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NOVEL TRIMETHACRYLATES: SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF NEW MONOMERS FOR IMPROVED DENTAL RESTORATIVES

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NOVEL TRIMETHACRYLATES: SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF NEW MONOMERS FOR IMPROVED DENTAL RESTORATIVES

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ABSTRACT

Two novel trimethacrylates, i.e., 1,1,1-tri-[4-(methacryloxyethoxy)-phenyl]ethane (TMPE) and 1,1,1-tri-[4-(2-methyl-2-methacryloxyethoxy)-phenyl]ethane (TMMPE), have been synthesized by reacting methacryloyl chloride with the corresponding hydroxyl intermediates. Both trimethacrylate monomers, having a low viscosity of 11.5 and 13.1 Pa.S, respectively, were blended with TEGDMA at three different weight ratios, i.e., 90/10, 70/30, and 50/50. The mixtures were made visible light-curable (VLC) by the addition of camphorquinone (0.5 wt%) and N,N-dimethylaminoethyl methacrylate (1.0 wt%). In addition to evaluation as cured neat resins, VLC formulations with 70% by wt. of silanated microfiller were also prepared and evaluated. The control in both cases was a VLC formulation of BisGMA/TEGDMA (70/30 and 50/50 wt/wt). These new, formulated resins have both improved physical properties and higher double bond conversion than the BisGMA control, as well as decreased linear polymerization shrinkage (LPS). The neat resin having 70/30 (wt/wt) ratio of TMPE/TEGDMA (T7T3, Table 2) exhibited a compressive strength (CS) of 496 (± 51) MPa compared to the 70/30 (wt/wt) ratio of BisGMA/TEGDMA control having 425(± 27) MPa. A filled resin having a 90/10 (wt/wt) ratio of TMPE/TEGDMA exhibited a flexural strength (FS) of

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122.6(\pm 23) MPa, compared with a similar filled BisGMA/TEGDMA (70/30, wt/wt) resin exhibiting 112.7(\pm 19) MPa. These and other results suggest that these new trimethacrylates have potential application in formulating dental composites with improved performance.

Key Words: Dental composites; Visible light-curing; Trimethacrylate; Photopolymerization; Polymerization shrinkage; Compressive strength; Crosslink density

INTRODUCTION

For decades, the dental profession has searched for an esthetic and safer material to replace the traditional amalgam restorative. To achieve this goal, two types of polymer based restoratives, i.e., composites and glass-ionomers have become the materials of choice in tooth restorations. In different ways, each restorative has fulfilled many, if not most, of the requirements for restorative materials [1, 2]. 2,2-Bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl]propane (BisGMA) was the first dimethacrylate based formulation exhibiting satisfactory clinical performance, especially for anterior restoration [3]. Nevertheless, there remains a number of problems associated with dental composites based on BisGMA, one of which is the high viscosity (>1200 Pa.S at r.t.) of BisGMA. Therefore, a low viscosity dimethacrylate, i.e., reactive diluent, is mandatory in order to obtain a workable viscosity (1-2 Pa.S) for highly filled formulations. Another drawback is associated with the use of a monomer having high viscosity, i.e., the higher the viscosity of the monomer the more limited is the mobility of the propagating radicals, which in turn brings about more rapid vitrefication during the polymerization. The latter in turn may lower the degree of C=C double bond conversion, leading to poorer mechanical properties for the composite. In addition, BisGMA based resins are also too susceptible to water sorption. These drawbacks associated with BisGMA use are more or less relevant to the hydroxyl groups on BisGMA. Based on the concept of improving BisGMA, many other dimethacrylates have been developed, which can be divided into three categories: a) monomers having lower viscosity, such as replacing the hydroxyl on BisGMA or changing the core structure of the BisGMA [4-7]; b) preparing monomers having decreased water sorption, such as fluorine substituted dimethacrylates [8, 9]; c) producing monomers having higher T_g with more bulky structural units, such as fluorine-based dimethacrylates [10], and exploring poly(isopropylidenediphenol) resin based oligomeric multi-methacrylates [11]. At the same time, many fundamental aspects about the polymerization behavior, evaluation and performance of polymeric composites in vivo and vitro, have been investigated [12]. Each of these new monomers or oligomers can improve some properties of restorative resins to

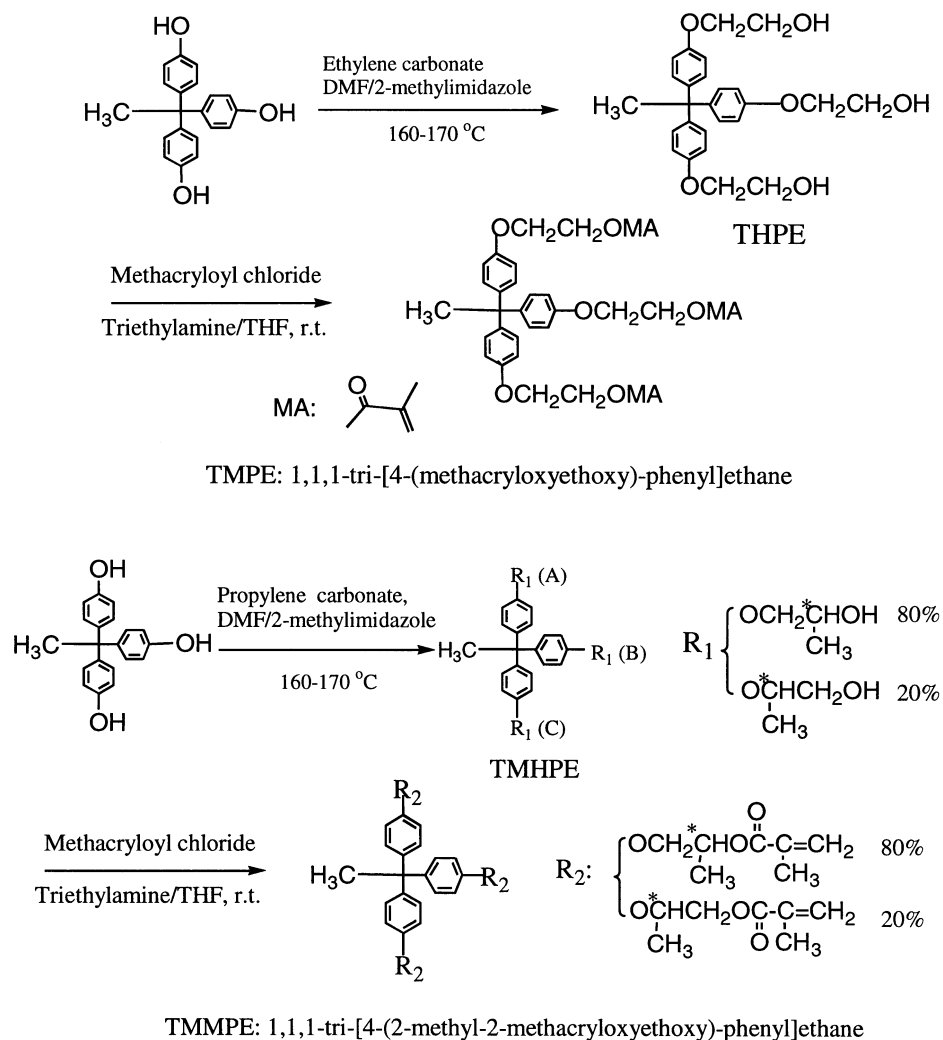
some extent, but often at the cost of losing one or more properties associated with the use of BisGMA. The OH based hydrogen bonding on BisGMA is mostly responsible for the high viscosity of the monomer, with elimination of the OH groups expected to significantly decrease its viscosity. But reducing only the BisGMA viscosity will not bring about a synergistic effect on the physical properties of the cured materials. For example, dimethacrylates with very low viscosity, such as triethyleneglycol dimethacrylate (TEGDMA) and hexamethylene dimethacrylate (HDMA) produce crosslinked materials having weaker mechanical properties than BisGMA based materials. This shows that BisGMA benzene rings play an important role in the improvement of mechanical properties. In comparison, restorative resins based on 2,2-Bis[4-(methacryloyloxyethoxy)phenyl]propane (BisEMA), which have no OH groups, have somewhat inferior strength compared to BisGMA based materials, but have superior wet strength compared to BisGMA based resins. Thus, the BisGMA OH groups make some contributions to mechanical strength. However, the lower viscosity of BisEMA, compared to BisGMA, may compensate for the absence of hydroxyl groups by allowing higher double bond conversion during visible light-curing (VLC).

It is obvious that trimethacrylate monomers, at equivalent C=C bond conversion, should have a higher cross-link density than dimethacrylates. Moreover, formulated resins having lower viscosity could allow for higher double bond conversion, as well as allow more filler loading, with both leading to better physical performance of the cured materials.

Following from the above brief discussion, we initiated an effort to synthesize and evaluate two low viscosity trimethacrylates having the aromatic ring structure. Starting from 1,1,1-tris-(4-hydroxyphenyl)ethane (THPE), we synthesized two novel trimethacrylates, 1,1,1-tris-[4-(methacryloyloxyethoxy)phenyl]ethane (TMPE) and 1,1,1-tris-[4-(2-methyl-2-methacryloyloxyethoxy)phenyl]ethane (TMMPE), as shown in Sch. 1, in a quantitative yield. The new monomers were mixed with TEGDMA in different composition to formulate neat resins as well as composites with 70 wt% glass microfiller. The solution viscosity before VLC, linear polymerization shrinkage (LPS), double bond conversion (DC), glass transition temperature (T_g) of cured resins, compressive strength (CS) and flexural strength (FS) of both neat resins and composites were briefly evaluated. The TMPE/TEGDMA and TMMPE/TEGDMA based resin properties were compared to a BisGMA/TEGDMA based resin used as a control.

EXPERIMENTAL

Starting materials and chemicals: BisGMA is a product of Cook Composites and Polymers (CCP), with a batch number of 811999090174. All



Scheme 1. Reaction scheme for new trimethacrylate synthesis.

other reagents and monomers, purchased from Aldrich Chemical Co., were used as received.

Synthesis of 1,1,1-Tri-[4-(Hydroxyethoxy)phenyl]ethane (THPE)

A 500 mL, three-necked flask, equipped with a magnetic stirrer, thermometer, reflux condenser and a nitrogen sparge tube, was charged with 30.6 g (0.1 mol) of 1,1,1-tri-4-hydroxyphenylethane, 30.8 g (0.35 mol) of ethylene carbonate, 200 mL of N,N-dimethylformamide (DMF), and 0.6 g (1.0 wt%) of 2-methylimidazole catalyst. After stirring and heating for 3 hours at

165–170°C, the mixture was transferred to a rotary evaporator to remove most of the DMF. The residue or slurry was poured into water to obtain the crude products. The earth colored powder was recrystallized from acetone/water (80/20 v/v) to obtain white crystalline THPE in a 38.5 g (87.9%) yield, with melting point 44–45°C. This compound has not been reported to date.

¹H NMR (DMSO-d₆, Broker 400 MHz), with δ 2.04 (s, -CH₃, 3H), 3.70 (t, -CH₂OH), 6H), 3.95 (t, ArO-CH₂-, 6H), (s, OH, < 3H), 4.85 (s, -OH), 6.83 (s, Ar-H, 6H), 6.93 (s, Ar-H, 6H).

¹³C NMR spectroscopy shows eight signals at 156.98, 141.7, 129.6, 114.0, 72.8, 59.9, 50.5, 30.7.

Synthesis of 1,1,1-Tri-[4-(2-Methyl-2-hydroxyethoxy)-phenyl]ethane (TMHPE)

Similar to the THPE procedure, a 30.6 g (0.1 mol) of 1,1,1-tri-4-hydroxyphenylethane, 35.7 g (0.35 mol) of propylene carbonate, 200 mL DMF and 1.0 wt% of 2-methylimidazole mixture was stirred and heated for 5 hours at 165–170°C. The mixture was transferred to a rotary evaporator to remove about 100 mL of DMF, the resulting slurry or mixture was poured into a large excess of water (2 L) to obtain a brown colored, crude product. After decanting the water, ethyl acetate (500 mL) was used to dissolve the crude material. The ethyl acetate solution was washed twice with 50 mL NaOH (10%) solution and twice with 50 mL HCl (5%) solution. The organic phase was then dried over anhydrous Na₂SO₄. The solvent was removed to obtain a 33.6 g (71%) yield of light yellow color TMHPE as a wax-like semi-solid. This compound has not been reported so far. ¹H NMR (CDCl₃, Broker 400 MHz), with δ 1.25 [t, -OCH₂CH(CH₃)OH, 9H], 2.08 (s, CH₃-C≡, 3H), 2.90 (s, -OH, 3H), 3.79 (t, -OCH(CH₃)CH₂OH, 2.4H) 3.87 (m, -OCH(CH₃)CH₂OH, -OCH₂CH(CH₃)OH, 3.5H), 3.95 (m, -OCH(CH₃)CH₂OH, 0.6H), 4.15 (m, -OCH₂CH(CH₃)OH, 2.4H), 6.77 (s, Ar-H, 6H), 6.96 (s, Ar-H, 6H).

¹³C NMR spectroscopy shows 11 signals at 157.0, 142.5, 130.1, 114.2, 74.8(weak, assigned to minor isomer, -OCH(CH₃)CH₂OH), 73.6, 67.4, 51.1, 31.2, 18.8, 17.4 (weak, assigned to minor isomer, -OCH(CH₃)CH₂OH).

From the NMR, it shows that about 20% isomer is produced during the reaction. The possible reason for this is that the phenol attacks at two different locations on the propylene carbonate, at the high reaction temperature. All attempts to recrystallize TMHPE, as was done with THPE, failed.

Syntheses of 1,1,1-Tri-[4-(Methacryloxyethoxy)-phenyl]ethane (TMPE) and 1,1,1-Tri-[4-(2-Methyl-2-methacryloxyethoxy)-phenyl]ethane (TMMPE)

A 500 mL, tree-necked, round-bottom flask, fitted a magnetic stirrer, thermometer, ice-water bath, condenser and nitrogen sparge tube, was charged with 0.05 mol of THPE or TMHPE, which were prepared as

previously described, along with 250 mL of dry THF, and 22 mL of triethylamine (0.16 mol). Methacryloyl chloride, 17.8 g (0.16 mol), was added slowly to the stirred mixture. The reaction mixture was then stirred overnight at room temperature. The precipitated solid was filtered off. After the addition of 0.05 wt% 2,6-di-tert-butyl-4-methylphenol (BHT) the solvent was removed. The very light yellow oil, crude product, was dissolved in diethyl ether and extracted twice with 10% Na₂CO₃ solution and with water. After drying over anhydrous MgSO₄, 0.05 wt% BHT was added and the solvent was removed in vacuum at ca. 40°C, obtaining a 28.4 g (88.5%) yield of TMPE and a 29.2 g (86.1%) yield of TMMPE, as viscous, light yellow colored oils. The IR and NMR spectra show no -OH functionality on the two novel trimethacrylates, which have viscosities at 25°C, respectively, of 11.5 and 13.1 Pa · S.

TMPE-¹H NMR (DMSO-d₆, Broker 400 MHz), with δ 1.89 [s, -C(CH₃)=CH₂, 9H], 2.05 (s, CH₃-C≡, 3H), 4.20 (t, -CH₂CH₂OH, 6H), 4.42 (t, -CH₂CH₂OH, 6H), 6.05 (m, -C(CH₃)=CH₂, 3H), 5.66 (d, -C(CH₃)=CH₂, 3H), 6.84 (s, Ar-H, 6H), 6.94 (s, Ar-H, 6H); ¹³C NMR: 166.8, 156.6, 141.7, 136.2, 129.8, 126.2, 114.2, 66.0, 63.8, 50.5, 31.6, 18.4.

TMMPE-¹H NMR (DMSO-d₆, Broker 400 MHz), with δ: 1.30 [m, -OCH₂CH(CH₃)OMA, 9H], 1.86 (s, -C(CH₃)=CH₂, 9H), 2.06 (s, CH₃-C≡, 3H), 4.08 [m, -OCH₂CH(CH₃)OMA, 2.4H], 4.21 [m, -OCH₂CH(CH₃)OMA, 2.5H], 4.25 [m, -OCH₂CH(CH₃)OMA and -OCH(CH₃)CH₂OMA, 3.6H], 4.72 [m, -OCH(CH₃)CH₂OMA, 0.6H], 5.65 (d, -C(CH₃)=CH₂, 3H), 6.00 (m, -C(CH₃)=CH₂, 3H), 6.76 (s, Ar-H, 6H), 6.96 (s, Ar-H, 6H). ¹³C NMR: 167.0, 157.0, 142.3, 136.4, 130.1, 126.4, 114.2, 74.8 (weak, assigned to a minor isomer, -OCH(CH₃)CH₂OR), 73.6, 67.4, 51.1, 31.2, 18.8, 18.4, 17.5 (weak, assigned to minor isomer, -OCH(CH₃)CH₂OR).

Viscosity. The Brookfield CAP 2000 Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) was used to measure the viscosity of each sample. Depending on the range of the viscosity for the sample, Cone #1, 3 and 5 were used, respectively. All samples were run three times at 25°C. The Bingham Plastic Math Model was then used to analyze the viscosity based on the linear regression of shear stress with the shear rate.

Preparation of VLC Resin and Composites Specimens and Mechanical Properties

TEGDMA comonomer was blended with the previously synthesized monomers in three different composition, with the sample code and its composition shown in Table 1. To obtain VLC formulations, camphorquinone (0.5 wt%) and accelerator N,N-dimethylaminoethyl methacrylate (1 wt%) were added to the mixtures. The mixtures were cured directly to obtain the crosslinked resins. The VLC mixtures were also combined with

70% by wt. microfiller (Schott Glass 1.0 μm) and cured to obtain the composites. After removal from the molds, all samples were conditioned in distilled water at 37°C for one week, prior to testing.

The compressive strength (CS) test samples, 4 mm in diameter \times 6 mm in thickness, and flexural strength (FS) samples, 25 \times 2 \times 2 mm, were visible-light cured for a total of five minutes, using an Optilux (Demetron Research Corporation) curing light. After removal from the mold, the sample surface was polished by using silicon carbide paper (FEPA P# 800). 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)

DC was measured by solid state ^{13}C -NMR: Specimens used for the FS test were ground into a powder for the solid state ^{13}C -NMR test. Spectra were obtained using a Bruker 300 spectrometer operating at 75.5 MHz. The integration of a signal at δ of 167.2 and 177.4, A_{167} and A_{177} , was used to represent the numbers of methacryloyl carbonyl groups on the un-polymerized and polymerized segments, respectively, in the resins after curing [13, 14]. Thus, $\text{DC} (\%) = A_{177}/(A_{177} + A_{167}) \times 100\%$

Linear Polymerization Shrinkage (LPS)

The LPS was determined for the experimental neat resins using the simple “deflecting disk” method described by Watts and Cash [15]. In this method, an LVDT displacement transducer is used to measure the displacement of a glass cover slip that is deflected as the resin shrinks during polymerization. The resin, usually 4 drops can produce 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, which was suspended by the the brass ring edges, see Fig. 2 apparatus scheme. 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 exposure, the total amount of LPS% was determined. For each sample, 6 specimen were tested and the average LPS was obtained.

Glass Transition Temperature (T_g)

The DSC curves were recorded with DuPont Differential Scanning Calorimeter 910 at temperatures over the range -60° to 250°C and with a scan rate of $10^\circ\text{C}/\text{min}$, with the T_g read from the mid-point of the tran-

sition by using the DSC 4.0 computer program supplied with the instrument. It should be noted that the T_g data obtained in this study is an apparent one, usually higher than the actual ones. However, the actual T_g could be obtained by scanning a sample at different scan rates and extrapolating to zero scan rate. But, since this was only a comparison study, only the apparent T_g was determined.

RESULTS AND DISCUSSION

The Syntheses of Trimethacrylates and Their Intermediates

As shown in Sch. 1, the TMPE and TMMPE trimethacrylate monomers, and their intermediates, can be obtained in good yields. HPLC (Shimadzu Class VP system) was used to check the purity of the sample, with the chromatography single peaks suggesting high purity for both monomers. Further, both IR and NMR confirmed the expected chemical structure. It is worth noting, great care or careful control of the crystallization condition is needed to get crystalline TMPE. However, all efforts to crystallize TMHPE failed. The reason is that TMHPE is actually a mixture of its isomers as well as enantiomers. As shown in Sch. 1, ether group A, B and C could be different, also the chiral carbon may have different chirality from each other. Attempts were made to use 2-chloro-isopropanol (containing >20% 1-chloro-propanol) and propylene oxide to prepare TMHPE. But, these reactions still provided a mixture, which could not be crystallized. Also, we could not optimize the latter reaction condition to prepare the desired intermediate at a yield higher than 10%.

The Viscosity and Polymerization Degree

As expected the TMPE and TMMPE trimethacrylates have much lower viscosity, 11.5 and 13.1 Pa.S, respectively, compared to the commonly used BisGMA having a viscosity of 1200 Pa.S [5] at 25°C. It is interesting to find that the viscosity of the two trimethacrylates have very similar viscosities, even though TMMPE has a much more disordered structure than TMPE. Since the two trimethacrylates have much lower viscosity than BisGMA, they can be formulated into resin with much less of a diluent monomer, such as TEGDMA, achieving a workable viscosity less than 1 Pa.S. With this in mind, three different TMPE/ and TMMPE/ TEGDMA formulations of the new monomers, versus a BisGMA/TEGDMA control, the viscosities were evaluated, as shown in Table 1.

There are a few ways to determine double bond conversion, such as differential photocalorimetry (DPC) [16] and IR [17, 18] techniques, with each of them having advantages and disadvantages. The exact conversion can

Table 1. The Formulations of VLC Resins

| Sample | Multi-methacrylate/ wt. Parts | TEG- MA/wt. Parts) | Viscosity* (cP) | DC** (%) | LPS* (%) | | T _g *(°C) |
|-----------|----------------------------------|--------------------------|--------------------|-------------|------------|-------------|----------------------|
| | | | | | Neat Resin | With Filler | |
| Control-1 | BisGMA/50 | 50 | 58(11) | 80.8 | 6.69(0.13) | 4.42(0.11) | 42.45(2.5) |
| T5T5 | TMPE/50 | 50 | 17(3) | 88.6 | 6.02(0.11) | 3.94(0.08) | 46.7(1.0) |
| TM5T5 | TMMPE/50 | 50 | 22(6) | 85.9 | 5.85(0.14) | 4.01(0.13) | 53.89(2.8) |
| Control-2 | BisGMA/70 | 30 | 744(93) | 77.6 | 4.86(0.10) | 3.28(0.07) | 45.92(2.4) |
| T7T3 | TMPE/70 | 30 | 223(30) | 87.5 | 4.10(0.20) | 2.55(0.11) | 52.4(1.8) |
| TM7T3 | TMMPE/70 | 30 | 187(14) | 86.3 | 3.49(0.16) | 2.48(0.08) | 55.74(2.0) |
| T9T1 | TMPE/90 | 10 | 793(50) | 86.6 | 3.89(0.14) | 2.21(0.12) | 54.2(3.0) |
| TM9T1 | TMMPE/90 | 10 | 875(50) | 83.7 | 4.02(0.14) | 2.03(0.08) | 56.2(2.1) |

* Entries are mean values (standard deviations) of five samples.

** Only one sample measured.

be clarified by an extraction test, i.e., extract the VLC cured resin with a solvent to obtain the weight loss over a certain span of time, giving monomer conversion not double bond conversion. For all cured resins in this study, the weight loss by acetone extraction, over 48 hour period, was between 1–2%, which needs clarification. We also used ¹³C-NMR to determine double conversion [13, 14], Fig. 1 gives the typical solid ¹³C-NMR spectra of two new trimethacrylate and BisGMA with TEGDMA formulated resins in weight ratio of 50/50. All those DC calculated from the NMR spectra were shown in Table 1. Benefiting from their low viscosity, the formulated trimethacrylate resins have higher double bond conversion than the BisGMA-based control. During VLC polymerization of the various formulations auto-acceleration and auto-deceleration are inevitable. Such reaction conditions are controlled by diffusion, which is related to the viscosity of the monomer systems. Thus, the formulations having the highest viscosity will have the earliest micro-gellation and be the first to reach vitrification. The latter consideration will cause more pronounced lack of homogeneity in the more viscous formulations, bringing about deleterious side-effects such as low polymerization conversion, long period of post-polymerization as well as deterioration of physical properties. In this study, the reduced viscosity of the TMPE and TMMPE formulations have about 10% higher double bond conversion than BisGMA based resins.

Linear Polymerization Shrinkage (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 [19]. Essentially,

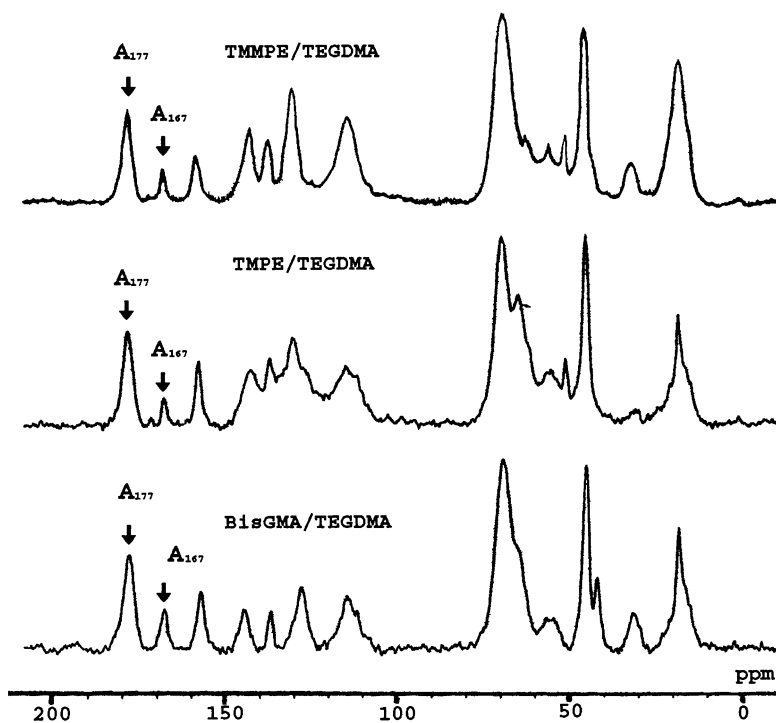


Figure 1. The ^{13}C -NMR spectra of TMPE/TEGDMA, TMMPE/TEGDMA, and BisGMA/TEGDMA (50/50 wt./wt.), cured by visible light; the peak with arrows indicated are used for calculation of double bond conversion.

the volume shrinkage of the methacrylate monomer brings about the intermolecular vicinity volume reduction during the polymerization process. Because the monomer molecules are “compacted” via the Van de Waals 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 crosslink 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 [11]. New kinds of spiro-orthoester monomer system having a characteristic of ring-opening polymerization have been developed lately [20–22]. Unfortunately, these new spiro-orthoester monomers can only be polymerized under specific conditions and the initiator systems are generally toxic. There is no doubt that to minimize or totally eliminate the polymerization shrinkage of resins for dental application will be a long-term challenge for

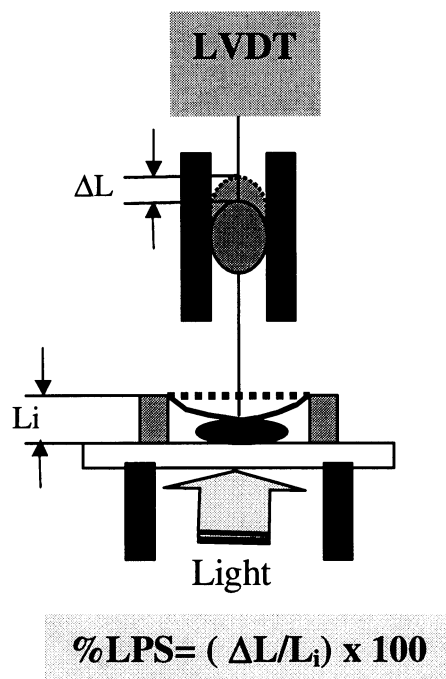


Figure 2. Diagram for linear polymerization shrinkage measurement.

dental materials investigators. Basically, to keep the order of multi-methacrylate molecules as high as possible will require developing methacrylate functionalized systems having higher order structures, such as liquid crystal, dendritic and hyperbranched architecture.

It is observed that along with the new trimethacrylate formulations have higher double bond conversion, they also have for both the neat resin and filled materials a slight reduced linear polymerization shrinkage, compared with the BisGMA control. The possible reason for this is that the bigger molar volume of the trimethacrylates is maintained during polymerization, compared to the BisGMA structure exhibiting more “free volume” squeezing out during polymerization.

Glass Transition Temperature of Neat Resins

Glass transition (T_g) is a ubiquitous and important phase transition phenomenon of amorphous polymer structures. But the molecular mechanism for the transition is not well understood, especially for crosslinked polymer networks [23]. Nielsen once put forward a very empirical correlation between T_g and crosslinking density of polymer networks [24]. But it is not overly reliable for low and moderate crosslinked polymer networks. Even so,

the characterization of T_g of crosslinked resin can still provide very useful information about phase morphology and prediction of physical properties of resins. Experimentally, differential scanning calorimetry (DSC) and dynamic mechanic analysis (DMA) are the most used methods to determine T_g of polymers, with the latter having higher sensitivity than the former usually revealing multi-transitions below T_g . If the assumption that polymer chain's "defreezing" motion leads to the observed amorphous polymer T_g can be applied to crosslinked polymer network, then for a highly (<100%) cross-linked polymeric network it is speculated that no glass transition temperature (T_g) could be observed. However, there is no such perfect polymer network. Usually one or more sub transitions, associated with movement of pedant branches and localized molecular segments may be observed. Depending on the determination approaches, preparation procedures for the crosslinked polymer network, such as photopolymerization or chemical curing and so on, a varied T_g for the cured BisGMA network has been published, i.e., 63°C [10], 72°C [25], 230°C [26] and even a double T_g of 64°C and 133°C [6]. For both the BisGMA control and new trimethacrylate formulations cured/prepared in this study, no T_g between 100–250°C was observed. Only a T_g ranging from 40–60°C was observed for each of the resins. For this low temperature transition, the new trimethacrylate resins have a slight higher T_g than the BisGMA control. The reasons for this may be twofold; first all the resins discussed earlier are highly crosslinked, from the double bond conversion data, and no main glass transition could be observed; second, the new trimethacrylate resins have higher double bond conversion, leading to the higher temperature for the pedant chains to start their movement. It is also interesting to find that the T_g doesn't change with the changing of composition of the two monomers, which does not agree with Jancar's experiment results [26]. The reason for this is unclear, with further exploration needed.

Mechanical Properties

The mechanical properties of polymers can be related to many factors, which can be categorized into intrinsic and extrinsic factors. Intrinsic factors include the chemical structure of the monomer used, polymerization methodology, molecular weight and its distribution, molecular topology and phase morphology and etc. Extrinsic factors include application environment, preparation history, testing methods, variation of personal operation and etc. For polymer composites, except all those aforementioned factors, the factors such as the utilization of filler, filler-matrix interface property and so on can also affect the performance of the materials. This situation makes it somehow difficult to judge different polymers or polymer composites from their mechanical properties. However, the extrinsic factor can be reduced to a minimum by using control specimens. With the control's comparison, eval-

uating the mechanical properties of a polymer or polymer composite by using standard testing procedure can give valuable prediction between structure and property of a polymer or polymer composite. In evaluation of dental neat resin or composites, compressive strength and flexural strength are usually used as the screening criteria for new restorative materials. In this paper, the neat resins and composites are briefly examined and compared with the BisGMA-TEGDMA control. Table 2 shows the primary results. For the resins with the same TEGDMA concentration, new monomer-formulated resins have both improved compressive strength and flexural strength. For compression testing, with increasing TEGDMA, the strain increased. TMPE and TMMPE based resins didn't change the strain compared with the BisGMA control, which might be related to the new monomers having the molecular structure of both a rigid benzene and flexural ethyloxyl part. Due to the low viscosity of the new monomers, the use of only 10% of TEGDMA raises the formulated resin viscosity to less 1 Pa.S. However, it is surprising that the CS and FS values of the cured resins and composites did not go up with raising the trimethacrylate concentration. The possible reason could be that the double bond conversion has the most determining affect on the strength. With utilization of filler, FS of composites are improved but CS are deteriorated compared to neat resins. The reason for this could possibly be something to do with the preparation of the specimen. For all formulations examined, The T7T3 neat resin has the highest compressive strength (CS) of

Table 2. The Mechanical Properties of VLC Resins Derived from New Trimethacrylates

| Sample | CS (MPa)* | Modulus (CS, GPa) | Strain (%) | FS (MPa)* | Modulus (FS, GPa) |
|--------------------|-----------|-------------------|------------|-------------|-------------------|
| Control-1 | 376(16) | 2.46(0.44) | 17.8(4.3) | 72.6(3.8) | 1.52(0.21) |
| T5T5 | 399(23) | 2.71(0.63) | 15.5(3.8) | 88.4(4.8) | 1.55(0.20) |
| TM5T5 | 391(23) | 2.71(0.38) | 14.9(4.2) | 84.4(6.8) | 1.88(0.23) |
| Control-1 (Filler) | 356(21) | 5.88(0.72) | 9.4(3.5) | 81.4(7.8) | 7.99(0.67) |
| T5T5 (Filler) | 339(31) | 5.44(0.86) | 8.8(2.2) | 85.0(7.4) | 7.25(0.66) |
| TM5T5 (Filler) | 341(40) | 6.12(0.58) | 8.4(3.0) | 79.6(10.6) | 7.88(0.83) |
| Control-2 | 425(27) | 3.11(0.23) | 14.6(2.6) | 105.3(4.4) | 1.98(0.2) |
| T7T3 | 496(51) | 3.45(0.22) | 15.0(3.0) | 97.2(4.6) | 1.86(0.11) |
| TM7T3 | 452(41) | 2.68(0.45) | 14.4(3.2) | 97.2(9.8) | 1.92(0.15) |
| Control-2 (Filler) | 345(6.6) | 6.37(0.22) | 8.9(1.8) | 112.7(9.3) | 9.17(0.76) |
| T7T3 (Filler) | 355(42) | 5.85(0.40) | 7.8(2.2) | 109.2(8.7) | 8.68(0.81) |
| TM7T3 (Filler) | 328(38) | 6.68(0.39) | 7.5(1.9) | 113.0(10.5) | 9.29(0.65) |
| T9T1 | 492(27) | 2.94(0.55) | 14.8(2.1) | 105.5(4.7) | 2.18(0.18) |
| TM9T1 | 488(20) | 3.57(0.50) | 13.5(2.0) | 99.7(5.5) | 2.02(0.19) |
| T9T1 (Filler) | 349(34) | 6.73(0.56) | 6.5(1.0) | 122.6(12.7) | 10.2(1.05) |
| TM9T1 (Filler) | 363(29) | 6.88(0.73) | 7.3(1.2) | 117.7(12.2) | 11.2(0.88) |

* Entries are mean values for five samples with standard deviations in parentheses.

496 ± 51 MPa compared G7T3 (control) of 425 ± 27 MPa. The T9T1 formulated composite has the highest FS of 122.6 ± 23 MPa compared with G7T3 composite of 112.7 ± 19 MPa. It is apparent that the moduli of composites are much higher than neat resins. But for neat resins, the moduli from CS are higher than those from FS, and it has a contrary tendency for composites. The reasons for this are not clear at this time. In general, through, the overall evaluation of mechanical strengths for the new trimethacrylate formulated resins and composites show advantages over BisGMA controls.

CONCLUSION

Two new, low viscosity trimethacrylates have been prepared in excellent yields. Evaluation of the trimethacrylates as potential alternatives for dental restoratives, compared to a BisGMA based control, showed that the new monomers could be used to formulate neat resins or composites having improved physical properties over the control. Due to more bulky molar volume and low viscosity, the new monomers exhibit higher double bond conversion as well as decreasing linear polymerization shrinkage (LPS), compared to a BisGMA control. The higher DC and lower LPS might be the reason for the improvement of the new formulated resins and composites. Thus, the new trimethacrylates could be a successful alternative to BisGMA for application in formulating dental composites.

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