Photopolymerizable bisallylcarbonate and bisacrylic monomers useful in the formulation of dental composite resins and in the crosslinking of methyl methacrylate

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ABSTRACT: Two new bisallylic monomers [allyl p-allyl carbonate benzoate (ApACBz) and 1,4-phenylenbis(methylene)diallyl carbonate (1,4-FMDAC)] and one bisacrylic monomer [1,4-bis(acryloyloxymethyl)benzene (1,4-BAMB)] were synthesized and used as crosslinking agents of methyl methacrylate (MMA) at different mass ratios (10, 20, 40, and 50%). All of the obtained copolymers showed improved thermal stability in comparison with that of the MMA homopolymer. Also, ApACBz and 1,4-FMDAC were used as bisphenol A glycidyl methacrylate (Bis-GMA) eluents to prepare dental resin composites. When compared to the control, the Bis-GMA–new eluent composites had a higher double-bond conversion, a higher solubility ($p < 0.05$) and a lower flexural strength ($p < 0.05$), whereas the elastic modulus and water sorption values were not statistically different ($p > 0.05$). The 1,4-FMDAC and ApACBz monomers are promising eluents of Bis-GMA for the preparation of dental composites with high degrees of conversion. In addition, the ApACBz, 1,4-FMDAC, and 1,4-BAMB monomers are potentially useful crosslinking agents when polymer networks of poly(methyl methacrylate) with a high thermal stability are desired. The application-oriented tests of the monomers in dental composite formulations showed a sufficient storage stability, high photocuring activity, excellent crosslinking of MMA, and good thermal and mechanical properties. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42920.

INTRODUCTION

Bifunctional monomer photopolymerization produces highly crosslinked polymers that have many potential applications in modern life.[1–3] In dentistry, photopolymerizable composite resins with a polymeric matrix and methyl methacrylate (MMA) acrylic resins are used in teeth restoration and replacement, respectively.[4–8] Dental composite resins consist of an organic matrix with filler particles bonded with a silane coupling agent. The main components of the organic matrix are bisphenol A glycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA). Additionally, a photoinitiation system constituted by camphorquinone and ethyl-4-dimethyl amino benzoate is used. The particles used as filling materials are often SiO_2 particles and add up to 80% of the

total mass.[8] The addition of inorganic filler particles helps to improve the mechanical and thermal properties of organic–inorganic hybrid composites. Hybrid composites can be prepared by the incorporation of inorganic filler or *in situ* sol–gel reactions of dually curable monomers.[9–11] For dental composites, the filler particles give the composites wear resistance and translucency. TEGDMA is used to dilute Bis-GMA in dental resins in concentrations ranging from 20 to 50% with the intention of improving the handling of the material and to obtain better double-bond conversion in the organic matrix.[12] On the other hand, the majority of the acrylic resins used to replace dental pieces are composed of MMA and a crosslinking agent, which usually is ethylene glycol dimethacrylate.[6] The role of the crosslinking agent is to allow the
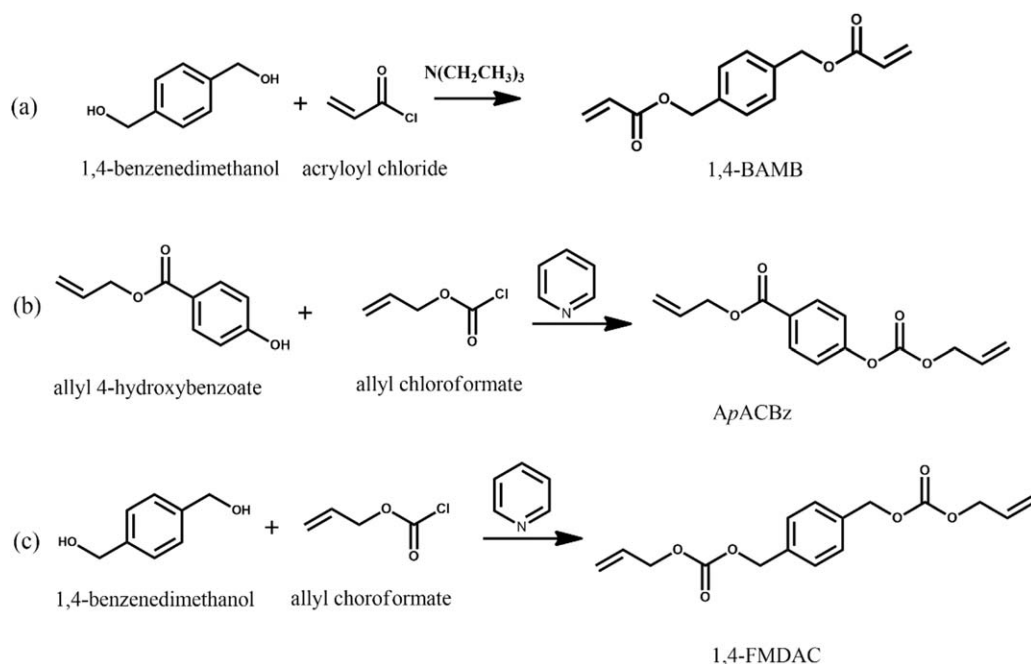
Figure 1. Monomer synthesis route.

formation of crosslinked poly(methyl methacrylate) (PMMA) networks with better mechanical properties. To enhance the physical properties of these groups of materials, a large amount of research centered on the development of new monomers that could replace those used nowadays to formulate composite and acrylic resins has been done. One of the main objectives has been to produce formulations with the highest possible double-bond conversion rates; this allows the prevention of the elution of some of the components of the polymeric matrix in the oral cavity and, hence, minimize the toxic, allergenic, and mutagenic effects that methacrylic monomers have on dental pulp.[13]

We were interested in the synthesis of bisallylcarbonate and bisacrylic monomers as Bis-GMA eluents as partial or total alternatives for the substitution of TEGMA in the formulation of new dental composite resins with enhanced or similar mechanical properties to those currently available.[14,15] In addition, the presence of two double bonds in the structure of the monomers allowed them to be used as crosslinking agents of acrylic monomers such as MMA. In this article, we report the synthesis of the monomers 1,4-bis(acryloyloxymethyl)benzene (1,4-BAMB), allyl *p*-allyl carbonate benzoate (A*p*ACBz), and 1,4-phenylenbis(methylene)diallyl carbonate (1,4-FMDAC) for use as Bis-GMA monomer diluents in the formulation of dental resins with high double-bond conversion rates. The mechanical properties of the resins formulated with allyl carbonate were compared with those of a composite resin formulated with Bis-GMA–TEGDMA. In addition, the monomers were crosslinking agents for MMA in the formulation of a polymeric network with a better thermal stability than that of the PMMA homopolymer.

EXPERIMENTAL
Materials and Instruments
All of the materials used to synthesize the monomers 1,4-BAMB, A*p*ACBz, and 1,4-FMDAC were acquired from Sigma-Aldrich and

were used as received. The MMA used in this research was donated by the Arias Co. (Mexico, Distrito Federal). The solvents used to synthesize the monomers were distilled and dried in accordance with techniques described in the literature.[16,17] ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Varian +400 (400-MHz) spectrophotometer with deuterated chloroform (CDCl$_3$) and tetramethylsilane as an internal reference. Fourier transform infrared (FTIR) spectra were obtained with a PerkinElmer Frontier IR spectrophotometer. Thermal analysis was done with a Mettler-Toledo 851 thermogravimetric analyzer. These measurements were obtained between 35 and 600°C at a heating rate of 10°C/min under a nitrogen atmosphere. The photopolymerization of the dental composite resin was done with a Bluephase 16i (Ivoclar-Vivadent) dental photocuring unit, which was equipped with a visible light-emitting diode. Three-point bending tests were performed with an Instron 4465 universal testing machine (Instron, Norwood, MA).

Synthesis of 1,4-BAMB
The compound 1,4-BAMB was synthesized by means of a nucleophilic acyclic substitution chemical reaction [Figure 1(a)]. An amount of 1 g (7.68 mmol) of 1,4-dimethanolbenzene dissolved in 50 mL of tetrahydrofuran was placed in a 100-mL, round-bottomed flask with a magnetic stirrer. The system was placed at 5°C under an argon atmosphere. Volumes of 1.8 mL (14.68 mmol) of acryloyl chloride and 2 mL (14.68 mmol) of triethylamine were added slowly. The system was covered from light and was kept under vigorous stirring for 24 h. At the end of the reaction, a heterogeneous mixture containing a yellow liquid and a white solid was obtained. The solid was separated by means of filtration, and the tetrahydrofuran was evaporated *in vacuo*. The remaining product was dissolved in dichloromethane, and three extractions with water were made. The organic phase was dried on anhydrous sodium sulfate, and the excess solvent was evaporated. The reaction mixture was purified by

means of column chromatography with silica as the stationary phase and dichloromethane as the mobile phase. The product was obtained as a white solid with a yield of 76%.

^{1}H-NMR (400 MHz, CDCl$_3$, δ, ppm): 7.42 (s, 4H, aromatic), 6.49 (d, J_{trans} = 16 Hz, 2H, CH_2=), 6.2 (m, 2H, =CH—), 5.89 (d, J_{cis} = 12 Hz, 2H, CH_2), 5.23 (s, 4H, —CH_2—). ^{13}C-NMR (400 MHz, CDCl$_3$, δ, ppm): 165.8 (C=O), 135.8 (aromatic), 131 (—OCO—CH=), 128.3 (aromatic), 128 (=CH$_2$), 65.7 (—CH$_2$—). FTIR (cm^{-1}): 2922 (vC—H), 1712 (vC=O), 1630 (vC=C), 1600 (vC=C aromatic), 1177 (vC—O), 818 (δC—H aromatic).

Synthesis of *Ap*ACBz

The synthesis of the monomer *Ap*ACBz was performed with the procedure suggested by López et al. [Figure 1(b)][18] to obtain a yield of 90%.

^{1}H-NMR (400 MHz, CDCl$_3$, δ, ppm): 8.1 (d, 2H, aromatic), 7.27 (d, 2H, aromatic), 6 (m, 2H, CH=), 5.35 (m, 4H, =CH_2), 4.78 (d, 4H, CH_2—CH). ^{13}C-NMR (400 MHz, CDCl$_3$, δ, ppm): 165.5 (—COO), 154.7 (aromatic), 152.9 (—OCOO), 132.2 (CH=), 131.4 (aromatic), 131.0 (CH$_2$=), 128.0 (aromatic), 127.7 (aromatic), 119.8 (=CH$_2$), 118.83 (=CH$_2$), 69.5(CH2 OCO), 65.75 (CH$_2$—OCOO). FTIR (cm^{-1}): 2951 (vC—H), 1762 (vC=O), 1717 cm^{-1} (vC=O), 1608 (vC=C), 1207 (vC—O).

Synthesis of the Monomer 1,4-FMDAC

The compound 1,4-FMDAC was synthesized by a one-step chemical reaction [Figure 1(c)]. First, a solution of 1 g (7.24 mmol) of 1,4-dimethanolbenzene, 1.28 mL (15.93 mmol) of pyridine, and 25 mL of dichloromethane was placed in a round-bottomed flask. After that, 1.69 mL (15.92 mmol) of allyl chloroformate was added dropwise. The reaction was made at 5°C under an argon atmosphere. The mixture was kept under constant stirring for 24 h. At the end of the reaction, a heterogeneous mixture containing a yellow liquid and a white solid was obtained. The solid was eliminated by means of decantation, and two extractions, one with 50 mL of HCl at 5% v/v and another with 50 mL of distilled water, were performed with the remaining liquid. The organic phase was dried on anhydride sodium sulfate, and the excess solvent was evaporated *in vacuo* to obtain a yellow liquid. The product was purified by means of column chromatography (silica gel) with a mixture of dichloromethane and acetone (90:10) as the mobile phase. The yield was 58.3%.

^{1}H-NMR (CDCl$_3$, 400 MHz, δ, ppm): 7.39 (s, 4H, aromatic), 5.92 (m, 2H, H$_2$C=CH—), 5.36 (dd, 2H, J_{trans} = 16 Hz, H$_2$C=), 5.27 (dd, 2H, J_{cis} = 8 Hz, H$_2$C=), 5.16 (s, 4H, —CH$_2$—Ar), 4.63 (d, 4H, J = 8.0 Hz, —CH$_2$—O). ^{13}C-NMR (CDCl$_3$, 400 MHz, δ, ppm): 155.0 (OCOO), 135.7 (aromatic), 131.6 (=CH—), 128.6 (aromatic), 119.2 (H$_2$C=), 69.3 (—CH$_2$—Ar), 68.8 (—CH$_2$—O). FTIR (cm^{-1}): 2956 (vC—H), 1745 (vC=O), 1655 (vC=C), 1230 (vC—O), 950 (δC—H aromatic).

Copolymerization of the 1,4-FMDAC, 1,4-BAMB and *Ap*ACBz Monomers with MMA

1,4-FMDAC, 1,4-BAMB, and *Ap*ACBz were tested as MMA crosslinking agents with different weight percentages. The concentra-

tions used in all cases were 50:50, 70:30, and 90:10 w/w (MMA–crosslinking agent). Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) at 3 wt % were used for 1,4-FMDAC as the thermal initiators, whereas only BPO was used for 1,4-BAMB and *Ap*ACBz. The mixtures were prepared in test tubes, and then, argon was bubbled through them for 5 min. Later, the tubes were sealed and placed in a water bath at 90°C for 1 h to accomplish the polymerization reaction. The gel percentage of the polymers was obtained by sol–gel extractions. For this procedure, the samples were triturated, weighed, and placed with agitation in ethanol for 24 h. Then, the insoluble part, the denominated gel, was separated and dried. Once it was dried, the mass for each of the samples was measured to obtain the gel percentage formed.

Silanization of Filling Material

The filling materials were silanized in accordance to the procedure reported by Chen and Brauer.[19] Amounts of 5 g of micrometer-sized (0.2–0.3 μm) silica, 100 mL of cyclohexane, 0.1 g of *n*-propyl amine, and 0.44 g of 3-trimethoxysilyl propyl methacrylate were placed in a round-bottomed flask. The mixture was stirred at room temperature for 30 min and was then heated to 60°C for other 30 min. The mixture obtained from the reaction was placed in a rotary evaporator at 65°C for 15 min and then at 95°C for 1 h. Finally, the solid obtained was dried in a vacuum oven for 18 h at 80°C.

Dental Resin Composite Preparation

The organic matrix of the composite material was prepared by the mixture of the monomers (1) Bis-GMA and 1,4-FMDAC and (2) Bis-GMA and *Ap*ACBz at weight ratios of 80:20. A photopolymerizable material was formulated for 1,4-FMDAC with the camphorquinone/ethyl-4-dimethyl amino benzoate initiating system with a 5 wt % concentration of each one. A thermally polymerizable system was formulated for the monomer *Ap*ACBz with BPO at 3% as an initiator. The composite resins were prepared by the mixture of the organic matrix with silanized silicon oxide in a 35:65 weight ratio. All of the materials were used immediately after their preparation. Finally, a formulation containing Bis-GMA–TEGDMA with a 80:20 ratio was used as a control group.

Flexural Properties

The flexural strengths of the prepared composite materials were evaluated in accordance with ISO-4049,[20] whereas the elastic moduli were evaluated in accordance with American National Standards Institute–American Dental Association (ANSI–ADA) specification No. 27.[21]

Bar specimens (25 × 2 × 2 mm^3) were prepared in a stainless steel mold. For the photopolymerizable material, samples were irradiated on both sides by the overlapping technique. Each overlap was light-cured for 10 s with an intensity of 460 mW/mm^2. In the case of the thermopolymerizable materials, the samples were heat-polymerized in an oven at 90°C for 1 h. After the polymerization process, flashes and irregularities were removed with 600- and 1200-grit abrasive paper, and their dimensions were measured with an accuracy of 0.01 mm with a digital caliper. The samples were kept in distilled water at 37°C for 24 h. A three-point flexural test was made in a universal mechanical testing machine with a 1-kN load cell at a crosshead speed of 1.00 mm/min until fracture

occurred. The flexural strength (σ) and elastic modulus (E; MPa) were calculated with the following equations:

$$\sigma = \frac{3Fl}{2bh^2}$$

$$E = \frac{F_1 l^3}{4bh^3 d}$$

where F_1 is the load exerted on the specimen (N), F is the maximum load exerted on the specimen at the point fracture (N), l is the distance between the supports (mm), h is the height of specimen measured immediately before testing (mm), b is the width of specimen measured immediately before testing (mm), and d is the deflection corresponding to F_1.

Water Sorption and Solubility

The water sorption and solubility of the composite materials were evaluated according to the method described in ISO 4049.[20] Sample discs were prepared in a stainless steel mold (15 mm in diameter and 1 mm in thickness). The samples were polymerized under the same conditions described in the Experimental/Flexural Properties section. After this, the samples were transferred to a desiccator, and their mass was monitored daily until a constant mass (m_1; μg) was obtained (mass loss of each specimen < 0.1 mg in a 24-h period). Then, the thickness and diameter of the samples were measured to calculate the volume (V; mm^3) for each one. The samples were immersed in distilled water at 37°C for a week. After that, they were weighed, and the mass obtained was registered as m_2 (μg). Finally, the samples were introduced again in a desiccator and were weighed daily until their mass remained constant (m_3; μg). The water sorption and solubility were calculated with the following equations:

$$w_{sp} = \frac{m_2 - m_3}{V}$$

$$w_{si} = \frac{m_1 - m_3}{V}$$

where w_{sp} is water sorption and w_{si} is water solubility.

Double-Bond Conversion

The double-bond conversion of the composite materials was determined by FTIR spectroscopy. IR spectra of the uncured and cured samples were obtained. The measurement was made in real time with an attenuated total reflection unit for the photopolymerizable materials. For the thermopolymerizable materials, the measurement was made with a transmittance unit. For each spectrum, we determined the height of the aliphatic C=C peak absorption at 1638 cm^{-1} and the aromatic C=C peak absorption at 1609 cm^{-1}. The aromatic C=C vibration was used as an internal reference. The double-bond conversion was determined in accordance with the following equation:[22]

$$\text{Double-bond conversion } (\%) = 100 \left[1 - \frac{\left(\frac{A_{1638}}{A_{1609}}\right)_{\text{Polymer}}}{\left(\frac{A_{1638}}{A_{1609}}\right)_{\text{Monomer}}} \right]$$

where A_{1638} is the maximum height of the band at 1638 cm^{-1}, A_{1609} is the maximum height of the band at 1609 cm^{-1}, and the polymer is the polymerized composite material and monomer is the unpolymerized composite material.

Statistical Analysis

A total of three values for the flexural strength, elastic modulus, water sorption, and degree of conversion were obtained for each material. The results were evaluated with a one-way analysis of variance. Statistical differences were considered significant when p was less than 0.05. Photopolymerizable and thermopolymerizable materials were evaluated separately.

RESULTS AND DISCUSSION

Monomer Synthesis

Figure 1 shows chemical structures for the monomers 1,4-FMDAC, 1,4-BAMB, and ApACBz. They were fully characterized with the FTIR and ^{1}H-NMR and ^{13}C-NMR techniques. The NMR spectra of these new monomers exhibited some characteristic signals that confirmed their chemical structure (Figure 2). The main evidence for the presence of monomers in the ^{1}H-NMR spectra were the signals observed in the range between 6.6 and 5.2 ppm, which correspond to the protons of the terminal double bonds, whereas the characteristic signal of the hydroxyl groups of the starting material did not appear in the spectra of the monomers. Also, in the FTIR spectra of the monomers, an absorption band appeared at 1638 cm^{-1}; this corresponded to the C=C vibration mode of the alkene groups present in both sides of each of the monomers. Furthermore, the absence of the absorption band at 3500 cm^{-1}, which corresponded to the stretching νOH present in the spectra of the raw materials, was evident.

Monomer Homopolymerization and Copolymerization

The monomers synthesized were evaluated as crosslinking agents for MMA through the percentage in gel after the copolymers were obtained. Figure 3 shows the gel percentage of the different copolymers synthesized and the gel percentages of their respective homopolymers with BPO and AIBN as initiator agents. The homopolymers corresponding to the acrylic monomers (MMA and 1,4-BAMB) presented the highest gel percentages. Acrylic monomers are very reactive; this allows them to polymerize quickly, yield high conversion degrees,[23] and in the case of 1,4-BAMB, high degrees of crosslinking. MMA only has a single acrylic group, and as such, a linear polymer was obtained; conversion degrees close to 80% were reached.[24]

The homopolymers poly(allyl p-allyl carbonate benzoate) [p(ApACBz)] and poly[1,4-phenylenbis(methylene)diallyl carbonate] presented relatively low gel percentages in comparison with the acrylic homopolymers. This behavior is typical in allylic monomers because they present a self-inhibiting phenomenon on polymerization because of their structure, and this leads to low gel percentages.[25] This types of monomers generally require higher concentrations of initiator than acrylic monomers (<3 wt %) and more energetic radiation sources, such as UV, electron, or γ radiation.[18] Although the allyl carbonate monomers exhibited this self-inhibiting process, both the ApACBz and 1,4-FMDAC monomers could efficiently copolymerize with MMA. This occurred because the initiator and MMA generated a large amount of free radicals in the reaction media, and this allowed the bisallylic monomer to react and copolymerize, even though low initiator concentrations (3 wt %) were used. In the case of the 1,4-FMDAC monomer, the use of the
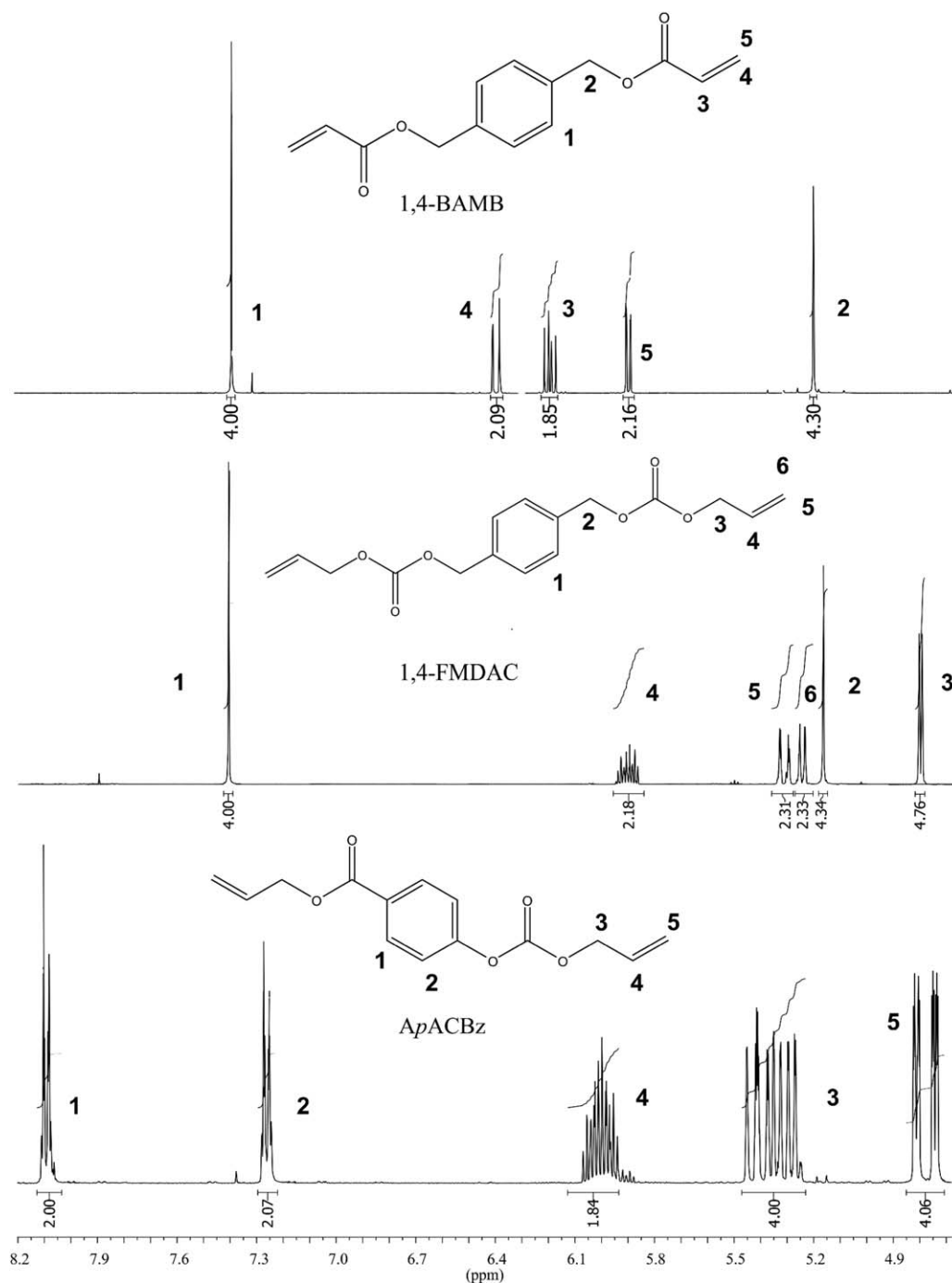
Figure 2. ^{1}H-NMR spectra of the synthesized monomers.

BPO or AIBN initiator did not represent a significant difference in homopolymerization or in copolymerization with MMA.

The copolymerization of the monomers was confirmed by means of IR spectroscopy analysis. Figure 4 shows the spectra corresponding to the 50:50 ApACBz–MMA copolymer, PMMA, and p(ApCBz). The FTIR spectrum of copolymer ApACBz–MMA 50:50 showed characteristics bands of both comonomers. The absorption band for the C=C elongation vibration mode of the aromatic ring, which came from the bifunctional monomer, was observed at 1600 cm^{-1}. The adsorption band corre-

sponding to the CH$_3$ vibration mode found at 1449 cm^{-1} belonged to MMA. The adsorption bands corresponding to the C=O vibration mode and belonging to the carbonate and ester groups were observed at 1771 and 1718 cm^{-1}, respectively. These bands were found in all of the synthesized copolymers, and this demonstrated how the new monomers acted as crosslinking agents for MMA, even at low concentrations. It is clearly shown in Figure 3 that even with 10 wt % crosslinking agent, the gel percentage increased up to 95%, whereas PMMA without a crosslinking agent had a 86% gel percentage.
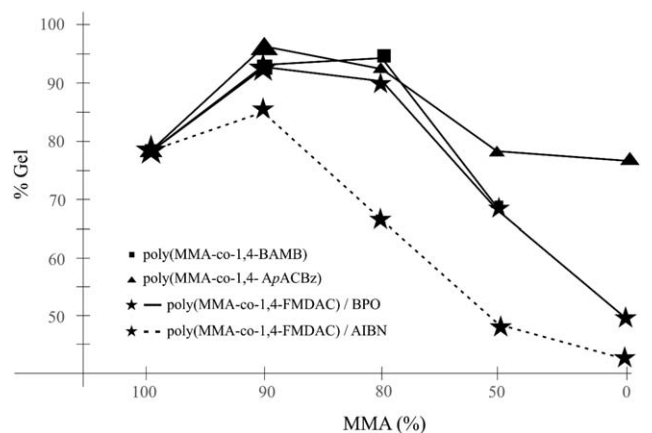
Figure 3. Sol–gel percentages of the synthesized copolymers; poly(MMA-co-1,4-BAMB), poly(MMA-co-1,4-ApACBz), poly(MMA-co-1,4-FMDAC) and poly(MMA-co-1,4-FMDAC).

Thermogravimetric Analysis

The thermal stabilities of all of the homopolymers and copolymers synthesized were analyzed by means of thermogravimetric analysis. The thermograms obtained are shown in Figure 5. On the basis of the analysis of the thermograms, it was possible to determine that the 1,4-FMDAC, 1,4-BAMB, and ApACBz monomers could crosslink and enhance the thermal stability of PMMA. According to previous research, PMMA degraded in three steps. The first stage at 160°C corresponded to the scission of head-to-head linkages (H—H); the bond dissociation of H—H linkages required the least amount of energy to occur. The next stage of degradation at 290°C corresponded to the breaking of the vinylic terminal bonds (—CH=CH$_2$), which did not react during the polymerization of MMA. The last stage of degradation, which occurred at 370°C, corresponded to the random scission of bonds within the polymer chain.[26,27] All of the copolymers obtained with either 1,4-FMDAC, 1,4-BAMB, or ApACBz as a crosslinking agent presented a single stage of degradation at 250°C. This increase in the thermal stability of the copolymer was independent from the concentration of the crosslinking agent used. The formation of three-dimensional networks, which occurred on the copolymers synthesized in this study, produced polymeric materials with high crosslinking densities, and hence, the amount of thermal energy that was necessary to degrade the polymeric networks was higher compared to that required by the linear PMMA homopolymer.[28,29] A direct relation between the degree of crosslinking of a polymer and its thermal stability was reported previously.[29] The 1,4-FMDAC, 1,4-BAMB, and ApACBz monomers were crosslinking agents for MMA at low or high concentrations and improved its thermal stability. When we compared the thermograms of the allylic monomers and 1,4-BAMB acrylic monomer, we observed that the latter formed more thermally stable copolymers. This result was confirmed with sol–gel experiments, where we observed that a greater gel percentage was obtained when 1,4-BAMB was used as a crosslinking monomer (Figure 3). For this case in particular, it may be possible that 1,4-BAMB, while being more reactive than the allylic monomers, allowed the formation of polymers with a higher degree of crosslinking.[30]

Flexural Properties

The average values and standard deviations for the flexural strength and elastic modulus of the prepared materials are presented in Tables I and II. The values obtained for the control group prepared with Bis-GMA–TEGDMA are also presented. Composite photopolymerizable resins were formulated with the 1,4-FMDAC monomer, and thermopolymerizable resins were formulated with the ApACBz monomer. The 1,4-BAMB monomer was not used to formulate a resin because it was a solid monomer with a low miscibility with the commercially available Bis-GMA and TEGDMA monomers.

The three-point flexural test is the most used mechanical test to evaluate materials for dental applications because it combines the effects of compression deformation and tensile stress in a single sample. With regard to the photopolymerizable materials, the system that contained the new monomer 1,4-FMDAC showed a lower flexural strength than the control. This reduction may have been caused by the difference in the reactivity between the allylic and acrylic monomers. As previously mentioned, allylic monomers have a self-inhibiting mechanism that yields lower conversion percentages than those of acrylic monomers.[25] It may have been possible that the presence of the allylic monomer in the formulation slightly reduced the crosslinking density of Bis-GMA within the polymer formed, and hence, its mechanical properties may have been affected. With regard to the elastic modulus, statistical analysis showed no significant differences between the evaluated groups. The elastic modulus is a property that describes the elasticity of a material and represents the amount of energy it can take without being permanently deformed. In a clinical situation, this property is very important because once a material deforms permanently, this stops its clinical service even if a visible fracture is not evident.[31]

The evaluation of dental restorations includes three groups of criteria: aesthetic, functional, and biological. Each of these
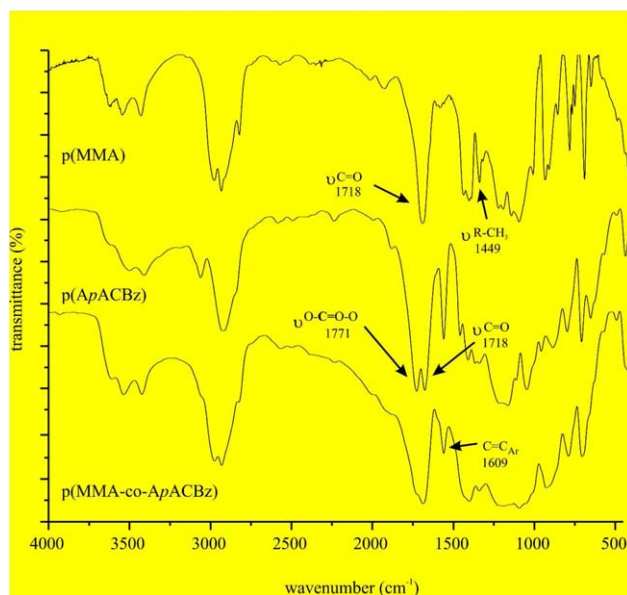

Figure 4. FTIR spectra of PMMA homopolymer, p(ApACBZ) homopolymer, and the p(MMA-co-ApACBz) copolymer.
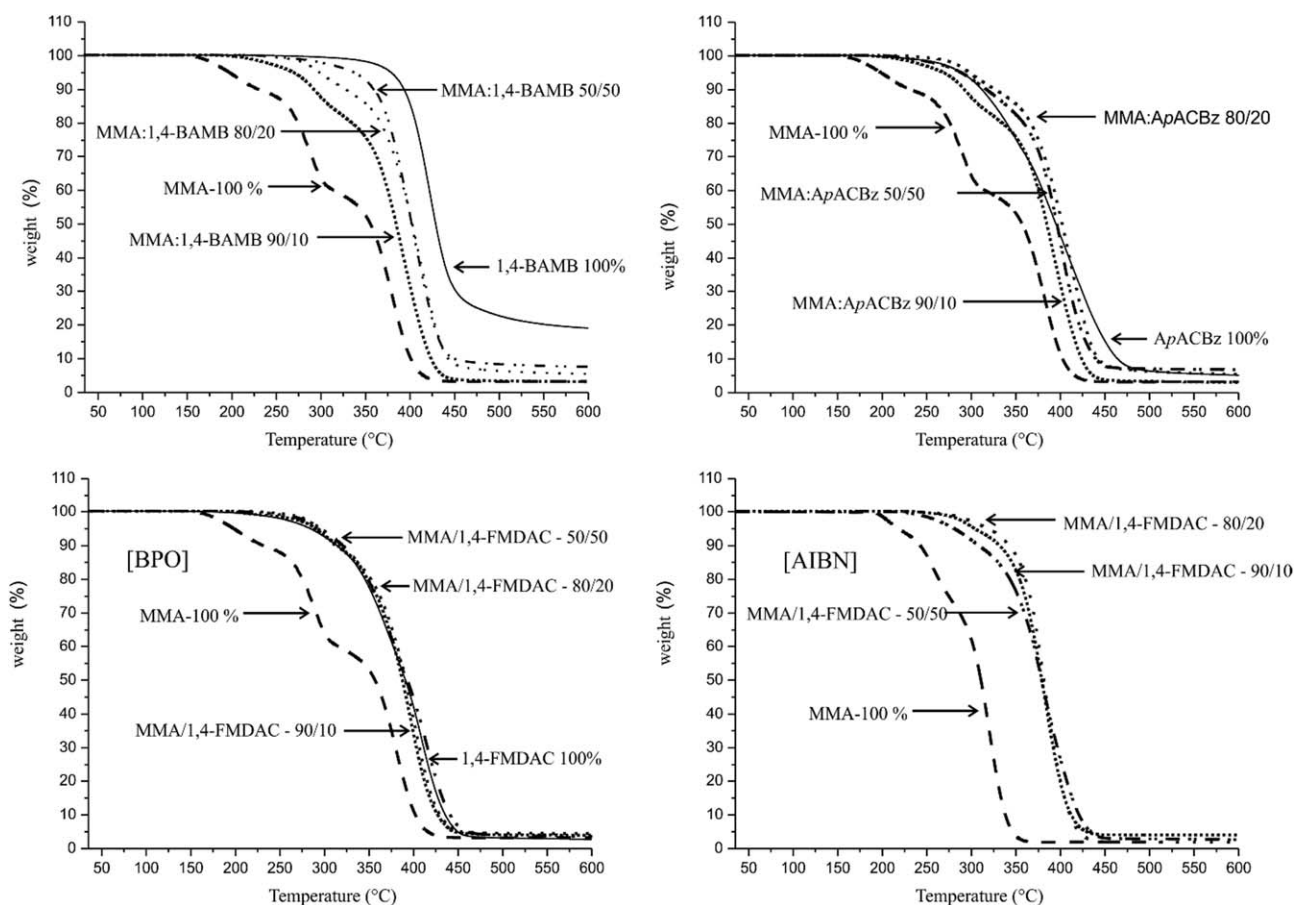
Figure 5. Thermograms of the synthesized homopolymers and copolymers.

groups has subgroups with 16 evaluation criteria in total.[32] Permanent deformation is not included in these criteria because it is very difficult to determine clinically; nevertheless, permanent deformation of a material could lead to several complications, including bacterial infiltration, hypersensitivity, and secondary decay.[33] The material formulated with the 1,4-FMDAC monomer fulfills some of the requirements needed for replacing lost tooth structures because, compared to the control material, it exhibited a similar elastic modulus and a lower flexural strength. This indicated that once a permanent deformation occurs in this material, it would fracture, and its replacement could be performed before the aforementioned complications appear.

Water Sorption and Solubility

Analysis made on the water sorption variable determined that there were no significant statistical differences between the con-

trol material and the material containing the 1,4-FMDAC monomer. With regard to solubility, the obtained value confirmed the presence of significant statistical differences between the control material and the material containing the 1,4-FMDAC obtained, which exhibited a higher weight loss. The water sorption and solubility phenomena in polymeric networks precede a large variety of physical and chemical processes that may deteriorate the structure of a polymeric material.[34] Aqueous sorption is a property that depends on many factors related to the polymeric network structure, including the hydrophilic characteristics of the monomers. The TEGDMA monomer had oxygen atoms in its ether groups, which were hydrophilic.[35] It is very important to mention that with regard to water sorption, both materials exhibited a value below 40 $\mu g/mm^3$; therefore, they complied with what is established in ISO 4049. It has been proven that polymers with a high degree of crosslinking possess a low solvent sorption.[36] Aqueous sorption is always accompanied by the

Table I. Mechanical Properties of the Thermopolymerizable Materials

Composite material	Flexural strength (MPa)	Elastic modulus (MPa)	Degree of conversion (%)	Water sorption ($\mu g/mm^3$)	Solubility ($\mu g/mm^3$)
Control	59.56 (4.1)[a]	8136.60 (549.03)[a]	61.69 (3.73)[b]	33.37 (7.47)[a]	5.27 (5.89)[a]
Resin Bis-GMA–A*p*ACBz	50.08 (1.6)[b]	6345.2 (113.57)[b]	79.00 (0.93)[a]	136.82 (15.80)[b]	29.00 (3.60)[a]

The same superscript letter indicates that no significant differences existed.

Table II. Mechanical Properties of the Photopolymerizable Materials

Composite material	Flexural strength (MPa)	Elastic modulus (MPa)	Degree of conversion (%)	Water sorption ($\mu g/mm^3$)	Solubility ($\mu g/mm^3$)
Control	62.21 (2.2)[a]	6400.60 (494.62)[a]	67.64 (1.35)[b]	39.19 (7.40)[a]	4.28 (2.24)[a]
Resin Bis-GMA–1,4-FMDAC	53.92 (2.8)[b]	6296.80 (326.20)[a]	90.82 (2.02)[a]	37.24 (2.01)[a]	11.3 (1.40)[b]

The same superscript letter indicates that no significant differences existed.

loss of some of the components of the polymeric material.[37] This fact explains the weight loss that the evaluated materials suffered after the solubility test. The statistical analysis demonstrated that the material elaborated with 1,4-FMDAC showed a higher solubility than the control. Differences in the solubility may have been due to the amount of monomers that remained unreacted. The unreacted monomer was solubilized and eluted from the composite material, and this contributes to its weight loss.[34]

Double-Bond Conversion

With regard to double-bond conversion, it is important to note that the system containing the 1,4-FMDAC monomer had a higher value than the control group ($p > 0.005$). Although allylic monomers are more stable than acrylic monomers,[25] it is possible that their high miscibility with Bis-GMA and the flexibility of the 1,4-FMDAC monomer could have favored this behavior. It has been reported that monomers with flexible groups may reach double-bond conversion percentages close to 100%.[12,38,39] In a study made by our research team in which an allyl carbonate monomer was used as the base monomer to formulate composite resins, higher double-bond conversion values were also obtained compared to the control group.[14] It has also been reported that allylic monomers only polymerize with radiation with high frequencies, such as γ, electron, and UV radiation. Despite this, the 1,4-FMDAC allylic monomer copolymerized with Bis-GMA with visible light. In the presence of the photoinitiator system, Bis-GMA generated the required amount of free radicals to promote the adequate copolymerization of the monomer system; this allowed the generation of a highly crosslinked Bis-GMA-co−1,4-FMDAC copolymer.

The analysis of thermopolymerizable materials that contained the *Ap*ACBz monomer as an eluent for Bis-GMA showed that they exhibited similar behavior to the 1,4-FMDAC system. The similarities in the evaluated properties may have occurred because the monomers shared some characteristics, such as the presence of aromatic rings in its structure and the presence of two double-terminal allylic groups.

CONCLUSIONS

Generally, the eluents for Bis-GMA are bisacrylic monomers. In this article, we have reported a bisallylic monomer 1,4-FMDAC, which was useful like an eluent in the formulation of dental composite resins. The new formulation obtained with 1,4-FMDAC was photopolymerizable with visible light, and it could be used for direct restoration in dentistry. Furthermore, the

three monomers *Ap*ACBz, 1,4-FMDAC, and 1,4-BAMB had the capacity of crosslinking MMA at low concentrations. The crosslinked MMA with the monomers reported in this article had better thermal properties, and it could be used in many dentistry applications.

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