

Synthesis and Characterization of a Chemico-structurally Modified *Bis*-GMA Analog for Dental Applications

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Received on: 30 April 2024; Accepted on: 31 May 2024; Published on: 23 September 2024

ABSTRACT

Aim: This study aimed to synthesize and characterize a novel *Bis*-GMA analog, termed *P-Bis*-GMA, through structural modification by replacing hydroxyl (–OH) groups with phosphonooxy [–O–P(=O)(OH)₂] groups and to evaluate and compare its viscosity with *Bis*-GMA.

Materials and methods: *Bis*-GMA, triethylamine, dichloromethane, and phosphoryl chloride were utilized for the synthesis of *P-Bis*-GMA through phosphorylation. Fourier discerned the chemical structure of the synthesized *P-Bis*-GMA transform infrared spectroscopy (FTIR), and its viscosity was assessed by rheometry in oscillatory shear mode over a frequency sweep range of 0.1–100 (ω , rad/s) at 25°C with a 25 mm parallel plate design and a 0.5 mm gap. The data was recorded and statistically analyzed.

Results: The FTIR analysis confirmed the successful synthesis of *P-Bis*-GMA, evidenced by the disappearance of hydroxyl (–OH) peaks and the emergence of phosphonooxy [–O–P(=O)(OH)₂] peaks in the *P-Bis*-GMA. Rheological testing demonstrated a notable reduction in viscosity for *P-Bis*-GMA (436.62 Pa.s) when compared to conventional *Bis*-GMA (1089.02 Pa.s), indicating improved handling characteristics.

Conclusion: *P-Bis*-GMA was successfully synthesized by phosphorylation reaction where the –OH groups responsible for the high viscosity in the *Bis*-GMA were replaced with the [–O–P(=O)(OH)₂] groups with significantly reduced viscosity.

Clinical significance: The development of *P-Bis*-GMA holds promise for simplifying dental procedures by reducing chairside time with uncooperative children. The *P-Bis*-GMA-based composites possess self-adhering properties thereby eschewing the etching and bonding procedures with reduced moisture contamination of the restoration during bonding. This ultimately leads to better clinical outcomes and improved patient experiences by reducing technical vulnerabilities.

Keywords: *Bis*-GMA, Composite resin, Phosphorylation, Self-adhering composite, Viscosity.

The Journal of Contemporary Dental Practice (2024): 10.5005/jp-journals-10024-3687

INTRODUCTION

Dental restorative resin (DRRs) composites have been extensively used in restorative treatments due to their excellent aesthetics when compared with conventional amalgam alloy restorations. Dental restorative resin composites mainly consist of organic matrix and inorganic fillers.¹ In children, there is a high technical defiance for dentists concerning restoration since the child's behavior often hampers dental restorative care. Therefore, clinicians must use restorative material with which they are most familiar to avoid prolonging clinical time, where isolation or a child's cooperation is in jeopardy, thereby contributing to a successful restoration.² Pediatric restorative dentistry is a dynamic area with rapid development of technology and new materials.² Among the materials used in pediatric dental restorations, self-adhering flowable composite resin systems have been proposed to reduce the technical vulnerabilities, chair-side time consumption, and postoperative sensitivity of the contemporary etch-and-rinse adhesive systems.³

However, flowable composites when compared with conventional hybrid composites, exhibit a lower modulus of elasticity and higher polymerization shrinkage due to their reduced filler content.⁴ Traditional flowable composite resins require a separate bonding system. On the contrary, the self-adhering flowable composite resin eliminates the need for a separate adhesive application. This outlines a functional treatment approach for children in practical working conditions. Nevertheless, for the

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How to cite this article: Ajay R, Selvabalaji A, Muthamilselvi M, et al. Synthesis and Characterization of a Chemico-structurally Modified *Bis*-GMA Analog for Dental Applications. *J Contemp Dent Pract* 2024;25(6):588–592.

Source of support: Nil

Conflict of interest: None

restoration of cavities in high load-bearing areas, the use of flowable composites is recommended only for cavity lining.⁵

In terms of organic matrix composition, *Bis*-GMA is commonly utilized as the main monomer of the dimethacrylate-based matrix for excellent mechanical performance.¹ Still the main drawback of the *Bis*-GMA monomer is related to its high viscosity attributed to the intermolecular hydrogen bonding between the hydroxyl groups present in the monomer structure.⁶ The hydroxyl groups of the *Bis*-GMA increase its high water sorption capacity.⁷ The high viscosity renders the *Bis*-GMA a poor candidate even for filler distribution raising handling issues and is accountable for the lesser degree of conversion of the monomer.⁸ This mandates the addition of a diluent comonomer like tri(ethylene glycol) dimethacrylate (TEGDMA). However, some adverse effects such as increased water sorption and shrinkage will be accompanied by the incorporation of a large amount of diluents.¹ Therefore, there is a need to develop a DRR with self-adhering capacity with less diluent and ample fillers without compromising its inherent physico-mechanical properties with enhanced clinical serviceability in children, where preservation of deciduous teeth is of paramount importance.

To overcome the shortcomings of the *Bis*-GMA, the researchers have made several substantial efforts to develop *Bis*-GMA analogs with low viscosity and high hydrophobicity. By replacing the hydroxyl groups in *Bis*-GMA, various analogs of *Bis*-GMA were synthesized with dramatically reduced viscosity.^{1,9-11} Hence, this instigated the idea of developing a novel *Bis*-GMA analogue with etching efficiency rendering the DRR self-adhering eschewing separate etch-rinse and bonding steps and thereby reducing the chairside time. Therefore, the present research aimed to synthesize and characterize a novel *Bis*-GMA analog with an acidic moiety via structural modification where the hydroxyl group would be replaced with phosphonoxy group (*P-Bis*-GMA). The null hypothesis was that the substitution of the *Bis*-GMA's hydroxyl groups with phosphonoxy moieties would not have any effect on its viscosity.

MATERIALS AND METHODS

The present *in-vitro* laboratory research was conducted for 7 months. *Bis*-phenol-A-glycerolate dimethacrylate (*Bis*-GMA), triethylamine, dichloromethane, and phosphoryl chloride were purchased (Sigma Aldrich Co., St Louis, MO, USA) and were used as received. The novel *P-Bis*-GMA was synthesized in the Department of Biomaterials (Green lab), Saveetha Dental College, Saveetha University.

Synthesis and Characterization

The novel *P-Bis*-GMA was synthesized by phosphorylation reaction. 15 mM of 2,2-*Bis*-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane (*Bis*-GMA) and 60 mM triethylamine were added to 30 mL of dichloromethane. 60 mM of phosphoryl chloride (POCl₃) was added to the mixture and stirred at 300 rpm at -15°C for 15 min. The solution is then maintained at 20°C for 2 h. 20 mL of deionized water was added to stop the reaction and kept overnight at 300 rpm. A rotary vacuum evaporator was used to concentrate the solution. The solution was recrystallized using ethyl acetate. The final reaction product 2,2-*bis*-(4-(2-phosphonoxy-3-methacryloyloxypropoxy)phenyl)propane (*P-Bis*-GMA) was stored at 4°C until further use. The synthesized *P-Bis*-GMA was characterized through the Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflection (ATR) mode (Tensor 27 model; Bruker Optik, GmbH,

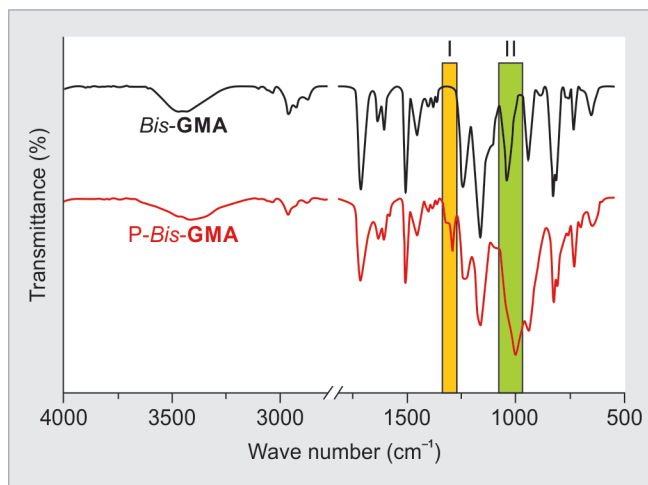


Fig. 1: Spectral differences in zones I and II of the *Bis*-GMA (black) *P-Bis*-GMA (red)

Germany). All the spectra were obtained from 64 scans and normalized at 4/cm spectral resolution.

Viscosity

The novel monomer *P-Bis*-GMA's and *Bis*-GMA's rheological properties were measured using a rheometer (Model: Bohlin Gemini II).¹² The experimental test was performed at the oscillatory shear mode over a frequency sweep range of 0.1–100 (ω , rad/s) at 25°C. The geometry used in this test was a 25 mm parallel plate design with a 0.5 mm gap as followed by Al-Odayni et al.¹³ Each sample was only measured in the appropriate linear viscosity values due to the wide variability in the viscosity values of the materials under research and the constraints of the used rheometer torque. Therefore, five replicate measurements ($n = 5$) were made per sample.

The data analysis was performed employing the Statistical Package for the Social Sciences software (SPSS Inc., Chicago, IL, USA; version 29.0). The obtained values were subjected to the Kolmogorov-Smirnov and the Shapiro-Wilk normality tests and found to be normally distributed ($p > 0.05$) and thus were presented as mean and SD. The paired *t*-test ($\alpha = 0.05$) was used to analyze the differences between the groups.

RESULTS

Fourier transform infrared confirmed the chemical structure of synthesized *P-Bis*-GMA. The phosphorylation took place at the hydroxyl groups which were replaced by phosphonoxy [$-\text{O}-\text{P}(=\text{O})(\text{OH})_2$] moieties. In the IR spectra of *Bis*-GMA, the broad band at 3467 cm^{-1} is attributed to the hydroxyl ($-\text{OH}$) groups. Moreover, the appearance of the $-\text{OH}$ band in the spectrum of *P-Bis*-GMA is due to the $\text{P}-(\text{OH})_2$ residues. Similarly in Zone I, the appearance of a new peak at 1295 cm^{-1} is owing to $\text{P}=\text{O}$ vibration in the *P-Bis*-GMA, which is absent in *Bis*-GMA. In zone II, the $\text{C}-\text{O}$ stretching ascribing secondary alcohol ($>\text{CH}-\text{OH}$) at 1040 cm^{-1} in the *Bis*-GMA was absent in *P-Bis*-GMA. This confirmed the completion of phosphorylation with the replacement of $-\text{H}$ in the $-\text{OH}$ by $-\text{O}-\text{P}(=\text{O})(\text{OH})_2$ moieties. Nevertheless, a new peak attributing $\text{P}-\text{O}$ stretching in $\text{P}-(\text{OH})_2$ and $\text{P}-\text{O}-\text{C}$ vibration at 1005 cm^{-1} in the *P-Bis*-GMA is absent in *Bis*-GMA. These three spectral differences in zones I and II confirm the synthesis of the *P-Bis*-GMA (Fig. 1). Table 1 tabulates the differences

Table 1: FTIR characterization of the functional groups

Functional groups	Group [Wave numbers (cm ⁻¹)]		Zone of differences
	Bis-GMA	P-Bis-GMA	
O–H stretching	3467.17	3410.32	
C–H stretching (–CH ₂ –)	2963.86–2874.06	2965.15–2874.06	
C=O stretching	1714.07	1715.90	
C=C aliphatic stretching	1635.91	1634.84	
C=C aromatic stretching (Bis-GMA)	1607.38	1607.46	
C–C stretching	1508.47	1508.57	
C–H bending (–CH ₃)	1454.83	1454.41	
C–H bending [gem 2(–CH ₃)]	1404.05–1382.18	1403.93–1381.44	
P=O vibration	Absent	1295.01	I
C–O–C stretching (alkyl-aryl etheral linkage)	1244.93	1242.92	
C–O–C stretching (aliphatic etheral linkage)	1160.95	1164.48	
C–O stretching of secondary alcohol (>CH–OH)	1040.90	Absent	II
P–O stretching in P–(OH) ₂ and P–O–C vibration	Absent	1005.36	
<i>trans</i> -C=C bending, di-substituted alkene	942.64–827.50	943.68–828.02	
<i>cis</i> -C=C bending, di-substituted alkene	735.73	734.69	
Ring C–H wagging	651.34	643.66	

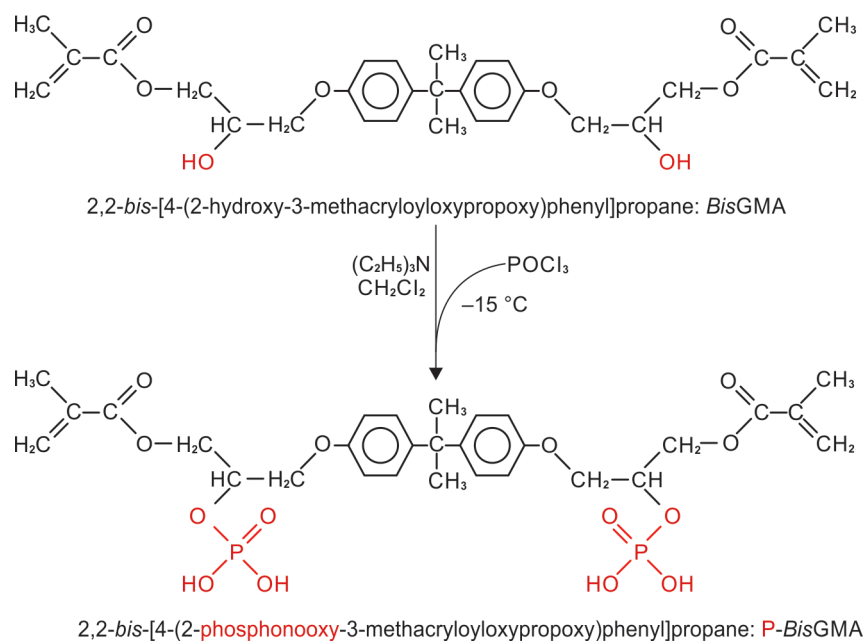

Fig. 2: Synthetic route of the P-Bis-GMA

Table 2: Paired *t*-test concerning the viscosity of the groups

Group	Mean (\pm SD) (Pa.s)	<i>t</i> -value	<i>p</i> -value
Bis-GMA	1089.02 (\pm 5.44)	175.697	<0.001
P-Bis-GMA	436.62 (\pm 5.11)		

in functional groups or moieties between Bis-GMA and P-Bis-GMA. Figure 2 depicts the schema of the P-Bis-GMA synthesis. Concerning the viscosity, the mean (\pm SD) viscosity of the Bis-GMA was 1089.02 (\pm 5.44) Pa.s and the P-Bis-GMA was 436.62 (\pm 5.11) Pa.s. There was a statistically significant difference in the viscosity between the

groups ($p < 0.001$; Table 2) where replacing the –OH groups of the Bis-GMA with the –O–P(=O)(OH)₂ moieties decreased the viscosity of the newly synthesized P-Bis-GMA.

DISCUSSION

In addressing the inherent limitations of Bis-GMA, the present research embarks upon a pioneering approach through the synthesis of a chemically modified Bis-GMA analog. Specifically, the –OH groups of Bis-GMA have been targeted by substituting them with phosphonoxy [–O–P(=O)(OH)₂] moieties. This innovative

modification represents a significant departure from conventional strategies and offers promising prospects for enhancing the performance of Bis-GMA-based materials as better restorative materials in terms of physico-mechanical properties. Through meticulous synthetic protocols and characterization, the current research aims to elucidate the potential of P-Bis-GMA in mitigating the challenges associated with conventional Bis-GMA while preserving its advantageous properties like high refractive index, low volatility, less diffusivity into tissues, formation of polymers with higher moduli and less volume shrinkage.¹⁴

In the present research, the chemical structure of the synthesized P-Bis-GMA was confirmed by FTIR. The disappearance of the broad peak at 3467 cm^{-1} in P-Bis-GMA is attributed to the replacement of -OH groups of Bis-GMA with $-\text{O}-\text{P}(=\text{O})(\text{OH})_2$ moiety. Moreover, the disappearance of the peak attributed to C-O stretching of secondary alcohol ($>\text{CH}-\text{OH}$) in P-Bis-GMA also ascribed to the replacement of -OH groups. This replacement of -OH groups resulted in the low viscosity of the P-Bis-GMA. Therefore, the amount of TEGDMA diluent could be decreased in the resin formulation due to its adverse effects such as increased water sorption as demonstrated by Kalachandra and Turner¹⁵ and high polymerization shrinkage as mentioned by Pałka et al.¹⁶ Pereira et al.⁹ replaced -OH groups with methyl groups that showed very low viscosity and utilized as diluent in place of TEGDMA. Khatri et al.¹⁷ replaced the -OH groups of the Bis-GMA with various chain lengths of the alkyl urethane substituents and found decreased viscosities for all the derivatives with low flexural strength with increasing chain length of the alkyl urethane substituent. Kim et al.¹ synthesized methoxylated-Bis-GMA replacing the -OH groups of the Bis-GMA with methoxy moiety that was confirmed by the disappearance of the -OH peak in the FTIR spectrum and found a drastic decrease in the viscosity when compared to Bis-GMA. Alrahalah et al.¹² altered the Bis-GMA by attaching a chlorine atom at the -OH site and found the viscosity of the modified monomer was 65 times lower than the Bis-GMA. Al-Odayni et al.¹³ modified Bis-GMA by attaching chlorine atoms at both the -OH sites and the viscosity of the dichloro-Bis-GMA drastically decreased. Song et al.¹⁸ synthesized a silyl-Bis-GMA by replacing the -OH group with silyl functionality and found decreased viscosity. Srivastava et al.¹⁹ synthesized fluorinated-Bis-GMA which exhibited low viscosity depicted the absence of the -OH peak in the IR spectrum that suggested the replacement of the former with a fluorinated molecule. Wang et al.¹¹ found that 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 and valeryl groups for -OH groups, respectively. Hence, from the above context, the P-Bis-GMA possessed low viscosity due to the completion of phosphorylation with the replacement of -H in the -OH by $-\text{O}-\text{P}(=\text{O})(\text{OH})_2$ moieties.

Advantages of lower viscosity self-etch adhesive monomers, such as the synthesized P-Bis-GMA, include ease of manipulation with ready flow into intricate cavities and voids, ensuring better adaptation to tooth surfaces, improved marginal integrity, less prone to trapping air bubbles during application, reducing the likelihood of void formation within the restoration. This helps in achieving a more homogeneous and durable restoration with reduced chairside time and improved patient comfort during dental procedures, especially in the anxious pediatric population.²⁰

Conventional self-etching monomers are strongly acidic (pH: 1.5–2.5) and contain mono- or di-hydrogenphosphate (10-methacryloyloxydecyl dihydrogenphosphate [10-MDP]), carboxylic (4-methacryloyloxyethyl trimellitic acid [4-META]), and phosphonic acid groups. They remove the smear layer, demineralize

the dental hard tissues, and percolate into the dentinal collagen layer to form a hybrid layer improving composite resin bonding.^{21–24} However, the addition of these acidic self-etching monomers in the Bis-GMA:TEGDMA composite matrix mixture resulted in compromised mechanical properties.^{25–28} This drop in mechanical properties could be partly attributed to the structure of the incorporated acidic monomers. Indeed, most of these monomers are aliphatic carboxylic acids and are not structurally analogous with the aromatic methacrylates commonly added in dental composites.²⁹ To address this problem, Mou et al.³⁰ suggested that the use of aromatic acidic monomers, structurally similar to the methacrylates incorporated in dental composites, should lead to materials exhibiting greater mechanical properties. Therefore, they prepared a new crosslinking methacrylate, similar to Bis-GMA, bearing two phosphonic acid groups on the aromatic rings. Although the monomer preparation was reported, its polymerization behavior was barely described.³¹ Moreover, this monomer exhibited a lower reactivity in free radical polymerization than Bis-GMA.³¹ This was attributed to a deactivation effect of the phosphonic acid groups.

Therefore, in the present research, the Bis-GMA was structurally altered at the -OH positions with the $-\text{O}-\text{P}(=\text{O})(\text{OH})_2$ moieties attached to oxygen atoms which is different from the phosphonic groups directly attached to the carbon atoms of the Bis-GMA's aromatic ring. In P-Bis-GMA, appearances of the new distinct peaks ascribing P=O vibration at 1295 cm^{-1} and P-O vibrations [P-(OH)₂ and P-O-C] at 1005 cm^{-1} determines the phosphorylation with the replacement of -H in the -OH group. The wavenumbers of the above peaks in the present research are corroborated with studies conducted by Thomas and Chittenden.^{32,33} Similarly, Catel et al.³⁴ observed conspicuous peaks attributing P=O vibration at 1220 cm^{-1} and P-O stretching at 980 cm^{-1} when phosphonic acid moiety was attached to aromatic methacrylates other than Bis-GMA. Sahin et al.³⁵ synthesized acidic monomers with both phosphonic and carboxylic acid moieties that were analogous to Bis-GMA where the peaks attributed to P=O and P-O were at $1260/\text{cm}$ and $1030/\text{cm}$, respectively. Mou et al.³⁰ structurally altered Bis-GMA by attaching phosphonic residues to the aromatic rings and the peaks attributed to P=O and P-O were observed at $1294/\text{cm}$ and $941/\text{cm}$, respectively. Sibold et al.³⁶ synthesized and characterized the acidic aromatic adhesive monomers since the aliphatic monomers containing acidic moiety possessed comparatively compromised mechanical properties.

Self-adhering light-cure flowable composites contain acidic self-etch adhesive monomers like glycerol phosphate dimethacrylate (Vertise Flow) and 10-MDP (Constic DMG). However, due to their aliphatic nature, these monomers could decrease the reactivity of the composites. Therefore, the current research developed a new acidic self-etch adhesive monomer, P-Bis-GMA, that could be used to develop either new self-adhering composites or self-etch adhesives as bonding agents. However, the P-Bis-GMA monomer is synthesized for the first time, its copolymerizing ability with other dimethacrylates, degree of conversion, etching capacity on enamel and dentin, physico-mechanical properties, and bond strength are yet to have experimented.

CONCLUSION

In conclusion, the structurally modified Bis-GMA, P-Bis-GMA, was synthesized successfully by substituting the former's -OH groups

with phosphonooxy moieties. The functional groups, the bond stretches and bends were characterized through FTIR spectroscopy. Nevertheless, this chemical alteration led to a reduction in the viscosity of the P-Bis-GMA.

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