Tailoring the Degree of Branching: Preparation of Poly(ether ester)s via Copolymerization of Poly(ethylene glycol) Oligomers (A_2) and 1,3,5-Benzenetricarbonyl Trichloride (B_3)

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Received November 30, 2004; Revised Manuscript Received February 1, 2005

ABSTRACT: A novel approach to tailor the degree of branching of poly(ether ester)s was developed based on the copolymerization of oligomeric A_2 and B_3 monomers. A dilute solution of poly(ethylene glycol) (PEG) (A_2) was added slowly to a dilute solution of 1,3,5-benzenetricarbonyl trichloride (B_3) at room temperature in the presence of triethylamine to prepare high molar mass gel-free products. PEG diols of various molar masses permitted the control of the degree of branching and an investigation of the effect of the distance between branch points. ^{1}H NMR spectroscopy indicated a classical degree of branching (DB) of 69% for a highly branched poly(ether ester) derived from 200 g/mol PEG diol. A revised definition of the degree of branching was proposed to accurately describe the branched poly(ether ester)s, and the degree of branching decreased as the molar mass of the PEG diols was increased. The effects of branching and the length of the PEG segments on the thermal properties of the highly branched polymers were investigated using differential scanning calorimetry (DSC). Amorphous branched poly(ether ester)s were obtained using PEG diols with number-average molar masses of either 200 or 600 g/mol. In-situ functionalization of the terminal acyl halide units with 2-hydroxylethyl acrylate provided novel photo-cross-linkable precursors.

Introduction

Tailored topology exerts a pronounced effect on the thermal, mechanical, and rheological properties of macromolecules.[1,2] For example, high-density polyethylene (HDPE) and low-density polyethylene (LDPE) are composed of nearly identical repeat units, which, however, exhibit dramatically different properties. Tailoring the extent and nature of branching in macromolecules has led to exquisite control of many physical properties. Branching during chain polymerization has received significant attention, and polyethylenes, for example, with diverse topologies that range from linear to dendritic structures are attainable via systematic changes in catalysts and reaction conditions.[1] Branching during step-growth polymerization also received considerable initial attention in the late 1970s for the preparation of unique branched architectures.[3−10] Linear macromolecules are typically prepared via step-growth copolymerization of either AB monomers or a combination of A_2 and B_2 monomers. On the other hand, highly branched polymers, such as hyperbranched polymers, are often prepared via the self-condensation of AB_n monomers.[11−27] Although Flory first described the synthesis of highly branched polymers via the self-condensation of AB_2 monomers or copolymerization of AB and AB_2 monomers in 1952,[11,12] hyperbranched polymers have received significant and renewed attention since the early 1990s. Webster and Kim first coined the term “hyperbranched” in the late 1980s, which referred to a dendrimer-like structure with a very high degree of branching.[13] Hyperbranched polymers are expected to exhibit inferior mechanical properties due to poor molar mass control and a lack of significant chain entanglements.[14,28] However, the continued discovery of many synthetic strategies for hyperbranched polymers and the realization of unique applications for highly branched polymers has resulted in the application of hyperbranched polymers as low-cost additives, dispersants, and compatibilizers.[20]

Other commercially viable, synthetic methods were reported earlier for the preparation of polymers with degrees of branching that range between linear and hyperbranched polymers. For example, copolymerization of A_2 and B_2 monomers with a low level of a B_3 monomer (<2 mol %) typically results in products with a very low degree of branching.[3,7,29−32] Gelation prevents the incorporation of higher levels of B_3 monomers that are required to obtain higher levels of branching. Flory also proposed the copolymerization of AB and AB_2 monomers and the corresponding degree of branching of the final structures.[11,12] This synthetic method does not result in gelation, and the molar ratio of AB to AB_2 monomers controls the degree of branching. Several families of polymers with different degrees of branching were prepared earlier based on this methodology, and the effects of branching on the physical properties were thoroughly investigated.[4,33−43] However, the limited availability of functionally nonsymmetrical AB and AB_2 monomers has prevented many industrial applications, and more facile synthetic methods are needed for further exploration of branching in macromolecules.

Recently, alternative methodologies to the polymerization of AB_n monomers for the preparation of hyperbranched polymers have received attention, and it was demonstrated that the copolymerization of A_2 and B_3 monomers proceeds without gelation.[44−60] In addition, A_2 and B_3 monomers are more readily available than AB and AB_2 monomers, which provides more facile

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10.1021/ma047534v CCC: $30.25

routes to several families of hyperbranched polymers. Our recent efforts have also focused on A_2 with B_3 synthetic methodologies in order to control the degree of branching in highly branched copolymers.[61] However, our approach involves the use of oligomers as A_2 or B_3 monomers for copolymerization without gelation. Although the reaction methodology is similar to the polymerization of low molar mass A_2 and B_3 monomers, the degree of branching was effectively tailored via the oligomeric A_2 or B_3 molar mass. Thus, macromolecules with a range of branched topologies were prepared without AB or AB_n monomers. Moreover, the final products exhibited a well-defined distance between B units due to the use of relatively narrow molar mass distribution A_2 oligomers. In contrast, branched polymers that are derived from the copolymerization of AB and AB_n monomers have a more ill-defined chain length between branch points.

This paper specifically describes the preparation of poly(ether ester)s with different degrees of branching via an oligomeric A_2 with B_3 methodology. These novel branched architectures are both fundamentally interesting and commercially viable. Poly(ethylene glycol) (PEG) is a semicrystalline, water-soluble thermoplastic that is used in a wide range of applications such as biocompatible materials, drug and gene delivery, optical devices, cosmetics, and thermoplastic elastomers.[62] Poly(ethylene oxide)s that contain alkali metal salts also exhibit acceptable mechanical properties and ionic conductivity.[63,64] Hawker and co-workers have reported the preparation of hyperbranched poly(ether ester)s as a new class of ion conducting materials via AB_2 condensation.[65] The introduction of branching in the polymer backbone disrupted crystallinity and completely amorphous polymers were obtained. However, a multistep synthesis of complex AB_2 monomers was required prior to polymerization, and the distance between branch points was significantly less than the critical molar mass for entanglement. The one-step oligomeric A_2 and B_3 methodology based on PEG diols offers a more facile approach to products with improved properties and performance. In addition, new applications such as highly branched poly(ether ester)s with ethyl acrylate end groups were also prepared to obtain photo-cross-linkable precursors.

Experimental Section

Materials. Ethylene glycol (EG), diethylene glycol (DEG), poly(ethylene glycol) (PEG) (M_n: 200, 600, 2000, and 3400 g/mol), 1,3,5-benzenetricarbonyltrichloride (BTC) (99%), anhydrous triethylamine (TEA) (99%), dimethyl isophthalate (DMI), titanium tetraisopropoxide (99%), 2-hydroxyethyl acrylate (96%) (2-HEA), phenol (99+%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%) were purchased from Aldrich. Chloroform was purchased from Burdick and Jackson (high purity), and methanol was purchased from EM Science. Chloroform and TEA were stirred over calcium hydride and distilled under nitrogen. EG, DEG, and PEG diols were dried in a vacuum oven (0.50 mmHg) at 70 °C for 18 h prior to polymerization. All other reagents were used as received unless otherwise stated.

Synthesis of Poly(ether ester)s. Synthesis of Linear Poly(ether ester)s from PEG-200 (L-200), PEG-600 (L-600), and PEG-2000 (L-2000) (L Denoting "Linear", xxx Denoting the PEG Precursor M_n). A single-neck, 250 mL round-bottomed flask was charged with 10.00 g of DMI (0.051 mol) and 10.30 g of PEG-200 (0.051 mol). Titanium tetraisopropoxide (20 ppm) was added to facilitate transesterification. The reaction flask, which contained the monomers and the catalyst, was degassed using vacuum and nitrogen three times and subsequently heated to 180 °C. The reactor was maintained at 180 °C for 2 h, and the temperature was increased to 200 °C over 2 h. Vacuum was applied (0.5 mmHg) for 30 min to ensure the removal of methanol. A similar synthetic method was used to prepare linear poly(ether ester)s from PEG-600 (L-600) and PEG-2000 (L-2000) with the exception that equimolar amounts of PEG-600 and PEG-2000 were used with DMI.

Synthesis of a Branched Poly(ether ester) from PEG-200 with Methyl Ester Terminal Groups (HB-200-Me-1) (HB-xxx-Me-*y*, HB Denoting "Highly Branched", xxx Denoting the PEG Precursor M_n, Me Denoting Methyl Ester Terminal Groups, *y* Denoting Sample Number). BTC (10.00 g, 0.038 mol) was dissolved in 70 mL of freshly distilled chloroform in a dried, 250 mL two-necked flask equipped with a magnetic stir bar and addition funnel. PEG-200 (7.54 g, 0.038 mol) and TEA (11.41 g, 0.113 mol) were dissolved in 80 mL of freshly distilled chloroform and transferred into the addition funnel. The oligomer solution was slowly added to the reaction flask over 2 h, and a homogeneous reaction was maintained at ambient temperature for 24 h. Excess methanol was subsequently added to quench the terminal acid chloride end groups, and the homogeneous solution was stirred for 6 h. The solution was washed with deionized water three times and precipitated into hexane at ~0 °C. A waxy, pale yellow product was collected and dried at 60 °C in a vacuum oven for 24 h. Typical yields ranged from 90 to 95%. ^{1}H NMR (chloroform-*d*, ppm): 8.70−8.95 (3H, aromatic protons from BTC), 3.50−4.60 (4H, protons from PEG, 3H, protons from methyl ester terminal unit), 4.44 ($-NCH_2CH_3$), 1.42 ($-NCH_2CH_3$). ^{13}C NMR (chloroform-*d*, ppm): 164.9 ($O{=}C{-}OCH_3$, methyl ester end groups), 164.4 ($O{=}C{-}OCH_2CH_2{-}$), 134.2 and 130.7 (BTC), 70.3, 68.7, and 64.4 (PEG), 52.3 ($-OCH_3$, methyl ester end groups), 61.4 and 13.9 ($-NCH_2CH_3$, TEA salt).

Synthesis of Branched Poly(ether ester)s from PEG-600 (HB-600-Me-*y*), PEG-2000 (HB-2000-Me-*y*), and PEG 3400 (HB-3400-Me) with Methyl Ester Terminal Groups. The synthetic method was similar to HB-200-Me-1 preparation with the exception that different poly(ethylene glycol)s were used as A_2 oligomers at the concentrations and reaction times in Table 1.

Synthesis of a Branched Poly(ether ester) from PEG-200 with Phenyl Ester Terminal Groups (HB-200-Ph) (HB-xxx-Ph, HB Denoting "Highly Branched", xxx Denoting the PEG Precursor M_n, Ph Denoting Phenyl Ester Terminal Groups). The synthetic method was similar to HB-200-Me-1 preparation with the exception that phenol (3.57 g, 0.038 mol) was dissolved in 10 mL of freshly distilled chloroform and added dropwise into the reaction flask over 30 min in place of the excess methanol. The homogeneous solution was stirred for 12 h, subsequently washed with deionized water three times, and precipitated into hexane at ~0 °C. A waxy, pale yellow product was collected and dried at 60 °C in a vacuum oven for 24 h. ^{1}H NMR (chloroform-*d*, ppm): 8.70−9.15 (3H, aromatic protons from BTC), 6.80−7.60 (aromatic protons from phenyl ester terminal unit), 3.50−4.60 (4H, protons from PEG), 4.44 ($-NCH_2CH_3$), 1.42 ($-NCH_2CH_3$). ^{13}C NMR (chloroform-*d*, ppm): 164.4 ($O{=}C{-}OCH_2CH_2{-}$), 163.1 ($O{=}C{-}O{-}Ar$, phenyl ester end groups), 150.2, 130.2, 125.9, and 121.1 ($O{=}C{-}O{-}Ar$, phenyl ester end groups) 134.2 and 130.7 (BTC), 70.3, 68.7, and 64.4 (PEG), 61.4 and 13.9 ($-NCH_2CH_3$, TEA salt).

Synthesis of Branched Poly(ether ester)s from EG (HB-EG-Ph), DEG (HB-DEG-Ph), and PEG-600 (HB-600-Ph) with Phenyl Ester Terminal Groups. The synthetic method was similar to HB-200-Ph preparation (at 0.40 M) with the exception that equimolar amounts of EG, DEG, and PEG-600 were used as A_2 oligomers to prepare HB-EG-Ph, HB-DEG-Ph, and HB-600-Ph, respectively.

**Synthesis of a Branched Poly(ether ester) from PEG-200 with Ethyl Acrylate (25 mol %) and Methyl Ester (75 mol %) Terminal Groups (HB-200-EA-1) and Subsequent Photo-Cross-Linking Using UV Light (HB-200-EA-*y*, HB

Table 1. Characterization Data for Linear and Highly Branched Poly(ether ester)s

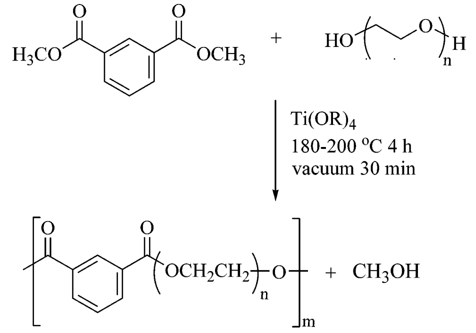
sample	A_2[a] (g/mol)	[M][b] (mol/L)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	[η][d] (dL/g)	α[e]	T_g (°C)	T_c (°C)	T_m (°C)
HB-200-Me-1	200	0.25	1230	12 300	56 500	0.065	0.284	−17		
HB-200-Me-2	200	0.40	1470	17 500	74 600	0.074	0.330	−15		
HB-200-Me-3[c]	200	0.40	1260	16 200	73 900	0.060	0.265	−17		
HB-200-Me-4	200	0.45	780	9 410	55 500	0.063	0.288	−14		
L-200	200		5970	15 900	24 800	0.176	0.569	−22		
HB-600-Me-1	600	0.10	1420	4 240	11 900	0.071	0.411	−53	−10	4
HB-600-Me-2	600	0.12	1660	9 860	29 600	0.100	0.396	−50		
HB-600-Me-3	600	0.16	2070	32 600	171 000	0.172	0.416	−53		
L-600	600		3940	11 300	17 400	0.172	0.581	−51	−19	8
HB-2000-Me-1	2000	0.10	6050	27 100	81 000	0.259	0.513	−43		40
HB-2000-Me-2	2000	0.12	5360	23 800	68 000	0.238	0.498	−51		40
HB-2000-Me-3	2000	0.15	2130	7 060	15 000	0.148	0.490	−42		40
L-2000	2000		7550	17 100	25 100	0.256	0.621			47
HB-3400-Me	3400	0.10	9860	35 200	120 000	0.340	0.550			47

[a] Number-average molar mass of PEG diols as A_2 oligomers. [b] Final concentration in highly branched poly(ether ester) synthesis. [c] Reaction time was 12 h. [d] *N,N*-Dimethylformamide/0.01 M $LiNO_3$, 35 °C. [e] α = Mark−Houwink exponent.

Denoting "Highly Branched", 200 Denoting PEG-200 Precursor, EA Denoting Ethyl Acrylate Terminal Groups, *y* Denoting Sample Number). BTC (10.00 g, 0.038 mol) was dissolved in 35 mL of freshly distilled chloroform in a dried, 250 mL two-necked flask equipped with a magnetic stir bar and addition funnel. PEG-200 (7.54 g, 0.038 mol) and TEA (11.41 g, 0.113 mol) were dissolved in 60 mL of freshly distilled chloroform and transferred into the addition funnel. The solution was slowly added to the reaction flask over 2 h, and the homogeneous reaction was maintained at ambient temperature for 12 h. The functionalization of branched polymers with 2-HEA, isolation processes, and the polymer film preparation were conducted with minimized light exposure; the reaction flask and addition funnel were covered with aluminum foil to avoid exposure to laboratory light. 2-HEA (1.10 g, 0.01 mol) was dissolved in 5 mL of freshly distilled chloroform and added to the reaction flask dropwise over 10 min. The homogeneous reaction was maintained at ambient temperature for 6 h, excess methanol was added to quench the remaining terminal acid chloride end groups, and the homogeneous solution was stirred for 6 h. The solution was washed with deionized water three times and precipitated into hexane at ~0 °C. A waxy, pale yellow product was collected and dried at room temperature in a vacuum oven for 96 h. ^{1}H NMR (chloroform-*d*, ppm): 8.70−8.95 (3H, aromatic protons from BTC), 3.50−4.60 (4H, protons from PEG, 3H, protons from 75 mol % methyl ester terminal unit, 4H, protons from 25 mol % ethyl acrylate terminal unit, $-OCH_2CH_2OCOCHCH_2$), 5.80−6.50 (3H, protons from 25 mol % ethyl acrylate terminal unit, $-OCH_2CH_2OCOCHCH_2$), 4.44 ($-NCH_2CH_3$), 1.42 ($-NCH_2CH_3$).

A 30 wt % solution of dried polymer was prepared in chloroform, and 4 wt % DMPA was added. Thin films were directly cast onto glass slides from the homogeneous solution and allowed to stand at ambient temperature for 24 h in the absence of light. The average thickness of the polymer films was ~12 μm. Completely dried films on glass slides were passed through a Fusion UV system (model LC-6B benchtop conveyor) at 10 ft/min at approximately 3.73 W/cm² (UVA) to initiate photo-cross-linking. Soxhlet extraction with chloroform was performed for 24 h on the photo-cross-linked films, and the gel content was determined upon drying at 60 °C.

Scheme 1. Synthesis of Linear Poly(ether ester)s via Melt Polymerization



Characterization. ^{1}H NMR spectroscopic analyses were performed on a Varian Unity 400 MHz spectrometer at ambient temperature. Size-exclusion chromatography (SEC) with viscometry detection (Viscotek model 110) in *N,N*-dimethylformamide (DMF) containing 0.01 M lithium nitrate at 35 °C using three Polymer Standards Services Gram Linear 8 × 300 mm columns was used to determine molar mass. Absolute molar masses were calculated from viscosity data based on a universal calibration curve that was constructed from narrow molar mass distribution poly(methyl methacrylate) standards. Thermal transition temperatures were determined using a Perkin-Elmer Pyris-1 at 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. MALDI-TOF/MS analyses were performed on a Kompact SEQ instrument using 100−180 power setting in positive ion linear mode. Laser wavelength was 337 nm, and the accelerating voltage was 20 kV in delayed extraction mode. The targets were prepared from a tetrahydrofuran (THF) solution with dithranol as the matrix and potassium trifluoroacetate as the cationization reagent. The concentration of the matrix, dithranol, was 10 g/L, and the cationization reagent concentration was 1 g/L. Polymer samples were also dissolved in THF at 10 g/L, and the three solutions were mixed at a ratio of 8:1:1 matrix:salt:polymer.

Results and Discussion

Polymerization. Two methods of step-growth polymerization were used to prepare poly(ether ester)s with degrees of branching ranging from linear analogues to highly branched polymers. Linear analogues with various distances between ester units were prepared via melt polymerization of DMI and PEG diols (Scheme 1). Compared to previous polyester products that were prepared using a similar methodology,[66−69] relatively low molar mass products were desired, and the linear analogues had absolute weight-average molar masses that were comparable to branched products prepared via the copolymerization of A_2 oligomers and a B_3 monomer (Table 1). A low amount of a trifunctional agent (typically 0.1−1.0 mol %) may be incorporated to prepare lightly branched polyesters via melt polymerization; however, gelation occurs at relatively low concentrations of trifunctional agent (>1.5 mol %), and a high degree of branching is not achievable.[70] To prepare highly branched polymers without gelation, the copolymerization of various molar mass PEG diols (A_2 oligomers) and a B_3 monomer was conducted in dilute solution. In an attempt to control the distance between branch points, PEG diols that have molar masses ranging from 200 to 3400 g/mol with very low molar

Scheme 2. Synthesis of Methyl Ester-Terminated Highly Branched Poly(ether ester)s via Polymerization of A_2 and B_3 Monomers

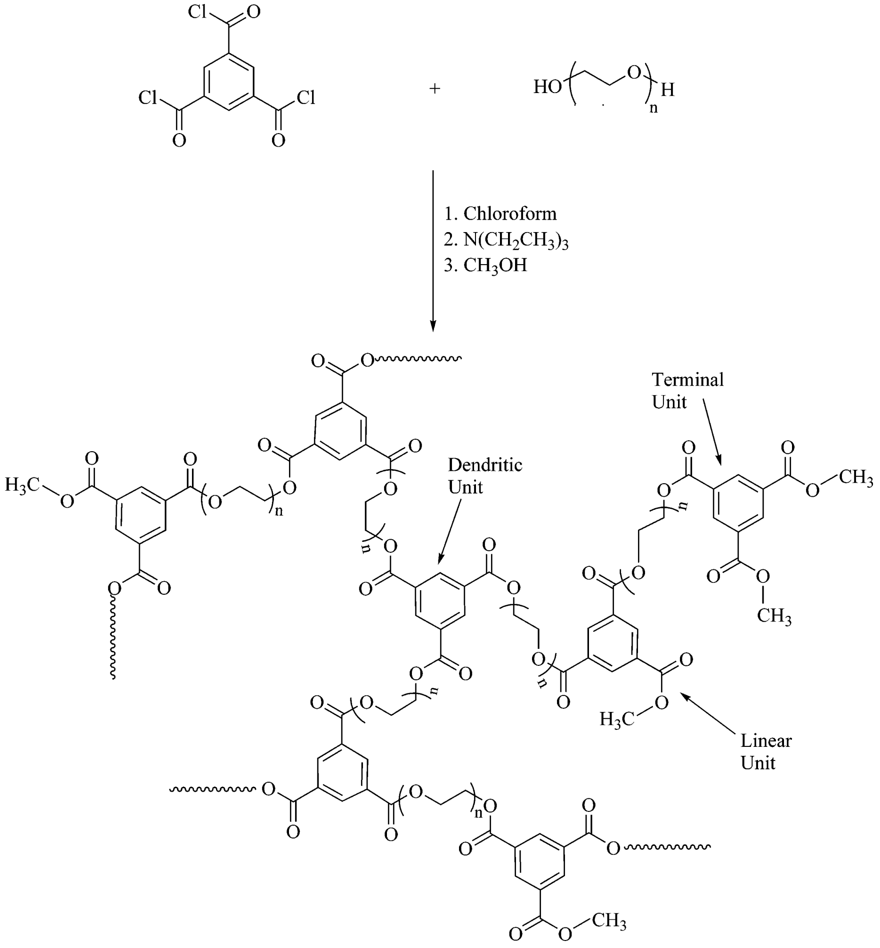


Table 2. Characterization of PEG Diols as A_2 Oligomers

A_2 (g/mol)	n^a	M_w/M_n	T_g (°C)	ΔC_p (J/(g °C))	T_m (°C)	ΔH (kJ/g)
200	4.1	1.02^b	−85	3.0		
600	13.2	1.02^b	−58	0.8	20	0.37
2000	45.0	1.05^c			52	0.47
3400	76.8	1.07^c			53, 59	0.09, 0.35

[a] Average number of repeat units. [b] Determined by MALDI-TOF/MS analysis. [c] Determined by SEC analysis.

mass distributions were used as A_2 oligomers (Table 2). Earlier studies have shown that copolymerization of low molar mass A_2 and B_3 monomers will result in a network. Moreover, a slow addition of A_2 to B_3 monomer in dilute solution avoids gelation, and hyperbranched aromatic polyesters were prepared earlier in a controlled fashion via low molar mass A_2 and B_3 copolymerization.[58,59] Thus, copolymerization of oligomeric A_2 with B_3 monomers for the preparation of branched poly(ether ester)s was utilized in our laboratories based on the slow addition approach (Scheme 2).

Others have reported reaction conditions that influence the final product in low molar mass A_2 and B_3 polymerization in dilute solution, and the type of solvent, order of monomer addition, monomer reactivity, reaction temperature, monomer concentration, reaction time, molar ratio of the monomers, and terminal groups are important parameters.[46,49,51,55,58,59] In our studies, chloroform was a suitable solvent for the oligomeric A_2 and B_3 copolymerization as both the starting materials, and the branched products were completely soluble in chloroform. The order of monomer addition was necessary to maintain a homogeneous, gel-free solution, and this observation was consistent with our earlier reports.[58,59] When a dilute solution of B_3 monomer was added to a dilute solution of A_2 oligomer, highly cross-linked products were obtained regardless of the rate of addition. In contrast, slow addition of the oligomeric A_2 solution to the B_3 solution yielded branched polymers. Recently, Fossum and Czupik demonstrated that the development of branched structures was dependent on the order of monomer addition.[60] When the A_2 monomer solution was added to the B_3 monomer solution, the initial products had linear topologies due to the excess of B_3 monomers. Slightly branched products were subsequently formed, and finally highly branched products formed through the continued addition of A_2 monomer. On the other hand, when the B_3 monomer solution was added to the A_2 monomer solution, the initial product was highly branched. In contrast to these earlier studies, the enhanced acid chloride reactivity in our approach significantly increased the risk of premature gelation. As a result, only the slow addition of PEG diol (A_2 oligomer) solution to the BTC (B_3) monomer solution was suitable for the preparation of highly branched products in the absence of gelation.

The polymerizations were conducted at room temperature, which is typical for the reaction of an acid chloride with an alcohol in the presence of TEA. As summarized in Table 1, monomer concentration, [M], has no obvious influence on the molar mass and the polydispersity of the final products. In general, the molar mass increases

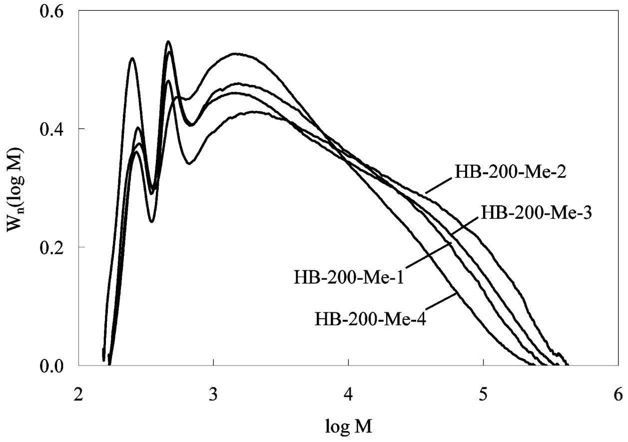


Figure 1. Molar mass distributions for highly branched poly(ether ester)s based on PEG-200.

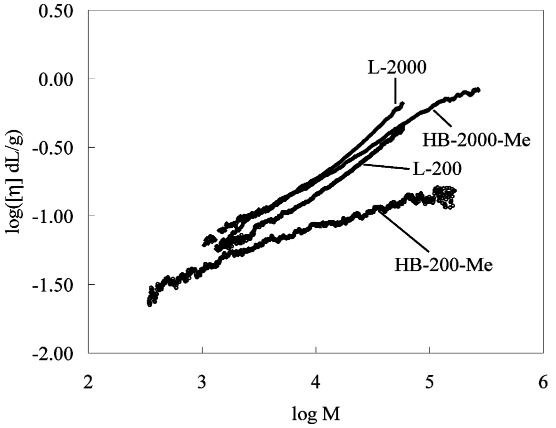


Figure 2. Mark−Houwink plots for PEG-200 and PEG-2000 based linear and highly branched poly(ether ester)s.

with increasing [M] for PEG-600, decreases with increasing [M] for PEG-2000, and changes nonsystematically for the samples derived from PEG-200. HB-2000-Me-3 (0.15 M) had a considerably lower molar mass than HB-2000-Me-1 (0.10 M) and HB-2000-Me-2 (0.12 M). Lower molar mass HB-2000-Me-3 was attributed to limited solubility of the A_2 oligomer and the branched products at higher concentrations. TEA salt that is generated during polymerization may also affect solubility during polymerization. At 0.18 M final monomer concentration for PEG-2000, premature gelation occurred during the polymerization. Similarly, gelation was observed at 0.50 and 0.18 M final monomer concentrations when PEG-200 and PEG-600 were used, respectively. In most cases, reactions were allowed to proceed for 24 h to ensure complete conversion; however, a branched polymer that was derived from PEG-200 was allowed to polymerize for 12 h (HB-200-Me-3), and a similar molar mass and polydispersity were obtained (HB-200-Me-2). Molar mass distributions broaden with increasing weight-average molar mass, as shown in Figure 1. Typical examples of Mark−Houwink plots (Figure 2) illustrate the effects of A_2 monomer length on dilute solution viscosity. Linear poly(ether ester) that was derived from PEG-2000 (L-2000) had a higher viscosity than linear poly(ether ester) derived from PEG-200 (L-200) at equivalent molar mass, indicating a more highly swollen or a less dense structure. A linear polymer derived from PEG-600 (L-600) (not shown) is intermediate between L-200 and L-2000. Highly branched poly(ether ester)s that were derived from PEG-200 had lower viscosities at equivalent molar mass than their linear analogues. The difference between the viscosities of linear and highly branched poly(ether ester)s derived from PEG-2000 is also apparent in Figure 2; however, it is less than the PEG-200 example, indicating a less highly branched structure. Highly branched poly(ether ester)s that are derived from PEG-600 (not shown) are also intermediate between the polymers derived from PEG-200 and PEG-2000. The slope of each curve in Figure 4 provides the Mark−Houwink constant (α) for each sample, which are also listed in Table 1. The value of α is known to be between 0.65 and 0.75 for linear random coils in a good solvent, whereas the value is approximately 0.25 for hyperbranched structures.[17,19,26] The value of α was in the range of 0.55−0.62 for linear poly(ether ester)s (L-200, L-600, L-2000). Highly branched poly(ether ester)s derived from PEG-200 (HB-200-Me) had much lower α values (approaching 0.25), which indicated a more compact or highly branched structure. As the distance between the B_3 units was increased to 600 (HB-600-Me) and 2000 (HB-2000-Me), α values increased and approached values of linear analogues, which indicated that the branching decreased as the length of A_2 oligomer was increased. As reported previously, the intersection of the branched and linear curves determines the approximate distance between the branch points.[71] As shown in Figure 2, such intersection occurs at $M > 5000$ for L-2000 and HB-2000-Me. The molar mass distribution of L-200 does not extend low enough to observe this intersection; however, if extended, the distance between the branch points would be much less than the PEG-2000 example. Overall, the viscosity of highly branched poly(ether ester)s compared to the linear analogues is consistent with the formation of branched architectures that differ in molar mass between branch points.

An explanation that accounts for successful polymerization of A_2 and B_3 monomers without gelation remains unclear. According to Flory, only low molar mass products are obtained since gelation occurs at very low monomer conversions.[11,12] However, Flory's theory is based on the following assumptions: (1) the reactivity of the functional groups remains constant during polymerization, and (2) the reactions do not involve cyclization. Deviations from these assumptions shift the gel point to higher conversions and the polymerizations result in high molar mass, highly branched structures.[55−57] Jikei and co-workers proposed that when a reaction was kinetically controlled, the first condensation reaction of A_2 and B_3 was faster than subsequent propagation and A-ab-B_2 type intermediates were formed.[46] Kricheldorf and co-workers reported that cyclization during polymerization was the major factor responsible for the gel point shift, and various cyclic species were identified using MALDI-TOF analysis.[55,57] In our studies, highly reactive acid chloride groups were used as B units, and it was assumed that cyclization prevented gelation in dilute solution. As a result of cyclization, a relatively large amount of low molar mass species is expected in the final product. As shown in Figure 3, MALDI-TOF analysis of HB-200-Me-2 indicated the complete consumption of PEG precursor and the presence of low molar mass species in the 600−1000 *m/z* range. The molar mass distribution in Figure 3 arises from the molar mass distribution of PEG-200 precursor with a mass difference of ~44 Da. Because of

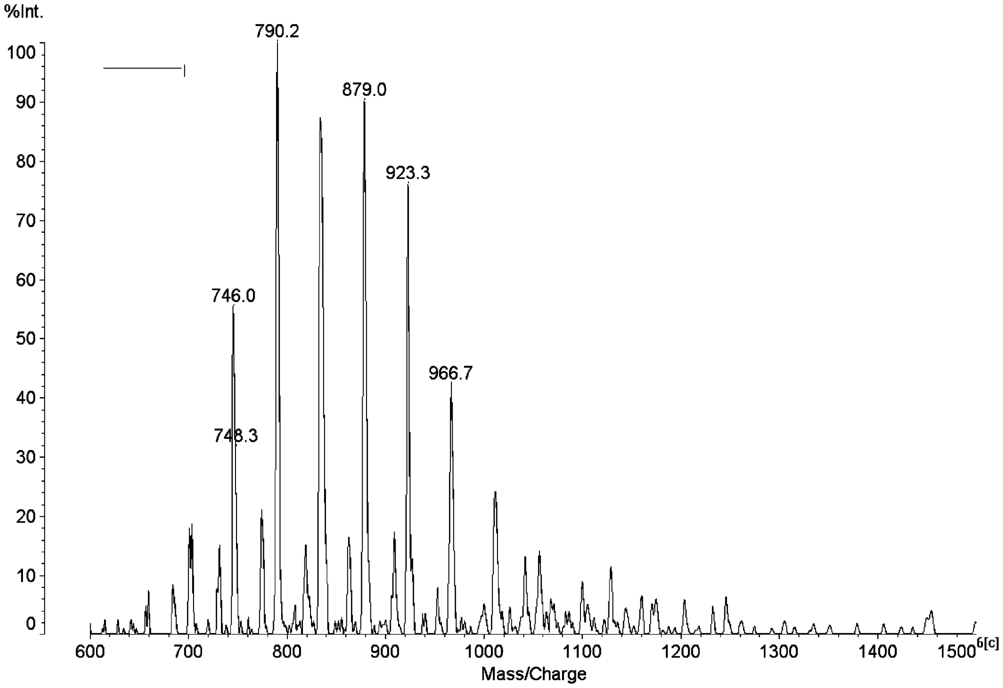


Figure 3. MALDI-TOF spectra of HB-200-Me-2.

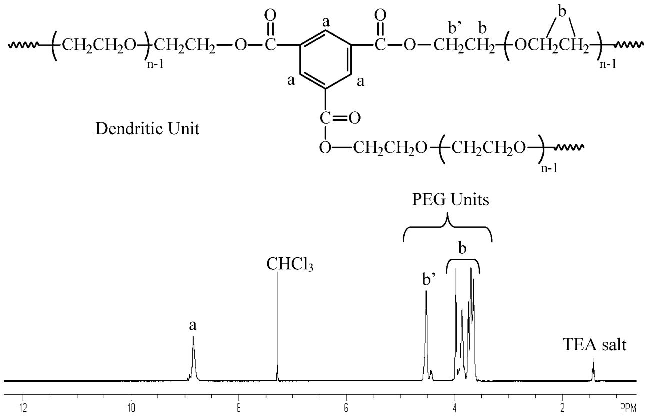


Figure 4. ^{1}H NMR spectrum of a methyl ester-terminated highly branched poly(ether ester) (HB-200-Me-2, 400 MHz, $CDCl_3$).

the molar mass distribution that arises from the PEG-200 precursor, a confident assignment of the chemical structures for these low molar mass species was not possible. However, these low molar mass compounds are presumed to be oligomeric or cyclic structures, which are characteristic of $A_2 + B_3$ polymerization. The critical concentrations for gelation when various molar mass PEG diols were used as A_2 oligomers also supported the occurrence of cyclization. In a previous report, when bisphenol A, a relatively rigid diol, was used as the A_2 monomer, the critical concentration (0.08 M) for gelation was significantly lower.[59] Consequently, it was assumed that cyclization was less pronounced for bisphenol A due to limited conformational mobility relative to PEG diols, and the higher final monomer concentrations that were required to obtain gel-free high molar mass products from A_2 oligomers suggested the occurrence of cyclization.

In-situ functionalization of the highly branched polymers was a powerful tool, especially at a molar ratio of A_2:B_3 = 1:1. A 1:1 molar ratio of A_2:B_3 corresponds to a 2:3 stoichiometric ratio of functional groups ([A]:[B]), and it was expected that the excess acid chloride functional groups were the terminal groups on the final branched polymers. The terminal acid chloride groups were reacted with methanol via in-situ functionalization to obtain methyl ester end groups, and structural characterization of the final products (Figure 4) was attempted using ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopic analysis was not quantitative with respect to the concentration of end groups in the methyl ester-terminated poly(ether ester)s; the resonances that were indicative of methyl ester protons (3.5 ppm) and poly(ethylene glycol) protons (3.5−4.5 ppm) overlapped. Moreover, ^{1}H NMR spectroscopy did not provide quantitative analysis of the dendritic, terminal, and linear units in the polymer backbone due to overlap of the aromatic protons corresponding to each unit. Thus, phenyl ester terminal groups, as described below, were pursued to determine the degree of branching. ^{1}H NMR spectroscopy also indicated the presence of low levels of residual TEA salts (5−8 mol %) (1.42 and 4.44 ppm) after purification (Figure 4).

Degree of Branching. Several equations were developed earlier to define the structure of hyperbranched polymers based on the self-condensation of AB_2 monomers.[13,15] In most cases, these equations are also applicable to the products of A_2 and B_3 polymerization. If the highly branched products, which contain the oligomeric A_2 unit, were considered hyperbranched in a fashion similar to earlier poly(arylene ester)s,[59] then each oligomer between two branch points was considered a single repeat unit. Thus, the degree of branching based on BTC units was calculated according to the Fréchet definition.[16] The degree of branching (DB) was described as the ratio of the sum of all fully branched and terminal units to the total number of units

$$\mathrm{DB} = (D + T)/(D + T + L) \qquad (1)$$

where D, T, and L correspond to total number of dendritic, terminal, and linear units, respectively. To determine the degree of branching in these branched

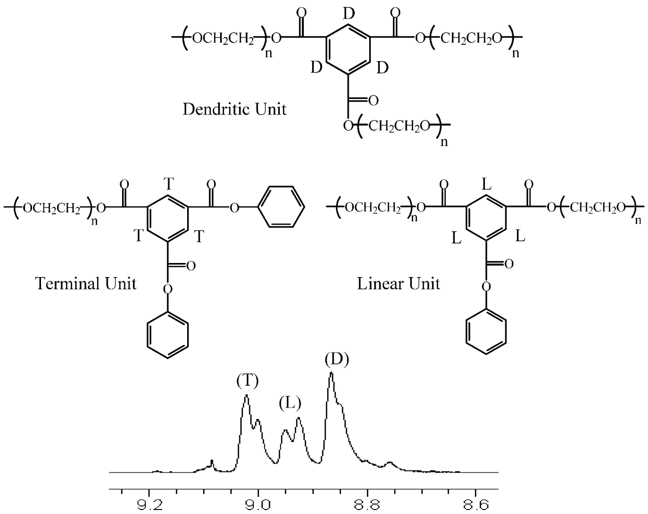


Figure 5. Aromatic region of ^{1}H NMR spectrum of a phenyl ester-terminated highly branched poly(ether ester) (HB-200-Ph, 400 MHz, $CDCl_3$).

Table 3. Degree of Branching of Highly Branched Poly(ether ester)s Using a Revised Equation

sample	A_2	n^a	classical DB (%)	revised DB (%)
HB-EG-Ph	ethylene glycol	1.0	62	31
HB-DEG-Ph	diethylene glycol	2.0	63	21
HB-200-Ph	PEG-200	4.1	69	14
HB-600-Ph	PEG-600	13.2	66	5

[a] Average number of repeat units in A_2 precursors.

poly(ether ester)s, acid chloride terminal units were reacted with phenol to afford phenyl ester-terminated poly(ether ester)s. The phenyl ring has increased electron-withdrawing capability relative to alkyl ester end groups. Thus, the phenyl ester end groups provided a higher resolution of the aromatic protons that corresponded to dendritic, terminal, and linear units and permitted an improved deconvolution of the resonances in the aromatic region (Figure 5). Resonances were assigned based on our earlier model compounds for hyperbranched poly(arylene ester)s.[59] Moreover, ^{13}C NMR spectroscopy of methyl ester-terminated poly(ether ester)s and phenyl ester-terminated poly(ether ester)s confirmed the structure and the quantity of both end groups. In this study, the chemical structures of the products were intermediate between linear and highly branched topologies since the A_2 oligomers have a relatively high molar mass. The Fréchet definition accurately described the branching structures only when each oligomer between the branch points was considered as a single repeat unit. Using eq 1, the degree of branching of the poly(ether ester)s that were derived from EG, DEG, PEG-200, and PEG-600 ranged from 62 to 69 mol % (Table 3). To properly characterize the oligomeric A_2 and B_3 products herein, eq 1 was revised as

$$\mathrm{DB} = (D + T)/(D + L + T + n) \tag{2}$$

where n was defined as the number of repeat units in the linear oligomer, and D, T, and L were defined as the dendritic, terminal, and linear units of BTC, respectively. As a result, the degree of branching of poly(ether ester)s that were derived from EG, DEG, and PEG oligomers decreased dramatically. As summarized in Table 3, the degree of branching for branched poly(ether ester)s decreased as the molar mass of PEG oligomers increased. Consequently, the oligomeric A_2 and B_3 polymerization was an effective method to prepare polymers with a range of DB values.

Thermal Analysis. The PEG oligomers with number-average molar masses (M_n) of 200 and 600 g/mol have glass transition temperatures (T_g) of −85 and −58 °C, respectively (Table 2). In addition, PEG-600 has a melting temperature (T_m) of 20 °C. Branched poly(ether ester)s derived from PEG-200 had glass transition temperatures ranging from −14 to −17 °C (Table 1). As expected, because of the presence of aromatic branch points (62−69 mol %), the branched poly(ether ester)s had higher glass transition temperatures than the precursor oligomers and linear analogues based on PEG-200 (L-200) also exhibited a T_g that was relatively close to the highly branched polymer (−22 °C).

Highly branched poly(ether ester)s that were prepared using an oligomeric A_2 with longer ethylene glycol chains (PEG-600) exhibited interesting thermal behavior depending on the final molar mass. The lower molar mass HB-600-Me-1 was semicrystalline with a T_g of −51 °C, crystallization temperature (T_c) of −10 °C, and a T_m of 4 °C. Similarly, a distinct crystallization and a melting peak were observed for the linear L-600. The linear and low molar mass branched poly(ether ester)s derived from PEG-600 had slower crystallization rates than the PEG-600 precursor. As the molar mass of the branched poly(ether ester) increased, the crystalline melting peak disappeared. Indeed, HB-600-Me-2 and HB-600-Me-3 exhibited a T_g of −50 and −53 °C, respectively; however, a T_c and T_m were not detected using identical DSC conditions.

The PEG-2000 and PEG-3400 precursors were highly crystalline and exhibited a T_m of 52 and 53−59 °C, respectively. It was reported earlier[65] that higher molar mass, linear poly(ethylene oxide)s (M_n = 15 000 g/mol) also have a T_g at −67 °C; however, a T_g was not evident for the PEG-2000 and PEG-3400 precursors under the DSC conditions used in this study. The linear poly(ether ester) based on PEG-2000 (L-2000) was also semicrystalline with a T_m of 47 °C. However, the branched poly(ether ester)s based on PEG-2000 (HB-2000-Me-1, HB-2000-Me-2, and HB-2000-Me-3) had T_g values ranging from −42 to −51 °C and a depressed T_m at 40 °C relative

Table 4. Summary of UV-Cross-Linking Experiments of Highly Branched Poly(ether ester) with Ethyl Acrylate Terminal Groups

sample	ethyl acrylate terminal groups (mol %)	A_2 (g/mol)	[M] (g/mol)	T_g (°C)^a	gel fraction (%)^b	T_g (°C)^b
HB-200-EA-1	25	200	0.45	−12	81	13
HB-200-EA-2	50	200	0.45		premature cross-linking	
HB-200-EA-3	100	200	0.45		premature cross-linking	

[a] Before UV-cross-linking [b] After UV-cross-linking.

to both the A_2 oligomer (PEG-2000) and the linear poly(ether ester) based on PEG-2000 (L-2000). These results are consistent with the crystallization behavior of branched polymers.[13] As the chain length of PEG precursor was increased to 3400 g/mol, only a depressed T_m at 47 °C was observed for the branched poly(ether ester) (HB-3400-Me) when compared to the PEG-3400 precursor with T_m of 53 and 59 °C. As clearly shown, highly branched poly(ether ester)s have a lower degree of crystallinity. Decreased crystallinity of PEG based ion conducting polymeric materials is an important phenomenon in terms of providing enhanced ion mobility.[64] A more detailed investigation of the morphology of this family of branched polymers and ion conductivity measurements will be reported in the future.

UV Cross-Linking. As summarized in Table 4, the branched poly(ether ester)s cross-linked during isolation of the products when the polymer contained 50 mol % (HB-200-EA-2) and 100 mol % (HB-200-EA-3) ethyl acrylate terminal groups. The branched poly(ether ester) with 25 mol % ethyl acrylate terminal groups (HB-200-EA-1) was isolated successfully without premature cross-linking. Soxhlet extraction using chloroform was subsequently conducted after the UV-cross-linking of HB-200-EA-1**.** The UV-cross-linked films typically contained 80 wt % gel. In addition, the T_g increased from −12 to 13 °C upon cross-linking, and a less tacky, free-standing film was prepared.

Conclusions

Oligomeric A_2 and B_3 polymerization is an effective method to control the degree of branching. A series of poly(ether ester)s with various degrees of branching were prepared via the addition of a dilute solution of PEG oligomer to a dilute solution of triacid chloride in the presence of TEA. The reaction conditions such as solvent, order of monomer addition, monomer reactivity, temperature, monomer concentration, reaction time, and type of terminal groups exerted pronounced effects on the properties of the branched copolymers. A revised equation was proposed to accurately determine the degree of branching of the final products, and the calculated results demonstrated that the degree of branching of highly branched poly(ether ester)s decreased with an increase in the molar mass of the oligomeric A_2 precursor. The relationship between intrinsic viscosity and molar mass also supported that products that were derived from lower molar mass PEG diols had more highly branched structures. Branched poly(ether ester)s based on PEG-200 and PEG-600 precursors were amorphous, and semicrystalline polymers were obtained from the higher molar mass PEG precursors (PEG-2000 or PEG-3400). Moreover, the branched polymers from PEG-200 were in-situ functionalized to obtain ethyl acrylate-terminated polymers. The ethyl acrylate-terminated polymers were UV-cross-linked to form less tacky, free-standing films with high gel contents.

Acknowledgment. This material is based upon work supported in part by the U.S. Army Research Laboratory and U.S. Army Research Office under Grant DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also thank Eastman Chemical Co. for financial support.

Supporting Information Available: ^{13}C NMR spectra of HB-200-Me-2 and HB-200-Ph. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA047534V