Self-Controlled Synthesis of Hyperbranched Poly(ether-ketone)s from $A_2 + B_3$ Approach in Poly(phosphoric acid)

IN-YUP JEON,[1] LOON-SENG TAN,[2] JONG-BEOM BAEK[1]

[1]School of Nano Bio Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 194, Banyeon, Ulsan, 689-805 South Korea

[2]Nanostructured and Biological Materials Branch, Materials and Manufacturing Directorate, Air Force Research Laboratory, AFRL/RXBN, Wright-Patterson Air Force Base, Dayton, Ohio 45433-7750

Received 5 February 2009; accepted 11 March 2009
DOI: 10.1002/pola.23402
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Self-controlled synthesis of hyperbranched poly(ether-ketone)s (HPEKs) were prepared from "$A_2 + B_3$" approach by using different monomer solubility in reaction medium. 1,3,5-Triphenoxybenzene as a hydrophobic B_3 monomer was reacted with commercially available terephthalic acid or 4,4′-oxybis(benzoic acid) as a hydrophilic A_2 monomer in a hydrophilic reaction medium, polyphosphoric acid (PPA)/phosphorous pentoxide (P_2O_5). 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 B_3 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-optical[3] and medical[4] 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

Additional Supporting Information may be found in the online version of this article.

Correspondence to: J.-B. Baek (E-mail: jbbaek@unist.ac.kr)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 47, 3326–3336 (2009)
© 2009 Wiley Periodicals, Inc.

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2009		**00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE
Self-Controlled Synthesis of Hyperbranched Poly(etherketone)s from A2 + B3 Approach in Poly(phosphoric acid)

5a. CONTRACT NUMBER
5b. GRANT NUMBER
5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
5e. TASK NUMBER
5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory,Nanostructured and Biological Materials Branch, Materials and Manufacturing Dire,AFRL/RXBN,Wright-Patterson AFB,OH,45433-7750

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. 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 4,40-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

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**11**	

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.[4] 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.[2,3]

The synthesis of HBPs can be divided into three main strategies: (i) step-growth polycondensation of AB_x[7] and $A_2 + B_3$ monomers,[8] (ii) self-condensing vinyl polymerization of AB* monomers,[9] and (iii) multibranching ring-opening polymerization of latent AB_x monomers.[4,22] The most common approach is HBPs from specially designed AB_x ($x \geq 2$) monomers. Although a few HBPs were prepared from commercially available AB_x monomers,[7d,e,f] the synthesis of AB_2 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 "$A_3 + B_2$" or "$A_2 + B_3$" polymerization,[8] which requires tedious reaction control to prevent gelation as predicted in Carother's and Flory's equations.[10] There are many reports to address the gelation problem. Hitherto, the commonly used approaches are stoichiometrically unbalanced systems[11] and the slow addition of a dilute monomer solution into the reaction mixture containing the comonomer at relatively lower concentration and reaction temperature.[12] However, both approaches often resulted in gelation. Thus, as an alternative to AB_x-monomer approach, AB'_2-monomer has been *in situ* generated from $A_2 + BB'_2$ and polymerized to HBPs.[13] Although the gelation can be prevented, the availability of the BB'_2 monomer is still limited.

We have previously described the discovery of a new "self-controlled" polycondensation methodology via different solubility of monomers in the reaction medium, poly(phosphoric acid) (PPA)/phosphorous pentoxide (P_2O_5), to prepare hyperbranched poly(ether-ketone)s (HPEK's) directly from commercially available A_3 and B_2 monomers without any problem of gelation.[5]

In this article, we would like to report our continued effort on the preparation of HPEKs via "$A_2 + B_3$" monomers system, which is a "reverse" system to previously reported "$A_3 + B_2$" monomers system.[14] 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-triphenoxybenzene (TPB) as a hydrophobic B_3 monomer was synthesized with 1,3,5-tribromobenzene and phenol. Commercially available terephthalic acid (TA) or 4,4′-oxybis(benzoic acid) (OBA) as a hydrophilic A_2 monomer was reacted with TPB in hydrophilic reaction medium PPA/P_2O_5 as a "direct" Friedel-Crafts acylation condition.[14] 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 chromatograph 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 DVB 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.

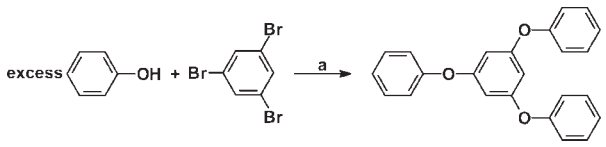
Synthesis of 1,3,5-Triphenoxybenzene

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, 0.472 mol), and copper(I) iodide (4.0g) were placed. Dimethyl acetamide (DMAc) (300 mL) and toluene (50 mL) were then carefully poured in the flask. The mixture was then heated to 160 °C. The water generated during the reaction was removed by toluene azeotropic distillation for 4–5 h. After completion of dehydration, the mixture was further stirred under reflux for 90 h. The mixture was filtered and the filtrate was poured into distilled water containing 50 mL of conc. hydrochloric acid. The precipitate that formed was collected by filtration and air-dried. Some impurities and colors from the product were removed by treating with activated carbon, and then the product was recrystallized from heptane to afford 28.21 g (62.6%) of yellow crystals: mp 110.2–111 °C (lit. mp not reported).[15] Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.34%; H, 5.12%. Found: C, 80.91%; H, 5.47%. FT-IR (KBr, cm^{-1}): 694, 753, 859, 1215, 1460, 1582, 3076. ^{1}H NMR (DMSO-d_6, δ in ppm): 6.26 (s, 3H, Ar-*H*), 7.07-7.09 (d, 6H, Ar—*H*), 7.15-7.18 (t, 3H, Ar—*H*), 7.37-7.41 (t, 6H, Ar—*H*). ^{13}C NMR (DMSO-d_6, δ in ppm): 102.2, 119.4, 124.4, 130.2, 155.3, 159.3.

Polymerization of Terephthalic Acid (A_2) + 1,3,5-Triphenoxybenzene (B_3) (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, 2.8 mmol), 1,3,5-triphenoxybenzene (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 (**1a**): $[\eta] = 0.20$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Calcd. for $C_{32}H_{20}O_5$: 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-triphenoxybenzene (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 (**1b**): $[\eta] = 0.22$ dL/g (0.5% solution in MSA at 30.0 ± 0.1 °C). Calcd. for $C_{36}H_{21}O_6$: C, 78.68%; H, 3.85%. Found: C, 77.05%; H, 4.36%.



Scheme 1. Synthesis of 1,3,5-triphenoxybenzene (TPB): a. K_2CO_3, CuI, DMAc/toluene.

Polymerization of 4,4′-Oxybis(benzoic acid) (A_2) + 1,3,5-Triphenoxybenzene (B_3) (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**): [η] = 0.16 dL/g (0.5% solution in MSA at 30.0 ± 0.1 °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 1.87g (96.9% yield) of cherry red powder (**2b**): [η] = 0.21 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_2CO_3 and CuI in a DMAc/toluene mixture. The purified yield of TPB was ~63%. The structure was ascertained by ^1H 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_2O_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

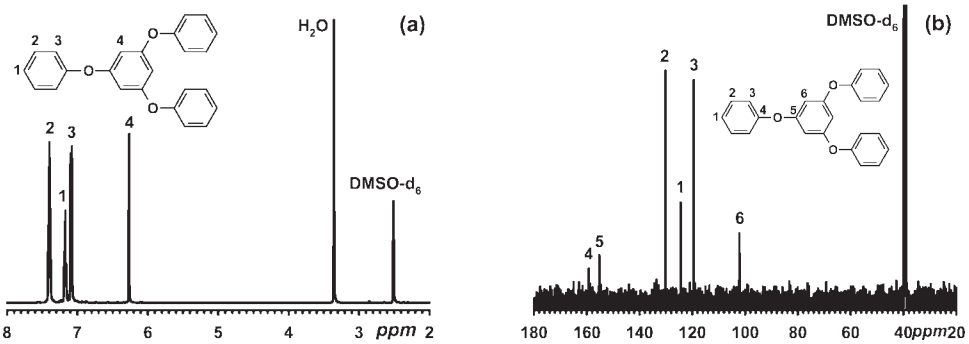
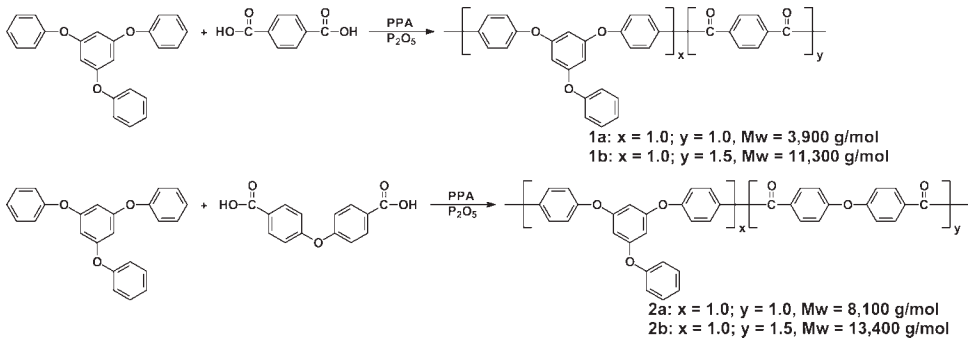


Figure 1. (a) ^1H and (b) ^{13}C NMR spectra of 1,3,5-triphenoxybenzene in DMSO-d_6.



Scheme 2. Self-controlled synthesis of HPEKs from "$A_2 + B_3$" monomers approach.

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 AB_2 monomer onto the surface of multiwalled carbon nanofiber (CNF) is able to support the speculations.[17] The final hyperbranched PEK-grafted CNF (HPWK-g-CNF) 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/P_2O_5 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 arisen 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 A_2 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 phenoxy groups. That explained how hydrophilic A_2 monomers have higher chance to react than hydrophobic B_3 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-pyrrolidone (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

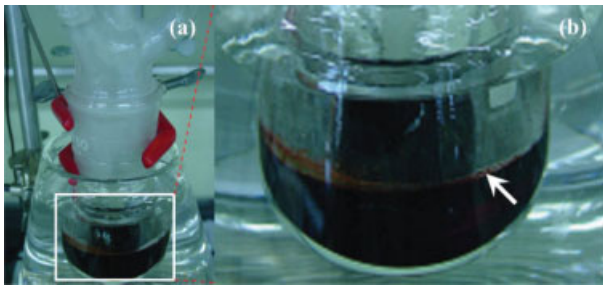


Figure 2. Digital photographs: (a) reaction flask containing HPEK 1a; (b) magnified image from (a). The floatation of clear molten 1,3,5-triphenoxybenzene can be observed on the surface of dark brown reaction mixture (arrowed). The lower homogeneous, dark brown mixture was an indication of reaction progress.

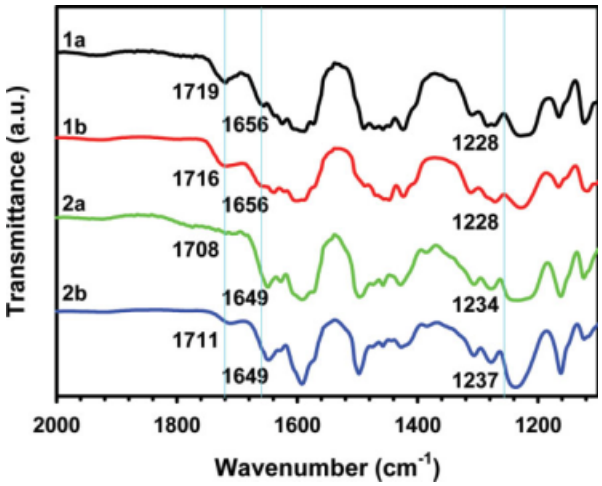


Figure 3. FTIR (KBr pellet) spectra of HPEKs.

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),[9a,18] 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.[19] 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 1. SEC Results of HPEKs

Sample	Intrinsic Viscosities (η)[a] (dL/g)	Number Average MW (g/mol)	Weight Average MW (g/mol)	Molecular Weight Distribution
1a	0.20	2,800	3,900	1.4
1b	0.24	6,500	11,300	1.7
2a	0.16	5,100	8,100	1.6
2b	0.21	7,500	13,400	1.8

[a] Intrinsic viscosities (MSA, 30 ± 0.1 °C) determined by the extrapolation of two concentration points at 0.25 and 0.50 g/dL.

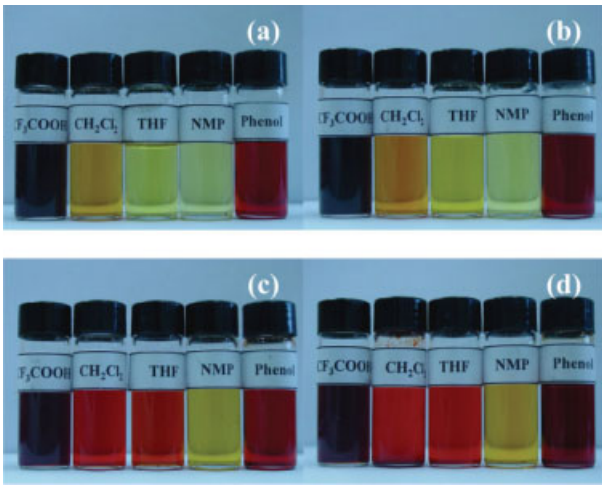


Figure 4. Digital photographs of sample solutions (10 mg/3 mL): (a) **1a**; (b) **1b**; (c) **2a**; (d) **2b**.

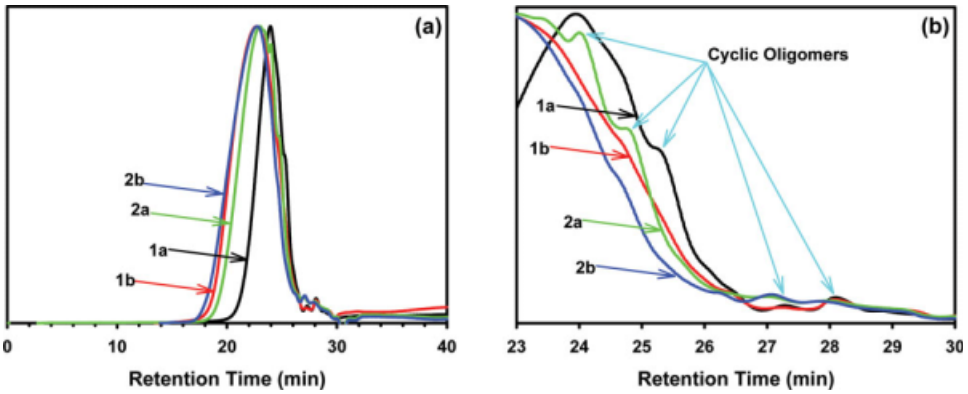


Figure 5. SEC curves of samples. The molecular weights of **1a** and **2a** were relatively lower than corresponding **1b** and **2b**, respectively. The **1a** and **2a** were prepared from equimolar monomer feed and **1b** and **2b** were equifunctional monomer feed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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.[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

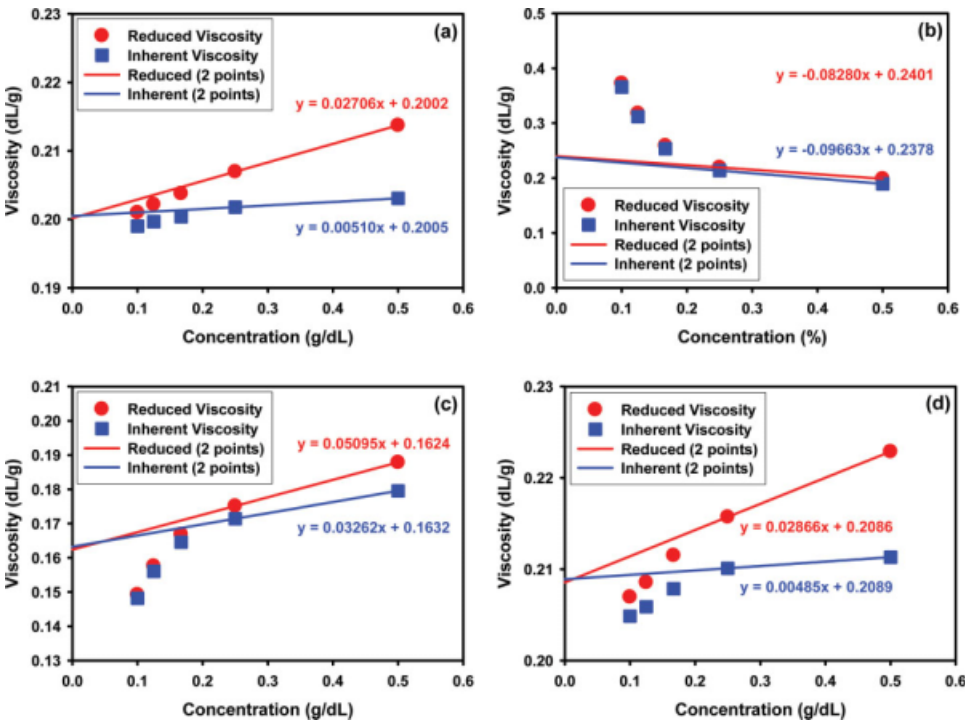


Figure 6. Solution viscosities with respect to sample concentrations: (a) **1a**; (b) **1b**; (c) **2a**; (d) **2b**. The samples **1a**, **2a** and **2b** displayed "inverse" polyelectrolyte behaviors in strong acid MSA solution. The "inverse" polyelectrolyte behavior is that solution viscosity is drastically decreased as the concentration decreased. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. Elemental Analysis, Intrinsic Viscosities, and Thermal Properties of HPEKs

	Elemental Analysis					TGA[b]			
	Calcd.		Found			In Air at 800 °C		In N_2 at 800 °C	
Sample	C (%)	H (%)	C (%)	H (%)	DSC[a] T_g (°C)	$T_{d5\%}$ (°C)	Char (%)	$T_{d5\%}$ (°C)	Char (%)
1a	79.33	4.16	75.33	4.87	193	284	2	294	57
1b	78.68	3.85	75.04	3.93	170	286	0	303	63
2a	79.16	4.20	75.87	4.15	174	292	1	297	56
2b	78.59	3.96	75.61	4.02	–	292	0	303	57

[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.

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, (Table 2). 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 *m*PEK 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

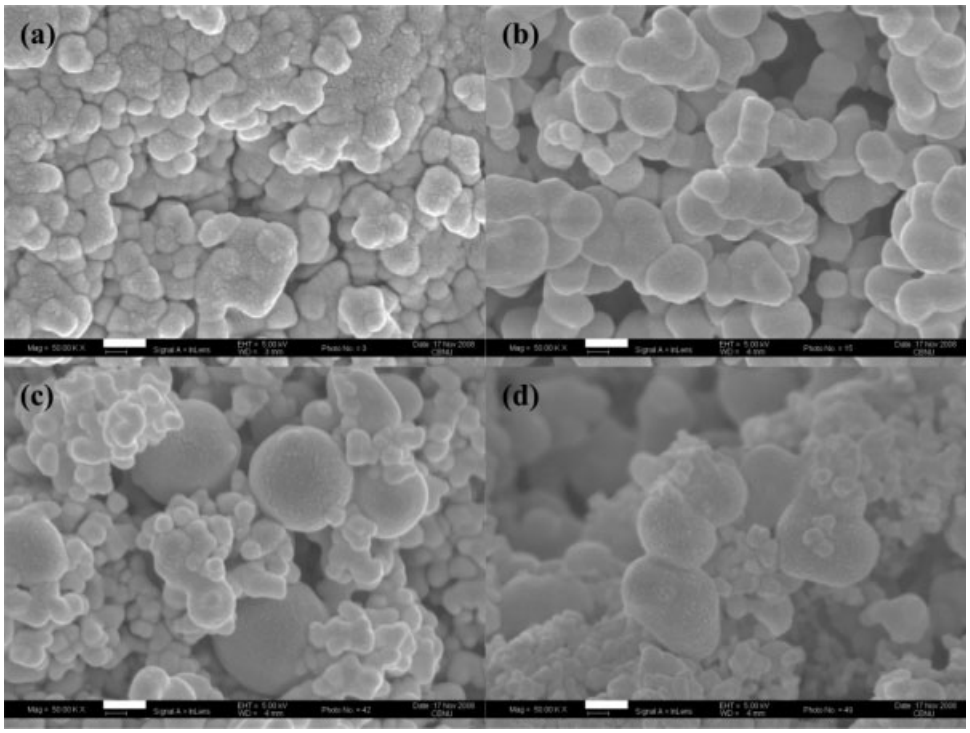


Figure 7. SEM images of HPEKs: (a) **1a**; (b) **1b**; (c) **2a**; (d) **2b**. The scale bars are 200 nm.

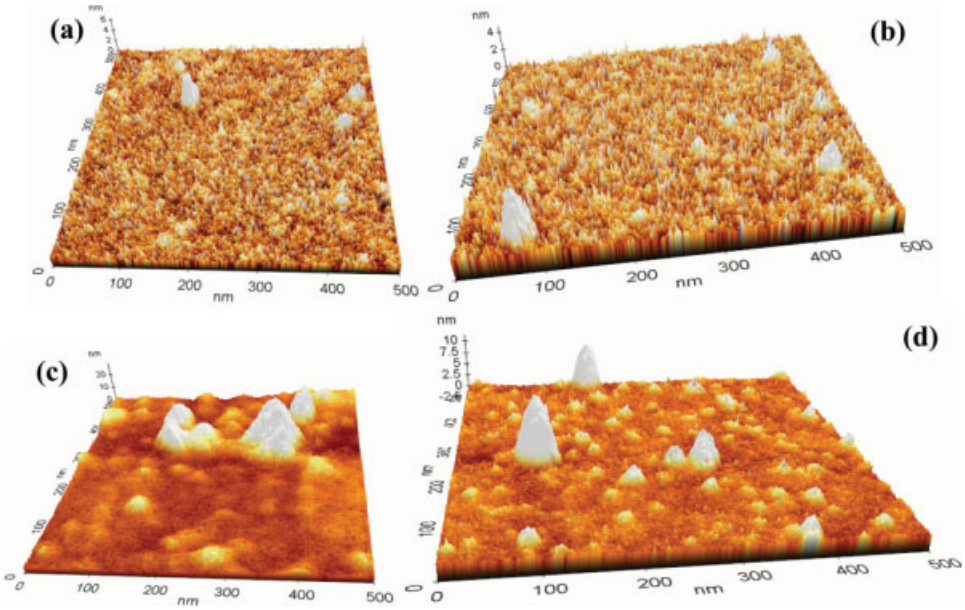


Figure 8. AFM tapping three dimensional topographic images of HPEKs obtained from the deposits of THF solutions on silicon wafers: (a) **1a**; (b) **1b**; (c) **2a**; (d) **2b**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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 A_2 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 A_2 and B_3 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 crosslinked polymers was synthesized from hydrophilic A_2 and hydrophobic B_3 monomers in a hydrophilic reaction medium, PPA/P_2O_5. 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,[19] 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 "$A_3 + B_3$" monomers system and even higher functionality system have remained challenges to demonstrate the feasibility of the reaction conditions described here.

This project was supported by funding from US Air Force Office of Scientific Research, Asian Office of Aerospace R and D (AFOSR-AOARD) and Korea Science and Engineering Foundation (R01-2007-000-10,031-02).

REFERENCES AND NOTES

1. (a) Jikei, M.; Kakimoto, M. Prog Polym Sci 2001, 26, 1233–1298; (b) Kim, Y. H. J. Polym Sci Part A: Polym Chem 1998, 36, 1685–1698; (c) Hult, A.; Johansson, M.; Malmström, E. Adv Polym Sci 1999, 143, 1–34; (d) Inoue, K. Prog Polym Sci 2000, 25, 453–571; (e) Voit, B. J Polym Sci Part A: Polym Chem 2000, 36, 2505–2525; (f) Hult, A.; Malmström, E.; Johansson, M. In Polymeric Materials Encyclopedia; Salamone, J., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 5 H-L, p 3171.
2. (a) Fréchet, J. M. J. Science 1994, 263, 1710–1715; (b) Majoral, J. P.; Caminade, A. M. Chem Rev 1999, 99, 845–880; (c) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. Prog Polym Sci 1998, 23, 1–56; (d) Bochkarev, M. N.; Katkova, M. A. Russ Chem Rev 1995, 64, 1035–1048; (h) Tomalia, D. A.; Hedstrand, D. M.; Wilson, L. R. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1990; p 46; (i) Burchard, W. Adv Polym Sci 1983, 48, 1–124; (j) Turner, S. R.; Voit, B. I.; Mourey, T. H. Macromolecules 1993, 26, 4617–4623.
3. (a) Lee, B. L.; Yamamoto, T. Macromolecules 1999, 32, 1375–1382; (b) Baek, J.-B.; Chien, L.-C. J Polym Sci Part A: Polym Chem 2004, 42, 3587–3603; (c) Cui, Y.; Zhang, X.; Jenekhe, S. A. Macromolecules 1999, 32, 3824–3826; (d) Justin Thomas, K. R.; Lin, J. T.; Tao, Y. T.; Chuen, C.-H. Chem Mater 2002, 14, 2796–2802; (e) Thlelakkat, M. M.; Posch, P.; Schmidt, H.-W. Macromolecules 2001, 34, 7441–7447; (f) Jonforsen, M.; Johansson, T.; Inganäs, O.; Andersson, M. R. Macromolecules 2002, 35, 1638–1643; (g) Zhan, X.; Liu, Y.; Wu, X.; Wang, S.; Zhu, D. Macromolecules 2002, 35, 2529–2537; (h) Bangcuyo, C. G.; Ellsworth, J. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. Macromolecules 2003, 36, 546–548; (i) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. J Am Chem Soc 2000, 122, 12385–12386; (j) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. J Am Chem Soc 2000, 122, 1175–1185.
4. Grayson, S. M.; Fréchet, J. M. J. Chem Rev 2001, 101, 3819–3868.
5. Malmstrom, E.; Hult, A. J Macromol Sci-Rev Macromol Chem Phys 1997, 37, 555–579.
6. Bolton, D. H.; Wooley, K. L. J Polym Sci Part A: Polym Chem 2002, 40, 823–835.
7. (a) Flory, P. J. J Am Chem Soc 1952, 74, 2718–2723; (b) Hawker, C. J.; Fréchet, J. M. J. Macromolecules 1990, 23, 4726–4729; (c) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. Angew Chem Int Ed Engl 1994, 33, 82–85; (d) Kim, Y. H. J. Am Chem Soc 1992, 114, 4947–4948; (e) Yang, G.; Jikei, M.; Kakimoto, M. Macromolecules 1998, 31, 5964–5966; (f) Yang, G.; Jikei, M.; Kakimoto, M. Macromolecules 1999, 32, 2215–2220; (g) Tomalia,

D. A.; Durst, H. D. Top Curr Chem 1993, 165, 193–313 and references therein.
8. (a) Jikei, M.; Chon, S.-H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. Macromolecules 1999, 32, 2061–2064; (b) Hao, J.; Jikei, M.; Kakimoto, M. Macromolecules 2002, 35, 5372–5381; (c) Hao, J.; Jikei, M.; Kakimoto, M. Macromolecules 2003, 36, 3519–3528; (d) Komber, H.; Voit, B.; Monticelli, O.; Russo, S. Macromolecules 2001, 34, 5487–5493; (e) Emrick, T.; Chang, H.-T.; Frechet, J. M. J. Macromolecules 1999, 32, 6380–6382; (f) Emrick, T.; Chang, H.-T.; Fréchet, J. M. J. J Polym Sci Part A: Polym Chem 2000, 38, 4850–4869; (g) Sato, M.; Matsuoka, Y.; Yamaguchi, I. J Polym Sci Part A: Polym Chem 2007, 45, 2998–3008; (h) Xu, H.; Chen, K.; Guo, X.; Fang, J.; Yin, J. J Polym Sci Part A: Polym Chem 2007, 45, 1150–1158; (i) Sato, M.; Nakashima, A.; Sato, Y.; Yamaguchi, I. J Polym Sci Part A: Polym Chem 2008, 46, 6688–6702.
9. (a) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Geubbs, R. B. Science 1995, 269, 1080–1083; (b) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. Macromolecules 1997, 30, 5192–5194; (c) Matyjaszewski, K.; Gaynor, S. G.; Müller, A. H. E. Macromolecules 1997, 30, 7034–7041; (d) Matyjaszewski, K.; Gaynor, S. G. Macromolecules 1997, 30, 7042–7049; (e) Matyjaszewski, K.; Gaynor, S. G. Macromol Rapid Commun 1998, 19, 665–670.
10. (a) Carothers, W. H., Trans. Faraday Soc. 1936, 32, 39; (b) Flory, P. J. J Am Chem Soc 1941, 63, 3083–3096.
11. Kricheldorf, H. R.; Hobzova, R.; Vakhtangishvili, L.; Schwarz, G. Macromol Chem Phy 2005, 206, 2133–2142.
12. (a) Fang, J.; Kita, H.; Okamoto, K. Macromolecules 2000, 33, 4639–4646; (b) Fang, J.; Kita, H.; Okamoto, K. J Membr Sci 2001, 182, 245–256; (c) Czupik, M.; Fossum, E. J Polym Sci Part A: Polym Chem 2003, 41, 3871–3881; (d) Lin, Q.; Long, T. E. Macromolecules 2003, 36, 9809–9816; (e) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. Macromolecules 2003, 36, 4337–4344; (f) Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. J Polym Sci Part A: Polym Chem 2002, 40, 2967–2978.
13. (a) Chang, Y.-T.; Shu, C.-F. Macromolecules 2003, 36, 661–666; (b) Liu, Y.; Chung, T.-S. J Polym Sci Part A: Polym Chem 2002, 40, 4563–4569; (c) Wang, S. J.; Fan, X. D.; Kong, J.; Wang, X.; Liu, Y. Y.; Zhang, G. B. J Polym Sci Part A: Polym Chem 2008, 46, 2708–2720; (d) Lin, Y.; Dong, Z. M.; Liu, X. H.; Li, Y. S. J Polym Sci Part A: Polym Chem 2007, 45, 4309–4321; (e) Lin, Y.; Dong, Z. M.; Li, Y. S. J Polym Sci Part A: Polym Chem 2008, 46, 5077–5092; (f) Wang, D.; Zheng, Z. J.; Hong, C. Y.; Liu, Y.; Pan, C. Y. J Polym Sci Part A: Polym Chem 2006, 44, 6226–6242.
14. Baek, J.-B.; Tan, L.-S. Polymer 2003, 44, 4135–4147.
15. Moroz, A. A.; Shvartsberg, M. S. Russ Chem Rev 1974, 43, 679–689.
16. Oguz, C.; Gallivan, M. A.; Cakir, S.; Yilgor, E.; Yilgor, I. Polymer 2008, 49, 1414–1424.
17. Wang, D. H.; Mirau, P.; Li, B.; Li, C. Y.; Baek, J.-B.; Tan, L.-S. Chem Mater 2008, 20, 1502–1515.
18. Baek, J.-B.; Harris, F. W. Macromolecules 2005, 38, 297–306.
19. Choi, J.-Y.; Tan, L.-S.; Baek, J.-B. Macromolecules 2006, 39, 9057–9063.
20. Wesolowski, M.; Konarski, T. J Therm Anal Calorim 1999, 55, 995–1002.
21. Fyfe, C. A.; McKinnon, M. S. Macromolecules 1986, 19, 1909–1912.
22. (a) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. Macromolecules 1999, 32, 4240–4246; (b) Huber, T.; Böhme, F.; Komber, H.; Kronek, J.; Luston, J.; Voigt, D.; Voit, B. Macromol Chem Phys 1999, 200, 126–133; (c) Liu, M.; Vladimirov, N.; Fréchet, J. M. J. Macromolecules 1999, 32, 6881–6884; (d) Trollsås, M.; Löwenhielm, P.; Lee, V. Y.; Möller, M.; Miller, R. D. Hedrick, J. L. Macromolecules 1999, 32, 9062–9066.