table 1 were obtained...
by initial two-point extrapolation to the origin. It should be noted that this extrapolation might have either overestimated or underestimated the values for these HPEKs.

**Thermal Properties**

The DSC samples in power form were subjected to two cycles of heating from room temperature to 250 °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. HPEKs 1a, 1b, and 2a displayed $T_g$'s at 193 °C, 170 °C, and 174 °C during the second heating scan, respectively. In the case of 2b, baseline shift was not clear to determine $T_g$. The $T_g$ values are 34–56 °C higher than that of mPEK homopolymer ($T_g = 137$ °C) prepared under the same condition.$^{11}$ This $T_g$ increase could be because of the presence of carboxylic acids in HPEKs and their compact molecular architecture, restricting their mobility.

The thermooxidative stabilities of the samples were determined by the temperatures at which

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Analysis</th>
<th>Thermal Properties</th>
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<tbody>
<tr>
<td></td>
<td>Calcd.</td>
<td>Found</td>
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<tr>
<td>1a</td>
<td>79.33 4.16</td>
<td>75.33 4.87</td>
</tr>
<tr>
<td>1b</td>
<td>78.68 3.85</td>
<td>75.04 3.93</td>
</tr>
<tr>
<td>2a</td>
<td>79.16 4.20</td>
<td>75.87 4.15</td>
</tr>
<tr>
<td>2b</td>
<td>78.59 3.96</td>
<td>75.61 4.02</td>
</tr>
</tbody>
</table>

$^a$Glass transition temperature ($T_g$) determined by DSC with heating and cooling rates of 10 °C/min.
$^b$The temperature at which 5% weight loss occurred on TGA thermogram obtained with heating rate of 10 °C/min.

![Figure 7](image-url) SEM images of HPEKs: (a) 1a; (b) 1b; (c) 2a; (d) 2b. The scale bars are 200 nm.
5% weight loss ($T_{d5\%}$) in air. The $T_{d5\%}$’s of HPEKs 1a, 1b, 2a, and 2b were at 284 °C, 286 °C, 292 °C, and 292 °C and those in nitrogen were at 294 °C, 303 °C, 297 °C, and 303 °C, in that order (Table 2). All samples obtained from equimolar stoichiometry and equifunctional stoichiometry displayed similar thermal stability. The result implies that the presence of carboxylic acids in HPEKs. The observed temperature for thermal decomposition of aromatic carboxylic acid derivatives agreed well with the temperature range. 20 Char yields of the samples were 0–2 wt % at 800 °C in air and 56–63 wt % at 800 °C in nitrogen. The early weight loss could be attributable from the terminal carboxylic acids, which started decarboxylation around 300 °C.21

**SEM**

The SEM images were obtained from powder HPEK samples. The morphology of the HPEK 1a appears to be uniform globular sphere agglomerates [Fig. 7(a)]. The size distribution of the 1a agglomerates is in the range of 100–200 nm. The 1b agglomerates has the size distribution in the range of 200–300 nm [Fig. 7(b)], which is much larger than that of 1a. In the cases of 2a and 2b, the size distribution of the agglomerates is much broader than 1a and 1b, and it is in the range of 50–500 nm [Fig. 7(c) and 7(d)]. It is noteworthy that the size distributions of HPEKs 1a and 1b are quite uniform when compared with those of 2a and 2b. Although the size of the agglomerates may not necessarily be correlated to the architecture or molecular weight as the nature of the precipitation process may very well influence the size of the agglomerates, the morphology differences between samples are coincidently related to the different molecular architectures and molecular weights. For example, 4,4'-oxybis(benzoic acid) as an A2 monomer for the HPEKs 2a and 2b more reactive than terephthalic acid for 1a and 1b. The resultant HPEKs were expected to have higher molecular weights and more flexible backbone, resulting in broader molecular weight distributions as well as wider size distribution of agglomerates. In addition, the samples 1a and 2a were prepared from equimolar amount of A2 and B3 monomers and it implied that 50% molar excess amount of B-functional groups were presented in the system. Thus, the samples 1a and 2a were supposed to have lower molecular weights than corresponding 1b and 2b, respectively, which were prepared from equifunctional monomer feed ratio. As a result, the average size of 1b and 2b agglomerates is appeared to be larger than corresponding counterparts 1a and 2a.
AFM

To further characterize the shape and dimension of HPEKs, AFM images were recorded in tapping mode. The images obtained from the sample 1a and 1b show that ~10–50 nm sized molecules are uniformly distributed on silicon substrates [Fig. 8(a) and 8(b)]. Interestingly, both HPEK molecules are vertically aligned to the surface. On the contrary, the HPEK 2a and 2b prefer to be flattened on the same surface [Fig. 8(c) and 8(d)]. As expected, due to the stronger monomer reactivity, the average molecular sizes of the 2a and 2b appear to be much larger than those of 1a and 1b. The samples 1b and 2b reveal their height almost three times larger than 1a and 2a, respectively. The characteristic molecular alignments could be related to the molecular rigidity. The samples 1a and 1b are relatively more rigid than 2a and 2b.

CONCLUSIONS

A series of organo-soluble HPEKs instead of cross-linked polymers was synthesized from hydrophilic A₂ and hydrophobic B₃ monomers in a hydrophilic reaction medium, PPA/P₂O₅. On the basis of solubility test, the resultant HPEKs were all soluble in most of the organic solvents. With the collective evidence from solubility, SEC, viscosity experiments and morphology studies, the hyperbranched structures could be originated from the different solubility of monomers in the reaction medium. Together with our previous observation, the result suggested that the polymerization proceeded in a “self-controlled” manner without forming gelation to a maximum conversion (equifunctional feed ratio of monomers). In addition, the reaction medium was indeed strong enough to efficiently drive polycondensation of heterogeneous mixture. The results of this work could portend that proper selection of monomers and reaction medium would provide the cost-effective production of hyperbranched polymers. Hereafter, more difficult systems such as the “A₃ + B₃” monomers system and even higher functionality system have remained challenges to demonstrate the feasibility of the reaction conditions described here.

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REFERENCES AND NOTES


