Highly Branched Poly(ether ester)s via Cyclization-Free Melt Condensation of A_2 Oligomers and B_3 Monomers

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ABSTRACT: This paper reports the first synthesis of $A_2 + B_3$ highly branched polyesters with the minimal formation of cyclics in the absence of a polymerization solvent. Highly branched poly(ether ester)s were synthesized in the melt phase using an oligomeric $A_2 + B_3$ polymerization strategy. Condensation of poly(propylene glycol) (M_n ~1060 g/mol) and trimethyl 1,3,5-benzenetricarboxylate in the presence of titanium tetraisopropoxide generated highly branched structures with high molar mass when the reaction was stopped immediately prior to the gel point. Size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy were used to monitor molar mass as a function of monomer conversion and to determine the gel point. Monomer conversions at both the theoretical and experimental gel points for an A_2:B_3 = 1:1 molar ratio agreed well. Thus, cyclization reactions, which are common in $A_2 + B_3$ polymerization in solution, were negligible in the melt phase. The degree of branching (DB) increased with an increase in monomer conversion and molar mass, and the final product contained 20% dendritic units. Monofunctional end-capping reagents were also used to avoid gelation in the melt phase, and high molar mass final products were obtained with nearly quantitative monomer conversion in the absence of gelation. The presence of a monofunctional comonomer did not affect the molar mass increase or the formation of branched structures due to desirable ester interchange reactions.

Introduction

Hyperbranched polymers have emerged as popular alternatives to dendrimers in the past 15 years.[1−4] Dendrimers are perfectly branched macromolecules that are synthesized via multistep divergent or convergent methods,[5] whereas hyperbranched polymers possess structural irregularities but are typically synthesized with much less effort.[1−4] Despite few irregularities in branching, hyperbranched macromolecules possess similar characteristics to dendrimers such as low hydrodynamic volume, low solution and melt viscosity, good solubility, a multitude of functional end groups, and nonentangled chains.[1−4] Initial studies focused on the synthesis of hyperbranched polymers via the self-condensation of AB_n ($n \geq 2$) type monomers.[2,6,7] Although several studies reported the synthesis and characterization of various types of hyperbranched step-growth polymers via the self-condensation of AB_n type monomers,[1−4] limited availability of these functionally nonsymmetrical monomers has stymied industrial applications and fundamental studies of branching in macromolecules.

Although Kienle[8−10] and Flory[11,12] initially studied these processes in the 1940s, the polymerization of functionally symmetric monomer pairs such as A_2 and B_3 type monomers has received renewed interest in the past decade as a convenient approach to synthesize hyperbranched polymers.[4,13,14] Significant effort has been devoted to understanding the influence of the reaction parameters on gel formation in $A_2 + B_3$ systems, and gelation is retarded at optimum A_2:B_3 molar ratios (generally 1.0 or higher) to obtain high molar mass products. For example, gelation is predicted at 86.6% A group conversion (57.7% with respect to B) for a 1:1 molar ratio of A_2:B_3 monomers (A:B = 2:3) that are homogeneously mixed at the onset of polymerization.[7] A few common strategies are used to avoid gelation in $A_2 + B_3$ polymerization. Stopping the reaction immediately prior to gelation results in partial conversion of functional groups; however, fully soluble highly branched products are prepared.[13,14] Polymerization in dilute solution promotes cyclization reactions, which effectively avoid gelation, and the reaction proceeds with complete consumption of the limiting reagents.[15−17] Slow addition of one monomer into the reaction mixture is also commonly employed especially for highly reactive monomer pairs.[18,19] The slow addition strategy is generally related to one of the first two techniques; either the functional groups are only partially converted or cyclization reactions occur.[16] Finally, nonideal conditions tailor the relative reactivity of one of the functional A or B groups on A_2 or B_3, resulting in AA* or B_2B* monomers.[20−27] A* and B* groups exhibit different reactivities than A and B groups, respectively.

The vast majority of hyperbranched polymers via $A_2 + B_3$ polymerization reported in the literature were synthesized in solution.[14−19,22,23,28−33] However, only two studies reported polycondensation of A_2 and B_3 monomers in the melt phase.[34,35] For example, melt polymerization of adipic acid (A_2) and glycerol (B_3) resulted in highly branched aliphatic polyesters without gelation.[35] However, glycerol bears two primary alcohols and a secondary, which possess significantly different reactivity in the polymerization. Hence, glycerol effectively acts as a B_2B* monomer, and gelation is avoided even at molar ratios of A_2:B_3 = 2:1. Other than polycondensation of A_2 and B_3 monomers, Fréchet and co-workers reported the synthesis of aliphatic polyether epoxies in bulk via the proton-transfer polymerization from a diepoxide (A_2) and triol (B_3).[13,36] A feed molar ratio of A_2:B_3 = 3:1 was employed to introduce epoxide chain ends. Polymerizations were stopped before the full conversion of limiting reagents prior to gelation, and the molar mass increase was monitored with time.

This paper describes the synthesis of a highly branched poly(ether ester) via the melt condensation of poly(propylene glycol) (A_2 oligomer) and trimethyl 1,3,5-benzenetricarboxylate (TMT, B_3 monomer). The conversion of each monomer was monitored during the polymerization to understand the onset of gelation in the melt phase. The equal reactivity of the B_3 monomer does not promote a B_2B* scenario, and oligomeric A_2 provides the

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opportunity for entanglements between branch points. Finally, the introduction of a monofunctional comonomer is reported as a novel strategy to avoid gelation in $A_2 + B_3$ polymerization.

Experimental Section

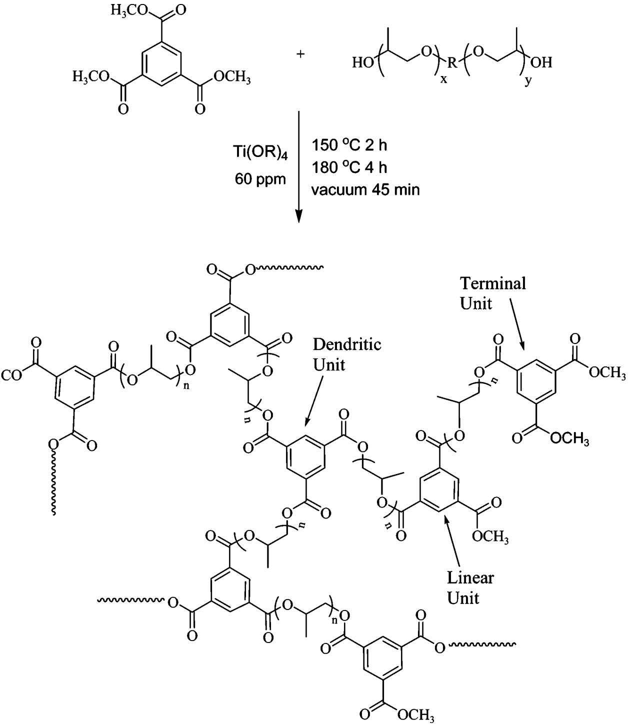
Materials. Poly(propylene glycol) (PPG-1000), which consisted of secondary hydroxyl end groups and a number-average molar mass (M_n) of 1060 g/mol (^{1}H NMR), was kindly donated by Bayer MaterialScience under the commercial name Arcol PPG-1000. Trimethyl 1,3,5-benzenetricarboxylate (98%) (TMT), dodecanol (DD), poly(propylene glycol) monobutyl ether (PPG-M-1000, $M_n = 1200$ g/mol by ^{1}H NMR), dimethyl terephthalate (DMT), and titanium tetraisopropoxide (99%) were purchased from Aldrich. PPG-1000 and PPG-M-1000 were dried in a vacuum oven (0.50 mmHg) at 50 °C for 18 h. TMT was purified by sublimation at 150 °C. All other reagents were used as received unless otherwise stated.

Synthesis of Highly Branched Poly(ether ester)s. TMT (5.00 g, 19.82 mmol) and PPG-1000 (21.01 g, 19.82 mmol) were added to a 100 mL, two-necked flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser. Titanium tetraisopropoxide (60 ppm) was added to facilitate transesterification. The reaction flask was degassed using vacuum and nitrogen three times and subsequently heated to 150 °C. The reactor was maintained at 150 °C for 2 h, and the temperature was increased to 180 °C over 4 h. Vacuum was gradually applied (0.30 mmHg), and the reaction proceeded for 1 h at 180 °C. Aliquots (0.40 g) of the reaction mixture were removed with a pipet at different reaction times and analyzed using ^{1}H NMR spectroscopy and SEC to monitor molar mass and monomer conversion. The final, low glass transition temperature product was simply isolated from the reactor with a spatula and analyzed without further purification.

Two methods (I and II) were used to synthesize both poly(propylene glycol) end-capped highly branched poly(ether ester)s (HBPEE-PPG) and dodecyl ester end-capped highly branched poly(ether ester)s (HBPEE-DD). In the first method (I), the end-capping reagent was introduced at the onset of polymerization. For the synthesis of HBPEE-PPG-I, PPG-M-1000 (11.89 g, 9.91 mmol) was added to the reaction flask with TMT (2.50 g, 9.91 mmol), PPG-1000 (10.51 g, 9.91 mmol), and titanium tetraisopropoxide (60 ppm). The same multistep temperature sequence was used as above with the exception that the reaction was allowed to proceed for 4 h at 180 °C in the second step, and vacuum was applied for 4 h at 180 °C in the third step. HBPEE-DD-I was synthesized using the identical procedure as HBPEE-PPG-I with the exception that DD (1.85 g, 9.91 mmol) was initially added to the reaction flask in place of the PPG-M-1000. In the second method (II), the DD end-capping reagent was introduced at a later stage of polymerization. For the synthesis of HBPEE-DD-II, TMT (2.50 g, 9.91 mmol), PPG-1000 (10.51 g, 9.91 mmol), and titanium tetraisopropoxide (60 ppm) were added to the reaction flask and allowed to react at 150 °C for 2 h. Temperature was increased to 180 °C over 4 h and vacuum was gradually applied (0.30 mmHg) for 10 min. The reaction was paused, and DD (1.85 g, 9.91 mmol) was added to the reaction flask. The reaction flask was maintained at 180 °C for 2 h, and gradual vacuum was applied (0.30 mmHg) for 4 h.

Synthesis of Linear Poly(ether ester)s. A single neck, 100 mL round-bottomed flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser was charged with DMT (5.25 g, 27.04 mmol) and PPG-1000 (27.29 g, 25.75 mmol). Titanium tetraisopropoxide (60 ppm) was added to facilitate transesterification. The reaction flask was degassed under vacuum and nitrogen three times and subsequently heated to 180 °C. The reactor was maintained at 180 °C for 4 h, and the temperature was increased to 200 °C over 2 h. Vacuum was applied (0.5 mmHg) for another 1 h to ensure the removal of methanol.

Scheme 1. Synthesis of Highly Branched Poly(ether ester)s via Melt Condensation of PPG-1000 (A_2) and TMT (B_3)



Characterization. ^{1}H NMR spectroscopic analyses were performed on a Varian Unity 400 MHz spectrometer at ambient temperature. Triple-detection size-exclusion chromatography (SEC) was conducted in THF (40 °C, 1 mL min^{-1}, polystyrene standards) on a Waters 717 Autosampler equipped with three in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. Thermal transition temperatures were determined using a Perkin-Elmer Pyris-1 at 10 °C/min under helium, and reported data were obtained from the second heating.

Results and Discussion

Polymerization. Conventional transesterification was used to prepare highly branched poly(ether ester)s in the melt phase using titanium tetraisopropoxide as catalyst. We previously reported the polymerization of poly(ethylene glycol) (PEG, A_2 oligomer) with B_3 acyl halides in dilute solution to prepare highly branched poly(ether ester)s.[16] Variations in the molar mass of the PEG oligomer controlled the distance between branch points. However, synthesis in dilute solution, which is generally associated with a significant amount of cyclization, resulted in a mixture of high molar mass, highly branched polymers and low molar mass oligomers or cyclic compounds. Thus, melt polymerization was employed to overcome the need for large quantities of polymerization solvent, eliminate highly reactive acyl halides, and limit the formation of low molar mass products.

Various commercial polyesters that are commonly used as engineering thermoplastics, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and various polyether-based polyesters (i.e., Hytrel), are synthesized in the melt phase at temperatures ranging from 180 to 290 °C.[37−39] Polymerizations in the current study were conducted at relatively lower temperatures to avoid degradation of the polyether-based A_2 oligomer (PPG-1000). ^{1}H NMR spectroscopy of the final products did not reveal any unexpected resonances due to thermal degradation. Moreover, thermogravimetric analysis (TGA) also ensured no weight loss at polymerization temperatures.

PPG-1000 A_2 oligomer and TMT B_3 monomer were polymerized in a 1:1 molar ratio using a multistep temperature sequence in the presence of a transesterification catalyst, as shown in Scheme 1. A lower initial temperature (150 °C) was required

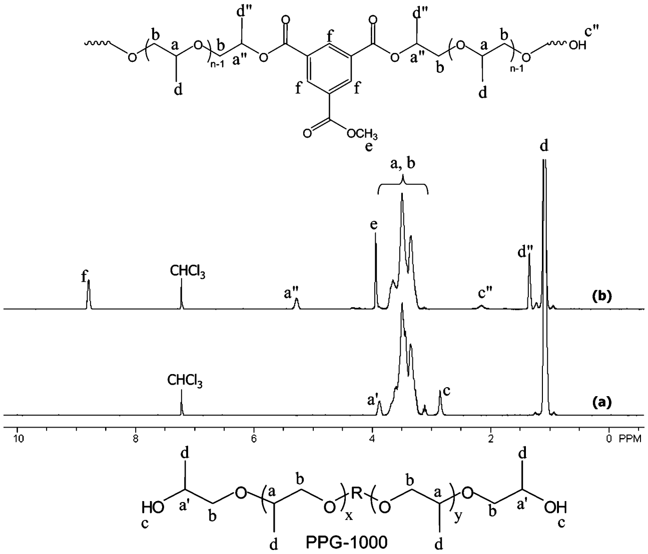


Figure 1. ^{1}H NMR spectra of (a) PPG-1000 and (b) reaction product at 86% conversion of hydroxyl (A) groups (400 MHz, $CDCl_3$).

to ensure the reaction of TMT with PPG-1000 and minimize stoichiometric changes due to TMT sublimation. After 2 h at 150 °C, the reaction temperature was raised to 180 °C over 4 h. A homogeneous reaction mixture was maintained in the absence of TMT sublimation. Finally, slight vacuum was applied at 180 °C for 45 min to ensure the removal of condensation byproducts and to obtain higher monomer conversions.

Aliquots of the reaction mixture were removed at different times during the course of the reaction and analyzed using ^{1}H NMR spectroscopy and SEC. PPG-1000 diol consists of secondary hydroxyl end groups and has characteristic NMR resonances that shift upon reaction with TMT (Figure 1a). In particular, the methyne resonances (3.88 ppm) and the resonances of the methyl groups that are adjacent to the hydroxyl end groups (1.08 ppm) shift slightly downfield (to 5.28 and 1.33 ppm, respectively). These two resonances were used to calculate the extent of reaction and monomer conversion for each sample. In addition, methyl ester resonances (3.93 ppm), which were expected to decrease as the reaction proceeded, were used to further confirm the calculations. Finally, aromatic resonances due to TMT were used to verify that the initial A_2:B_3 = 1:1 molar ratio was maintained throughout the reaction. Figure 1b shows the ^{1}H NMR spectrum of the reaction product at 85% hydroxyl (A) group conversion (p_A). Thus, ^{1}H NMR spectroscopy was a powerful tool to characterize reaction products and extent of reaction. Linear analogues of the highly branched poly(ether ester)s were synthesized for comparative purposes using dimethyl terephthalate (DMT), which was a suitable B_2 version of TMT (B_3). A 5% excess of DMT was charged to the reaction flask due to minor sublimation during the early stages of the reaction at 180 °C.

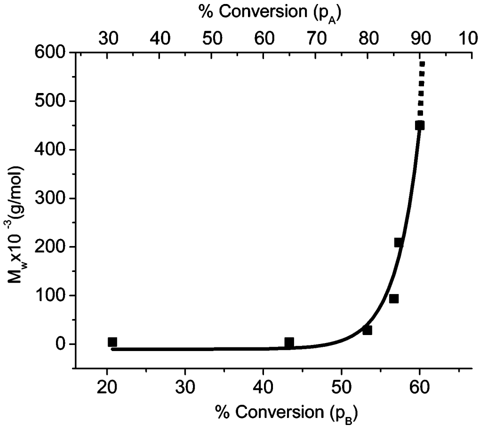


Figure 2. Weight-average molar mass as a function of monomer conversion.

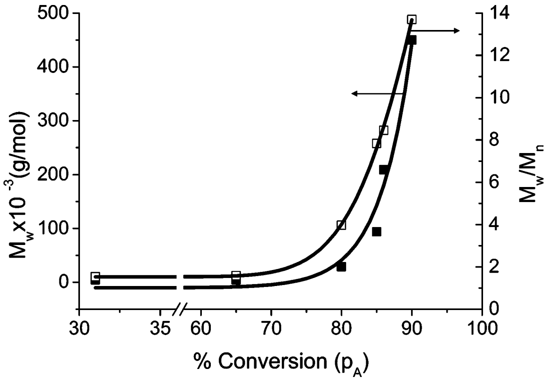


Figure 3. Weight-average molar mass and molar mass distribution as a function of monomer conversion.

SEC and ^{1}H NMR spectroscopy allowed us to monitor the molar mass increase as a function of monomer conversion. Figure 2 is a plot of absolute weight-average molar mass as a function of the percent conversion of hydroxyl (p_A) and methyl ester (p_B) groups. The reaction resembled a typical step-growth polymerization with a dramatic increase in molar mass at p_A = 80−85% and p_B = 53−57%. Gelation occurred at a critical monomer conversion, which is depicted in Figure 2 using a dotted line. A sudden increase in melt viscosity was also observed and associated with incidence of gelation. Multiple reactions were performed to determine the exact gel point and ensure reproducibility. A final soluble product was reproducibly obtained immediately prior to gelation at p_A = 90% and p_B = 60%, and solubility tests in chloroform and tetrahydrofuran confirmed that the product at p_A = 90% was fully soluble. SEC analysis of highly branched poly(ether ester)s revealed an absolute weight-average molar mass (M_w) of 450 000 g/mol and a molar mass distribution of 13.8, which are exceptionally high for a step-growth polymerization. It should be noted that PPG-1000 contributes ~1060 g/mol to each repeat unit, which should be taken into account during the evaluation of the degree of polymerizations for these highly branched polymers. Fréchet and co-workers also monitored the molar mass increase hyperbranched aliphatic polyether epoxies via $A_2 + B_3$ proton-transfer polymerization and observed a similar step-growth behavior.[13,36] However, a molar ratio of A_2:B_3 = 3:1 was employed, which would result in gelation at moderately lower monomer conversions, and a relationship between the monomer conversion and gel point was not established. In our studies, the experimental critical monomer conversion values for gelation (p_A = 90%, p_B = 60%) correlated well with the theoretical calculations (p_{Ac} = 87%, p_{Bc} = 58%) for an A_2:B_3 = 1:1 system. Close agreement between experimental and theoretical results indicated that there were negligible cyclization reactions that would have accounted for a delayed gel point. Figure 3 is a plot of molar mass distribution vs monomer conversion for the same series of samples. The molar mass distribution increased as a function of reaction extent and reached a maximum value of 13.7. The SEC traces in Figure 4 clearly show a polymodal distribution with a growing fraction of high molar mass hyperbranched polymer and a decreasing fraction of low molar mass oligomers with increasing monomer conversion. As expected for an A_2 + B_3 polymerization process, the final product (p_A = 90%) showed multiple shoulders at the high molar mass elution times.

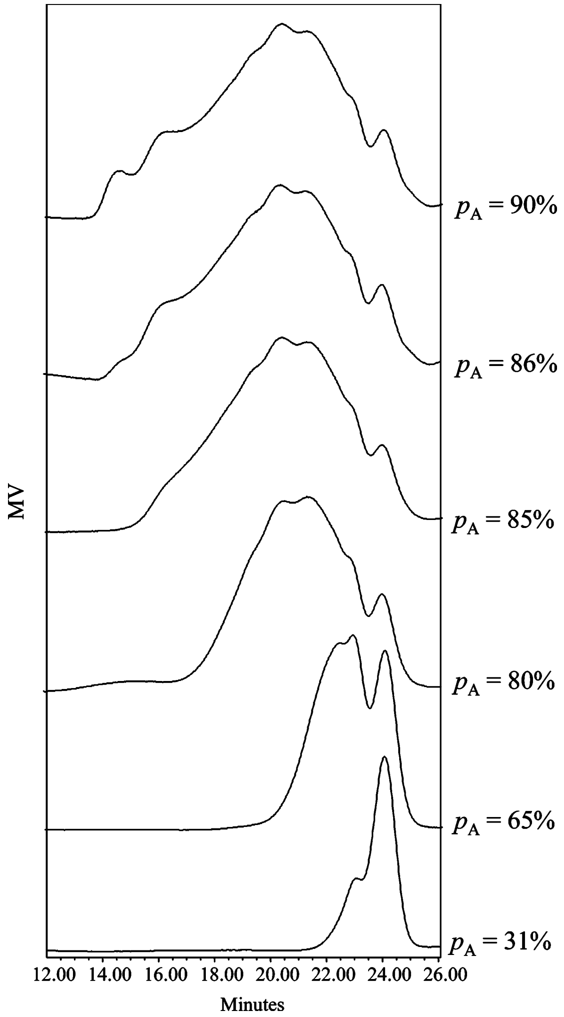


Figure 4. SEC traces of highly branched poly(ether ester)s as a function of monomer conversion.

The final products were stable and did not show gelation or a molar mass change under ambient storage conditions, indicating acceptable shelf life storage. However, as expected for polyesters, the polymerization is presumed to continue at higher temperatures, in the presence of vacuum, due to the presence of a large number of functional end groups. Thus, an end-capping strategy was developed in $A_2 + B_3$ polymerizations to prevent gelation in the melt phase at higher monomer conversions and improve the stability of the final products even at high temperatures in the presence of vacuum.

Synthesis of Highly Branched Poly(ether ester)s with Monofunctional End-Capping Reagents To Avoid Gelation. Low levels of trifunctional agent (typically 0.1−1.0 mol %) are commonly used to synthesize lightly branched (long-chain branched) condensation polymers via the conventional $A_2 + B_2$ methodology, and it is widely recognized that the introduction of monofunctional comonomers prevents gelation and allows higher levels of branching.[39] However, $A_2 + B_3$ polymerization enables the incorporation of equimolar levels of multifunctional reagents, which is a significantly higher level of branching than $A_2 + B_2$ methodologies in the presence of B_3.

In our studies, either poly(propylene glycol) monobutyl ether (PPG-M-1000) or dodecanol (DD) was introduced as end-capping reagent (monofunctional comonomers, A) in hyperbranched polymers to avoid gelation during $A_2 + B_3$ polymerization. Both end-capping strategies allowed the polymerization to proceed to very high conversions (p_A and $p_B \geq 98\%$) without gelation, while in the absence of end-capping, gelation occurred at $p_A = \sim90\%$ and $p_B = \sim60\%$. PPG-M-1000 (A monomer) was introduced into the reaction flask at the onset of polymerization to synthesize HBPEE-PPG-I. The molar ratio of monomers was set at A_2:B_3:A = 1:1:1, targeting the end-capping of all residual methyl ester functionalities that are expected in an A_2:B_3 = 1:1 system. Additional polymerization time was required to ensure complete monomer conversion. Gelation was not observed after 2 h at 150 °C, 4 h at 180 °C, and 4 h under vacuum (180 °C). ^{1}H NMR spectroscopy of the final product indicated p_A and $p_B > 98\%$. As summarized in Table 1, the final product (HBPEE-PPG-I) had a weight-average molar mass of 416 000 and a molar mass distribution of 23.3.

Table 1. Characterization Data for Highly Branched Poly(ether ester)s That Were Synthesized Using End-Capping Strategies

sample	end-capping reagent (A)	A_2:B_3:A[c]	M_w (g/mol)	M_w/M_n	g'
HBPEE-PPG-I	PPG-M-1000[a]	1:1:1	416 000	23.3	0.23
HBPEE-DD-I	dodecanol[a]	1:1:1[d]	cross-linked product		
HBPEE-DD-II	dodecanol[b]	1:1:1	302 000	14.2	0.27

[a] Introduced at the onset of polymerization. [b] Introduced during the polymerization (at $p_B = \sim56\%$). [c] Molar feed ratio. [d] ^{1}H NMR analysis indicated 15% loss of DD (A) during polymerization.

When DD was used as the end-capping reagent (A) and added to the reaction flask at the onset of polymerization, the reaction resulted in gelation (HBPEE-DD-I). ^{1}H NMR analysis of the product indicated a 15% DD loss during polymerization, which was presumed to favor gelation. Therefore, when DD was used as the end-capping reagent (A), an alternate strategy, end-capping during polymerization, was utilized. In this approach, the polymerization was started using A_2 oligomer and B_3 monomer only, and DD (A monomer) was added to the reaction flask at a later stage of the polymerization ($p_B = \sim56\%$, $p_A = \sim84\%$ at the time of A introduction). A sharp decrease in p_A was expected upon DD addition because of an increase in the concentration of unreacted A functional groups (hydroxyl). Following the addition of DD, the reaction proceeded for 2 h at 180 °C and vacuum was applied for 4 h. ^{1}H NMR spectroscopy of the final product (HBPEE-DD-II) revealed p_A and p_B of ~98%. The final polymer was gel-free and fully soluble with M_w of 302 000 g/mol and molar mass distribution of 14.2 (Table 1).

In addition to prevention of gelation during the synthesis, end-capping strategy is also expected to increase the stability of these polymers at high temperatures and under vacuum.

Characterization of Branching. Degree of branching (DB), which is defined as the ratio of dendritic and terminal units to the sum of all dendritic, linear, and terminal units, is a convenient method to characterize branching in hyperbranched polymers.[40] In a hyperbranched polymer that is synthesized via AB_2 polymerization, the approximate distribution of dendritic, terminal, and linear fractions is expected to be 25, 25, and 50%, respectively, resulting in a DB = ~50%. However, as reported previously, the fractions of dendritic and terminal are not necessarily equal in an $A_2 + B_3$ polymerization system.[19] On the other hand, the classical degree of branching does not properly characterize our systems due to the presence of oligomeric sequences rather than single monomer units between each branch point. Nevertheless, it provides useful information on the branching efficiency of the B_3 monomer and describes the branched structures when each oligomer between the branch points is considered as a single repeat unit. Detailed investigation of the ^{1}H NMR spectra of each sample at different conversions demonstrated the formation of dendritic, linear, and terminal

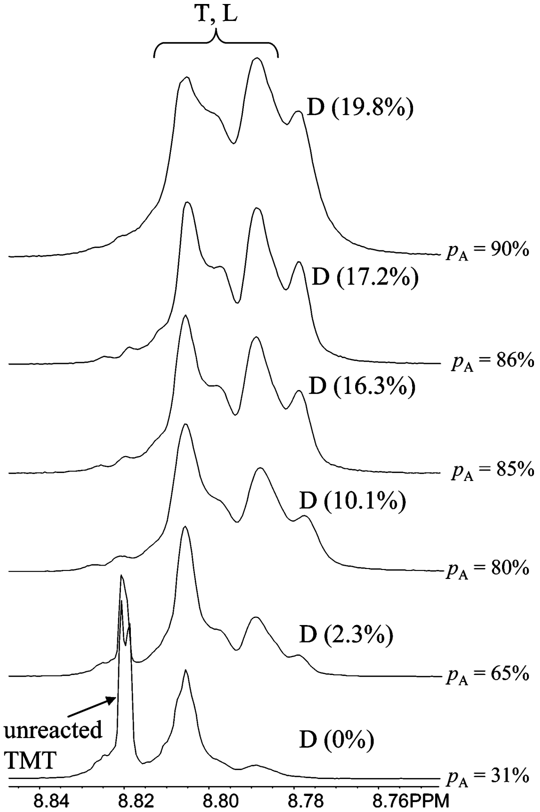


Figure 5. ^{1}H NMR spectra of aromatic region of highly branched poly(ether ester)s provide information on the structural changes and branching at various monomer conversions (400 MHz, $CDCl_3$).

units as a function of monomer conversion (Figure 5). At early stages of the polymerization ($p_A = 31\%$), only terminal and linear units were present. As the reaction proceeded, a dendritic shoulder (8.78 ppm, see Supporting Information) was more significant, especially through the end of the reaction. Deconvolution of each resonance in Figure 5 revealed that the final product ($p_A = 90\%$) had ~20% dendritic units, which is slightly lower than 25% dendritic fraction that is anticipated in a hyperbranched polymer synthesized via AB_2 polymerization at 100% conversion of A groups. However, it should be noted that the feed molar ratio of A and B groups and monomer conversion is expected to play an important role on the distribution of dendritic, linear, terminal units in an $A_2 + B_3$ polymerization. Therefore, 20% dendritic fraction is acceptable at 90% and 60% conversion of A and B groups, respectively.

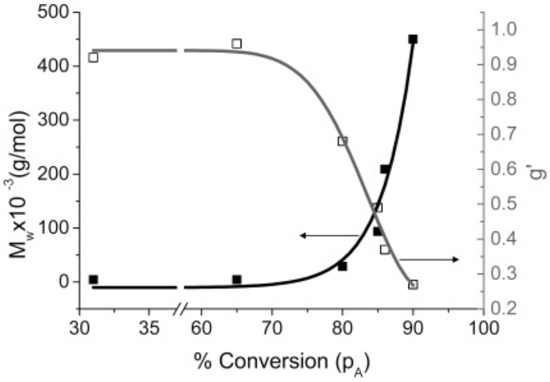


Figure 6. Branching index (g') as a function of monomer conversion.

The branching index (g'), which is derived from SEC viscometric data, was also used to characterize branching.[41] The value g' provides a direct comparison of the hydrodynamic volume of a branched molecule with its linear analogue and is calculated as $g' = [\eta]_{branched}/[\eta]_{linear}$, where $[\eta]_{branched}$ and $[\eta]_{linear}$ are the intrinsic viscosities of branched and linear polymers of equivalent weight-average molar mass. The g' values are closer to unity for linear polymers and decrease as branching increases. To calculate g' for any branched polymer, $[\eta]_{branched}$ is obtained directly from SEC, and $[\eta]_{linear}$ is calculated at an equivalent molar mass using the Mark–Houwink equation ($[\eta]_{linear} = KM_w{}^a$) with appropriate K and a values. It is important to note M_w was only used as an approximation for viscosity average molar mass, M_v, for the calculation of $[\eta]_{linear}$ values, whereas the measured $[\eta]_{br}$ values obtained from SEC-viscometry detector utilized the M_v.[7] The Mark–Houwink relationship $[\eta]_{linear} = 10^{-3.45}M_w{}^{0.65}$ was established using the SEC-viscometry detector for the linear poly(ether ester) (M_n 19 800 and M_w = 39 200 g/mol) in this study. Figure 6 depicts g' and weight-average molar mass as a function of monomer conversion. Only linear structures formed at early stages of polymerization ($p_A < \sim70\%$). Branching increased above $p_A = 70\%$ and g' ultimately reached a value of 0.27, which indicated a highly branched polymer.

A monofunctional reagent is theoretically expected to terminate some of the B functionalities and decrease the branching probability of a B_3 unit, resulting in a less branched structure. Furthermore, introducing the end-capping reagent late in the polymerization rather than at the onset is expected to yield a more highly branched polymer due to the formation of a branched intermediate prior to addition of the end-capping reagent. However, characterization of highly branched poly(ether ester)s that were synthesized in the presence of monofunctional end-capping reagents suggested that these considerations were not influential during the polymerization. The highly branched poly(ether ester)s that were synthesized in the presence of monofunctional end-capping reagents had g' values (Table 1) similar to the final product that was synthesized in the absence of end-capping reagent and obtained immediately prior to gelation ($p_A = 90\%$, $p_B = 60\%$). This suggested that the presence of a monofunctional reagent did not significantly influence the formation of branched structures. Moreover, the point at which the monofunctional end-capping reagent was introduced (at the onset of polymerization vs at a later stage) did not alter the final structure. Such discrepancies between theoretical considerations and g' data were attributed to ester interchange reactions. Clearly, B functionalities that have reacted with the end-capping reagent continue to undergo ester-interchange with unreacted A groups. Thus, a nonideal $A_2 + B_3$ system was envisioned, where a B_3 monomer reacted with an end-capping reagent and formed a B_2B^* type intermediate (B^* denotes the reacted B group that undergoes ester interchange at a lower rate). In this system, the final products are expected to branch randomly, regardless of the presence of an end-capping reagent or the point in the polymerization at which the end-capping reagent is introduced.

Conclusions

Melt condensation of an A_2 oligomer (poly(propylene glycol)) with a B_3 monomer (trimethyl 1,3,5-benzenetricarboxylate) resulted in gelation at ~90% conversion of A ($p_A = 90\%$) and ~60% conversion of B groups ($p_B = 60\%$). However, fully soluble, highly branched, products with M_w of ~450 000 g/mol and M_w/M_n of 13.7 were obtained by stopping the reaction immediately prior to the gel point. The close approximation between the experimental ($p_A = 90\%$, $p_B = 60\%$) and theoretical ($p_{Ac} = 87\%$, $p_{Bc} = 58\%$) gel points suggested that cyclization reactions, which would inhibit gelation even at 100% conversion of A groups, were not significant in the melt phase. Moreover, gelation was successfully avoided when monofunctional end-capping reagents were introduced to the reaction flask either at the onset of polymerization or during the reaction. Greater than 98% of the A and B functionalities were consumed. The B functionalities that reacted with the end-capping reagent continued to undergo ester interchange and reacted with unreacted A groups. As a result, the final products were similar to highly branched polymers that were synthesized in the absence of an end-capping reagent, and the point at which the monofunctional end-capping reagent was introduced (at the onset of polymerization versus at a later stage) did not influence the final structure. It should be noted that various other short chain or long chain diols, including monomeric or oligomeric poly(ethylene glycols), are viable candidates for the synthesis highly branched polyesters using melt $A_2 + B_3$ polymerization.

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Supporting Information Available: Experimental details of synthesis of a dendritic model compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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