

Synthesis of Two Bis-GMA Derivates with Different Size Substituents as Potential Monomer to Reduce the Polymerization Shrinkage of Dental Restorative Composites

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Abstract

Organic matrixes of commercial dental composites generally consist of diluent such as triethylene glycol dimethacrylate (TEGDMA) to decrease viscosity. However, the increasing dilution exhibited adverse effects such as higher polymerization shrinkage and water uptake of resin materials. Therefore, the viscosity of the resin matrix should be as low as possible to fabricate resin composites with a minimum content of diluent. To overcome the high viscosity of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl] propane (Bis-GMA) caused by hydrogen bonding between hydroxyl groups, 2,2-bis[4-(2-benzoyl-3-methacryloyloxypropoxy) phenyl] propane (Bz-Bis-GMA) and 2,2-bis[4-(2-valeryl-3-methacryloyloxypropoxy) phenyl] propane (Vr-Bis-GMA) were synthesized by esterification reaction using benzoyl and valeryl as substituent groups for hydroxyl groups. A series of resin composites containing various resin mixtures of Bis-GMA, Bz-Bis-GMA, Vr-Bis-GMA and TEGDMA and the same filler composition with 70 wt% loading were fabricated. The results suggested that the viscosity of Bis-GMA was dramatically reduced from 820 Pa.s to 2.7 Pa.s and 1.6 Pa.s by regulating substituent size of benzoyl and valeryl groups for hydroxyl groups, respectively. Consequently, the amount of TEGDMA included in the Bz-Bis-GMA matrix could be minimized to 20 wt%, as a substituent for the commonly used resin formulation (Bis-GMA/TEGDMA=50/50, wt/wt), resulting in the reduced polymerization shrinkage (2.1%), adequate flexural strength (93.3 MPa) and compressive strength (212.4 MPa) of the corresponding composites, which might provide a new strategy for the design of novel monomer for dental restorative materials with a decreased polymerization shrinkage and acceptable mechanical performance.

Keywords: Bis-GMA derivates, viscosity, reaction kinetics, polymerization shrinkage, mechanical properties

1. Introduction

Dental restorative composites have been extensively used as filling materials for clinical treatments ranging from small anterior restorations to large posterior restorations, and even fixed partial dentures instead of conventional amalgam alloys, due to their distinguished characteristics such as aesthetics, manipulative qualities, biocompatibility, and physical properties (J. Kim, L. Kim, C. Kim, Cho, & O. Kim, 2006; Wang, Zhu, Li, Zhang, & Wang, 2011). However, restorative dentistry is still fraught with various problems such as postoperative sensitivity, secondary caries, and pulpal pathoses resulting from inherent curing shrinkage accompanying the polymerization process of resin composites (Jeon, Yoo, J. Kim, C. Kim, & Cho, 2007; Kim et al., 2003; El-housseiny, & Farsi, 2002). Therefore, the development of new monomers eliminating or decreasing volume shrinkage during polymerization process is essential and profound for dental resin composites.

Commercial organic matrix generally contains bisphenol A glycerolate dimethacrylate (Bis-GMA) as a base resin and tri (ethylene glycol) dimethacrylate (TEGDMA) as a diluent. Rigid aromatic backbone structures in Bis-GMA provide superior toughness to resin composites, while a main disadvantage is its high viscosity attributed to intermolecular hydrogen bonding between hydroxyl groups, necessitating a diluent monomer (Khatri, Stansbury, Schultheisz, & Antonucci, 2003). The addition of TEGDMA improves handling characteristics and filling loading, however, dilution also increases polymerization shrinkage and water sorption

(Davy & Braden, 1991; Podgórski 2011).

To overcome adverse diluent effects on properties of dental composites, several studies aimed at developing Bis-GMA alternatives with lower viscosities have been performed (Jeon et al., 2007; El-housseiny et al., 2002; Khatri et al., 2003; Pereira, Osoriob, Toledanob, & Nunes, 2005; Podgórski et al., 2010; Lovell, Stansbury, Syrpes, & Bowman, 1999; Podgórski 2012). These attempts have been partially successful in reducing polymerization shrinkage, but TEGDMA is still required and present in the majority of commercial dental formulations and there are still problems with mechanical performance of corresponding resin composites. Furthermore, these synthetic processes have inherent limitations, especially the complicated synthetic procedures and strict conditions.

In the previous research, we had explored acetyl-substitution Bis-GMA derivate (Ac-Bis-GMA) as a base resin to develop dental restorative composites with low curing shrinkage and excellent mechanical properties (Wang et al., 2013). Based on our best knowledge, removal of the hydroxyl groups in Bis-GMA and increase the steric hindrance in the chain packing of the polymer could be effective strategies for viscosity reduction (J. Kim et al., 2006; Nystrom, Kjoniksen, & Iversen, 1999). Bulky group substitution for hydrogen on the phenyl ring in the Bis-GMA could be an example. In this present work, two novel organic Bis-GMA derivates, including benzoyl and valeryl groups instead of hydroxyl groups in Bis-GMA, i.e. 2,2-bis[4-(2-benzoyl-3-methacryloyloxypropoxy) phenyl] propane (Bz-Bis-GMA) and 2,2-bis[4-(2-valeryl-3-methacryloyloxypropoxy) phenyl] propane (Vr-Bis-GMA) were synthesized by substituting bulky benzoyl and valeryl for hydroxyl groups in Bis-GMA through a simple one-step esterification reaction with different carbonyl chlorides. The viscosities and photopolymerization kinetics of resin matrixes were assessed. Polymerization shrinkage and mechanical properties of corresponding dental resin composites fabricated from various polymer matrixes were also investigated.

2. Materials and Experimental

2.1 Materials

Bis-GMA, TEGDMA, camphorquinone (CQ, 97%) and ethyl 4-dimethylamino benzoate (4-EDMAB, 99%) were obtained from Aldrich Chemical Co. (Milwaukee, USA). Nanosized (Aerosil OX50, average diameter of 40 nm) and microsized silica (particle size distribution of 0.4~1.2 μm) were supplied by Evonik Degussa Co. Ltd. (Shanghai, China) and Tongda Weipeng Electric Co. Ltd. (Zhejiang, China), respectively. Cyclohexane (C_6H_{12} , 99%), n-propylamine ($\text{C}_3\text{H}_9\text{N}$, 99%), 3-methacryloyloxypropyl trimethoxysilane (γ -MPS, 99%), benzoyl chloride (Bz), valeryl chloride (Vr), dichloromethane and triethylamine (TEA) were provided from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Dichloromethane and TEA were dried and distilled before use, and other chemicals were directly used without further purification.

2.2 Methods

2.2.1 Synthesis of Bz-Bis-GMA and Vr-Bis-GMA

Two novel Bis-GMA derivates, Bz-Bis-GMA and Vr-Bis-GMA, were synthesized by substituting benzoyl and valeryl groups for hydroxyl groups in Bis-GMA by the esterification reaction, shown in Figure 1.

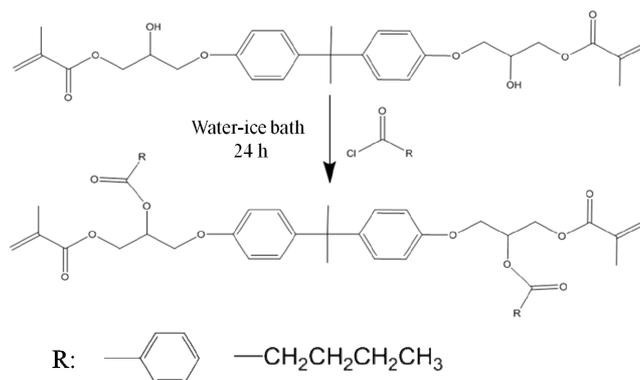


Figure 1. Synthetic route of acyl-substituted Bis-GMA derivates

According to our previous work (Wang et al., 2013), all reactions were carried out under an inert atmosphere of

nitrogen. Benzoyl chloride or valeryl chloride (1.5 mol), was added dropwise over 30 min to the solution of Bis-GMA (1 mol) and TEA (1.5 mol) in dichloromethane (100 mL), respectively. After stirring for 6 h under ice water bath, the resulting mixture was further performed at room temperature for 24 h to ensure the complete substitution of hydroxyl groups in Bis-GMA. The mixture was then transferred through a sintered glass funnel containing a small pad of silica gel. The resulting organic solution was washed with saturated aqueous NaHCO_3 , deionized water, dried over anhydrous MgSO_4 and concentrated by rotary evaporation. Finally, the synthesized Bz-Bis-GMA and Vr-Bis-GMA were vacuum-dried at 40 °C for 48 h.

2.2.2 Preparation of the Samples

(1) Unfilled Bis-GMA derivatives and their mixtures with TEGDMA

Organic matrixes were prepared with Bis-GMA (or its derivatives) as base resin, TEGDMA as the diluent, 0.02 wt% CQ and 0.08 wt% ethyl 4-EDMAB as the photo-initiator system. To investigate the viscosities and polymerization kinetics properties of the organic matrix, a series of Bis-GMA (or its derivatives)/TEGDMA mixtures were prepared, with a content of 20, 30, 40, and 50 wt% of TEGDMA. Among these organic mixtures, Bis-GMA/TEGDMA=50/50 (wt/wt) mixture was selected as the control group for comparison (Khatri et al., 2003; Lovell et al., 1999).

(2) Filled experimental resin composites

The resin composites contained 70 wt% silanized co-fillers including micro- and nano-size silica with the optimum weight ratio of 58:12 (Wang et al., 2013), and the representative silanization procedure was described in the previous work (Wilson, Zhang, & Antonucci, 2005). The silanized co-fillers were premixed into the resin matrix by hand spatulation, and then blended into a three-roll extruder (EXAKT 80E, Exakt Apparatebau GmbH & Co., Norderstedt, Germany) with 40 rpm at room temperature for optimal dispersion of fillers in the resin matrix.

The uncured resin composites were inserted into appropriate silicon rubber molds, covering the surface with a thinner glass slide, and polymerized using a LED light unit (Blue light, 430~490 nm, SLC-VIII B, Hangzhou Sifang Medical Apparatus Co., Ltd., Zhejiang, China) for 90 s on each side. The cured composite specimens were then stored in the dark for 2~3 days and then polished with silicon carbide abrasive paper (grit numbers of 800 #, 1500 # and 2000 #) before test.

2.3 Characterization

2.3.1 Characterization of Molecular Structures

Molecular structures of Bis-GMA, Bz-Bis-GMA and Vr-Bis-GMA were confirmed by ^1H NMR (Bruker Avance-400, Switzerland) and FT-IR (Nicolet NEXUS-670, USA) analyses. ^1H NMR was registered with chloroform-d (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal standard. Base resins were placed in a KBr vessel for FT-IR analysis.

2.3.2 Measurement of Rheological Properties

Viscosity measurements of organic matrixes without the initiating system were characterized with a rotational rheometer (TA ARES-RFS, USA). The measurements were carried out at 25 °C in the shear frequency ranging from 0.1 to 100 rad/s.

2.3.3 Measurement of Photopolymerization Kinetics

The polymerization characteristics of organic matrixes were investigated by the differential scanning calorimeter (DSC, TAQ-2000, USA) with a photocalorimetric accessory offering 380~480 nm light source, and 2.5 mW/cm² light intensity. All mixtures were purged with nitrogen for 10 min before irradiating as well as throughout the reaction to ensure oxygen did not inhibit the polymerization. The exothermic heat flux detected from the DSC was transformed into the rate of polymerization by comparing with the theoretical heat of reaction per methacrylate double bond (13.1 kcal/mol) (Lovell et al., 1999). The rate versus time data was then numerically integrated to give the reaction rate as a function of double-bond conversion.

2.3.4 Polymerization Shrinkage

Polymerization shrinkage of each resin composite was calculated according to Archimedes' principle (Rüttermann, Dluževskaya, Großsteinbeck, Raab, & Janda, 2010). The densities of uncured and cured resin materials were determined with the electronic balance (JA5003, Changzhou Keyuan Electronic Instrument Co., Ltd., Jiangsu, China). For each material, five specimens were carefully examined, and the curing time was set at 60 s on each side for obtaining the cured specimens. Every specimen was stuck on a light fiber and fixed on the

steelyard hook of the balance, so each sample was weighed in air and in deionized water and the density of each uncured and cured composite was calculated with the following equation:

$$\rho = \left(\frac{m_a}{m_a - m_w} \right) \times (\rho_w - \rho_a) + \rho_a \quad (1)$$

Where ρ = density of sample (g/cm^3), m_a = the mass of the sample in air (g), m_w = mass of sample in deionized water (g), ρ_w = density of the sample in deionized water at the exactly measured temperature in $^{\circ}\text{C}$ (g/cm^3), and ρ_a = air density ($0.0012 \text{ g}/\text{cm}^3$).

Finally, the polymerization shrinkage of each resin material was determined by the following formula (Sideridou, Karabela, & Vouvoudi, 2011):

$$\text{Polymerization shrinkage (\%)} = \left(\frac{\rho_{\text{cured}} - \rho_{\text{uncured}}}{\rho_{\text{cured}}} \right) \times 100 \quad (2)$$

Where ρ_{uncured} and ρ_{cured} is the density of the uncured and cured resin composite, respectively.

2.3.5 Mechanical Properties

Six rectangular-shaped specimens ($25 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$) and cylindrical specimens ($\Phi 4 \text{ mm} \times 6 \text{ mm}$) were made from each resin materials for flexural and compressive strength tests, respectively. According to the ISO-4049 specification, flexural strength of the cured resin composites was measured with the three-point bending test, using a universal testing machine (WDW-300, Changchun Kexin Equipment Co., Ltd., Changchun, China), with span of 20 mm, crosshead speed of 0.75 mm/min. Compressive strength was also evaluated with this universal testing machine at a cross-head speed of 0.75 mm/min.

3. Results and Discussion

This present work was designed to ascertain how the conversion of hydroxyl groups in Bis-GMA to its derivatives without hydroxyl groups but with bulky acyl group substituents of different size would affect critical properties of new monomers, including viscosity and vinyl conversion, as well as polymerization shrinkage and mechanical properties of corresponding resin composites. From this work, it was clear that both the nature of hydrogen bonding and the size of acyl substituents are considered to be important parameters to design the monomer or monomer systems with optimum properties (Khatri et al., 2003).

3.1 Characterization of Bz-Bis-GMA and Vr-Bis-GMA

The molecular structure of Bz-Bis-GMA and Vr-Bis-GMA was fully confirmed by ^1H NMR and FT-IR. Figure 2 indicated ^1H NMR results of Bis-GMA, Bz-Bis-GMA and Vr-Bis-GMA, respectively. The spectrum of Bz-Bis-GMA and Vr-Bis-GMA was exactly the same with that of Bis-GMA, except the peaks at 7.28, 7.46, and 8.05 ppm, due to the aromatic protons from benzoyl groups (Hawker, 1994), and the peaks at 0.89, 1.32, 1.62, and 2.33 ppm, representing the protons from valeryl groups (Li, Lin, & Rustum, 2008). The peak representing the proton in hydroxyl groups in Bis-GMA (2.2 ppm) was not observed in the spectra of its derivatives. Besides, the peaks at 4.06, 4.29, and 4.38 ppm arising from protons adjacent to hydroxyl groups in Bis-GMA were shifted upfield in Bz-Bis-GMA and Vr-Bis-GMA, due to the electrophilic effect of benzoyl and valeryl groups, respectively (Podgórski, 2011). Figure 3 exhibits FT-IR spectra of Bis-GMA and its derivatives. The broad absorption peak of about 3500 cm^{-1} representing hydroxyl groups in Bis-GMA was completely disappeared in its derivatives, indicating the complete replacement of hydroxyl groups. Both results of ^1H NMR and FT-IR suggested that hydroxyl groups in Bis-GMA were replaced with benzoyl and valeryl groups, respectively.

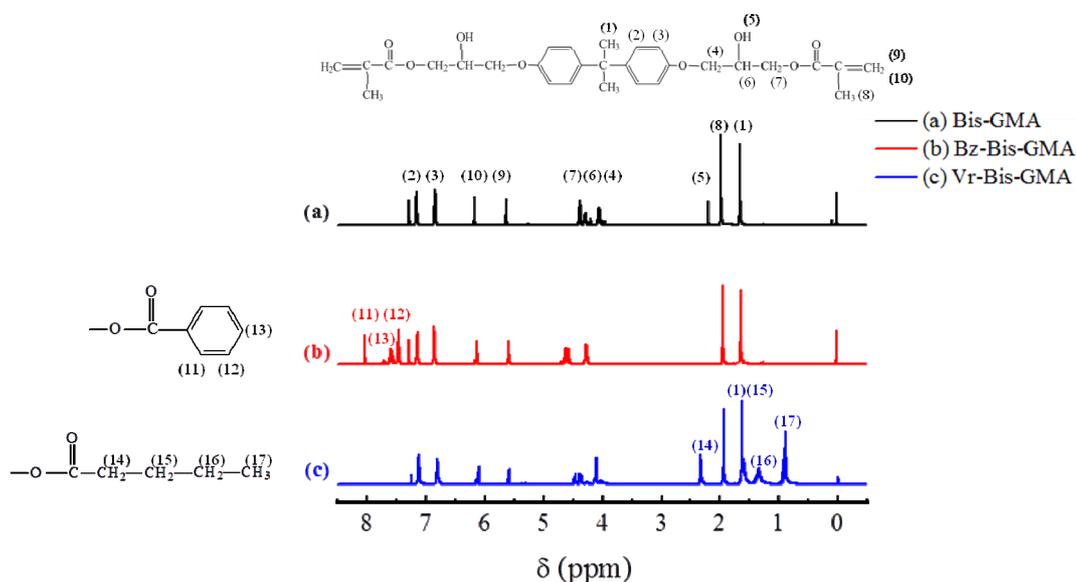


Figure 2. ^1H NMR spectra of Bis-GMA (a), Bz-Bis-GMA (b), and Vr-Bis-GMA (c)

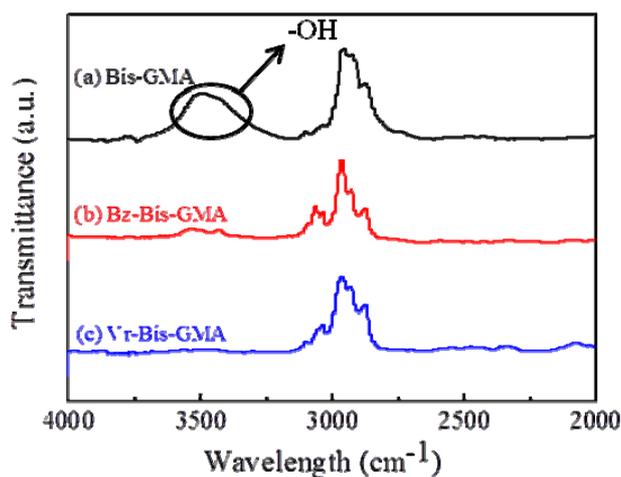


Figure 3. FT-IR spectra of Bis-GMA (a), Bz-Bis-GMA (b), and Vr-Bis-GMA (c)

3.2 Viscosities of Bis-GMA and Its Mixtures with TEGDMA

Viscosities of Bis-GMA, Bz-Bis-GMA, Vr-Bis-GMA and their mixtures with TEGDMA as a function of shear frequency was depicted in Figure 4. A monomer mixture of Bis-GMA/TEGDMA=50/50 (wt/wt) was selected as a control group, due to the commonly utilized formulation for organic matrix (Khatri et al., 2003). In Figure 4(a), the viscosities of acyl modified Bis-GMA derivatives were significantly lower than those of Bis-GMA (820 Pa.s), which could be attributed to the presence of alkyl pendant substituents from the side chains and the weaker intermolecular hydrogen bonding of acyl groups in comparison of the stronger hydrogen bonding interactions of the hydroxyl groups of Bis-GMA (Khatri et al., 2003). Vr-Bis-GMA with increasing length of substituent than acetyl groups and reducing intermolecular hydrogen bonding (Podgórski et al., 2010; Wang et al., 2013) hence exhibited the lowest viscosity of 1.6 Pa.s.

With the increasing supplement of TEGDMA from 0 to 50 wt%, as displayed in Figure 4(b) and (c), viscosities of corresponding resin mixtures decreased gradually. Besides, comparing with the control group, the amounts of diluent could be minimized to 20 wt% and 30 wt% by using Bz-Bis-GMA and Vr-Bis-GMA instead of Bis-GMA, indicating adverse effects caused by TEGDMA on properties of resin composites such as water uptake and polymerization shrinkage could be further minimized. For Ac-Bis-GMA, the essential amount of TEGDMA increased to 40 wt%, attributed to its relative high viscosity (Wang et al., 2013).

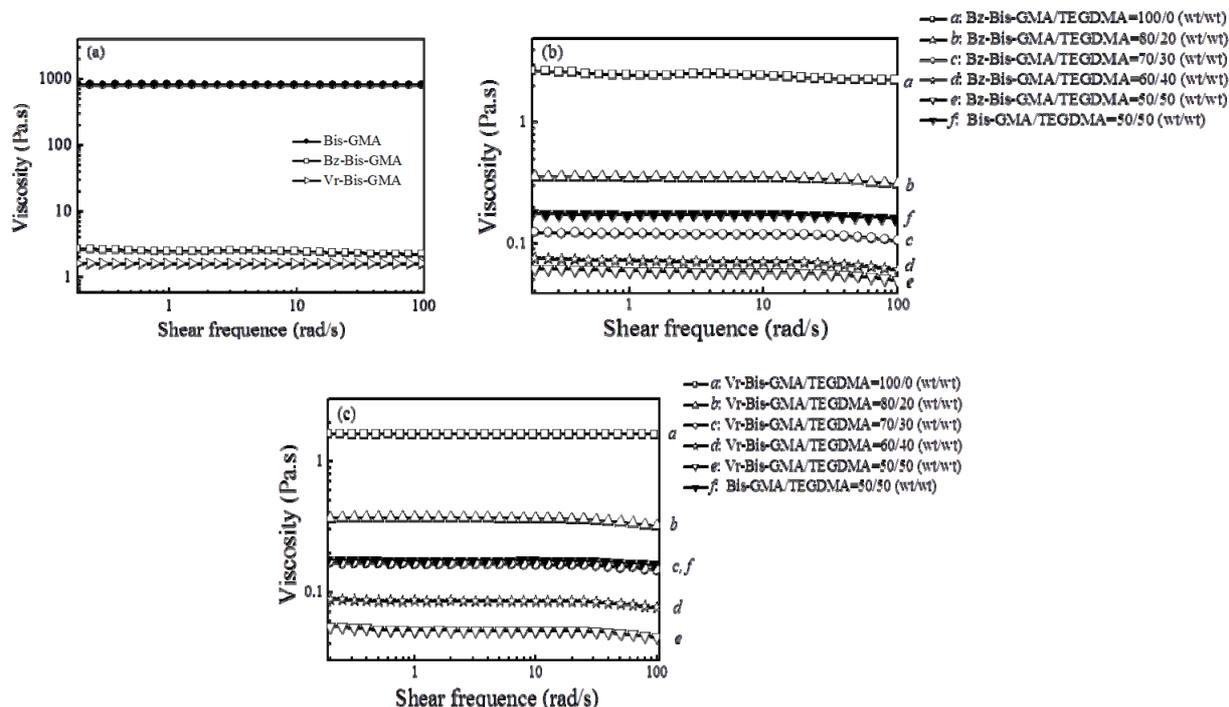


Figure 4. Measured viscosities of Bis-GMA, Bz-Bis-GMA, and Vr-Bis-GMA (a), Bz-Bis-GMA and its mixture with TEGDMA (b), and Vr-Bis-GMA and its mixture with TEGDMA (c) as a function of shear frequency, respectively

3.3 Copolymerization Characteristics of Monomer Mixtures

Conversion of double bonds in the multifunctional methacrylates ranges from 55% to 75%, which is rarely complete due to immobilization, gelation, vitrification or steric isolation (Podgórski et al., 2010). Figure 5(a) illustrates the characteristic behaviour of Bis-GMA and its two derivatives with 50 wt% TEGDMA. All mixtures exhibited the typical auto-acceleration effect in the early stages for the movements of molecular chain and net are limited. As the polymerization progresses, the cross-linking degree and viscosity of the resin matrix system increase continuously. At the later stage, the mobility of the radicals is decreased due to the high viscosity, and finally the reaction rate tapers off to zero (Lovell et al., 1999). When these three kinds of organic matrices are copolymerized with an equal weight diluent TEGDMA, respectively, the maximum reaction rate occurring at 9% conversion was achieved by the Bz-Bis-GMA group, which could be attributed to the strongest electrophilic effect of benzoyl groups in Bz-Bis-GMA. Besides, combining with our previous finding (Wang et al., 2013), conversion values of Ac-Bis-GMA and Vr-Bis-GMA systems were higher compared with Bis-GMA system. This could be attributed to the relatively weaker hydrogen bonding of acyl groups in these two Bis-GMA derivatives, which is in accordance with their lower viscosities, compared to the stronger hydrogen bonding of the hydroxyl groups of Bis-GMA (Khatri et al., 2003). Furthermore, for novel Bis-GMA derivatives in this work, the decreased viscosity in the Vr-Bis-GMA system allows for higher conversion of 85%, whereas the increased steric hindrance of benzoyl group in Bz-Bis-GMA leads to the lowest value of 62%, compared to that of 75% for the Bis-GMA control group.

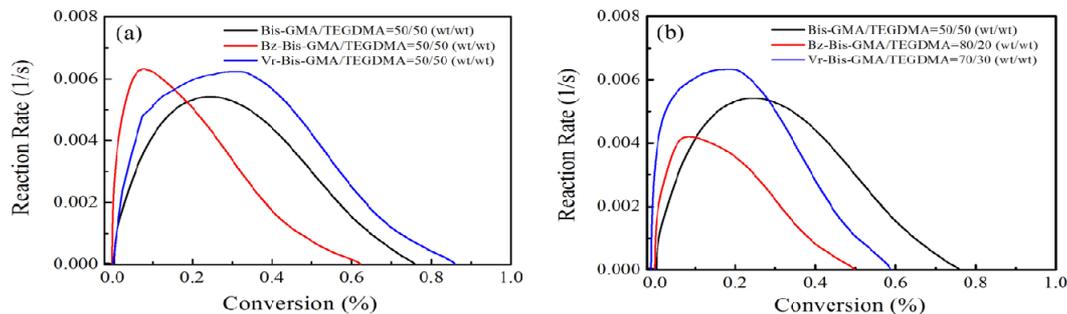


Figure 5. Copolymerization of monomers and their mixtures with TEGDMA

It has been proved that lower viscosities and weaker hydroxyl bonding of monomer mixtures increase the mobility of the monomer system, thereby allowing the material to reach a much higher double-bond conversion (Lovell et al., 1999). Therefore, in order to explore the effect of molecular structure and substitute size of new monomers on degree of vinyl conversion individually, copolymerization behaviours of monomer mixtures with nearly the same viscosity were also investigated, shown in Figure 5(b). According to our previous work, the Ac-Bis-GMA system (Ac-Bis-GMA/TEGDMA= 60/40, wt/wt) with increased mobility of monomer molecules and weaker intermolecular interactions possessed the highest conversion of 82%, compared to Bis-GMA system with stronger hydrogen bonding. Besides, flexibility of monomer molecules were inhibited with increasing the size and the steric hindrance of substituent, especially for benzoyl group in Bz-Bis-GMA, resulting in the lowest conversion of 49% for the Bz-Bis-GMA mixture, compared to that of 58% for the Vr-Bis-GMA mixture. These results suggested that viscosities of monomer mixtures (i.e. the condition of reaction environment) and molecular structure of monomers are essential for vinyl conversion, and therefore affect the properties of resin composites (Podgórski et al., 2010).

3.4 Polymerization Shrinkage of Dental Resin Materials

All dental resins analyzed in this study were consisted of the same composition and filler loading of co-fillers (Micro- and nano-size silica with optimum ratio of 58:12) (Wang et al., 2013). Based on this, all findings about polymerization shrinkage were discussed only taking into account the influence of the monomer systems. It has been reported that the polymerization shrinkage decreases when the molecular volume of monomer is increased (Podgórski et al., 2010; Matsukawa, Hayakawa, & Nemoto, 1994). Accordingly, the polymerization shrinkage of new Bis-GMA monomer based resin composites with the same amount of TEGDMA (50 wt%) was decreased with the increasing molecular weight, shown in Figure 6(a), compared with that prepared from the Bis-GMA/TEGDMA=50/50 (wt/wt) mixture, which displayed the highest shrinkage of 3.0%. Among all Bis-GMA derivatives based materials shown in Figure 6(a), considering the influence of chemical structure on polymerization shrinkage of resin materials, the presence of benzoyl group could be a reason for the increased molecular volume of Bz-Bis-GMA, and thus resulted in the lowest polymerization shrinkage of 2.3% of corresponding composites. Meanwhile, the value of composite prepared from Vr-Bis-GMA with relatively high molecular weight showed a slightly decreased value of 2.7%, compared with that of Ac-Bis-GMA (2.8%).

Furthermore, the effect of the amount of dilute TEGDMA on polymerization shrinkage of resin composites was also assessed in Figure 6(b). It could be observed that all Bis-GMA derivatives based composites presented reduced shrinkage values compared with that of the Bis-GMA based composites, attributed to the reduced content of TEGDMA. The abrupt decrease in the shrinkage of the composite, which was as low as 2.1%, prepared from the Vr-Bis-GMA/TEGDMA=80/20 (wt/wt) polymeric mixture was remarkable, which is in accordance with the finding that the shrinkage of resin materials was reduced with decreasing the amount of dilute in resin matrix (L. Kim, J. Kim, & C. Kim, 2006). Besides, for the other Bis-GMA alternatives based composites, the shrinkage values were 2.8% and 2.5% for Ac-Bis-GMA and Vr-Bis-GMA group, respectively, which were higher than that of Bz-Bis-GMA group, due to the increasing essential amount of TEGDMA. Therefore, the polymerization shrinkage could be regulated by the structure of organic monomer and the amount of diluent. In comparison with the previously reported work, the shrinkage of composites could be reduced even below 1% (L. Kim, J. Kim, & C. Kim, 2006), which was significantly lower than that of 2.1% in this present work, which could be attributed to the new structure of the Bis-GMA alternative 2,2-bis [3,5-dimethyl, 4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (TMBis-GMA) and the diluent 4-tert-butylphenoxy-2-methoxypropyl (t-BP-M-GMA).

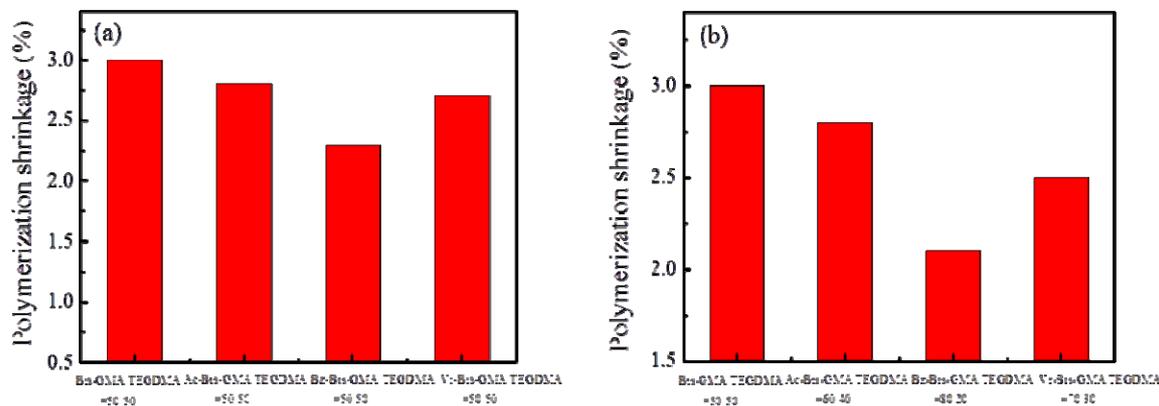


Figure 6. Polymerization shrinkage of Bis-GMA and its derivatives with different amount of TEGDMA

3.5 Mechanical Properties of Resin Composites

An important consideration in the formulation of durable dental resin composites is not only low polymerization but also adequate mechanical properties to bear forces in oral cavity. Compressive strength and the flexural strength of the conventional resin composites filled with hybrid fillers are in the range of 150 to 250 MPa, and 70 to 130 MP (Samuel, Li, & Mukherjee, 2009; Wang et al., 2011), respectively. In this present work, mechanical properties of resin composites remained at a relatively high level, and results are displayed in Figure 7. It could be easily observed that all modified Bis-GMA based resin composites exhibited lower flexural and compressive strengths compared with those of the Bis-GMA based composites, attributed to the absence of strong intermolecular hydrogen bonding caused by hydrogen groups in Bis-GMA.

In order to further investigate the effect of chemical structure of Bis-GMA and its derivatives, and the amount of TEGDMA on mechanical performance of corresponding resin composites, all resin matrices were enhanced with 70 wt% silica co-fillers in this present work. As shown in Figure 7(a, c), the amount of TEGDMA was fixed at 50 wt% of every resin matrix, and Bz-Bis-GMA group showed the lowest compressive strength of 223.7 MPa and flexural strength of 109.7 MPa, due to the lowest vinyl conversion of its resin matrix (62%), compared with the other two Bis-GMA derivatives matrix. Meanwhile, the highest mechanical values were obtained by Ac-Bis-GMA group among all Bis-GMA derivatives, possessing flexural strength and compressive strength of 252.8 MPa and 125.2 MPa, respectively, resulted from the higher conversion of its resin matrix (88%), which were still slightly lower than those of Bis-GMA control group (264.1 MPa and 125.6 MPa, respectively), due to the existence of hydrogen groups.

Additionally, mechanical performance of resin composites could be decreased with the reduced viscosities of monomer systems reflected by the reduced amount of dilute TEGDMA, as is shown in Figure 7(b, d), which displays mechanical properties of resin composites with the synthesized Bis-GMA derivatives at the least amount of diluent, compared with that of Bis-GMA control group. It could be easily observed that the lowest compressive strength (212.4 MPa) and flexural strength (93.3 MPa) were obtained by Bz-Bis-GMA/TEGDMA (80/20, wt/wt) based resin materials, which could be due to the minimum content of TEGDMA and therefore its lowest vinyl conversion of its resin matrix (49%). As is expected, for Ac-Bis-GMA group, compressive strength and flexural strength were increased to 237.2 MPa and 123.8 MPa, respectively, with the content of TEGDMA increased to 40 wt% of its resin matrix. Besides, mechanical performance of the Vr-Bis-GMA group was between the other two Bis-GMA derivatives based materials.

However, it was encouraging that although excellent mechanical properties of resin composites could be achieved by introducing Bis-GMA into the resin matrix through the intermolecular hydrogen bonding from its -OH groups, all experimental resin composites using Bis-GMA derivatives and TEGDMA as organic matrices still presented acceptable flexural and compressive strengths for clinical application potentially.

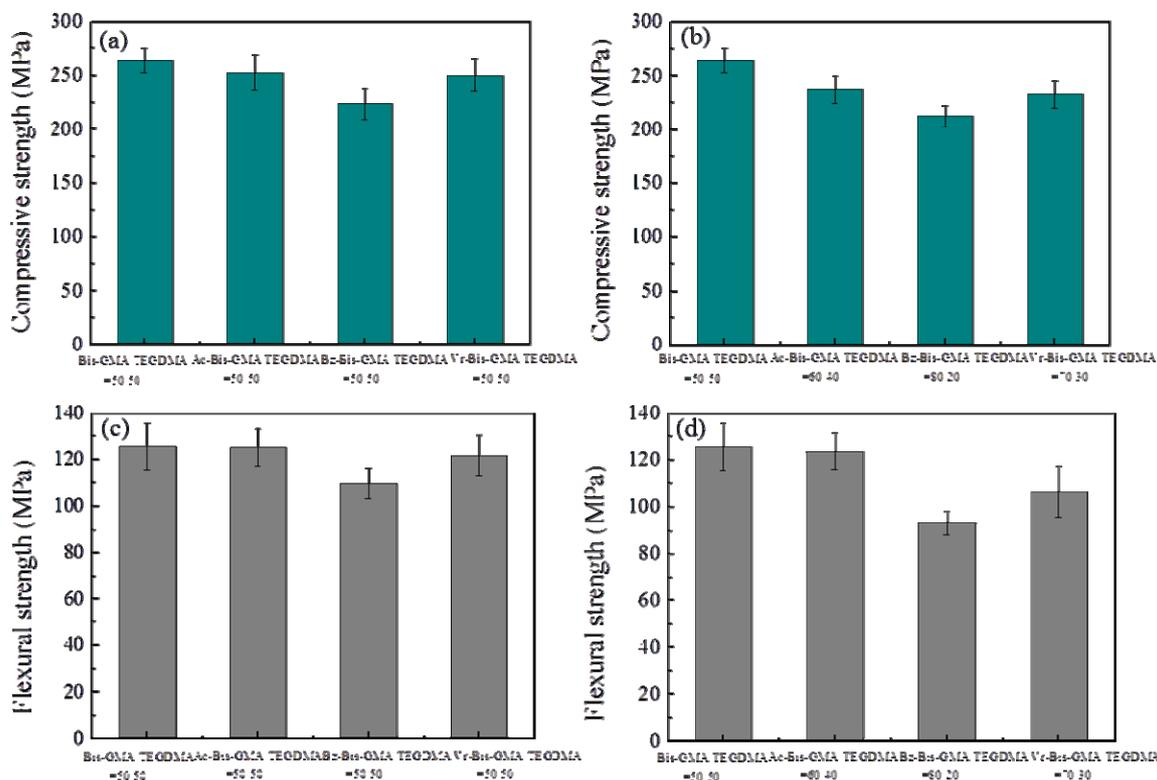


Figure 7. Compressive strength (a, b) and flexural strength (c, d) of Bis-GMA and its derivatives based dental resin composites with different amount of TEGDMA

In summary, acyl substitution of Bis-GMA derivatives with optimum amount of dilute TEGDMA could be a promising strategy for obtaining dental composites possessing improved properties. The results explored here indicate that a dental resin composite with reduced polymerization shrinkage along with adequate mechanical properties could be obtained by introducing the mixture of Bz-Bis-GMA/TEGDMA = 80/20 (wt/wt) as a resin matrix.

4. Conclusions

To minimize diluent TEGDMA amount in the resin matrix, Bz-Bis-GMA and Vr-Bis-GMA were successfully synthesized by substituting different acyl groups for hydroxyl groups in Bis-GMA. The molecular structure of Bis-GMA derivatives were confirmed by ^1H NMR and FT-IR. The viscosity of Bis-GMA was dramatically reduced from 820 Pa.s to 2.7 Pa.s and 1.6 Pa.s by substituting benzoyl groups and valeryl groups for hydroxyl groups, respectively. Consequently, the amount of TEGDMA in the comparison resin matrix (Bis-GMA/TEGDMA=50/50, wt/wt) can be decreased from 50 wt% to 20 wt% by replacing base resin from Bis-GMA to Bz-Bis-GMA, compared to that of 30 wt% TEGDMA in the Vr-Bis-GMA resin matrix, due to the weakest intermolecular interactions in Bz-Bis-GMA. Comparing the polymerization shrinkage of resin composite containing Bz-Bis-GMA/TEGDMA=80/20 (wt/wt) with that prepared from Bis-GMA/TEGDMA=50/50 (wt/wt) as the resin matrix, the reduction in shrinkage was about 26%, attributed to reduced amount of dilute TEGDMA. Furthermore, Bz-Bis-GMA based resin composites exhibited adequate mechanical performance, with flexural strength of 93.3 MPa and compressive strength of 212.4 MPa. In summary, physical-mechanical properties of resin composites are influenced by the size of substituent groups in Bis-GMA derivatives, indicating that the monomer with bulky superhydrophobic substituent groups is beneficial to reduce the amount of dilute such as TEGDMA, therefore leading to reduced polymerization shrinkage which is desirable in application. Thus, further work should be targeted for the clinical performance of this novel resin based composite.

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