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HYPERBRANCHED POLYESTER WITH MIXED METHACRYLOYL ANDALIPHATIC ESTER TERMINAL GROUPS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION IN DENTAL RESTORATIVE FORMULATIONS

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HYPERBRANCHED POLYESTER WITH MIXED METHACRYLOYL ANDALIPHATIC ESTER TERMINAL GROUPS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION IN DENTAL RESTORATIVE FORMULATIONS

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ABSTRACT

Boltron H30 is a polyester polyol with a dendritic structure, developed by Perstop Corp. Complete methacrylated H30 oligomers were obtained by using three different reaction routes, i.e., treatment of H30 with methacrylic anhydride, methacryloyl chloride and 2-isocyanatoethyl methacrylate (IEM). The viscosities of the three H30 hyperbranched materials at 45°C were 22.4, 23.5, and 42.8 Poise, respectively, compared to commonly used BisGMA having a viscosity of 33.5 Poise at 45°C. All three completely methacrylated H30 materials were combined with TEGDMA (50/50, wt/wt) to formulate visible light-curable (VLC) neat resins. The experimental VLC resins exhibited significant reduction of polymerization shrinkage and higher C=C double bond conversion, compared to the VLC BisGMA/TEGDMA (50/50, wt/wt) control. The three new resins, with the exception of the H30-IEM based formulation, have mechanical properties comparable to a BisGMA/TEGDMA control. But, the VLC H30-IEM based resin exhibited higher compressive and flexural strengths than the BisGMA/TEGDMA control, possibly due to hydrogen bonding. H30 was also esterified by using different acid chlorides to investigate the effect of other ester terminal groups on H30,

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in relation to the viscosities of the oligomers. The results show that the viscosities of the esterified H30 are strongly depended on the ester groups, where benzoate > acetate > propionate > isobutyrate ester > butyrate ester. However, the T_g of the cured resins depends more on the level of hydrogen bonding, rather than the terminal ester groups. A H30 oligomer, with half of the terminal hydroxyl groups replaced by methacrylate residues and half by different carboxylates, such as acetate, propionate, butyrate and isobutyrate ester, were prepared and used to formulate VLC resins. All these formulated resins, with partly methacrylated H30, have much higher double bond conversion and less linear polymerization shrinkage. But, they exhibited lower T_g values and less attractive mechanical properties. The latter was especially true in comparing acetate to butyrate ester terminal groups. A third series of partly methacrylated H30 were prepared, where methacrylation was achieved by combining acetyl chloride/methacryloyl chloride in the 70/30, 50/50 and 30/70 (wt/wt) ratios, respectively, were prepared and used to formulate VLC resins. The results showed that higher methacrylation of the terminal hydroxyls on H30 failed to bring about better mechanical properties for the cured resins, when the replacement portion was >50%.

Key Words: Hyperbranched polyester; Dendritic polymer; Post-synthetic reaction; Multi-methacrylate; Dental composite

INTRODUCTION

Designing, tailoring, and assembling of macromolecular structures is a highly important approach in searching for improved materials. The flourish of research and development of dendritic macromolecules, i.e., hyperbranched polymers and dendrimers greatly exemplifies this point [1–4]. From the statistical condensation of ABx monomer, three different structural units may be formed, i.e., linear, branched and terminal. The molar fraction of branched and terminal units in all polymerized units is defined as the degree of branching (DB). Obviously, the DB of an ideal dendrimer is 1, with linear polymer having $\mathrm{DB} = 0$, while the hyperbranched polymer has a DB between 1 and 0. No doubt, the DB is a key parameter for the determination of dendritic architecture, even though it is difficult to get a correct DB. Chemical degradation [5] and NMR spectroscopy [6] can be used to determine DB. However, spectroscopic methods may not be applicable in many cases where the difference in the monomer is subtle or the spectra are too complex for interpretation.

Based on different topological molecular architecture, dendrimer, hyperbranched polymer, and linear polymer behave differently, exhibiting wide variation of properties. Dendrimers are perfectly built, monodisperse structures assembled around a central core moiety, while hyperbranched polymers are polydispersed and allowed the incorporation of linear segments. Therefore, dendrimers are considered to be globular shape with high symmetry, having very different properties compared to their linear counterparts. Hyperbranched polymers are somewhere in between. Also, the difference between dendrimers and hyperbranched materials can be illustrated by their preparative procedures. Dendrimers are not made from condensation polymerization but built up in step by step fashion, with purification between each step. In contrast, hyperbranched polymers are synthesized in a one-pot reaction, with portion-wise feeds of starting materials. From a commercial point of view, hyperbranched polymers have more practical significance due to the cost-effectiveness and easy preparation. Studies and investigations on dendritic macromolecules are both intensive and extensive; hundreds of papers keep appearing in publication each year since 1990, as well as many monograph books on the subject [7a–d].

Since hyperbranched polymers have no chain entanglement, which is an attribute contributing to the polymer's unique viscosity profile. Hyperbranched polymers (HBPs) have poor mechanical properties. But, they may be put into more and more applications via modification of their terminal chemistry [8]. In other words, after the hyperbranched polymers have been obtained their shell or terminal chemistry becomes the most important factor determining their possible application. It has been found that the terminal groups on HBPs have great influence on their molecular behavior, such as glass transition temperature, viscosity and solubility. So far, there are only a few commercialized HBPs, among them Perstop's materials trademarked Boltorn. These HBPs are hyperbranched polyester polyols which has been successfully applied in some industry products such as adhesives and coatings [9, 10]. Modified Boltorns have also been shown to have potential application for formulating low shrinkage dental restoratives [11, 12]. As demonstrated in Figure 1, Boltorn H30 is prepared by condensation of a pentaerythritol core molecule with 2,2-dimethylol propionic acid (BisMPA). It has a core/shell structure with an essentially inert interior and a reactive shell with 32 hydroxyl groups, which can be molecularly modified in diverse ways for different applications. In our previous work [12], we reported that with addition of 10 wt% fully methacrylated Boltron H30 to a BisGMA based formulation, modified resins could be produced with 30–50% reduction of polymerization shrinkage and about 15% increase in mechanical strength, compared to a BisGMA control. But we found that the fully methacrylated H30 has the drawback of high viscosity. Meanwhile, it was found that the solubility and intrinsic viscosity of hyperbranched polymer are strongly depended on the type of terminal groups on the shell. Therefore, questions on how various terminal groups, such as acetate, propioate, butyrate, isobutyrate, and benzoate ester, would influence the viscosity of the esterified H30 were raised. Answers to various questions were explored in this effort. Such as, will the neat resin formulated with a completely methacrylated H30 have advantage over BisGMA? Will the partially methacrylated H30 oligomers exhibit desired lower polymerization shrinkage? How will the replacement level of methacrylate for shell hydroxyls on H30 oligomer influence the mechanical properties of formulated VLC resins? To seek answers to these and other questions, we first synthesized completely methacrylated H30 via three different methacrylation reactions, i.e., treatment with methacryloyl chloride, methacrylic anhydride and isocyanatoethyl methacrylate, in order to optimize the methacrylation procedure. Second, we investigated the effect of terminal groups on the viscosity of H30 polyesters, which have terminal -OH groups replaced by acetate, propionate, butyrate, isobutyrate and benzoate ester groups. Next, we prepared esterified H30 by having the shell -OH half methacrylated and half esterified by the aforesaid carboxylic acid chlorides. These partially methacrylated and additionally esterified H30 oligomers were also formulated with TEGDMA and evaluated as VLC resins. Finally, a series of esterified H30 oligomers having varied levels, 30/70, 50/50, and 70/30, of acetate and methacrylate functionalities, were prepared and evaluated. The viscosity before VLC, double bond conversion (DC), linear polymerization shrinkage (LPS), compressive (CS) and flexural strength (FS), as well as Vicker hardness, were evaluated for all formulated resins.

EXPERIMENTAL

Materials

Boltorn H30 was a gift from Perstorp Specialty Chemicals, Lot. 2889206, with Hydroxyl number = 8.72 mmol/g-resin, $M_w = 3500$ (theoretical calculated 3604), polydispersity = 1.5 and T_g of 40°C. 2-Isocyanatoethyl Methacrylate was purchased from Monomer-Polymer & Dajac Labs, Inc., BisGMA was purchased from Cook Composites and Polymers Inc, batch # 811999090174. All other chemicals, purchased from Aldrich Chemical, were used as received.

Syntheses

Figure 1 shows the synthesis route for all H30 hyperbranched oligomers prepared in the study.

Synthesis of a Completely Methacrylated H30

Prepared by Using Methacryloyl Chloride

A 250 mL three-neck flask, fitted with a nitrogen sparge tube, magnetic stirrer and condenser, was charged with 10 g H30 (87.2 mmol -OH by titration), 15 mL triethylamine, 25 mg hydroquinone(HQ) and 100 mL absolute

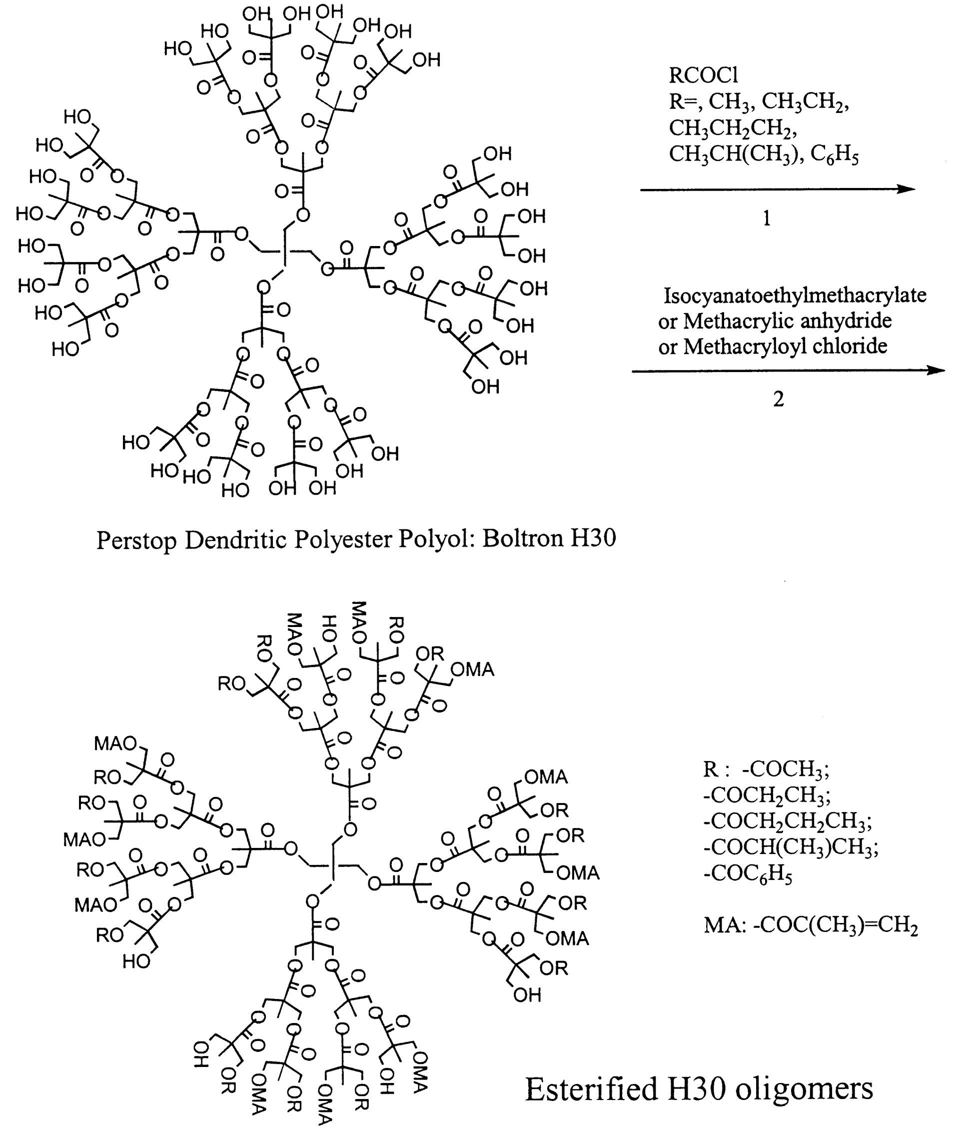

Figure 1. Synthetic route for hyperbranched polyester with mixed methacryloyl and aliphatic ester terminal groups in this study.

dry tetrahydrofuran (THF). After cooling to 0°C, 10 g methacryloyl chloride, dissolved in 10 mL dry THF, was added dropwise within 1 hour. After acid chloride addition, the mixture was kept stirring overnight at room temperature. The reaction, monitored by IR, was run until all hydroxyls were consumed. Any precipitated solid was removed by filtration, followed by solvent removal to leave crude yellowish oil. The crude product (oil) was dissolved in 200 mL ethyl acetate, followed by the solution extracted twice with a 50 mL Na_2CO_3 (10%) solution and with a 20 mL HCl (10%) solution. After drying over anhydrous Na_2SO_4, 10 mg 2,6-di-tert-butyl-4-methylphenol (BHT, 0.05 wt%) was added and the solvent was removed to obtain yellowish colored, viscous oil in a 9.6 g (60.9%) yield.

The IR spectrum and hydroxyl titration showed that there was no remaining hydroxyl group on the H30 oligomer. The NMR spectrum showed only a hint of methylene protons for $-CH_2OH$. Figure 2 shows the H^1-NMR spectrum of H30 and the fully methacrylated H30 oligomer.

^{1}H-NMR (DMSO-d_6, Broker 400 MHz), with δ 1.08 (s, 2.63H, $-CH_3$ from H30), 1.90(s, 3.02H, $-CH_3$ from methacrylate), 3.48 (m, 0.21H, $-CH_2OH$), 4.12 (m, 3.46H, $-CH_2$-O-), 5.76(s, 1H, $>C=CH_2$), 6.03 (s, 1H, $>C=CH_2$). **^{13}C-NMR:** 176 (carbonyl of H30), 167 (carbonyl of methacryloyl), 137 (methane carbon of vinyl), 126 (methylene carbon of vinyl), 65, 63 ($-CH_2O-$), 55, 54 (C), 17.3–18.4 (methyl of H30 and methyl carbon of methacryloyl).

Prepared by Using Methacrylic Anhydride

Using the same setup as procedure 1.1, the reaction flask was charged with 10 g H30, 15 g methacrylic anhydride, 25 mg HQ and 100 mL mixed

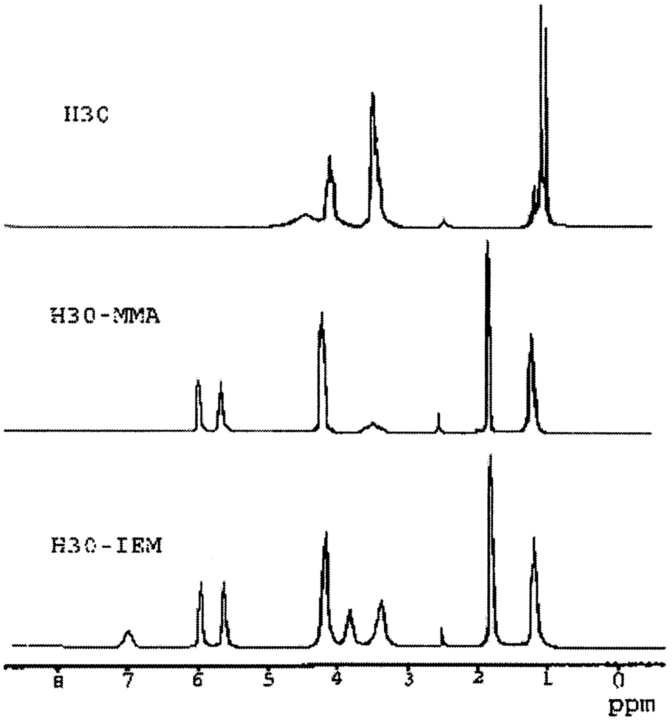

Figure 2. ^{1}H-NMR of H30 and its methacrylated oligomers.

solvent of THF/pyridine (70/30 vol). The mixture was heated to reflux (ca. 80°C), with the reaction monitored by IR until the anhydride was consumed (as shown by absence of the 1850 cm^{-1} absorption band). The reaction was then stopped; the solvent and methacrylic acid were removed by an evaporator under high vacuum (0.5 mmHg) at below 80°C. The residue was dissolved in 200 mL ethyl acetate, followed by the solution extracted twice with 30 mL Na_2CO_3 (10%) solution 20 mL HCl solution (10%), and drying over anhydrous Na_2SO_4. After solvent removal, a 8.8 g (55.8%) yield yellowish oil was obtained.

The IR spectrum and titration effort showed no apparent -OH, but the H^1-NMR spectrum showed a hint of methylene protons for the $-CH_2OH$ moiety. The ^{1}H-NMR and ^{13}C-NMR spectra was identical to that prepared by the methacryloyl chloride procedure, as shown in Fig. 2.

Prepared by Using 2-Isocyanatoethyl Methacrylate (IEM)

A 250 mL three-neck, round-bottom flask, fitted with a magnetic stirrer, nitrogen sparge tube, and cooling finger, was charged with 10 g H30, 14 g IEM (90 mmol), 100 mL dry THF and 0.1 g DABCO (triethylenediamine), followed by heating in an oil bath at 45°C. IR was employed to monitor the reaction until the $\nu_{C=N}$ absorbance at 2270 cm^{-1} disappeared, showing stopping point for the reaction. After solvent removal, the crude yellowish oil was dissolved in ethyl acetate and extracted twice with a 20 mL NH_4Cl solution (10%), twice with a 20 mL Na_2CO_3 solution (10%) and finally with a 20 mL NaCl (10%) solution. After drying over anhydrous Na2SO4, 10 mg of 2.6-di-tert-butyl-4-methylphenol (BHT, 0.05 wt.%) was added and the solvent was removed to obtain a 16.5 g (70.3%) yield of a viscous oil, with Fig. 1 showing the ^{1}H-NMR spectrum of the product. **^{1}H-NMR** (DMSO-d_6, Broker 400 MHz), with δ 1.15 (s, 2.43H, $-C\boldsymbol{H}_3$, from H30 itself), 1.88 (s, 2.97H, $-C\boldsymbol{H}_3$ from methacrylate), 3.28 (t, 1.98H, $-CONH-C\boldsymbol{H}_2$-,) 3.48 (m, 0.12H, $-C\boldsymbol{H}_2OH$ from H30), 3.60 (t, 2.01H, $-CONHCH_2C\boldsymbol{H}_2O$-), 4.14 (m, 5.38H, $-C\boldsymbol{H}_2-O$- from H30), 5.76 (s, 1H, $>C=C\boldsymbol{H}_2$), 6.03 (s, 1H, $>C=C\boldsymbol{H}_2$), 7.02 (m, $-CON\boldsymbol{H}-CH_2O$-). **^{13}C-NMR:** 176 (carbonyl of H30), 167 (carbonyl of methacryloyl), 157(carbonyl carbon of amino ester), 136 (methane carbon of vinyl), 127 (methylene carbon of vinyl), 65, 63 ($-CH_2O$-), 55, 54 (C), 38 ($-CONH-CH_2$-), 17.5–18.4 (methyl of H30 and methyl carbon of methacryloyl).

Esterification of H30 with Different Carboxylic Acid Chlorides

The carboxylic chlorides used in this work include acetyl chloride, propyl chloride, butyl chloride, isobutyl chloride and benzoyl chloride. All those esterification procedures were basically the same, as explained for the preparation of H30-AC. A 250 mL three-neck, round bottom flask, fitted with a N_2

sparge tube, magnetic stirrer, and condenser, and placed in an ice-water bath, was charged with 10 g H30, 100 mL dry THF and 10 g triethylamine. A solution of 7.8 g (100 mmol) of acetyl chloride in 20 mL THF was added dropwise over a 1 hour. The reaction was stirred overnight at r.t. IR was used to monitor the reaction, showing that all hydroxyls were consumed. The precipitated solid was removed by filtration. After solvent removal, the crude yellowish oil was dissolved in diethyl ether. The ether solution was extracted twice with a 20 mL Na_2CO_3 solution (10%) and with water. After drying over anhydrous Na_2SO_4), the solvent was removed to obtain a 12.4 g (90.5%) yield of a slightly yellow colored, viscous oil. Both IR and titration showed no remaining -OH. **^{1}H-NMR:** signals at $\delta = 3.5$ (-CH_2OH) disappear but show up the methyl proton of acteyl group at $\delta = 2.05$. **^{13}C-NMR:** signals at $\delta = 65.5$ (-CH$_2$OH) disappear but the methyl carbon of acetyl group showed up at $\delta = 21.4$, carbonyl carbon of acetyl overlapped around $\delta = 174$. For the preparation of esterified H30 from benzoyl chloride, chloroform was used to extract crude product instead of ethyl ether. The IR and NMR confirmed the chemistry of product.

Half Methacrylated H30 Oligomers with Half Carboxylate Replacement for Shell-OH Groups

Half of the shell-OH groups on the H30 oligomer were first esterified with reactants such as acetyl, propyl, butyl, isobutyl, etc., chlorides. To assist in having random esterification of the OH groups on each H30 molecule occur, a small amount of pyridine was added to the reaction mixture to make H30 completely soluble before each esterification reaction. The half carboxylic acid esterified H30 was separated and purified to be the intermediate for the subsequent methacrylation reaction. Each intermediate was titrated, using the method described in this paper, to determine the remaining amount of hydroxyl on the esterified H30. For all esterified H30 intermediates, the residual -OH ranged from 47–49%. The partially esterified intermediates were then methacrylated, using the previously described 1.1 procedure. The samples were named according to the acid chloride employed and shown as in Table 3. The H^1-NMR and IR spectra verified the desired structures of the targeted oligomers.

Partly Methacrylated H30 Oligomer with Varying Methacrylation Degree

Using the previously described procedure, H30 was esterified with acetyl chloride at different (30, 50, and 70%) esterification levels. The resultant intermediates were titrated to determine the remaining -OH fraction. The partially esterified intermediates were then methacrylated at the remaining -OH residues, to prepare a series of new acetyl/methacryloyl H30 derivitives, assigned according to the composition of terminal groups as shown in Table 4. NMR and IR were used to confirm the structures.

Determination of Hydroxyl Number: Titration with NaOH

The sample is acetylated under reflux using an excess of acetic anhydride and pyridine as a solvent. For the multi-methacrylate sample, 0.5 wt% of HQ was added. The remaining acetic anhydride was hydrolyzed with water, with the formed acetic acid determined by titration with sodium hydroxide. The hydroxyl number is calculated from the difference between the sample and a blank.

A typical procedure is as follows: 0.5–0.6 g sample was weighed into a dry 250 mL flask. A pipette was used to add 10.00 mL of the acetylation mixture (freshly prepared by mixing one part of acetic anhydride with 9 parts of pyridine). The mixture was heated at reflux for 20–25 minutes, with occasional shaking, making sure the sample was fully dissolved. After cooling to room temperature, the condenser was washed with approximately 20 ml of acetone, before flask removal. Water (20 mL) and a few drops of phenolphthalein indicator were added to the flask. The reaction mixture was titrated with a NaOH (1.00M) solution under vigorous stirring until a pink color appears and remains for five seconds. Due to the slow reaction rate the last two ml of NaOH must be added dropwise. The titrimetric volume was read as V_2. The blank test is run by the same procedure, only without the H30 sample, with the titrimetric volume read as V_1. The hydroxyl number is calculated in mol $= (V_1 - V_2)*C/w$ (mol/g-resin), while C is molar concentration of NaOH and w is amount of sample (g).

Measurement of Viscosity

The Brookfield CAP 2000 Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) was used to measure the viscosity of each sample. All resin samples were run at 25°C using a #1 cone at a speed of 800 rpm, and the oligomer samples were run at 45°C using a #6 cone at a speed of 600 rpm. Before testing, the viscometer was always calibrated using a standard fluid at the corresponding temperature. For each resin or oligomer, 6 samples were tested to obtain an average value.

Molecular Weight Determination

Size exclusion chromatography (SEC) was used to estimate the molecular weight of the oligomers synthesized in this study. The oligomers were dissolved in THF at a concentration of 10 mg/mL. Measurements were performed with a Shimadzu HPLC set with columns of Jordi Gel divinyl benzene with porosity 500 and 1000 A° using THL as an eluent at 25°C and polystyrene standards for calibration. It should be noted, since hyperbranched polymers possess a different hydrodynamic volume than the standard, the molecular weights may be underestimated. But this affect would be systematic to all oligomers and the ultimate molecular weight is not our main goal in the study.

Linear Polymerization Shrinkage (LPS)

The LPS was determined for the experimental neat resins using the simple "deflecting disk" method described by Watts and Cash [13]. In this method, an LVDT transducer is used to measure the displacement of a glass cover slip that is deflected as the resin shrinks during polymerization. The resin, usually was made into a disk of ca. 7 mm diameter, was placed in the center of a 1.5 mm thick brass ring and a glass coverslip placed over the liquid resin, suspended by the edges on the brass ring. The resins were light cured for 60 seconds (Optilux, Demetron Research Corporation) and the displacement continuously monitored for a total of three minutes. After 3 minutes, the total amount of recorded shrinkage and the % LPS was determined. For each sample, 6 specimens were tested and the average LPS was obtained.

Preparation of VLC Resin Specimens and Mechanical Property Testing

Both full methacrylated H30 oligomers (Table 1) and partial methacrylated H30 oligomers (Tables 3 and 4) were blended with TEGDMA (50/50, wt/wt) to formulate neat resins. Camphorquinone (CQ), 0.5 wt.%, and 1.0 wt% N,N-dimethylaminoethyl methacrylate were combined with the mixtures to give visible light-curing (VLC) capability. The resins were cured directly to obtain specimens for both compressive (CS) and flexural strength (FS) testing. After removal from the molds, all samples were conditioned in distilled water at 37°C for one week, prior to testing.

The CS (4 mm in diameter × 6 mm in thickness) and FS (25 × 2 × 2 mm) samples were visible-light cured for a total of five minutes. The sample surface was polished by using silicon carbide paper (FEPA P# 800) after removal from the mold. The CS and FS tests were carried out using a screw-driven mechanical testing machine (Model 4204, Instron Corp., Canton, MA) with a constant crosshead speed of 0.5 mm/min. For each sample, six specimens were tested.

Double Bond Conversion (DC)

The DC of formulated resins was measured by solid-state ^{13}C-NMR. The specimen used for CS testing was ground into a powder and used to record the solid-state ^{13}C-NMR spectrum. Spectra were obtained using a Bruker 300 spectrometer, operating at 75.5 MHz. For BisGMA based dental resins, integration of the carbonyl carbon signals can be used to determine the double bond conversion using an equation as follows: DC $(\%) = A_{177}/(A_{177} + A_{167}) \times 100\%$.

The A_{167} and A_{177} are the integration of the signal at δ 167.2 and 177.4, which represent the number of unpolymerized methacryloyl and polymerized methacryloyl carbonyl residues, respectively, on the resin after VLC [14, 15].

In the case of methacrylated H30 based resin, the H30 and methacryloyl carbonyls overlap, not allowing the above equation to be used to determine the DC of methacrylated H30 based dental resins. However, the ^{13}C-NMR spectra of H30 oligomer formulated resins, before and after polymerization, provided a vinyl carbon signal suitable for this purpose, i.e., the methylene and methinyl carbons, respectively, are at 126 and 136 ppm before polymerization, but show as an overlapped peak center at 45 ppm after polymerization. Their integration area represented as A_{126}, A_{136} and A_{45}, with the following equation useful to determine DC:

$$\mathrm{DC}\ (\%) = A_{45}/(A_{126} + A_{136} + A_{45}) \times 100\%$$

Similarly, the above equation cannot be used to determine DC of resins of monomer systems containing aromatic structure because of the signal overlap of benzene carbon and methylene carbon of the double bond.

Glass Transition Temperature (T_g)

DSC curves was recorded with a DuPont Differential Scanning Calorimeter 910 at temperatures over the range −60° to 250°C, with scan rate of 10°C/min. The T_g was obtained from the mid-point of the transition by using the DSC 4.0 computer program supplied with the instrument.

Vicker Hardness

The Barber Colman Co. hardness tester (model GYZJ-934-1 was used, per ASTM D-2583 method. For each sample, tests are made twenty times and the mean values were recorded.

RESULTS AND DISCUSSION

Synthesis and Characterization of Esterified H30 Oligomers

Complete Methacrylation of H30

Pyridine and DMF are reasonably good solvents for H30, whereas the hyperbranched oligomer is only partially soluble in THF or acetone. There are three routes to prepare methacrylate functionalized H30, i.e., use of methacrylic anhydride, methacryloyl chloride and 2-isocyanatoethyl methacrylate. For the chloride approach, THF is used as solvent. However, H30 dissolves only over time, by the end of reaction, after all terminal hydroxyl on H30 are converted into ester residues, providing in all cases products viscous oils. Acetone is a better solvent than THF for H30. However, the final reaction mixture is difficult to filter off with acetone as a solvent. For the methacrylic anhydride approach, addition of pyridine brings H30 into solution as well as complete the conversion of hydroxyl groups to ester groups. But, pyridine gives a deeper coloration to the final product. While IEM provides a route to a clear product, the methacrylated oligomer has higher viscosity and takes longer reaction time. All methacrylated H30 produced are shown in Table 1. The reaction yields for methacrylation of H30 are rather low (usually <70%). Low yields are associated with the purification of the methacrylated H30. The crude product was dissolved in ethyl acetate for washing; the problem encountered was that separation between the organic and aqueous phases takes a long time; the ethyl acteate/H_2O system tends to form a relatively stable emulsions. Efforts to use diethyl ether/water, $CHCl_3/H_2O$, and CH_2Cl_2/H_2O to purify the crude product gave even worse separation results. The problem was previously mentioned [9]. Attempts to salt out the product helped to some degree.

Methacrylation greatly changes the solubility of the oligomers. Before esterification H30 is somewhat soluble in DMSO, DMF and pyridine and partially soluble in THF and acetone. After methacrylation, the oligomers are soluble in most organic solvents. M_w from SEC of methacrylated H30 oligomer are somewhat lower than the theoretical values. This may imply that the hyperbranched structure of H30 is far from the perfect dendritic structure. Unfortunately, the DB of H30 could not be predicted simply from its NMR. With the replacement of terminal -OH groups on H30 by methacryloyl, the viscosity of the oligomer are greatly reduced, since the strong hydrogen bonding between the terminals -OH groups is eliminated. However, H30-MA-IEM still has a higher viscosity than desired, since a new type of hydrogen bonding is introduced to the structure. H30 has two glass transition temperatures, which are 21.45 and 50.66°C, respectively. The first T_g might

Table 1. Complete Methacrylation of H30

Sample	Theoretical Mw	Viscosity (Poise)*	Mw (SEC)	Mw/ Mn	Yield (%)	T_g (°C)
H30	3604	Solid	3500**	1.60		21.45, 50.66
H30-MA-Anh	5676	23.5(0.7)	5374	2.04	60.9	− 17.16, 52.42
H30-MA-Chl	5676	22.4(1.1)	5566	2.68	55.8	− 17.23, 51.88
H30-MA-IEM	8460	42.8(3.3)	6984	2.26	70.3	8.31, 54.74

*The entries are mean values for five specimens with standard deviations in parentheses.
**Molecular weight data is provided by Perstorp, the maker of Boltron H30.

be related to the hyperbranched molecules' translation movement, which might be associated with the size and polarity of the terminal groups of hyperbranched polymers. The intromelecular segmental movement contributes the second T_g, which is the reason why the second T_g doesn't show apparent change upon methacrylation.

Esterification of H30 with Carboxylic Acid Chlorides

As discussed in the Introduction, the terminal groups of hyperbranched polymer have strong effects on its solubility and viscosity. A few carboxylic acid chlorides were used to esterify H30, as a route to prepare low viscosity oligomers. The results are shown in Table 2.

One distinction related to the esterification of H30 as compared to the methacrylation of H30 was that the esterified yields were much higher. The reason for this is that we used diethyl ether/water to purify crude products, giving cleaner and faster separation between organic and aqueous phases during product isolation.

Since the H30 is not soluble in THF, we did not obtain its molecular weight under the same testing conditions. The M_W data of H30 was provided by Perstop. It is reported that Boltron H30 has a large part of isomers having cycled structure [16]. The authors gave a method to estimate molecular weight by using the NMR spectrum of hyperbranched polymer; according the method we found the Boltron H30 polymer provided by Perstop only has a molecular weight of 580. Obviously the value is far apart from the one from Perstorp. However, we found that the molecular weight of esterified H30 oligomers by using SEC is pretty close to the theoretical calculation for all of the esterified H30 oligomers. But, molecular weight distributions are somehow broadened. Theoretically, it is not correct to test the molecular weights of H30 oligomers by using SEC calibrated with polystyrene standards. Since, hyperbranched polymers possess a different

Table 2. Esterification of H30 by Carboxylic Acid Chloride

Sample	Theoretical MW	Mw (SEC)	Mw/ Mn	Viscosity (Poise)*	Yield (%)	T_g (°C)
H30	3604	3500	1.60	Solid	–	21.45, 50.66
H30-Ac	4980	5310	2.18	17.3(2.4)	90.5	– 27.20, 54.20
H30-Pr	5428	5766	2.35	12.6(1.5)	87.7	– 16.60, 52.59
H30-Bu	5876	5376	2.72	3.48(0.1)	91.7	– 39.44, 51.89
H30-iBu	5876	5370	2.66	11.3(0.4)	92.5	– 14.23, 56.07
H30-Bz	6964	5810	2.58	27.2(1.8)	91.8	– 22.31, 53.46

*The entries are mean values for five specimens with standard deviations in parentheses.

hydrodynamic volume than the standard, the molecular weights are underestimated. We failed to notice an apparent low molecular weight for esterified H30 oligomers. This may show that the Boltron H30 does not have a perfect dendritic architecture.

The benzoate functionalized H30 oligomer gave the highest viscosity, compared to the other esterified H30 oligomers, with their viscosities having an order of acetate > propionate > isobutyrate > butyrate ester. The DSC revealed that esterified H30 had two T_gs. The lower temperature T_g appears dependent on the terminal groups on H30, with the second one associated with other transitions. The real reason is not clear now. However, as we discussed about the methacrylated H30, the first T_g is related to the hyperbranched molecule translation movement. Hence, the first T_g has an abrupt drop upon conversion of most of the hydroxyl groups into the different ester groups. Therefore, the second T_g has something to do with the thermal movement or local molecular segment of the hyperbranched polymer; it is not affected by the change of terminal groups on the hyperbranched oligomer.

Half Methacrylated H30 Oligomers

To compare the viscosity data of esterified H30 oligomers in Table 2 and H30-MMA in Table 1, we found that the H30 oligomer having butyrate terminal groups has the lowest viscosity. Also, It can be shown that these partially aliphatic ester and methacrylate ester oligomers reduce polymerization shrinkage of the cured materials. Thus, we prepared a series of new methacrylated H30 oligomers having half hydroxyl groups esterified by various aliphatic carboxylic acid chlorides and half by methacryloyl chloride, with results shown in Table 3. The combined esterified H30 oligomers have similar molecular weight by SEC. The terminal groups of these esterified H30 oligomers have some affect on their viscosities, but causing little change in their T_gs.

Table 3. Combined Esterification of H30 using an Equivalent Molar Composition of Carboxylic Acid and Methacryloyl Chloride

Sample	Theoretical Mw	Mw (SEC)	Mw/ Mn	Viscosity (Poise)*	T_g (°C)
H30-Ac-MA	5364	5733	2.71	18.5(1.2)	− 24.5, 53.1
H30-Pr-MA	5588	5344	2.68	14.1(1.6)	− 20.6, 51.2
H30-Bu-MA	5972	5528	2.43	10.8(0.7)	− 22.4, 50.4
H30-iBu-MA	5972	5623	2.70	20.4(1.4)	− 16.2, 54.3

*The entries are mean values for five specimens with standard deviations in parentheses.

Partly Methacrylated H30 Oligomer with Varying Methacrylation Degree

We chose acetyl chloride and methacryloyl chloride to prepare partly methacrylated H30 oligomers with varied methacrylation degree. In addition to the H30-MA-Ac sample, we prepared another two methacrylated H30 oligomers, having 70% and 30% of hydroxyl esterified by acetyl chloride and the remaining hydroxyl groups esterified with methacryloyl chloride. The results and characterization of the oligomers produced are shown in Table 4.

Evaluation of Partial or Fully Methacrylated H30 Oligomer

Both complete methacrylated H30 oligomers (Table 1) and partial methacrylated H30 oligomers (Tables 3 and 4) are used to blend with TEGDMA (50/50, wt/wt) to formulate VLC neat resins. The viscosities of the resins before VLC, linear polymerization shrinkage (LPS), double bond conversion (DC), glass transition temperature (T_g) and the hardness were characterized, with results are shown in Table 5.

Viscosity

H30-MA-anh and H30-MA-chl, which are fully methacrylated H30 oligomers, obtained by the methacrylic anhydride and methacryloyl chloride reaction, respectively, have slightly reduced viscosities compared to the BisGMA control. But H30-IEM, which is methacrylated by IEM, has a higher viscosity than BisGMA, probably because of the existence of hydrogen bonding formed from amine. For half formulated methacrylated H30 oligomers resins, their viscosities have a rough correspondence to their H30 oligomers. In general, the half-methacrylated H30 oligomers have lower viscosity than either the full methacrylated H30 oligomers or the BisGMA control.

Table 4. Controlled Methacrylation of H30 Using Acetyl and Methacryloyl Chloride

Sample	Theoretical MW	Mw (SEC)	Mw/ Mn	Viscosity (Poise)*	T_g (°C)
H30-Ac-100	4980	5310	2.18	17.3(2.4)	− 27.2, 54.2
H30-7Ac-3MA	5198	5444	2.53	15.9(2.0)	− 23.5, 50.6
H30-5Ac-5MA	5364	5733	2.71	18.5(1.2)	− 24.5, 53.1
H30-3Ac-7MA	5530	5568	2.22	20.2(1.8)	− 21.1, 52.4
H30-MA-100	5676	5566	2.68	22.4(1.1)	− 17.2, 51.8

*The entries are mean values for five specimens with standard deviations in parentheses.

Table 5. VLC of Partial (Full) Methacrylated H30 Oligomers

Sample	Vis. (Poise)*	LPS*	DC (%)	T_g (°C)*	Hardness**
Control	1.62(0.21)	6.69(0.13)	78.4	42.45(2.5)	104(5)
H30-MA-chl	1.11(0.10)	4.97(0.20)	81.4	45.22(1.8)	93(5)
H30-MA-anh	0.98(0.08)	5.21(0.22)	81.6	48.10(2.1)	87(5)
H30-IEM	2.04(0.15)	4.52(0.18)	80.2	48.53(1.5)	95(5)
H30-Ac-MA	0.81(0.10)	3.93(0.41)	84.8	50.33(2.8)	92(5)
H30-Pr-MA	0.45(0.08)	3.66(0.32)	85.1	47.45(3.2)	42(5)
H30-Bu-MA	0.13(0.02)	3.71(0.34)	83.6	51.20(2.5)	<23
H30-iBu-MA	1.07(0.20)	3.27(0.40)	90.9	48.82(3.0)	<23
H30-7Ac-3MA	0.82(0.12)	3.22(0.35)	83.6	50.10(1.7)	75(5)
H30-5Ac-5MA	0.81(0.10)	3.93(0.41)	84.8	50.33(2.8)	92(5)
H30-3Ac-7MA	0.94(0.08)	3.87(0.45)	82.1	51.11(2.3)	98(5)

Entries are the mean values (standard deviation) of a group of five specimens.

LPS

The unintended polymerization shrinkage seems inevitable for multi-methacrylate-based resins due to a certain amount of volume (22.5 mL/mol) consumption for each methacrylate group that polymerizes [16]. Because the monomer molecules are ‘‘compacted’’ via the Van de Walls interaction and the intermolecular vicinity is bigger than that between the chemical bonded polymer units, it can be visualized that some ‘‘free volume’’ is squeezed out through polymerization. Minimizing the total number of methacrylate groups or utilizing monomers of larger molar volume could reduce the volume shrinkage. But this also could lead to unintended side effects, such as lowering cross-link density as well as producing materials of poor strength. It is reported that oligomeric multi-methacrylates with high molecular weight could offset the polymerization shrinkage to some extent [17]. As desired, all methacrylate-substituted H30 oligomer based formulations produce materials having lower LPS. The possible reason for this is that the bigger molar volume of the hyperbranched H30 is maintained during polymerization, compared to the BisGMA structure exhibiting more ‘‘free volume’’ squeezing out during polymerization.

Double Bond Conversion (DC)

Figure 3 shows the solid NMR of BisGMA/TEGDMA control, H30-MA-chl/TEGDMA, and second series of half methacrylated H30 oligomers formulated and cured. From the NMR results, full methacrylated H30 oligomers have the same double bond conversion as the BisGMA control. However, it is significantly higher for those of the half-methacrylated H30

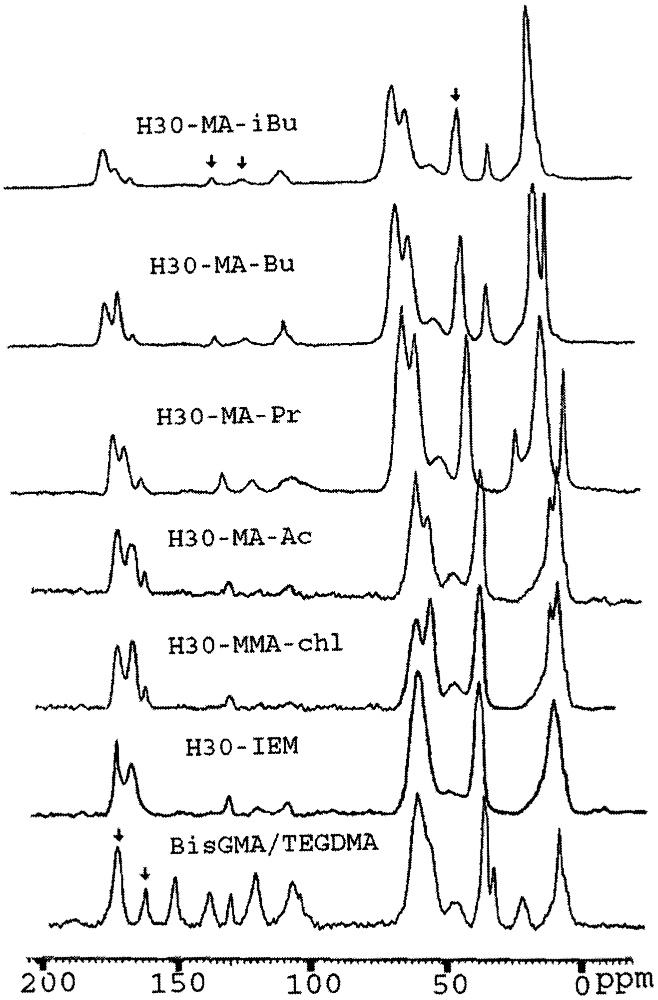

Figure 3. ^{13}C-NMR spectra of methacrylated H30 oligomer/TEGDMA resins and BisGMA control cured by visible light; the peaks with arrows indicted are used for calculation of double bond conversion.

oligomer formulated resins than BisGMA control. This phenomenon may be related with the low viscosity of those oligomers.

Glass Transition Temperature (T_g)

There is only one glass transition temperature observed for each VLC neat resin. The sub transition temperatures, which usually appeared below 0°C in the DSC profiles of those oligomers and may be related with the translation movement of oligomers, were no longer observed. The observed

T_gs reveal the thermo-movement of short pendant chains and very local chain segment of the crosslinked resins.

Hardness

Through the estimation of hardness for VLC samples, it is found the H30 oligomers formulated into resins have a low hardness number than the BisGMA control, it especially of true for those half methacrylated H30 oligomers with longer carboxylate groups such as propionate and butyrate ester.

Compressive and Flexural Strength

Both compressive and flexural strengths are important evaluating criteria for dental materials. All cured neat resins were tested for CS and FS; Table 6 shows the overall results. Among the VLC resins formulated from three methacrylated H30 oligomers, H30-IEM has both improved CS and FS strengths. But, for unknown reason, H30-MMA-chl and H30-MMA-anh only have the same range of CS and FS values as the BisGMA-based control. All three types of cured resins have stronger deflection ability than the control, as shown by the strain data. It was unexpected that both CS and FS have a sharp drop for those partly methacrylated H30 oligomer formulations. The higher the aliphatic carboxylate attached to the oligomer

Table 6. Evaluation of Resins Formulated from Partial (Full) Methacrylated H30 Oligomers

	Compressive Strength Test*		Flexural Strength Test*		
Sample	CS (MPa)	E (GPa)	Strain (%)	FS (MPa)	E (GPa)
Control	376(16)	2.46(0.4)	17.8(4.3)	72.6(3.8)	1.52(0.21)
H30-MA-chl	355(22)	2.38(0.3)	24.4(3.7)	74.2(6.4)	1.44(0.28)
H30-MA-anh	344(31)	2.09(0.3)	25.7(4.5)	69.5(4.8)	1.49(0.24)
H30-IEM	415(40)	2.65(0.2)	22.3(4.7)	80.1(5.5)	1.75(0.25)
H30-Ac-MA	347(34)	2.34(0.2)	31.6(4.0)	69.5(3.3)	0.92(0.19)
H30-Pr-MA	275(38)	1.67(0.1)	42.4(5.3)	67.2(4.4)	0.55(0.12)
H30-Bu-MA	92(24)	0.49(0.2)	42.3(4.8)	36.4(2.9)	0.33(0.15)
H30-iBu-MA	101(29)	0.58(0.3)	45.8(5.4)	39.5(3.2)	0.36(0.12)
H30-7Ac-3MA	201(24)	1.09(0.2)	44.2(4.2)	44.7(3.8)	0.55(0.20)
H30-5Ac-5MA	347(34)	2.34(0.2)	31.6(4.0)	69.5(3.3)	0.92(0.19)
H30-3Ac-7MA	359(28)	2.28(0.3)	25.4(5.0)	67.3(4.6)	0.84(0.21)

*The entries are mean values for five specimens with standard deviations in parentheses.

terminal, as a replacement of the shell -OH, the more the drop of the mechanical strength of the cured resins was noted. For example, with half shell -OH replaced by acetate, the half methacrylated H30 resin has $CS = 347\,MPa$ and $FS = 69.5\,MPa$, but with half of the shell -OH groups replaced by butyrate ester groups, the resin's CS and FS drop to 92 MPa and 36.4 MPa, respectively. From Table 5, those half-methacrylated H30 resins have much lower hardness numbers; in other words, they become more plasticized with the replacement of a higher aliphatic carboxylate for the shell -OH. Also their break strains are almost double those fully methacrylated H30 oligomers. Again, the possible reason for this may be that replacing OH groups with longer aliphatic carboxylate entities plays a role of "plasticizer" for the VLC neat resins. As shown, the higher the aliphatic carboxylate chain length the greater the plasticization effect. This part of result is not what we desired. However, if part of the shell -OH on H30 were replaced by much higher aliphatic carboxylates, e.g., laurate or stearate, the modified H30 oligomers might well be useful as ompatibilizer for blending of polyester, PET or PBT, with polyolefins, such as PE or PP. For the third series of partially methacrylated H30, it is interesting to find out that when the methacrylate replacement number exceeds 50%, the further increasing of methacrylate number seems not increase the mechanical strength.

CONCLUSION

Three series of methacrylated hyperbranched polyester polyol, Boltron H30, have been prepared through the controlled esterification of the hyperbranched material. It was briefly shown that all the methacrylated H30 oligomers have low linear polymerization shrinkage and comparable or higher double bond conversions, compared to a similar VLC BisGMA based control resin. VLC resins formulated from fully methacrylated H30 oligomer, also have improved mechanical properties, especially for H30-IEM formulation, which is prepared by treating H30 with 2-isocyananoethyl methacrylate. No doubt this is due to the existence of hydrogen bonding in the matrix. The neat VLC resins formulated from partially methacrylated H30 oligomers have significant increased double bond conversion, but less attractive mechanical properties, due to esterification of some of the shell –OH groups with higher aliphatic carboxylate groups. With the replacement of more acetate for the shell –OH, partially methacrylated H30 maintained mechanical strength until the replacement degree was >50%. In conclusion, partly methacrylated H30 oligomers with half of its shell hydroxyls replaced by acetate groups could be utilized to replace fully methacrylated H30 in the formulation of low shrinkage dental restoratives.

Additional work needs to be done to functionalize the terminal OH groups on hyperbranched polyester(s) to achieve other polymerization profiles.

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