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# METHACRYLOYL DERIVITIZED HYPERBRANCHED POLYESTER. 1. SYNTHESIS, CHARACTERIZATION, AND COPOLYMERIZATION

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# METHACRYLOYL DERIVITIZED HYPERBRANCHED POLYESTER. 1. SYNTHESIS, CHARACTERIZATION, AND COPOLYMERIZATION

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Key Words: Hyperbranched Polymer, Multi-Methacrylates, Thermal Polymerization, FT-IR or NMR Characterization

## ABSTRACT

Three hyperbranched multi-methacrylates (H20-MMA, H30-MMA and H40-MMA) have been synthesized by reacting Boltorn dendritic polyols with methacrylic anhydride and methacryloyl chloride. Their structures were characterized by FT-IR and NMR ($^1$H and $^{13}$C) and molecular weights were measured by GPC. These multi-methacrylates (H-MMAs) mixed well with a variety of monomers such as acrylic acid (AA), methacrylic acid (MA), methyl methacrylate (MMA), 2-hydroxy-ethyl methacrylate (HEMA), tri(ethylene glycol) dimethdimethacrylate (TEGDMA), and bisphenol A glycidyl dimethacrylate (BisGMA). The initial studies on thermal polymerization activities of 10% of H-MMAs with AA, MA, and MMA showed that they gave higher polymerization enthalpy than the corresponding homopolymerization. The resulting materials showed one glass transition temperature, indicating a typical single-phase resin. The H-MMAs can effec-

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tively copolymerize with AA, MA, and MMA, with essentially no homopolymers produced, as indicated by acetone extraction studies. This indicated that the hyperbranched multi-methacrylates have the potential to be used as crosslinking agents or modifiers with a number of monomers to produce new thermosets.

## INTRODUCTION

The concept of hyperbranched polymers or dendrimers was initially predicted and theoretically studied by Flory about half a century ago [1, 2]. It is within the last fifteen years that the hyperbranched polymers were synthesized and characterized [3]. Hyperbranched polymers or dendrimers have unique molecular structure and shape in contrast to their linear analogues [4-6]. Review papers and books have addressed this issue [4-8].

Typically, hyperbranched polymers are made from $AB_2$ type monomers in which A groups will only react with B groups and vice verse, through the addition reaction of free radical living molecules or condensation reaction of carboxylic acid with hydroxyl or amine groups. Most of the research done in this area has been focused on searching for appropriate ways to synthesize a variety of new hyperbranched polymers and characterize their physical properties [6, 9-11]. Only limited work has been reported to find possible applications of hyperbranched polymers, which has already shown promise as processing-promoting agents [12], toughening agents [13-14], reinforcing agents [15], and in coatings and adhesives [16]. It has been found that hyperbranched polymers can improve the mechanical properties of composite materials while maintaining a desirable viscosity. For example, with the addition of 5% of hyperbranched polyphenylene polymers, the fracture toughness of a glass fiber reinforced epoxy more than doubled from 0.63 to 1.54 MPa $m^{1/2}$ [13] and $G_{IC}$ increases 6 fold [14]. Blending hyperbranched polymers with polycarbonate increases the tensile modulus by 32% and compression modulus by 15%, but with a decrease in tensile elongation [15].

Boltorn is a commercial hyperbranched polyol, synthesized by a condensation reaction of a pentaerythritol (I) core with 2,2-bis(hydroxymethyl) propionic acid (BHPA, II) [17]. Pentaerythritol forms ester linkages with the BHPA, giving a molecule with eight hydroxyl end groups. These eight hydroxyl groups will produce 16 hydroxyl groups after a second shift reaction with BHPA, then 32, 64 . . . etc. However, besides this idealized situation, some branches may grow more than the others, which may give rise to a distribution of molecular weight and not an idealized spherical shape. In addition, Burgath *et al.* [18]

reported that cyclization may occur during chain growing, which would influence the molecular structure and molecular weight, especially for the higher generation products. Theoretically, Boltorn H20 is reported as having an average molecular weight 1750 with theoretically 16 primary hydroxyl groups, H30 MW 3600 with 32 hydroxyl groups, and H40 MW 7300 with 64 hydroxyl groups. They are amorphous yellow solids at room temperature, dissolving in only several special solvents such as pyridine, dimethyl sulfone, and N-methyl-pyrrolidinone. The number of hydroxyl groups on the oligomers makes them moisture sensitive, easily absorbing water.

In order to use Boltorn polyesters to reinforce methacrylate systems, we esterified the hydroxyl groups with polymerizable carbon-carbon double bonds (C=C). Generally hydroxyl groups can be methacrylated through reaction with methyl methacrylate, methacrylic anhydride or methacryloyl chloride. There are some reports regarding the esterification or methacrylation of hydroxyl terminated polymers [19-22], but the polymers studied had molecular structures different from those in this paper. Also, the experimental and characterization details were not fully given from those studies.

The purpose of this study is to synthesize multi-functional hyperbranched polymers, based on Boltorn polyols, characterize their structures and molecular weight, and evaluate their possible applications as modifiers with common carbon-carbon double bond containing monomers. To the best of our knowledge, no such research has been reported.

## EXPERIMENTAL

### Materials

Dendritic Boltorn polyols suppplied by Perstorp Inc., Sweden, were used as received. Methacrylic acid anhydride and methacryloyl chloride (Aldrich Chemical) were distilled before use. BPO was recrystallized from acetone. AR grade acrylic acid (AA), methacrylic acid (MA), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and solvents were used as received from Aldrich.

### Syntheses

Boltorn-methacrylate is synthesized through two steps: (1) Boltorn was reacted with methacrylic anhydride to give an intermediate product (Boltorn-MA) with hydroxy groups partly converted into methacrylate; (2) Boltorn-MA was further reacted with methacryloyl chloride to have most of hydroxy groups converted into methacrylate (Boltorn-MA-MC). The typical reaction conditions are as follows:

### *Boltorn with Methacrylic Anhydride*

Boltorn H30 (44 g) was partly dissolved into 200 ml tetrahydrofuran (THF) in a 500 ml three-neck rounded-bottom flask at 65-70ºC under nitrogen. Then, 88 g of methacrylic anhydride with 0.9 g hydroquinone, dissolved into 50 ml THF, was added dropwise into the Boltorn solution. After addition, the reaction was continued for 8 hours.

The THF was removed by using a Dean-Stark evaporator. The crude product was dissolved in chloroform, followed by washing the chloroform solution with 2% NaOH solution twice and distilled water several times, until pH = 7. After drying over anhydrous sodium sulfate and removal of solvent, 85 g of a light-yellow viscous liquid was obtained.

### *Boltorn-MA was Further Reacted with Methacryloyl Chloride*

The H30-MA (44 g) was dissolved in a mixture of 250 ml THF and 80 ml triethyl amine, using magnetic stirring under Nitrogen. Then, 60 g of methacryloyl chloride was added dropwise, keeping the temperature below 10ºC in an ice-salt water bath. The reaction was run for about 15 hours.

The precipitate was removed by filtration, after which the solution was washed with 2% of HCl, 2% of NaOH, and distilled water several times until pH=7. The raw product was dissolved in chloroform and dried over anhydrous sodium sulfate. After evaporation of the chloroform, 54 g H30-MMA was obtained.

## IR and NMR Characteristics

The IR spectra (Figure 2) were obtained by using a MIDAC FT-IR Spectrophotometer (MIDAC Corp., Costa Mesa, CA). The $^{1}H$ and $^{13}C$ NMR were obtained on a Bruker 400 Hz NMR equipment, using dimethyl-$d_6$ sulfoxide as a solvent and tetramethylsilane (TMS) as a reference (Figures 3 and 4).

## GPC Measurement of Molecular Weight

GPC was used to estimate the molecular weight of multi-mthacrylate oligomers by using a Shimadzu HPLC (Figure 5). The columns are Jordi Gel divinyl benzene with porosity 500 and 1000 A, with THF solvent and molecular weights being calculated using polystyrene standards (Table 1).

### DSC Testing

Thermal polymerization of monomers and monomers/H-MMAs with 0.5% BPO were evaluated by using 910 Differential Scanning Calorimeter (TA Instruments, Wilmington, DE) (Table 2). The mixtures (about 8 mg) were weighed into a sealed aluminum pan and heated from 10 to 200°C, at a heating rate of 10°C/min, to get the thermal polymerization enthalpy ($\Delta H$). After cooling, the samples were reheated from 10 to 200°C at the same heating rate. The glass transition temperatures were estimated by DSC.

In addition, DSC was used to measure the glass-transition temperature of thermal-polymerized resins. MMA and MMA/10% H-MMAs and 0.5% BPO was first heated to 70°C for about 6 hours, then at 120°C for 2 hours. After the reaction, the resulting resins were tested by using DSC from 10 to 180°C at the heating rate of 10°C/min, see Figure 6.

## RESULTS AND DISCUSSION

The reaction route for preparing hyperbranched multi-methacrylates (H20-, H30- and H40-MMA) is schematically shown in Figure 1. The IR spectra of H30 polyol and its multi-methacrylate derivative are shown in Figure 2.

For the starting material, Boltorn H30, there is a strong, wide absorption peak for aliphatic -OH around 3450 cm$^{-1}$. After reaction with methacrylic anhydride and methacryloyl chloride, almost no peaks can be detected around 3100 to 3600 cm$^{-1}$. However, stronger bands appear at 2877 and 2990 cm$^{-1}$, indicating addition of $-CH_2$ and $-CH_3$ groups of methacrylates. As for the region between 1800-1500 cm$^{-1}$, the starting polyols did not have a peak at 1638 (C=C) cm$^{-1}$, while the reaction product showed a middle to strong peak at 1638 (C=C) cm$^{-1}$, corresponding to the addition of methacrylates.

FT-IR suggests that most of the hydroxyl groups on the Boltorn starting material have been converted to methacrylates. Similar results can be seen for the H20 and H40 and their reaction products.

The $^1$H and $^{13}$C NMR spectra of H30 and its methacrylated product were also examined (Figures 3 and 4). From the $^1$H NMR spectrum, the starting Boltorn mainly contains three groups of hydrogen, that is $-CH_3$ (1.08 ppm), $-CH_2O-$ (4.1 ppm), and $-CH_2OH$ (3.5 ppm). After reaction, two new groups associated with methacrylate vinylic $CH_2$ (6.0 ppm) and connected $-CH_3$ (1.9 ppm) appear, supporting the addition of methacrylate. For $^{13}$C NMR, the starting Boltorn has four kinds of carbons: carbonyl C=O, $-CH_2O$, C-, and $-CH_3$.

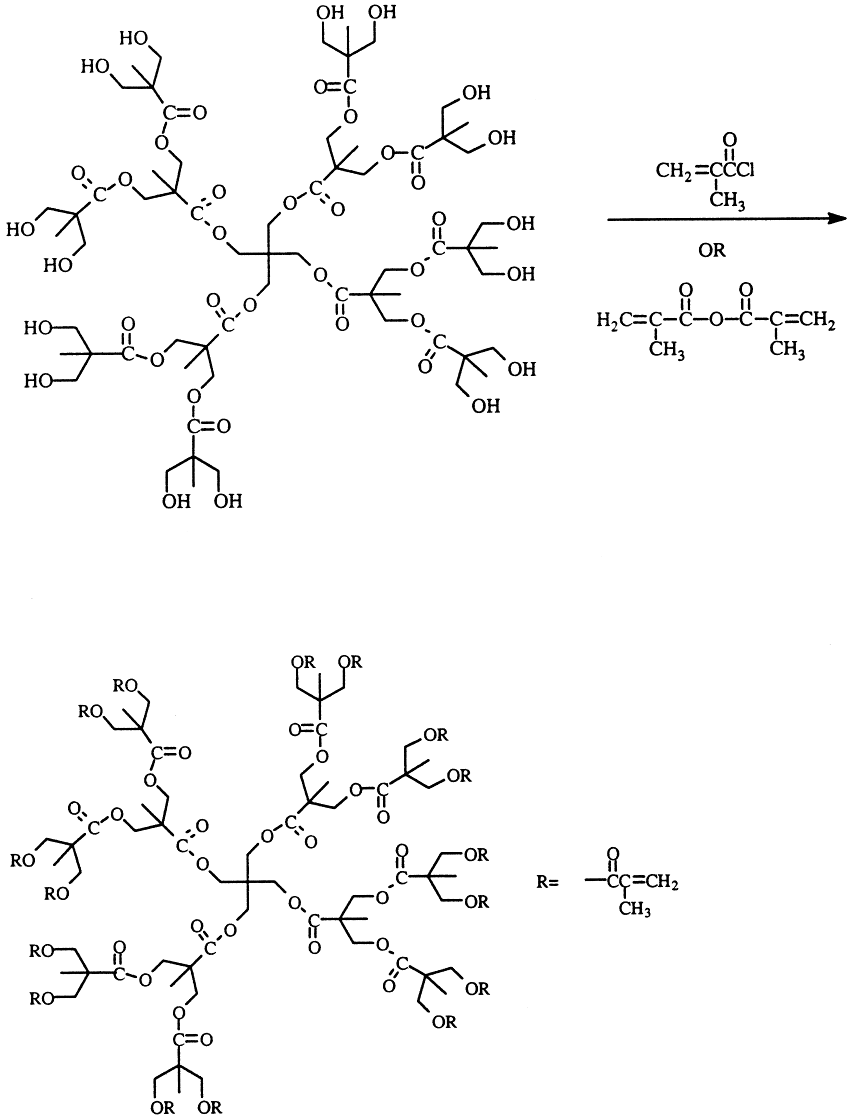

Figure 1. Schematic synthesis route of H-MMA.

After the reaction, the –OH groups are converted into methacrylates, generating new vinylic, methyl, and carbonyl carbon signals. Both FT-IR and NMR confirmed the structures of our products.

The molecular weights of the H-MMAs (H20-, H30-, H40-MMA) were evaluated by using GPC (Figure 5) and compared with the theoretical calculation, assuming complete conversion of hydroxyl groups into methacrylates (Table 1).

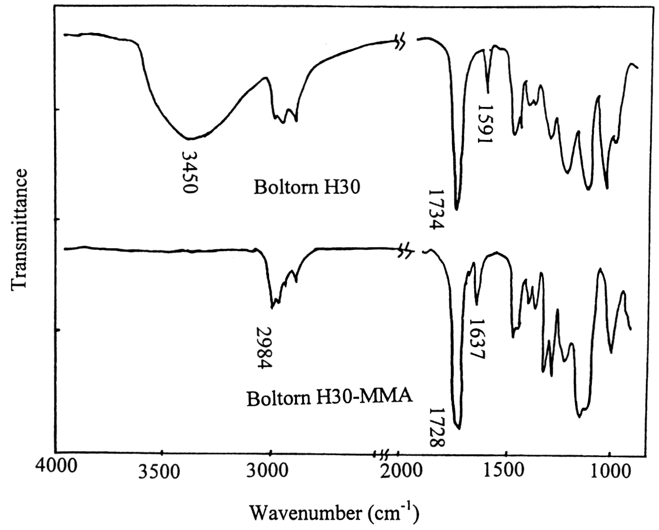

**Figure 2.** The FT-IR spectrum of Boltorn H30 and H30-MMA.

Table 1 showed the GPC results of molecular weight. For both starting materials and final products, with the molecular weight increases, the molecular weight differences between the theoretical calculation and GPC measurement increases and the polydispersity index becomes larger. This may be partly explained by cyclization during the preparation of hyperbranched polyesters, whick decreases the molecular weight, especially for the higher generation [18]. Another problem may be due to the GPC technique itself in estimation of molecular weight of hyperbranched polymers in lieu of linear polystyrene standards. Due to their unique globular structure, GPC results of hyperbranched polymers generally give lower molecular weight than they should be. However, GPC can still be used to estimate the molecular weight of hyperbranched polymers. Assuming complete esterification, the molecular weights of the resulting multi-methacrylates should be about 3188, 5676, and 9452 for H20-MMA, H30-MMA, and H40-MMA, respectively, which are in good aggrement with our GPC results. Thus, the results further suggested that most of the hydroxyl groups on Boltorn polyols are converted to methacrylates.

The H-MMA products are light-yellow, highly viscous materials. They are miscible with many monomers, such as AA, MA, MMA, HEMA, TEGDMA, and BisGMA. Due to their multi-functional carbon-carbon double bonds, H-MMAs may have wide application as modifiers or crosslinking agents as briefly evaluated and demonstrated. DSC was used to evaluate the thermal poly-

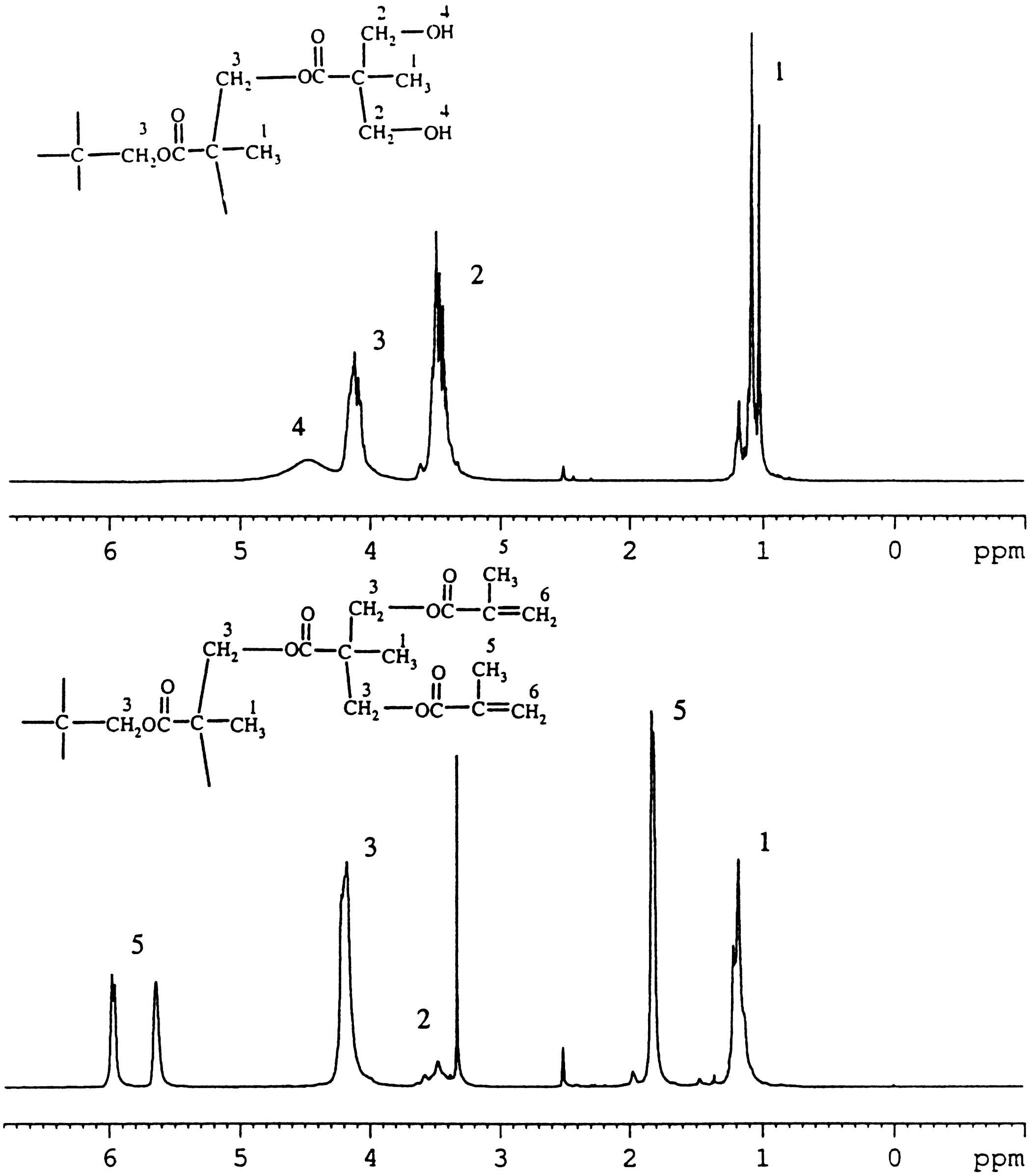

**Figure 3.** $^1$H NMR spectrum of Boltorn H30 (top) and H30-MMA (bottom) in Dimethyl-$d_6$ Sulfoxide.

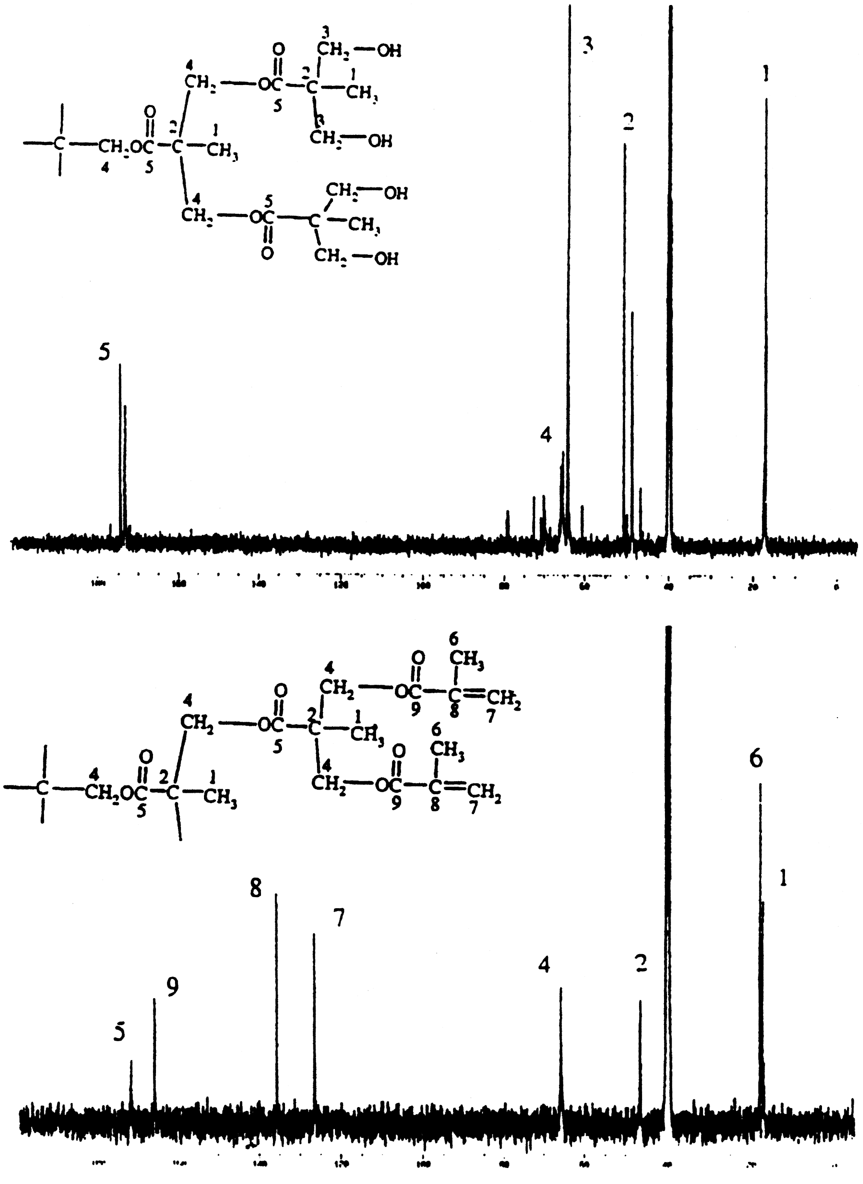

**Figure 4.** $^{13}$C NMR spectrum of Boltron H30 (top) and H30-MMA (bottom) in Dimethyl-d$_6$ Sulfoxide.

merization of the hyperbranched multi-methacrylates with the above common vinyl monomers, with the results shown in Table 2.

Mixtures of 10% of H-MMAs in methacrylic acid or acrylic acid or methyl methacrylate have higher thermal polymerization enthalpy (ΔH) than the

TABLE 1. GPC Results of H-MMAs in THF

| | Theoretical Calculation | GPC Results | | |
|---|---|---|---|---|
| | MW | Mw | Mn | Polydispersity |
| H20* | 1747 | 2100 | 1500 | 1.4 |
| H30* | 3604 | 3500 | 2187 | 1.6 |
| H40* | 7316 | 5100 | 2550 | 2.0 |
| H20-MMA | 3188 | 3075 | 2778 | 1.11 |
| H30-MMA | 5676 | 5340 | 4360 | 1.24 |
| H40-MMA | 9452 | 7229 | 5238 | 1.38 |

* Data provided by the manufacturer.

TABLE 2. Thermal Polymerization Characteristics of 10% of H-MMAs Modified Monomers by DSC Testing

| **Monomers** | **ΔH (J/g)** | **Peak Temp. (°C)** | **Tg (°C)** |
|---|---|---|---|
| **AA** | **880.9** | **129** | **91** |
| **AA+H20-MMA** | **906.9** | **122** | **103** |
| **AA+ H30-MMA** | **910.9** | **115** | **100** |
| **AA+ H40-MMA** | **1044.0** | **110** | **111** |
| **MA** | **587.2** | **127** | **-** |
| **MA+ H20-MMA** | **538.5** | **132** | **-** |
| **MA+ H30-MMA** | **555.8** | **125** | **-** |
| **MA+ H40-MMA** | **589.9** | **124** | **-** |
| **MAA** | **476.5** | **140** | **104** |
| **MAA+H20-MMA** | **400.5** | **116** | **110** |
| **MAA+H30-MMA** | **485.1** | **131** | **110** |
| **MAA+H40-MMA** | **483.5** | **122** | **111** |

corresponding pure monomers, with some exceptions. Considering H-MMAs have less density of double bonds per unit weight (1 mole/200 g) than AA (1 mole/72 g), MA (1 mole/86 g), and MMA (1 mole/100 g), multi-methacrylates of H-MMAs have thermal polymerization activities at least as good as pure monomers.

Another noticeable change of H-MMAs modified monomer mixtures is that they have lower peak temperature upon thermal polymerization. Once the polymerization is initiated, it can reach the peak early. From the second run of the DSC, glass transition temperatures ($T_g$) can be detected. H-MMAs modified resins have higher $T_g$ than the corresponding homopolymers, possibly due to the higher molecular weight of H-MMAs and higher crosslinking density.

In order to further characterize the polymerized resins, cylindrical resin samples were prepared by heating the mixture of H20-MMA with MMA and 0.5% of BPO at 70°C for 6 hours, then 120°C for 2 hours. The resulting polymer products are transparent, indicating that the poly (H-MMA)/PMMA thermoset, formed a single phase system. After acetone extraction for three days, no weight loss is detected for these copolymers of MMA/H-MMAs. This shows that hyper-branched multi-methacrylates can effectively co-polymerize with MMA, and no PMMA homopolymer is produced.

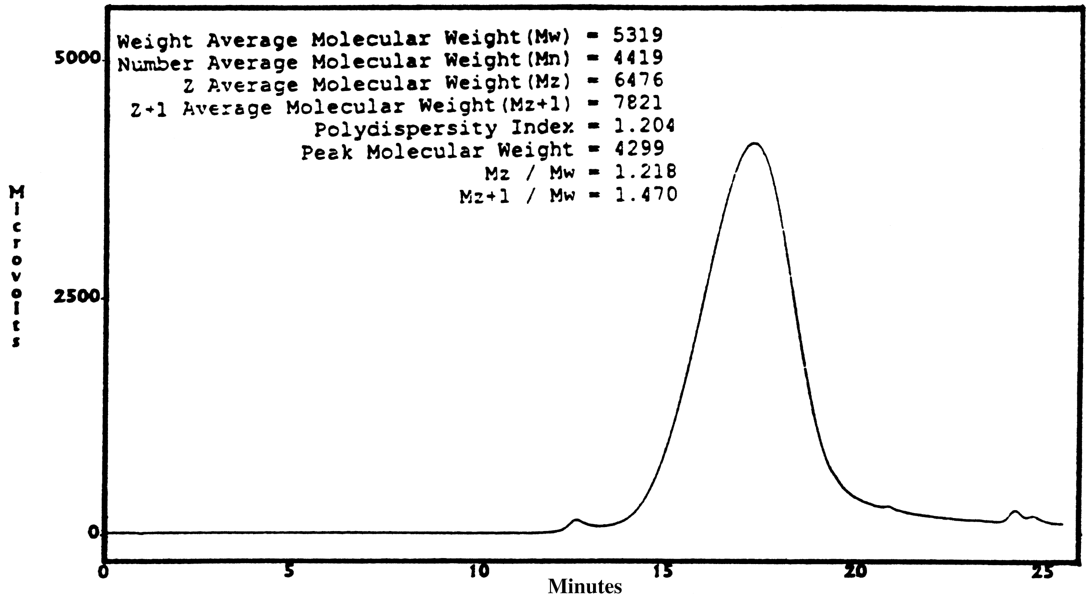

**Figure 5.** GPC result of H30-MMA in THF.

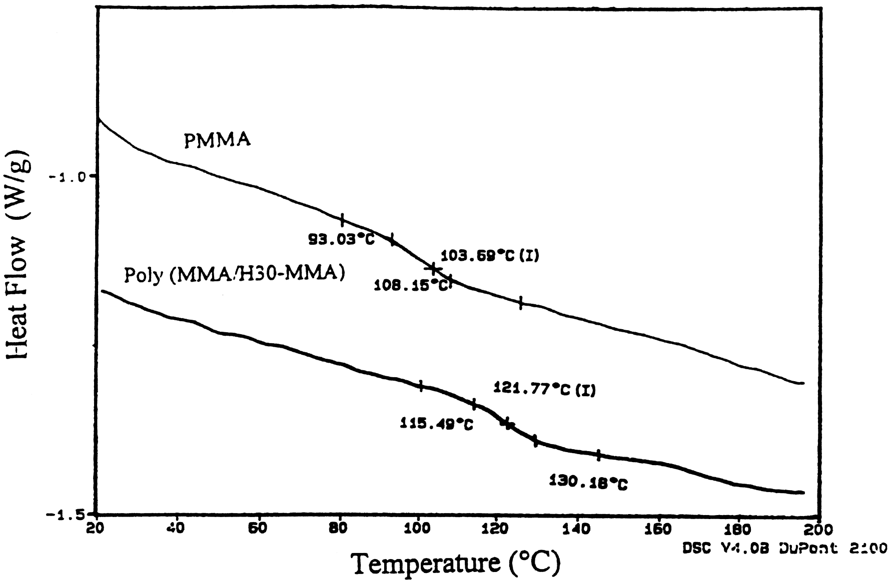

**Figure 6.** DSC curves of PMMA and Poly (MMA/H30-MMA) after thermal polymerization at 70°C, 6 hours and 120°C, 2 hours.

For these thermally polymerized resins, the glass transition temperatures were also measured by using DSC, with the curve for one experiment shown in Figure 6. As shown, H-MMA modified resins have higher $T_g$ (H20-MMA 122.3, H30-MMA 121.3, and H40-MMA 126.5°C) than PMMA (103.6°C), confirming our previous results.

## CONCLUSION

It has been shown that Boltorn hyprebranched polyols may be functionalized with methacrylate end groups. The produced methacrylated hyperbranched polyesters (H-MMA) mix well with a variety of vinyl monomers such as acrylic acid, methacrylic acid, methyl methacrylate, 2-hydroxyethyl methacrylate, and triethylene glycol dimethacryalte. The initial studies on thermal polymerization activities of 10% of H-MMAs with AA, MA, and MMA, and HEMA showed that H-MMA could effectively co-polymerize with vinyl monomers, with essentially no homopolymers produced. The resulting H-MMA/MMA resin showed one glass transition temperature, indicating a typical single-phase resin.

This indicated that Boltorn hyperbranched multi-methacrylates have potential to be used as crosslinking agents or modifiers with a number of monomers, for development of new thermosets for a variety of applications.

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