Synthesis and Characterization of Branched Polymers from Lipase-Catalyzed Trimethylolpropane Copolymerizations

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Lipase-catalyzed terpolymerizations were performed with the monomers trimethylolpropane (B_3), 1,8-octanediol (B_2), and adipic acid (A_2). Polymerizations were performed in bulk, at 70 °C, for 42 h, using immobilized lipase B from *Candida antartica* (Novozyme-435) as a catalyst. To determine the substitution pattern of trimethylolpropane (TMP) in copolymers, model compounds with variable degrees of acetylation were synthesized. Inverse-gated ^{13}C NMR spectra were recorded to first determine the chemical shift positions for mono-, di-, and trisubstituted TMP units and, subsequently, to determine substitution of TMP units along chains. Variation of TMP in the monomer feed gave copolymers with degrees of branching (DB) from 20% to 67%. In one example, a hyperbranched copolyester with 53 mol % TMP adipate units was formed in 80% yield, with M_w 14 100 (relative to polystyrene standards), M_w/M_n 5.3, and DB 36%. Thermal and crystalline properties of the copolyesters were studied by thermogravimetric analysis and differential scanning calorimetry.

Introduction

Hyperbranched polymers (HBPs) have unique physical and chemical properties that have stimulated many scientists to explore their synthesis and properties for a wide range of industrial and biomedical applications.[1−12] The diversity of chemical entities that can be incorporated in HBPs such as polyesters,[13,14] polyamides,[15] polyurethanes,[16,17] and others[9] expands the ability of synthetic scientists to specifically tailor structure−property relationships of HBPs.

Synthetic strategies have been developed to prepare HBPs with controlled molecular weights and branching as well as lower polydispersities. Important examples include: (a) core dilution/slow addition,[18−20] (b) postsynthetic modifications,[18,21] and (c) copolymerization of AB_2 with AB monomers. By introducing AB monomers control is gained over the average distance between branch points.[22] Problems encountered with current chemical methods include: (i) use of toxic catalysts such as 4-(dimethylamino) pyridinium-4-toluenesulfonate (DPTS) and triphenyl phosphite,[23] (ii) need for activation of AB_m or B_3 monomers,[14,24] (iii) harsh reaction conditions such as temperatures above 150 °C,[13,14] and (iv) use of high boiling organic solvents[25,27,28] to attain homogeneous reaction media. An additional problem is restrictions on reaction conditions to avoid gelation.[23] For example, the synthesis of hyperbranched poly(arylesters)[23a] from $A_2 + B_3$ monomers is performed by slow addition of a dilute solution of A_2 monomer to a dilute solution of B_3 monomer where the final concentration of monomers is kept below 0.08 M to avoid gelation. The potential of lipase-catalyzed routes to hyperbranched polyesters is that, due to steric constraints at enzyme active sites, enzymes can provide better control over branching while avoiding cross-linking reactions. This will be further discussed below.

Lipase-catalyzed condensation and ring-opening polymerization methods in addition to chemoenzymatic methods are gaining increased recognition as safe catalysts that bring benefits to polymer synthesis.[29−33] Unlike many organometallic catalysts, they do not require strict exclusion of air and/or moisture during reactions.[29] This allows for inclusion of thermally sensitive building blocks and creation of novel structures.[32] Lipase B from *Candida antartica* (CAL-B), physically immobilized on Lewatit beads (Novozyme-435), was found to be an effective lipase catalyst for polyesterifications to prepare linear polyesters with a polydispersity of around 2.0.[32a−c] Our laboratory reported that by agitating and heating mixtures of highly polar monomers such as sorbitol with adipic acid and 1,8-octanediol, monophasic liquid reaction media were attained without the addition of solvent.[30,31] For example, CAL-B-catalyzed bulk polymerization of sorbitol and adipic acid proceeded with high regioselectivity (85% ± 5%) at primary hydroxyl groups to give a water-soluble product with M_n 10 880 and M_w/M_n of 1.6. Skaria et al.[22] used Novozyme-435 to catalyze concurrent ring-opening and condensation reactions between ϵ-caprolactone and 2,2′-bis(hydroxymethyl) butyric acid (BHB). Reactions proceeded slowly in solvent so that, when the molar ratio of ϵ-caprolactone to BHB in the monomer feed was 92 to 8, the copolymer M_w after 24 h at 85 °C was 3500 g/mol. Our laboratory reported the synthesis of hyperbranched glycerol copolyesters by heating ternary monophasic mixtures of glycerol ($B'B_2$) with adipic acid (A_2) and 1,8-octanediol (B_2) monomers.[35a] Variation of reaction time and glycerol in the monomer feed gave copolymers with degrees of branching varying from 0% to 58%.

Thus far, our understanding of regioselectivity during lipase-catalyzed polyol−polyester synthesis is limited. By exploring a wider range of polyols and reaction conditions, we expect it will be possible to fine-tune degrees of branching and contents of hydroxyl groups along chains. This paper describes a simple, one-pot, enzymatic synthesis to prepare hyperbranched copolymers from trimethylolpropane (TMP), a monomer with three primary hydroxyl groups. Terpolymerizations of adipic acid (A_2), 1,8-octanediol (B_2), and TMP (B_3), catalyzed by Novozyme-435, were performed. Inverse-gated carbon (^{13}C) NMR

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was used to determine copolymer degree of branching (DB). The composition of the monomer feed was systematically varied to determine its effect on degree of branching and copolymer molecular weight. Thermal and crystalline properties of new copolymers were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Experimental Section

Materials Adipic acid, 1,8-octanediol, and trimethylolpropane (TMP) were purchased from Aldrich, USA, and were used without further purification. Novozyme-435 (specific activity 7000 PLU/g) was a gift from Novozymes (Bagsvaerd, Denmark). Deuterated chloroform (chloroform-d_1) was obtained from Aldrich, USA. Chloroform and methanol were purchased from Pharmaco, USA. All solvents were of HPLC grade and were used as received without any further purification. All chemicals were obtained in the highest possible purities available.

Instrumentation. *Nuclear Magnetic Resonance*. The polyesters formed were characterized using proton (^{1}H NMR) and inverse-gated (quantitative) ^{13}C NMR spectroscopy. The instrumentation parameters used were the same as those described earlier.[35a]

Molecular Weight Measurements. The number- and weight-average molecular weights (M_n and M_w, respectively) were determined by size exclusion chromatography (SEC) relative to polystyrene standards. Details of the equipment and method used are identical to those published elsewhere.[35a,c]

Thermal Analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a TA instruments DSC 2920 and a high-resolution TA instruments TGA2950, respectively. For both TGA and DSC, sample quantities were between 7 and 13 mg, the heating rate was 10 °C/min, and experiments were conducted with a nitrogen purge. DSC measurements were performed by first heating the samples from −30 to 110 °C (first heating scan), cooling at 10 °C/min from 110 to − 30 °C, and then performing a second heating scan with a 10 °C/min heating rate.

Synthetic Methods. *General Procedure for Lipase-Catalyzed Poly-(trimethylolpropane-adipate) Synthesis.* Adipic acid (2.93 g, 20 mmol) and trimethylolpropane (2.683 g, 20 mmol) were transferred into a 100 mL round-bottom flask. The mixture was heated with stirring to 115 °C for 30 min, after which it formed a liquid with two distinct phases. The temperature of the reaction mixture was lowered to 80 °C, and dried Novozyme-435 beads (490 mg; dried at 25 °C, 10 mmHg, 24 h) were added to the reaction mixture. During the first 2 h, the reaction flask was maintained at 80 °C under atmospheric pressure with mixing by magnetic stirring (IKA Werke RCT basic magnetic stirrer) set at 220 rpm. During this time, the immiscible monomer mixture became a translucent monophasic liquid. From 2 h to when the reaction was terminated, the mixture was maintained at 80 °C, with magnetic stirring, under vacuum (40 to 60 mmHg). The reaction was terminated by adding excess chloroform, stirring for 15 min, and filtration to remove the enzyme. The reaction product was purified by dissolving it in 80 mL of chloroform and washing with 50 mL of water three times in a separatory funnel. The chloroform layer was dried with anhydrous sodium sulfate and filtered, the solvent was stripped by rotoevaporation, and the resulting oily product was obtained in 40% yield after drying in a vacuum oven (30 mmHg, 30 °C, 24 h). The oil obtained was soluble in methanol and tetrahydrofuran (THF) but insoluble in water. It was characterized by ^{1}H and inverse-gated ^{13}C NMR spectroscopies and SEC.

General Procedure for Novozyme-435-Catalyzed Copolymerizations of TMP with Adipic Acid and 1,8-Octanediol. Adipic acid (2.93 g, 20 mmol) and a mixture totaling 20 mmol of 1,8-octanediol and trimethylolpropane were transferred into a 100 mL round-bottom flask. The mixture was heated with stirring at 70 °C for 10 min, and then dried Novozyme-435 beads (560 mg; dried at 25 °C, 10 mmHg, 24 h) were added. During the first 2 h, the reaction flask was maintained at 70 °C under atmospheric pressure with mixing as above. From 2 h to when the reaction was terminated, the mixture was maintained at 70 °C as described above. The polymerization was terminated after 42 h by dissolving the reaction mixture in chloroform, removing the enzyme by filtration, and stripping the solvent in vacuo. A small portion of product was precipitated by slowly transferring a chloroform solution of the product into a rapidly stirred flask containing excess cold methanol, and the resulting precipitate was isolated by filtration. The precipitated product was dried in a vacuum oven (30 mmHg, 30 °C, 24 h) and then characterized by ^{1}H and inverse-gated ^{13}C NMR spectroscopies and SEC.

Results and Discussion

Poly(adipate-*co*-octanediol-*co*-trimethylolpropane), P(A-*co*-O-*co*-TMP), consisting of octanediol−adipate and trimethylolpropane−adipate repeat units, was synthesized at 70 °C (42 h) using Novozyme-435 as a catalyst. Adipic acid (A_2) was copolymerized with varying ratios of 1,8-octanediol (B_2) to trimethylolpropane (B_3) (Scheme 1 and Table 1, entries 2−4). For entry 5 (Table 1), the molar feed ratio of adipic acid to trimethylolpropane was 1:1. In all the entries, it was assumed that trimethylolpropane reacts as a diol. Scheme 1 illustrates general characteristics of hyperbranched polymers formed as a result of polycondensation reactions with varying feed ratios of A to O to TMP. The hyperbranched architecture is comprised of linear units of octanediol−adipate and TMP−adipate formed by reactions between hydroxyl groups of 1,8-octanediol and two of three hydroxyl groups of TMP, respectively, with carboxylic acid groups of adipic acid. Similarly, dendritic trimethylolpropane adipate (TMPA) repeat units are formed as a result of reactions between carboxylic acid groups of adipic acid with all three TMP hydroxyl groups. Terminal T_{TMP}, T_o, and T_A units are formed by reaction of only one functional group of TMP, 1,8-octanediol, and adipic acid, respectively. The copolymer yield for entries 2−4 after precipitation of products from chloroform solutions into cold methanol was high (80−94%. No-enzyme control experiments showed that little (<3%) esterification of hydroxyl monomers took place in the absence of Novozyme-435. Proton and ^{13}C NMR experiments were used to determine degree of substitution of TMP units (see below).

Studies by ^{1}H and Inverse-Gated ^{13}C NMR Spectroscopy. Inverse-gated ^{13}C NMR spectra were recorded to eliminate the nuclear Overhauser effect and thereby obtain quantitative results. The ^{1}H NMR spectra of copolymers prepared by using monomer feed ratios of adipic acid to 1,8-octanediol to trimethylolpropane (A/O/TMP) of 100:100:0 and 100:80:20 are shown in Figures 1a and 1b, respectively. Assignments of protons for P(OA) given in Figure 1 are based on those described previously in reports by Kulshrestha et al.[35a] TMP methyl protons h ($-CH_3$) appear as a broad signal at 0.89 ppm whereas TMP methylene protons i (CH_3CH_2-) overlap with signals due to 1,8-octanediol protons c and d, giving a broad signal from 1.2 to 1.4 ppm. Signals due to TMP methylene protons g′ (CH_2OH) appear upfield at 3.45 ppm relative to terminal protons a′ of 1,8-octanediol at 3.60 ppm. Signals corresponding to methylene protons g and a ($-CH_2-O(C=O)$) of TMP and 1,8-octanediol, respectively, are unresolved at 4.05 ppm. The ratio of O−A to TMP−A repeat units was determined from relative integration intensities of TMP methyl protons h at 0.89 ppm and the total of adipate methylene protons e ($-CH_2CH_2(C=O)-O-CH_2-$) and e′ ($-CH_2CH_2(C=O)-O-H$) at 2.34 ppm.

To determine the relative ratio of total free hydroxyl to carboxyl groups at chain ends and along chains (Table 1), experiments were performed where ^{1}H NMR spectra of poly-

Scheme 1. Novozyme-435-Catalyzed One-Pot Polymerization of Trimethylolpropane To Form Terpolyesters

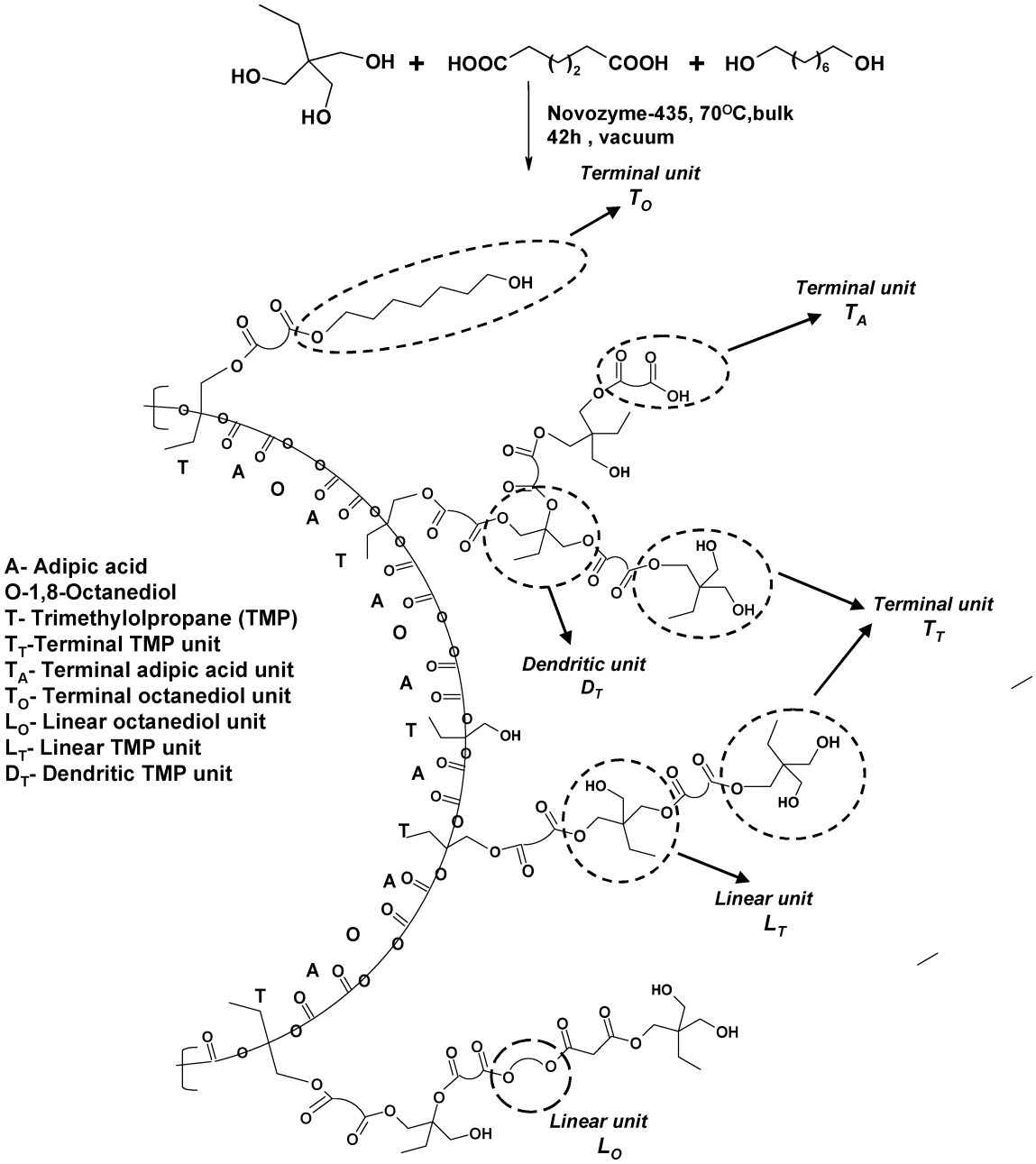


Table 1. Trimethylolpropane-Containing Hyperbranched Polyesters by Lipase Catalysis

entry	A/O/TMP feed ratio[b]	observed[c] OA/TMPA (mol %)	yield[d] (%)	total[e] OH/COOH	mono-[f] T_{TMP} (%)	di-[f] L_{TMP} (%)	tri-[f] D_{TMP} (%)	M_w[g] $\times 10^{-3}$	PDI[g]	DB[h] (%)
1	1:1:0	100:0	94	n.d				26.1	2.8	
2	1:0.8:0.2	84:16	89	2.1:1	4	47	49	22	4.5	20
3	1:0.7:0.3	66:34	86	2.9:1	12	50	38	22.4	6.6	26
4	1:0.5:0.5	47:53	80	3.2:1	25	51	24	14.1	5.3	36
5	1:0:1	0:100	40	2.9:1	46	44	10	2.7	2.2	67

[a] Reaction conditions: 70 °C, in bulk, Novozyme-435 was 10% by wt relative to total monomers, 42 h, in vacuo (40−60 mmHg). [b] A is adipic acid, O is 1,8-octanediol, and TMP is trimethylolpropane. [c] The mol % of trimethylolpropane adipate in the copolymers was determined from the relative intensity of ^{1}H NMR signals corresponding to adipic acid and TMP. [d] For entries 1−4, the percent insoluble product is that which precipitated into methanol where for entry 5 the % insoluble product is that which remained after repeated washing with water. [e] Determined by oxalyl chloride derivatization and subsequent ^{1}H NMR analysis. [f] Determined from the relative intensities of ^{13}C NMR signals corresponding to quaternary carbons of mono-, di-, and trisubstituted trimethylolpropane. [g] Determined by SEC relative to polystyrene standards. [h] Degree of branching calculated by the Frechet equation.

esters with varying TMP contents were recorded after oxalyl chloride derivatization. Oxalyl chloride treatment was performed in an attempt to resolve signals of protons e and e′ at 2.34 (Figures 1a and b). Figure 1c displays ^{1}H NMR spectra of oxalyl-chloride-modified P(OA-*co*-16 mol %-TMPA). Experimental details of oxalyl chloride derivatization are described elsewhere.[32f] Derivatization resulted in a downfield shift of terminal octanediol and TMP −C*H*$_2$OH protons a′and g′ from

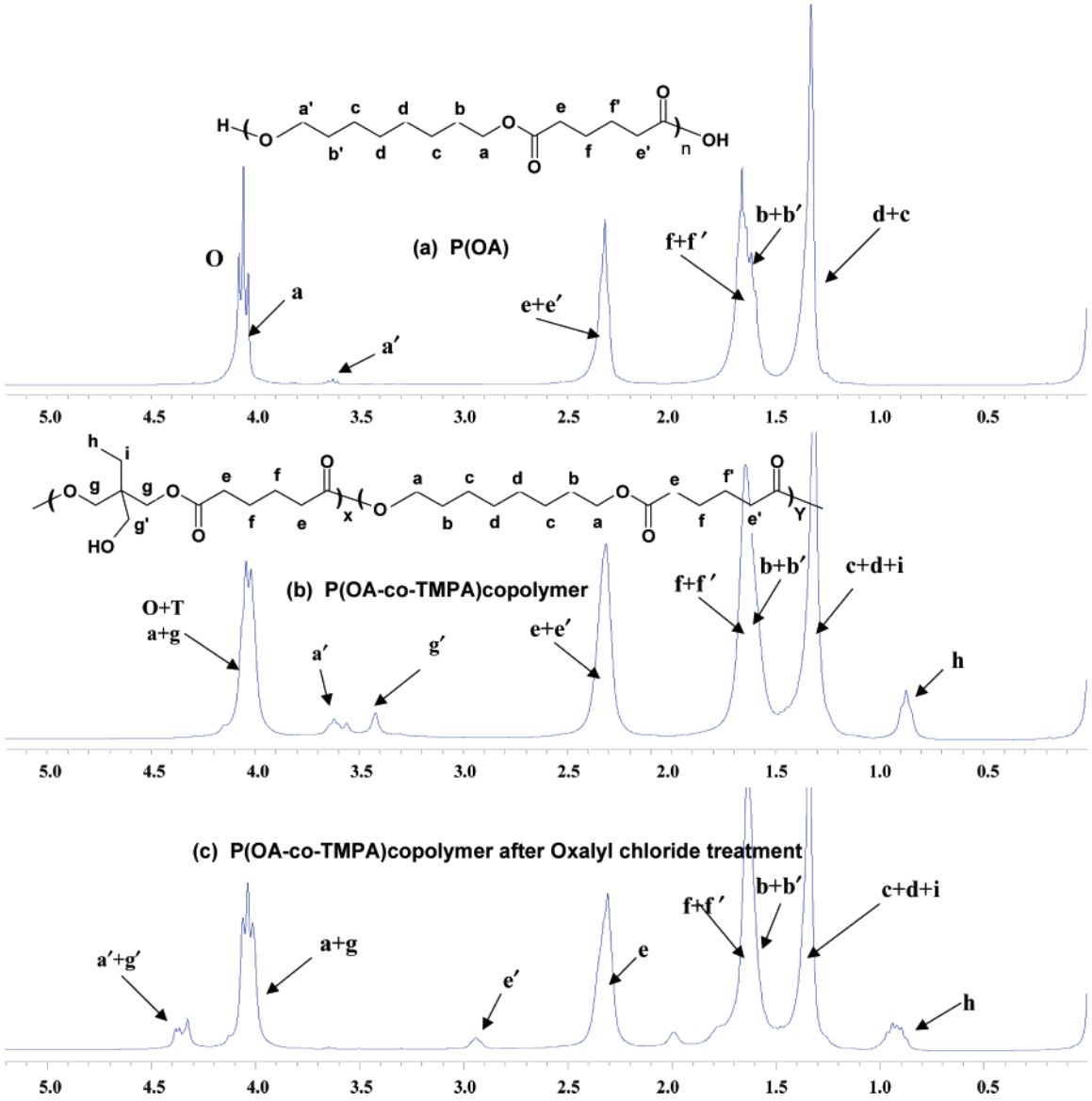
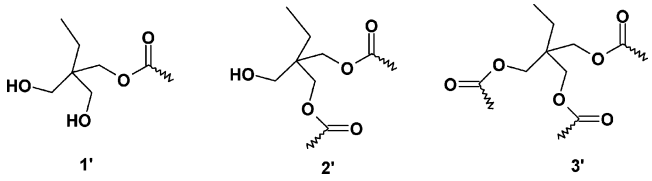


Figure 1. ^{1}H NMR spectra of (a) poly(octanedioladipate), P(OA), (b) poly(octanedioladipate-*co*-16 mol %-trimethylolpropaneadipate), P(OA-*co*-16 mol %-TMPA), and (c) P(OA-*co*-16 mol %-TMPA) after oxalyl chloride treatment.

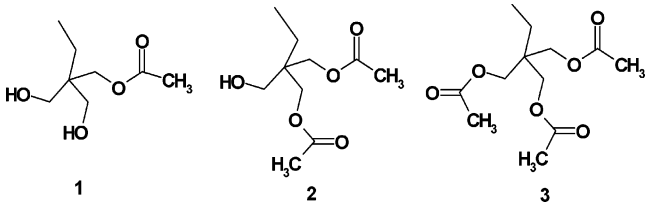
Scheme 2. Possible Combinations of Sites to Which Trimethylolpropane Units May Be Linked When Incorporated within or at the Terminus of Poly(OA-*co*-TMPA) Polymer



3.4−3.7 to 4.35−4.4 ppm. Also, derivatization of terminal adipate (−CH_2CH_2(C═O)OH) methylene protons e′ resulted in a signal at 2.9 ppm. The relative integration intensities of signals at 4.35−4.4 to 2.9 ppm after oxalyl chloride derivatization gave the ratio of hydroxyl to carboxylic acid groups in copolyesters.

Scheme 2 shows that there are three different ways that polymerized TMP units can be substituted. Structures **1′**, **2′**, and **3′** are terminal, linear, and dendritic units, respectively. To discriminate between these substitution patterns, mixtures of model compounds **1**−**3** (Scheme 3) were prepared by acetylation of TMP with acetic anhydride according to a literature procedure.[35c] Inverse-gated ^{13}C NMR spectra of TMP copolymers and model compounds **1**−**3** were recorded. A distinguishing feature of these spectra is the chemical shift(s) corresponding to TMP unit quaternary carbons. Figures 2a and 2b show expanded quaternary carbon regions of quaternary carbon signals for the synthesized mixture of compounds **1**−**3** with and without addition of non-acetylated TMP. Well resolved signals at 42.53 and 42.08 ppm correspond to quaternary carbons of non-acetylated TMP and model compound **1**, respectively. Signals at 41.49 and 40.01 ppm correspond to quaternary carbons of model compounds **2** and **3**, respectively. The observed upfield shift of quaternary carbon per acyl substituent is consistent with

Scheme 3. Mixture of Model Compounds Synthesized To Discriminate between the Possible Substitution Patterns of Trimethylolpropane in the Poly(OA-co-TMPA) Polymer



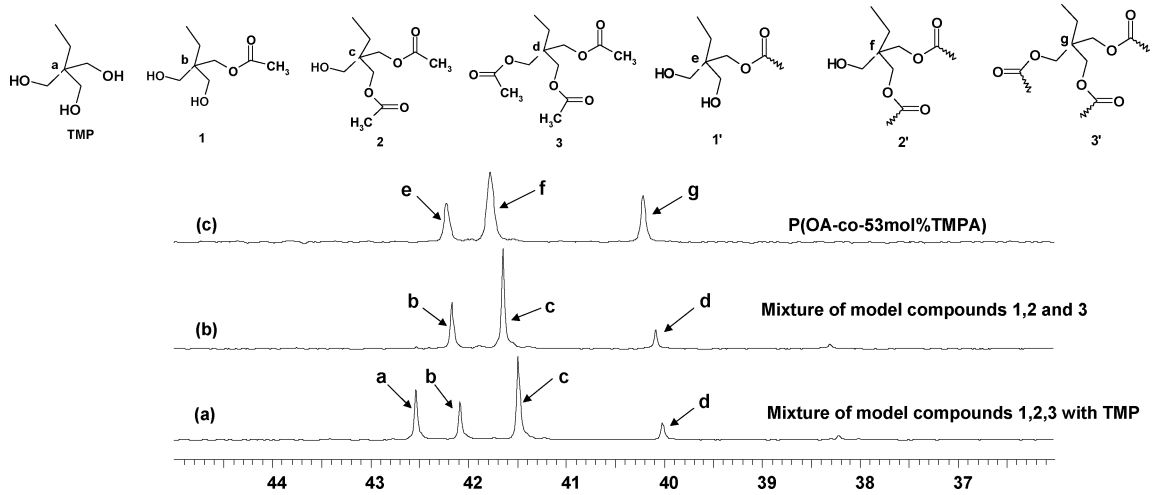


Figure 2. ^{13}C NMR spectra showing (a) a mixture of model compounds **1**, **2**, and **3** with externally added trimethylolpropane, (b) a mixture of model compounds **1**, **2**, and **3** without trimethylolpropane, and (c) poly(OA-*co*-53 mol %-TMPA) copolymer.

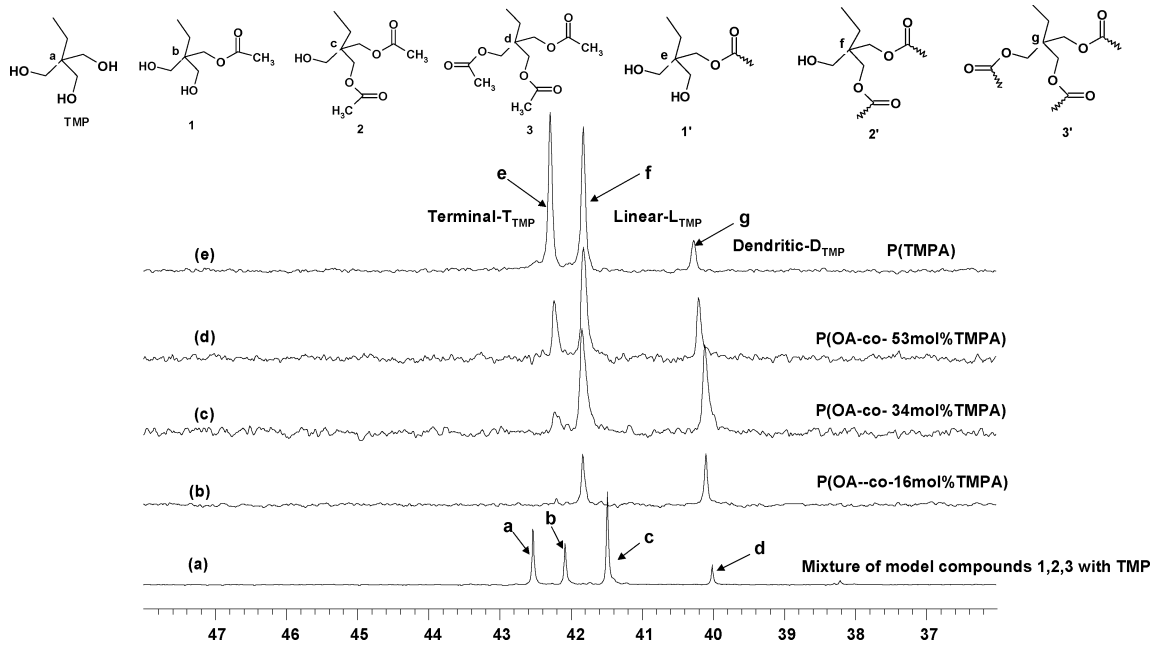


Figure 3. Expanded region of inverse-gated ^{13}C NMR (75.13 MHz) spectra that show signals corresponding to the quaternary carbons of trimethylolpropane for the copolymer series described in Table 1.

previous literature reports.[37] Comparison of Figures 2a, 2b, and 2c shows that neither the mixture of model compounds nor P(OA-*co*-53 mol %-TMPA) contains unreacted TMP. Furthermore, assignment of TMP unit quaternary carbon signals for the copolymer follows by comparison to spectra of the model compounds. Hence, the quaternary carbon signals of P(OA-*co*-53 mol %-TMPA) at 42.22, 41.79, and 40.23 are assigned to monosubstitued or terminal (T_T), disubstituted or linear (L_T), and trisubstituted or dendritic (D_T) TMP units, respectively.

In addition to TMP end groups, inverse-gated ^{13}C NMR spectra of copolymers allowed identification and quantification of other chain end groups. Terminal adipate unit (T_A) carboxylic acid ($-CH_2-(C{=}O)-OH$) carbons were observed at 176.33 ppm. Also, methylene carbons of terminal (T_O, CH_2-CH_2-OH) and linear (L_O, $-CH_2-O-(C{=}O)-$) 1,8-octanediol units were observed at 62.5 and 64.4 ppm, respectively. Figures 3b−e show expansions of inverse-gated ^{13}C NMR spectral regions where signals for TMP unit quaternary carbons are observed for the series of P(OA-*co*-TMPA) copolymers described in Table 1. By integration of relative peak areas as described above, substitution of TMP units was determined.

Branching and Copolymer Architecture. The average degree of branching (DB) of TMP copolymers was calculated by eq 1

$$DB = [\Sigma D + \Sigma T]/[\Sigma D + \Sigma L + \Sigma T] \quad (1)$$

where ΣD, ΣT, and ΣL are summations of dendritic, terminal, and linear repeat units, respectively. To satisfy this equation, dendritic units must be present in the polymer. For linear polymers DB is 0 while hyperbranched polymers have DB less than 100. The additive values of terminal, linear, and dendritic units were calculated as follows: (i) $\Sigma T = T_T + T_A + T_O$, (ii) $\Sigma L = L_T + L_O$, and (iii) $\Sigma D = D$. Since poly(TMPA) lacks 1,8-octanediol units, this copolymer has no contribution from terms T_O and L_O. Hence, for P(TMPA), $\Sigma T = T_T + T_A$ and $\Sigma L = L_T$. Relative percentages in P(OA-*co*-TMPA) of D, T_T, T_A, T_O, L_T, and L_O units were determined by integration of the corresponding signals from inverse-gated ^{13}C NMR spectra (see above). Since copolymers consist of OA and TMPA dyads, it follows that D, L_T, and T_T units are comprised of TMP and neighboring adipate. Similarly, L_O and T_O units are comprised

of OA units. Relative percentages of these dyads in copolymers are listed in Table S-1 of the Supporting Information.

Table 1 lists DB values calculated using eq 1. As the content of TMPA units in copolymers increased from 16 to 34, 53, and 100 mol %, the mol % of copolymer monosubstituted or terminal TMP units increased from 4 to 12, 25, and 46%, respectively (Figure 3 and Table 1). Thus, relative to 1,8-octanediol terminal units, TMP terminal units are less reactive, thus hindering chain growth. At low TMP feed ratios (i.e., 10 mol %), the fraction of trisubstituted (i.e., dendritic) TMP units is high (49%, Table 1). By increasing the TMP content in the monomer feed, copolymers with a lower fraction of trisubstsituted TMP units were obtained. This trend in substitution follows from simple arguments based on monomer feed stoichiometry. Tests of copolymer solubility for products described in Table 1 showed that they were completely soluble in chloroform, THF, and benzene but were insoluble in methanol and water. Regardless of that, TMP copolymers of relatively high molecular weight and branching were formed (Table 1); in no case was an insoluble or gel-like product fraction observed. In other words, by the enzyme-catalyzed route described herein, there was no formation of product with extensive cross-linking leading to network formation.

The presence of dendritic TMP units along chains suggests that copolyesters formed at 42 h are hyperbranched. The general structural features of hyperbranched copolyesters formed herein are displayed in Scheme 1. The hypothetical copolymer structure includes cyclics formed by intramolecular esterification.[38,39] Thus far, attempts by us to analyze the cyclic content of hyperbranched P(OA-*co*-TMPA) by MALDI-TOF mass spectrometry have failed due to difficulties in identifying a suitable matrix to ionize the polymers as well as poorly resolved signals. As an alternative approach, we are currently analyzing copolymer architecture by atomic force microscopy.

Molar Mass Measurements. Molar masses of copolyesters relative to polystyrene standards in THF were determined using a refractive index detector. Table 1 shows how variations in the monomer feed affected the relative molecular weight averages of synthesized hyperbranched polyesters. Hyperbranched TMP copolyesters prepared using lipase catalysis have M_w values up to 22 400 g/mol. The highest molecular weight products were from entries 2 and 3 with 16 and 34 mol % TMPA units. The product of the lowest M_w was from entry 5 without 1,8-octanediol. With the exception of entry 5, copolymers were obtained in high yield (80−94%) with M_w/M_n values from 2.2 to 6.6. Thus, by increasing the content of TMP in the monomer feed, the synthesized copolymers generally had lower molecular weights and were isolated in lower yields. However, the DB increased regularly by increasing the copolymer TMP content. The trend of decreased molecular weight with increasing copolymer TMP content may be explained by: (i) Increased branching results in more compact and dense structures that decrease the binding and reactivity of chain ends at the active site, and (ii) formation of trisubstituted TMP units deviates from the assumption that TMP reacts as a diol. The latter implies that the stoichiometry of carboxyl to hydroxyl groups deviates from 1:1, which will limit the extent of chain growth during step-condensation polymerizations. Work is in progress to determine how copolymer molecular weight and DB are affected by varying the relative ratio of OH/COOH in the monomer feed.

Thermal and Crystalline Properties. Figure 4a shows DSC thermograms recorded from first heating scans of poly(OA), poly(OA-*co*-16 mol %-TMPA), poly(OA-*co*-34 mol %-TMPA), poly(OA-*co*-53 mol %-TMPA), and poly(TMPA) copolymers.

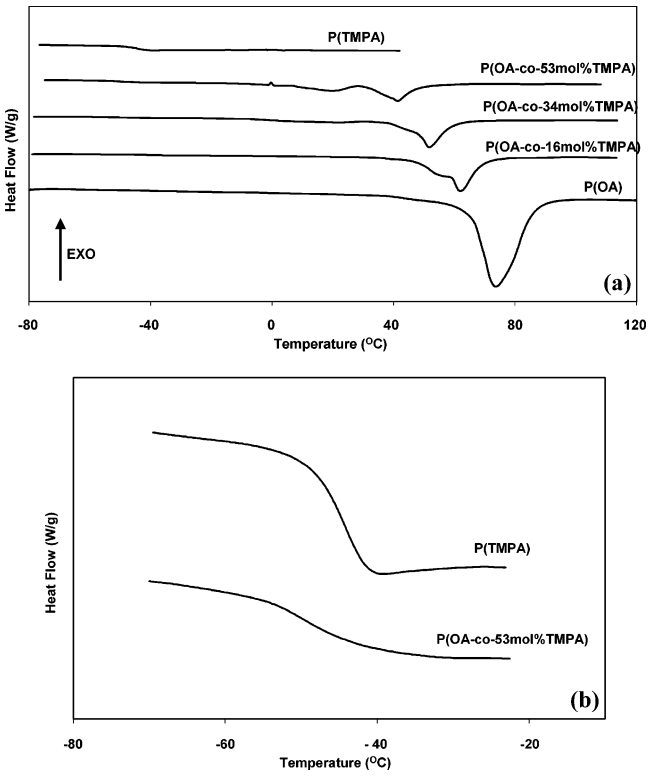


Figure 4. (a). DSC melting endotherms of P(OA-*co*-TMPA) copolymers during first heating scans. **(b)**. Expansion of DSC melting endotherms of P(TMPA) and P(OA-*co*-34 mol %-TMPA) copolymers to show glass transitions.

Table 2. Thermal Properties from DSC and TGA Analyses of P(OA-*co*-TMPA) Copolymers

entry	observed OA/TMPA (mol %)	T_m[a] (°C)	ΔH_f[b] (J/g)	T_g[a] (°C)	Δm[d] (wt %)	T_{max}[e] (°C)
1	100:0	74	136	−28[c]	0.2	441
2	84:16	62[f]	92	n.d.	1.2	446
3	66:34	52	49	n.d.	1.7	450
4	47:53	41[g]	25	−49	1.7	440
5	0:100			−44	9.0	424

[a] Determined by DSC from the first heating scan. [b] Determined by DSC from the first heating scan and is the summation of all melting transitions. [c] Determined by direct multicomponent analysis and reported elsewhere;[18] n.d., not determined. [d] The wt % loss at 300 °C measured using the following equation Δm = (wt % remaining at room temperature − wt % remaining at 300 °C); the wt % remaining at room temperature is 100%. [e] Determined from thermogravimetric analysis. [f] Another small peak at 59 °C. [g] Another small peak at 20 °C with ΔH_f of 9 J/g.

In Figure 4b, the first heating DSC scans of P(TMPA) and P(OA-*co*-53 mol %-TMPA) shown in Figure 4a were expanded to show the glass transition. Table 2 lists results of DSC analyses as a function of the copolymer compositions. Melting endotherms with peaks at 41−74 °C (T_m values) were the dominant thermal transitions observed in DSC curves except for P(TMPA). P(OA-*co*-TMPA) copolymers, as well as P(OA), are semicrystalline except for the P(TMPA), which is completely amorphous with a glass transition at −44 °C. While a glass transition at −49 °C was observed for P(OA-*co*-53 mol %-TMPA) (Figure 4b), glass transitions were not observed for P(OA-*co*-16 mol %-TMPA) and P(OA-*co*-34 mol %-TMPA). Weak glass transitions from DSC experiments led Sunder et al.[18] to use dynamic mechanical analysis to analyze the glass transition temperature of P(OA). Generally, by increasing the TMP content in copolymers, their crystal structure was disrupted, causing a decrease in T_m and heat of fusion (ΔH_f) values.

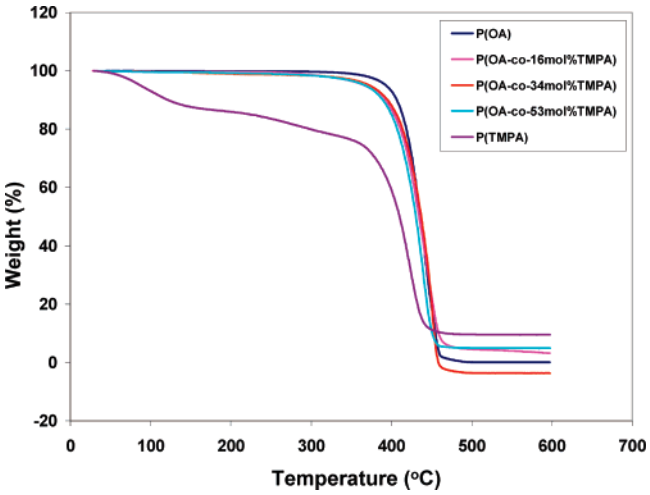


Figure 5. Thermogravimetric analysis of P(OA-*co*-TMPA) copolymers.

For example, increasing the TMPA content from 16 to 53 mol % caused T_m and ΔH_f to decrease from 62 to 41 °C and 92 to 25 J/g, respectively.

TGA analyses of P(OA), P(OA-*co*-16 mol %-TMPA), P(OA-*co*-34 mol %-TMPA), and P(OA-*co*-53 mol %-TMPA) were performed, and results of this work are listed in Table 2. TGA curves (Figure 5) of P(OA-*co*-TMPA) showed a single weight loss step centered at a temperature (T_{max}) nearby P(OA) at 441 °C. Relative to the TGA curve of P(OA), increases in copolymer TMPA content resulted in small decreases in thermal stability evident by comparison of weight loss values at 300 °C (Δm). Increase in copolymer TMPA mol % from 0 to 16, 34, and 53 mol % resulted in Δm values of 0.2, 1.2, 1.7, and 1.7, respectively. In contrast, P(TMPA) has two weight loss steps centered at 84 and 424 °C, respectively.

Summary and Conclusions

This work showed that TMP is a suitable polyol monomer for introduction of branch points along chains during Novozyme-435-catalyzed bulk polycondensations (70 °C, 42 h). Variation of TMP in the monomer feed gave copolymers with degree of branching (DB) from 20% to 67%. In general, molecular weight decreased with increased TMP in the monomer feed. This trend may be explained by: (i) Increased branching results in more compact and dense structures that decrease chain end binding at the active site, and (ii) formation of trisubstituted TMP units results in a deviation from 1:1 in reactive carboxyl and hydroxyl groups in the condensation polymerization.

P(TMPA) is completely amorphous and has a glass transition at −44 °C while P(OA-*co*-TMPA)'s are semicrystalline materials. By increasing TMPA content in copolymers from 16 to 53 mol %, T_m and ΔH_f values decreased from 62 to 41 °C and 92 to 25 J/g, respectively.

The synthetic method described herein gave highly functional branched copolymers of substantial molecular weight with no gel content. The polymerizations were conducted in bulk without activation of diacids. Also, polymerizations were conducted without taking special precautions to avoid gels such as kinetically freezing the reactions or conducting polymerizations in dilute solution.

Supporting Information Available. Relative percentages of all possible linear, terminal, and dendritic units present in hyperbranched polyesters containing varying contents of trimethylolpropane. This material is available free of charge via the Internet at http://pubs.acs.org

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