Synthesis of Hyperbranched Poly(glycerol-diacid) Oligomers

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ABSTRACT: Novel oligomeric prepolymers were synthesized by acid-catalyzed condensation of glycerol with iminodiacetic, azelaic, or succinic acid. The prepolymers were obtained, on average, in 62% yield and were characterized by ^{13}C NMR, ^{1}H NMR, matrix-assisted laser desorption ionization-time of flight-mass spectrometry, and gel permeation chromatography. The synthesized oligomers had an average M.W. of 1543 Daltons (average polydispersity (PD) = 1.34, average degree of polymerization (DOP) = 5.5). Hyperbranching was evident in the oligomers produced when using azelaic acid and succinic acid as co-monomers with glycerol, whereas the reaction between iminodiacetic acid and glycerol resulted in linear products bearing cyclic urethane structures.

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KEY WORDS: Diacids, glycerol, hyperbranching, polymers

Currently, there is a continuing effort to reduce U.S. dependence on foreign oil by using alternative, biobased fuels that also promote a clean environment. One approach to this goal is the use of biodiesel, a renewable fuel that is produced from fats and oils. With an increased production of biodiesel fuels, however, there also will be increased production of glycerol, the major co-product from the transesterification process used to produce biodiesel. As a consequence, glycerol production is predicted to increase to 1.1 million tons by 2008, a 38% increase from 1998 (1), and because of this there is a need to find new uses for glycerol. The development of new markets for glycerol also would have a significant impact on the economics of biodiesel production, since increased credit for this co-product would improve the economics of biodiesel and make it more commercially competitive with petroleum-derived diesel.

One approach to use large amounts of glycerol is to polymerize it. However, most strategies used to make polyglycerols do not us glycerol as the major propagating unit. Instead, monomers such as glycidol (2), a highly reactive epoxide, or *cis*-1,3-*O*-benzylideneglycerol (3) are used primarily since the condensation of glycerol is nonselective and requires high processing temperatures.

It was our goal to synthesize pre-polymers composed of glycerol units that could be further reacted to produce longer chains of hyperbranched polymers. Hyperbranched polymers belong to the family of macromolecules known as dendrimers, which are highly branched monodispersed molecules produced by multistep syntheses. In contrast, hyperbranched polymers are randomly branched molecules prepared by a simple one-step reaction. One of the earliest studies on hyperbranched polymers was performed by Flory (4) in which he described the critical gel point for hyperbranched polymers produced from AB_2 monomers. Since that time, condensation reactions involving di-functional monomers (A_2) with tri-functional monomers (B_3) have received considerable attention in the synthesis of branched polymers instead of AB_2 monomers (5–9). Hyperbranched polymers produced from diacids (A_2) and glycerol (B_3) are an example of this type of system. AB_2 monomers are not readily available, and kinetic calculations show that the first condensation reaction, which produces an AB_2 species, is faster than subsequent polymer propagation; thus, the remainder of the reaction progresses as polycondensations between AB_2-type species prior to the gel point. Several methods have been used to avoid gelation in $A_2 + B_3$ systems, including performing the reactions in dilute solutions (10) or reacting them in the absence of solvent while monitoring the viscosity of the system (6). Others have shown that gelation, branching, and M.W. can be controlled by lipase-catalyzed bulk polycondensations (7).

In this study, we wish to demonstrate the potential for using free glycerol to replace toxic monomers, such as glycidol, that are environmentally hazardous. To this goal, three structurally and chemically different diacids were reacted with glycerol to undertake a comparative study on the viability of using free glycerol as a polymer-propagating monomer. Such glycerol-based polymers are expected to render new surgical materials useful in orthopedic and ophthalmic applications, reconstructive surgery, and as drug delivery agents (11–13). These biocompatible polymers also are of interest for their potential uses as cosmetics, food additives, surfactants, lubricants, and azeotropic phase separators (14).

MATERIALS AND METHODS

Materials. Azelaic acid, iminodiacetic acid, glycerol, and titanium(IV) butoxide [$Ti(OC_4H_9)_4$] were purchased from Sigma-Aldrich (St. Louis, MO). Succinic acid was from Aldrich Chemical Co. (Milwaukee, WI). Deuterated NMR solvents (acetone-d_6, deuterium oxide, and dimethyl sulfoxide-d_6) were from Cambridge Isotope Laboratories (Andover, MA).

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Polymerizations. The diacid (0.10 mol), glycerol (0.105 mol), and 0.15% w/w catalyst, $Ti(OC_4H_9)_4$, were placed in a 100-mL two-necked round-bottomed flask and heated to 60°C under reduced pressure (~150 Pa) for 1 h. The reaction mixture subsequently was allowed to react for 2 h at 100°C, then 2 h at 120°C, and finally overnight at 150°C under reduced pressure (~150 Pa), for a total reaction time of approximately 16 h. The product resulting from the neat reaction of iminodiacetic acid and glycerol was dissolved in distilled water and vacuum-filtered to remove unreacted acid. The crude products derived from reactions of succinic acid or azelaic acid with glycerol were dissolved in acetone or chloroform, respectively. The solutions were subsequently vacuum-filtered to remove unreacted acid and the solvents were removed from the filtrate by rotary evaporation. The filtrate from iminodiacetic that was dissolved in water was passed through a column packed with Sephadex G-10 (Pharmacia Fine Chemicals, Piscataway, NJ) to remove any residual starting materials and catalyst. The rotary evaporated products derived from the reactions of azelaic acid or succinic acid with glycerol were dissolved in methanol and also passed through a column packed with Sephadex G-10. All products were dried by lyophilization before analyses.

Size exclusion chromatography. Poly(glycerol-iminodiacetic acid) (200 μL) was dissolved in 0.05 M $NaNO_3$ and injected into a Hewlett-Packard HP 1100 gel permeation chromatography (GPC) system with isocratic pump, equipped with a degasser, autosampler, in-line membrane filter, pre- and post-column set guards, three chromatography columns, multi-angle laser light-scattering detector (MALLS), Viscotec Corporation (Houston, TX) viscometer, and Wyatt Technology (Santa Barbara, CA) interferometric refractometer. The serially placed chromatography columns consisted of two Polymer Laboratories (Amherst, MA) PL-Aquagel OH-60 columns (7.5 × 300 mm) and one PL-Aquagel OH-40 column (7.5 × 300 mm). The electronic data were processed using Viscotec TriSec 3.0 GPC and ASTRA™ (v. 4.90.08) software.

Succinic acid-glycerol oligomers and the azelaic acid-glycerol oligomers were dissolved in THF in concentrations of 17.8 and 13.4 mg/μL, respectively, and 20–30 mL was injected into a Shimadzu Prominence HPLC (Columbia, MD) LC20AT system equipped with an SIL-10AF autosampler, a DGU-20A5 degassing unit, a Polymer Laboratories PLGel 5 μm column (7.5 μm × 300 mm) with 100 Å pore size, a CBM-20A communications BUS module, and a Sedex (Sedere, Alfortville, France) detector. The GPC was calibrated by the creation of a standard curve using standards from the "Polystyrene medium molecular weight kit" from Polymer Laboratories and, for lower M.W., tristearin, monostearin, and stearic acid. The detector was set to 40°C with a gain of 4.0 at 2.5 bar. The electronic data were processed with the EZ-Start Chromatography (Shimadzu) software.

MS. Spectra from matrix-assisted laser desorption/ionization mass spectrometry time-of-flight (MALDI-TOF) with automated tandem TOF fragmentation of selected ions (MALDI-TOF/TOF) were acquired with a 4700 Proteomics Analyzer mass spectrometer (Applied Biosystems, Framingham, MA) in the positive reflector mode with a 200 Hz Nd-YAG 355 nm laser. Spectra were obtained by averaging 1000 acquired spectra in the MS mode. Conversion of time of flight to mass (Da) for the monoisotopic ions, $[M + H]^+$, was based on calibration of the instrument with a peptide standard calibration kit (Applied Biosystems) that contained the following peptides: des-Arg^1-bradykinin (*m/z* 904.4681), angiotensin I (*m/z* 1,296.6853), Glu^1-fibrinopetide B (*m/z* 1,570.6774), ACTH (adrenocorticotrophic hormone: clip 1-17) (*m/z* 2,903.0867), ACTH (clip 18–39) (*m/z* 2.465.1989), and ACTH (clip 7–38) (*m/z* 3,657.9294). The 2,5-dihydroxybenzoic acid (DHB) matrix solution was prepared by dissolving 10 mg of DHB in a 1 mL aliquot of 10 mM sodium acetate solution. The 10mM sodium acetate solution was prepared in a 50/50 (v/v) mixture of acetonitrile-water. An aliquot (1μgL) of the polymer sample (1 mg/mL in H_20) was mixed with 24 μgL of DHB matrix solution and (7μgL) of the resulting solution was spotted on the MALDI plate for analysis.

NMR. ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature on a Varian Gemini 200-MHz spectrometer. Operating parameters for ^{1}H NMR were: cycle time (d1) = 1.0 s; acquisition time (aT) = 3.744 s; transmitter power (tpwr) = 57 Hz; pulse width (pw) = 90°; operating parameters for ^{13}C NMR were: cycle time (d1) = 2.0 s; aT = 2.399 s; tpwr = 52 Hz; pw = 45°. Spectra for iminodiacetic acid and iminodiacetic acid-glycerol oligomers were recorded in D_2O. Spectra for succinic acid, azelaic acid, and their oligomers with glycerol were recorded in DMSO-d_6.

^{1}H NMR of succinic acid-glycerol oligomers (DMSO-d_6, 200 MHz): δ 2.65 (*m*, –C<u>H</u>$_2$–CH$_2$–), 3.45 (*m*, –C<u>H</u>$_2$–CHOH–CH$_2$–), d 4.10 (*m*, –CH$_2$–CHO<u>H</u>–CH$_2$–). The following are the accompanying peaks due to linear and branched oligomeric repeat units at various distances from the succinic acid-glycerol core (R = H or ester): δ 3.55 (*m*, –CH$_2$–CHOR–CH$_2$–), 3.72 (*m*, –CH$_2$–CHOR–CH$_2$–), 4.27 (*m*, –CH$_2$–CHOR–CH$_2$–), 4.50 (*m*, –CH$_2$–CHOR–CH$_2$–), 4.73 (*m*, –CH$_2$–CHOR–CH$_2$–), 5.02 (*m*, –CH$_2$–CHOR–CH$_2$–), 5.37 (*m*, –CH$_2$–CHOR–CH$_2$–), 12.24 (*br*, –COOH, 1H). ^{1}H NMR of azelaic acid-glycerol oligomers (DMSO-d_6, 200 MHz; R = H or ester): δ 1.21 (*m*, –CH$_2$–C<u>H</u>$_2$–CH$_2$–), 1.49 (*m*, –CH$_2$–), 2.26 (*m*, –C<u>H</u>$_2$–COOH), 3.38 (*m*, –C<u>H</u>$_2$–CHOR–CH$_2$–). The following are the accompanying peaks due to linear and branched oligomeric repeat units at various distances from the azelaic acid-glycerol core (R = H or ester): δ 4.09 (*m*, –CH$_2$–C<u>H</u>OR–CH$_2$–), 4.62 (*m*, –CH$_2$–CHOR–CH$_2$–), 4.98 (*m*, –CH$_2$–CHOR–CH$_2$–), 5.25 (*m*, –CH$_2$–CHOR–CH$_2$–). ^{1}H NMR of iminodiacetic acid-glycerol oligomers (DMSO-d_6, 200 MHz): δ 3.45 (*m*, –OCH$_2$–), 3.64 (*m*, –CHO–), 4.12 (*d*, –CH$_2$N–). The following are the accompanying peaks due to linear and branched oligomeric repeat units at various distances from the iminodiacetic acid-glycerol core (R = H or ester): δ 3.85 (*m*, –C<u>H</u>$_2$–CHOR–C<u>H</u>$_2$–), 4.32 (*m*, –CH$_2$–CHOR–CH$_2$–), 4.99 (*m*, –CH$_2$–C<u>H</u>OR–CH$_2$–). ^{1}H NMR of iminodiacetic acid-glycerol oligomers (DMSO-d_6, 400 MHz): δ 3.58 (*m*, –OCH$_2$–), 3.67 (*m*, –OCH$_2$–), 3.78 (*m*, –CHO–), 4.01 (*m*, –CH$_2$–C<u>H</u>OR–CH$_2$–), 4.27 (*d*, –CH$_2$N–). The following are the accompanying peaks due to linear and branched oligomeric

repeat units at various distances from the iminodiacetic acid-glycerol core (R = H or ester): δ 4.47 (*m*, –CH_2–CHOR–CH_2–), 5.12 (*m*, –CH_2–CHOR–CH_2–), 5.29 (*m*, –CH_2–CHOR–CH_2–), 5.47 (*m*, –CH_2–CHOR–CH_2–). ^{13}C NMR of succinic acid-glycerol oligomers (DMSO-d_6, 200 MHz): δ 28.7 (*s*, –CH_2–CH_2–), 64.1 (*m*, –$\underline{C}H_2$–CHO–$\underline{C}H_2$–), 72.3 (*s*, –CH_2–$\underline{C}HO$–CH_2–), 172.2 (–COOH). ^{13}C NMR of azelaic acid-glycerol oligomers (DMSO-d_6, 200 MHz): δ 24.5 (–CH_2–), 29.8 (*m*, –CH_2–), 35.4 (*m*, –$CH_2\underline{C}H_2CH_2$–), 64.1 (–CH_2O–), 68.1 (*m*, –CH_2–$\underline{C}HO$–CH_2–), 71.1 (*m*, –CH_2OH), 173.8 (–$\underline{C}OOH$). ^{13}C NMR of iminodiacetic acid-glycerol oligomers (DMSO-d_6, 200 MHz): δ 38.3 (–CH_2N–), 46.2 (–CH_2N–), 47.1 (*m*, –CH_2N–), 47.9 (–CH_2N–), 50.8 (–CH_2N–), 59.6 (–CH_2O–), 61.5 (–CH_2O–), 61.9 (–CH_2O–), 65.2 (–$CH_2\underline{C}HOCH_2$–), 66.2 (–$CH_2\underline{C}HOCH_2$–), 66.7 (–$CH_2\underline{C}HOCH_2$–), 68.7 (–$CH_2\underline{C}HOCH_2$–), 71.7 (–CH_2-$\underline{C}HOCH_2$–), 76.2 (–$CH_2\underline{C}HOCH_2$–), 77.2 (–$CH_2\underline{C}HOCH_2$–), 166.0 (–COOH), 166.2 (–COOH), 169.2 (–COOH), 169.5 (–COOH), 171.6 (–COOH).

RESULTS AND DISCUSSION

Polymers resulting from the copolymerization of glycerol with diacids of varying carbon chain length, molecular structure, and composition were synthesized. Consistent with previous studies (6) of this type, gelation was not observed. The same synthetic strategy was used for each reaction. Purification and characterization of the oligomers were adjusted accordingly based on the solubility differences of the individual oligomers. After purification by chromatography, the products were obtained in an average yield of 62%. This is largely attributed to incomplete reaction, as inferred by NMR, during the allocated reaction time and a decrease in reaction rate due to increased viscosity of the solution. Increased viscosity limits the interaction between the reactants and the growing polymer. Solubility studies were performed for each product to determine the most effective method for product extraction and characterization by spectroscopic analysis. As expected, the water solubility of the oligomers decreased with increasing chain length of the diacid monomers used in preparing the oligomers. The iminodiacetic acid-glycerol oligomers were insoluble in nonpolar solvents such as hexane and chloroform but were very soluble in water and polar solvents such as methanol and dimethylformamide. Hydrogen bonding from the heteronitrogen atom in the iminodiacetic acid-glycerol oligomers likely contributes to their increased solubility in polar solvents. The succinic acid-glycerol oligomers were soluble in polar solvents such as acetone, only slightly soluble in water, and insoluble in nonpolar solvents. On the other hand, the azelaic acid-glycerol oligomers were not water soluble but, as expected from their increased FA chain-length, were soluble in nonpolar solvents such as toluene.

Table 1 lists the M.W., polydispersity, and degree of branching for each of the oligomers as determined by size exclusion chromatography (SEC). As described earlier, two types of GPC analyses were necessary because of the differences in the solubility of the oligomers. Polymerization was effective in forming the oligomeric products shown in Figures 2 and 3. The average M.W. for the three neat reactions were ~1543 Da with an average polydispersity index (PDI) of 1.34 (±0.13). Such low M.W. are common unless the reactions are carried out in dilute solutions (10) but a better comparison might be made by inspection of the degree of polymerization (DP), the average for the three reactions of which was 4.5 (±0.8). Polydispersity is likely to increase on polymerization since polydispersity for hyperbranched polymers is typically in the range of DP/2.Various synthetic strategies can be used to optimize the reaction and control the synthesis on further polymerization (8,9,15,16).

TABLE 1
Size Exclusion Chromatography (SEC) Data for Glycerol-Based Oligomers[a]

Co-monomer	M_n	PDI	DP
Iminodiacetic acid	1450	1.36	5.1
Succinic acid	992	1.28	3.
Azelaic acid	2316	1.30	4.9

[a]M_n = number average M.W.; PDI = polydispersity index; DP = degree of polymerization.

NMR spectroscopy supported the presence of branched structures in the glycerol oligomers as observed by repeating ^{1}H and ^{13}C resonances in their NMR spectra. In general, NMR resonances for the same type of repeat unit can appear upfield as repeating units get farther from the polymer core as a result of branching and linear propagation. All NMR spectral shifts are listed in the experimental section of this paper. The ^{13}C NMR spectra for the oligomers made by copolymerization of azelaic or succinic acid with glycerol both showed multiple overlapping peaks in the glycerol region (59.6–71.7 ppm region) and strong, distinct resonances for the azelaic and succinic acid units present in the aliphatic region (28–30 ppm). For azelaic acid and succinic acid polymerized with glycerol, the ^{13}C spectra did not provide sufficient detail to assign oligomer structures. However, the ^{13}C NMR spectra for the iminodiacetic acid-glycerol oligomers did show strong and well-defined resonances for both primary (core) and secondary (repeating) glycerol-diacid structural units (76–78 ppm). A better indication of oligomer structure could be made from the ^{1}H NMR spectra of the oligomers, which are shown in Figure 1. ^{1}H NMR resonances due to AB_2 repeating units were observed for the iminodiacetic acid-glycerol oligomers using the 200 MHz instrument. The proton resonances from the iminodiacetic acid repeat units (4.12 ppm) give two peaks for two different proton environments that overlap to give the illusion of a doublet. A doublet is impossible for this resonance; therefore, it is reasonable to assume that they are two overlapping singlets. These resonances are believed to be the result of cyclic and linear imine units. Repeating glycerol units resulting from branching give three repeats units that are observed in the 200 MHz instrument, both significantly shifted upfield (3.85, 4.32, and 4.99 ppm) with decreasing intensity. Additional resonances were only slightly more visible using a 400 MHz instrument in which small peaks are observed in the range of 4.73–5.37 ppm (Fig. 1A). Very strong ^{1}H NMR resonance peaks are observed for the primary (core) azelaic and succinic acid-glycerol

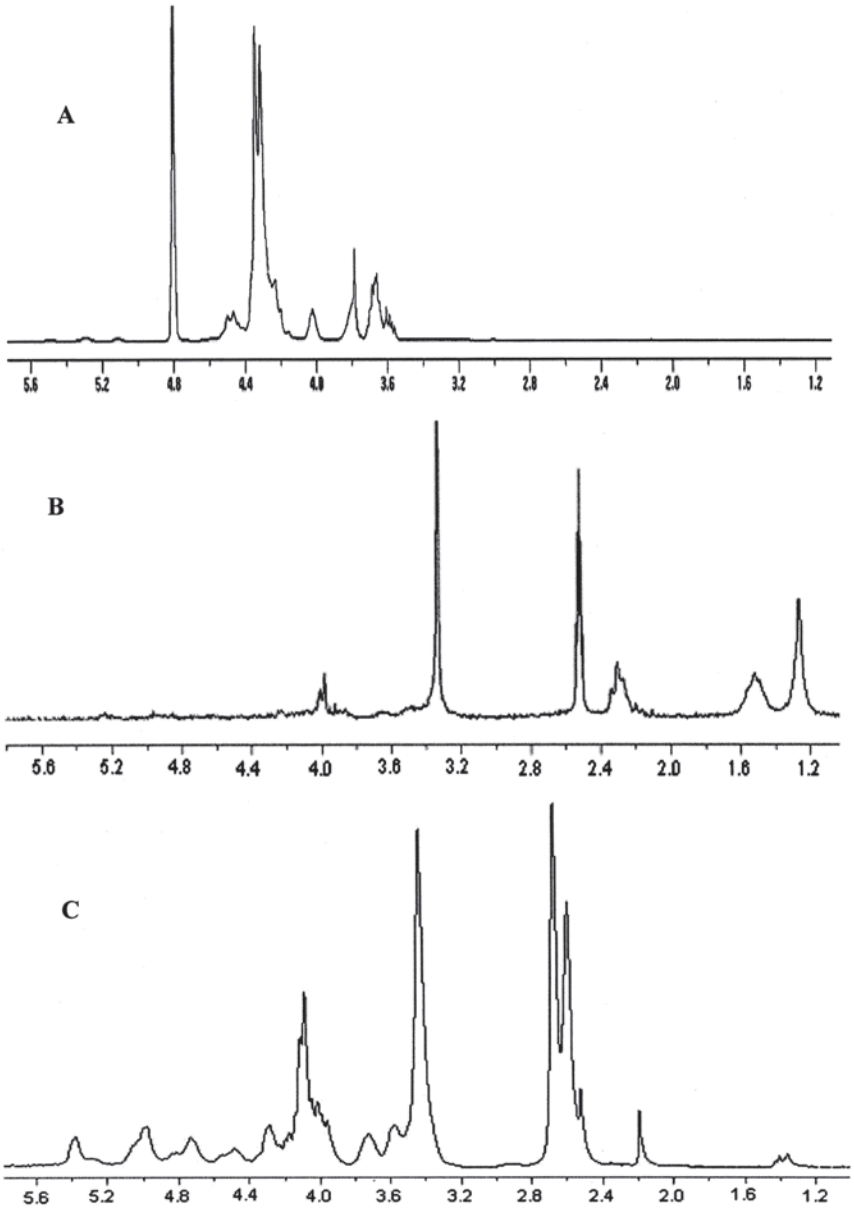


FIG. 1. ^{1}H proton NMR spectra of diacid-glycerol oligomers. (A) Iminodiacetic acid and glycerol (400 MHz); (B) azelaic acid and glycerol (200 MHz); (C) succinic acid and glycerol (200 MHz).

oligomer units as shown in their NMR spectra, Figures 1B and 1C, respectively. The secondary (branched) repeating succinic acid-glycerol units are broader and less defined but very observable (4.09–5.37 ppm). Unfortunately, the repeat units for the azelaic acid oligomers are not as distinct. Higher-frequency NMR spectra are required to improve the resolution of the peaks resulting from branching in the oligomers.

MS is a useful technique for the structural characterization of polymers resulting from linear, cyclic, or branching polymerization reaction pathways. Combining the MALDI ionization process with the TOF analyzer allows detection of compounds with high M.W. without the interference of significant fragmentation resulting from the metastable decay of ionized molecules that are associated with typical MS techniques. This technique is widely used to facilitate the analysis of biopolymers and synthetic polymers. Although MALDI ionization of biopolymers results in proton addition, synthetic polymers are more likely to add sodium and potassium. Traces of these cations are present in the solutions used for analysis. The ions reported in this work are positive sodiated species $(M + Na)^{+}$ derived from 10 mM sodium acetate that was added to the matrix solution. However, inclusion of sodium with the matrix did not eliminate the formation of potassium adducts, which for simplicity are not reported. In this study, samples for MALDI-TOF analysis were prepared by mixing the extracted and purified oligomers with DHB as matrix as outlined in the experi-

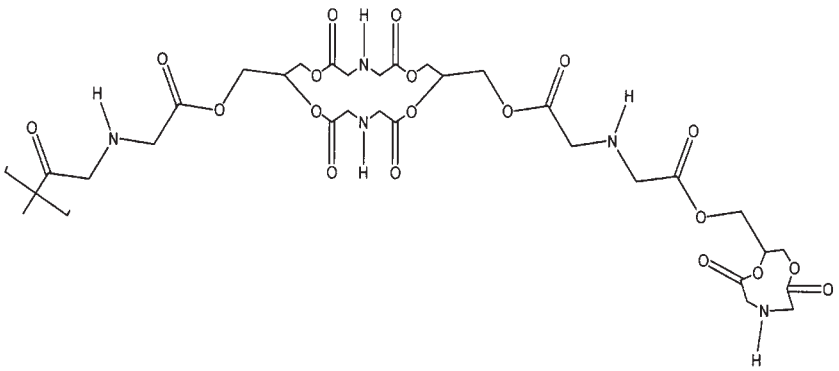


FIG. 2. Iminodiacetic acid-glycerol oligomers composed of terminal 9-membered rings and/or 18-membered rings along the propagating chain.

mental section. MALDI-TOF analyses of the oligomeric samples in this work have provided better mass detection than the other ionization technique available in our laboratory (i.e., atmospheric pressure ionization with a single quadrupole instrument). The use of a TOF analyzer in the reflectron mode provided a resolution between 15,000 and 20,000 full width half-maximum (FWHM) and an error in the mass determination below 50 ppm.

The spectra of polymer samples produced after reacting azelaic or succinic acid as copolymers with glycerol presented characteristic oligomeric chains separated by 244 and 174 Da, respectively. These molecular ions are consistent with a–(A-B)- polymeric elongation for each copolymer. Masses determined with MALDI-TOF for the individual oligomeric chains of succinic- and azelaic-glycerol products correlated, within experimental error, with the calculated mono-isotopic masses of the linear oligomeric structures reported in Table 2. MALDI mass spectra data are skewed below 500 Da owing to matrix interference; therefore, the masses reported in Table 2 only include oligomer structures masses above 500 Da. Nonetheless, the spectrum showed the more intense ions for these oligomeric products above the 500 Da limit, whereas no ions were detected above 2500 Da. Although the masses shown in Table 2 are consistent with a linear polymerization pathway, branched products are also possible. If branched products are formed at the secondary glycerol hydroxyl group, the spectrum of the oligomer should show characteristic ion masses that differ from those of the linear structures shown in Table 2. Structures having more than two free acid functionalities at the end-terminals can occur only after branching. The theoretical masses for these structures were calculated and are presented in Table 3. The mass spectrum of the oligomeric products confirms the presence of ions matching the masses expected for the branched species reported in Table 3 only up to entry 6. The addition of glycerol at the terminal carboxylic acids of these branched structures will produce isomeric structures indistinguishable by MS from the linear polymer reported in Table 2. The reaction of succinic acid with glycerol produced oligomers with M_n (number-average M.W.), PDI, and DP in good agreement with those determined by SEC (Table 1), whereas the values determined for azelaic acid-glycerol oligomers have a significant discrepancy.

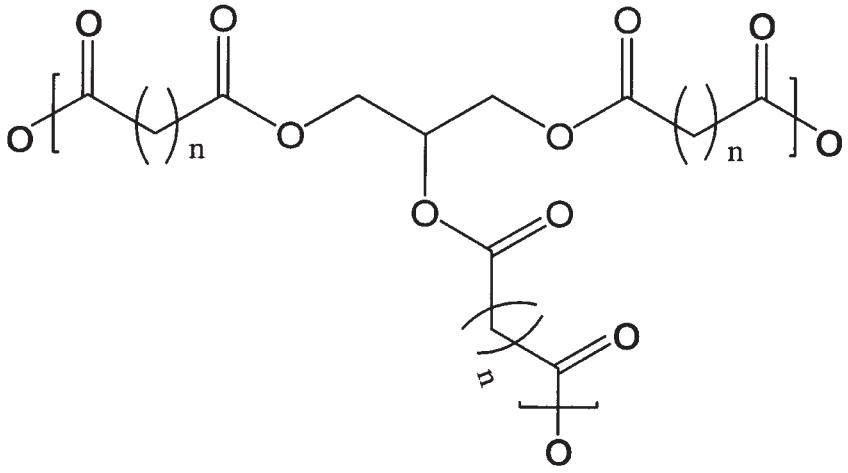


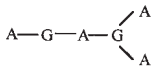
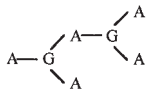
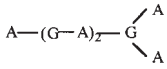
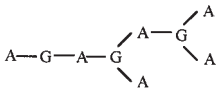
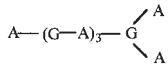
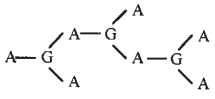
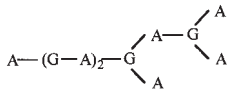
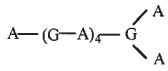
FIG. 3. Hyperbranched oligomers produced from the condensation of diacids with glycerol: n = 2, succinic acid glycerol oligomer; n = 7, azelaic acid glycerol oligomer.

TABLE 2
Mono-isotopic Masses Predicted of the Sodiated Ions for the Linear Co-oligomerization of Azelaic or Succinic Acids with Glycerol[a]

	$H–(A–B)_n–A$ $(M + Na)^+$		$H–(A–B)_n–OH$ $(M + Na)^+$		$B–(A–B)_n–OH$ $(M + Na)^+$	
n	Azelaic acid	Succinic acid	Azelaic acid	Succinic acid	Azelaic acid	Succinic acid
1		505.10				463.15
2	699.37	679.15	529.26		603.30	637.20
3	943.50	853.20	773.39	563.16	847.43	811.25
4	1187.63	1038.26	1017.53	737.21	1091.56	985.30
5	1431.76	1201.31	1261.66	911.27	1335.69	1159.36
6	1675.89	1375.36	1505.79	1085.32	1579.82	1333.41
7	1920.02	1549.42	1749.92	1259.37	1823.96	1507.46
8	2164.15	1723.47	1994.05	1433.42	2068.09	1681.51
9	2408.28	1897.50	2238.18	1607.49	2312.22	1855.57

[a]Only masses above 500 Daltons are reported.

TABLE 3
Suggested Structures and Predicted Mono-isotopic Masses of the Sodiated Molecular Ions for the Branched Form by Co-oligomerization of Azelaic and Succinic Acids with Glycerol[a]

Entry	Dendrimer polymer unit	Azelaic acid $(M + Na)^+$	Succinic acid $(M + Na)^+$
1		625.33	—
2		869.45	589.14
3		1039.56	689.16
4		1113.58	763.19
5		1283.68	863.21
6		1357.71	937.25
7		1453.79[b]	963.23[b]
8		1527.81	1037.26
9		1601.84	1111.30

[a]Only masses above 500 Daltons are reported.
[b]Ions not detected by matrix-assisted laser desorption ionization-time of flight mass spectrometric analysis of the oligomeric product.

The mass spectrum of the resulting product from the oligomerization of glycerol with iminodiacetic acid shows masses associated with individual chains that were inconsistent with linear or branched oligomer structures. Instead, the masses observed were 36 Da, or two H_2O molecules, below the expected masses. This suggests the presence of cyclic moieties resulting from intra-esterification of two glycerol secondary alcohols and free terminal carboxylic acids, as is shown by the structure proposed in Figure 2. The mass spectrum shows consistent oligomeric chains with mass distribution patterns of 97 and 189 Da apart. Increments of 189 Da between the oligomeric chains are in agreement with the polymeric elongation produced by the alternating co-polymers unit -(A-B)-. Increments of 97 Da between the oligomeric chains seem to be consistent with a reaction process where the carboxylic groups of the iminodiacetic acid (M.W. = 133.1) are being esterified to secondary middle-chain hydroxy groups of the oligomer rather than to the terminal group, producing an internal cyclic moiety as showed in Figure 2. Both processes have a shortening effect on the degree of polymerization and branching. The presence of similar cyclic structures has been reported previously (17–19); however, MALDI-TOF analysis cannot provide conclusive evidence for the formation of cyclic structures. Consequently, M_n, PDI, and DP were not determined by this technique.

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