

# Synthesis of Two PET Waste Derived Bisacrylic and Bisallylic Monomers and Their Potential Use as Crosslinking Agents and Dental Resin Composites

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**ABSTRACT:** Two novel bifunctional monomers obtained from PET waste glycolysis are reported. Bis(2-(acryloyloxy)ethyl) terephthalate and bis(2-(((allyloxy)carbonyl)oxy)ethyl) terephthalate (BACET) monomers were obtained from bis(hydroxyethyl) terephthalate derived from PET waste and acryloyl chloride and allyl chloroformate, respectively. The monomers were characterized by FTIR and <sup>1</sup>H-NMR spectroscopies. They were evaluated as crosslinking agents for acrylic acid (AA) and methacrylic (MA) acids using thermally initiated polymerization. The obtained copolymers showed higher thermal stability than the acrylic homopolymers. They were also tested for dental formulations as Bis-GMA substitutes in heat curing resin composites. In spite of its lower reactivity, only BACET was able to substitute Bis-GMA, due to its high solubility in the TEGDMA comonomer. Resin formulations containing nano-sized silica and the mixture Bis-GMA/TEGDMA or BACET/TEGDMA were prepared in order to compare physical and chemical properties. Water sorption, solubility, and flexural strength were found statistically similar for both formulations. However, flexural modulus was lower and double bond conversion was higher for the BACET resin, which could make it appropriate for its potential use in dental resin composites. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41487.

**KEYWORDS:** composites; copolymers; crosslinking; degradation; properties and characterization

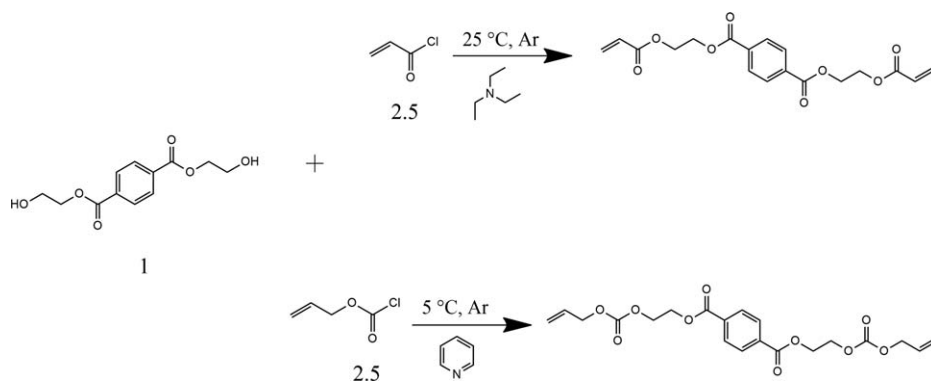
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## INTRODUCTION

Poly(ethylene terephthalate), PET, finds a widespread use, particularly in the beverage industry, and constitutes a substantial fraction volume in the plastics waste stream. For many years different efforts have been proposed to reuse or recycle PET to find a partial solution to the solid-waste problem and to the conservation of raw petrochemical products and energy.<sup>1</sup> One of these is the chemical recycling or reprocessing, which consists of the depolymerization of PET to obtain monomers such as terephthalic acid (TPA), dimethyl terephthalate (DMT), ethylene glycol (EG) and bis(2-hydroxyethyl) terephthalate (BHET). TPA, DMT, and EG can be repolymerized to obtain PET, while BHET and other PET glycolyzates find application as starting reactants for a range of different organic compounds. This method uses

processes such as hydrolysis, aminolysis, methanolysis, or glycolysis, being the last two methods the most studied for PET depolymerization on a commercial scale.<sup>1</sup> The glycolysis products are BHET or oligoesters containing terminal hydroxyl groups which can be further reacted to synthesize unsaturated polyester resins for polymer concretes and polymer mortars,<sup>2</sup> degradable copolyesters,<sup>3</sup> organic coatings,<sup>4</sup> alkyd–amino resins for coating applications,<sup>5</sup> or polyols and polyurethanes foams.<sup>6</sup> During the last decade, a novel modification of these glycolysis products is based on converting the hydroxyl groups into ultraviolet (UV) or electron beam irradiation curable acrylate or methacrylate moieties to obtain monomers with promising results from the point of view of their curability by UV and their mechanical properties.<sup>7</sup>



**Scheme 1.** Synthetic route to BAET and BACET.

Among the wide range of applications that bisacrylic monomers find, such as coating materials, superabsorbent polymers, and for the preparation of macroporous polymers,<sup>8,9</sup> their use as dental resins is very important because of their easy handling, good mechanical properties, and fast polymerization rates. Examples are methyl methacrylate (MMA), bisphenol A-glycidyl methacrylate (Bis-GMA), bisphenol A ethoxylated dimethacrylate (Bis-EMA), triethylene glycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA). MMA is the most widely used material for construction of dentures.<sup>10</sup> Bis-GMA and Bis-EMA are the primary components in the majority of commercial dental resins, TEGDMA is added as diluent to improve handling of the dental resin composite, as well as to achieve higher degrees of conversion,<sup>11</sup> while UDMA is less viscous and produces a more flexible and tough resin. Although these monomers are extensively used, the research on new compounds for dental applications is permanent in order to achieve monomers that fulfill a combination of characteristics, mainly non-shrinkage, hydrophobicity, high-strength, high double bond conversion, anticariogenic or antimicrobial requirements.<sup>12,13</sup>

On the other hand, some allyl esters containing two double bonds such as diallyl isophthalate or diethylene glycol bis(allyl carbonate) have found use in the manufacture of heat-resistant molding composites for electronic applications and eyeglass lenses, respectively. Besides, other polyfunctional allyl esters have been used for crosslinking or curing preformed vinyl-type polymers,<sup>14,15</sup> while some allyl esters are used as reactive diluents in the synthesis of unsaturated polyesters resins.<sup>16</sup>

In this article, we report the synthesis, characterization, and evaluation of two new acrylic and allylic monomers obtained from postindustrial PET waste as crosslinking agents for commercial acrylic monomers and their potential use in dental resin composites.

## EXPERIMENTAL

### Materials and Instruments

BHET was obtained through the depolymerization of postindustrial PET provided by the plastic containers supplier Graham Packaging Co. S. de R.L de C.V. located at Pachuca, Hgo. México. The viscosity average molecular weight measured in *o*-chlorophenol at 25°C was found to be  $4.8 \times 10^4$  mol/g.

The reagents used in the synthesis of bis(2-(acryloyloxy) ethyl) terephthalate (BAET) and bis(2-((allyloxy)carbonyl)oxy)ethyl terephthalate (BACET) are commercially available from Sigma-Aldrich and were used as received. The methylene chloride, ethanol, acetone, and tetrahydrofuran (THF) solvents were previously distilled from a convenient drying agent before using.

FTIR spectra were recorded on a Perkin Elmer Frontier spectrometer with attenuated total reflectance unit (ATR). They ranged between 4000 and 400  $\text{cm}^{-1}$  with a spectral resolution of 4  $\text{cm}^{-1}$ . The samples for the double bond conversion analyses were prepared using anhydrous KBr. <sup>1</sup>H-NMR spectra were recorded in a Varian Nuclear Magnetic Resonance 400 (400 MHz) spectrometer. The samples were prepared using deuterated chloroform ( $\text{CDCl}_3$ ) or deuterated acetone as solvent, with tetramethylsilane as internal reference. Thermograms were obtained in a Mettler-Toledo TGA/SDTA 851<sup>e</sup> equipment from 25 to 500°C using a temperature gradient of 1°C/min under a nitrogen atmosphere. Flexural properties were measured with an Instron 4465 universal testing machine.

### PET Depolymerization

Postindustrial PET particles, sieved between 7 and 18 mesh (1–2.8 mm), were depolymerized by glycolysis with EG using zinc acetate as promoter; 4 g (15.74 mmol) of PET and 0.08 g (0.43 mmol) of zinc acetate were added to a 25 × 200 mm test tube equipped with a stirrer, then 36 mL (579.5 mmol, 40 g) of EG were added. The test tube was sealed with a rubber septum and heated to 190°C in a sand bath under a constant stirring of 300 rpm. Inert atmosphere was not used. After 2 h, time for total dissolution of the PET particles, the reaction was cooled at room temperature and the reaction products were added to 80 mL of hot water at 80°C, temperature at which BHET is soluble. The liquid phase was separated from the solid after 30 s of centrifugation. The liquid was cooled to 5°C for 18 h. Then, the solid was filtered using a suction filter funnel with filter paper and washed three times with cold water to remove unreacted EG and catalyst. The final product was purified by recrystallization in water. The resulting solid was dried at 50°C under vacuum at 42.7 kPa. BHET was obtained as white needle crystals (mp: 106°C), with a yield of 89% (4.87 g). <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  (ppm): 8.16 (s, 4H, aromatic), 4.42 (t, 4H,

$\text{CH}_2\text{—OH}$ ,  $J = 4.0$  MHz), 3.89 (dd, 4H,  $\text{O—CH}_2$ ), and 4.16 (t, 2H,  $\text{OH}$ ).

#### Synthesis of BAET

BAET was synthesized by a typical condensation reaction. A solution of acryloyl chloride (0.89 g, 9.84 mmol), BHET (1 g, 3.93 mmol), and triethyl amine (0.99 g, 9.84 mmol) in 20 mL of acetone was placed in a 250 mL one necked round-bottomed flask, with constant stirring, under argon atmosphere during 24 h at room temperature (Scheme 1). The reaction mixture was filtered, the remaining liquid was eliminated under reduced pressure and the solid product was recrystallized from a mixture of ethanol and water in the ratio 2 : 5, filtered and dried in a vacuum oven at 50°C to give 1.2 g (3.30 mmol, 84% yield) of yellowish crystals (m. p. 86°C).  $^1\text{H}$  NMR (chloroform- $d$ )  $\delta$  (ppm): 8.15 (s, 4H; aromatic), 4.50 (t, 4H  $\text{O—CH}_2$ ), 4.55 (t, 4H  $\text{O—CH}_2$ ), 6.4 (t, 2H,  $\text{C=CH}$ ), 5.95 (t, 2H,  $\text{C=CH}_2$ ), and 6.2 (t, 2H,  $\text{C=CH}_2$ ).

#### Synthesis of BACET

BACET was synthesized by a typical Schotten-Baumann reaction. A solution of allyl chloroformate (1.18 g, 9.84 mmol), BHET (1 g, 3.93 mmol), and pyridine (0.77 g, 9.84 mmol) in an excess of dry THF, as a solvent, was placed in a 250 mL two necked round-bottomed flask, with constant stirring, under argon atmosphere during 24 h at room temperature. The reaction mixture was filtered and washed with THF. The colorless remaining liquid with the product was distilled under reduced pressure. After that, it was washed with water at 70°C, and purified in a chromatographic silica column using methylene chloride and 10% acetone. Finally, the monomer was dried in a vacuum oven at 50°C to give 0.55 g (1.4 mmol, 86% yield) of a white solid with melting point of 42°C.  $^1\text{H-NMR}$  (chloroform- $d$ )  $\delta$  (ppm): 8.15 (s, 4H; aromatic), 4.48 (t, 2.93H  $\text{O—CH}_2$ ), 4.57 (t, 2.93H  $\text{O—CH}_2$ ), 4.58 (m, 2.93H,  $\text{O—CH}_2$ ), 6.06 (m, 1H,  $\text{C=CH}$ ), 5.28 (m, 1.07H,  $\text{C=CH}_2$ ), and 5.42 (m, 1.07H,  $\text{C=CH}_2$ ).

#### Polymerization of BAET and BACET

**Bulk Polymerization with Thermal Initiators.** BAET and BACET monomers were crosslinked separately by dissolving the monomers and the initiators in acetone. Polymerizations were carried out in sealed Pyrex tubes using benzoyl peroxide (2 wt % for BAET and 5 wt % for BACET) at 90°C and AIBN (2 wt % for BAET and 5 wt % for BACET) at 90°C as initiators. Before polymerization, the acetone was removed at reduced pressure at room temperature and the tubes were degassed by the usual freezing and thawing technique under vacuum and then sealed off. The percentage of insoluble crosslinked polymer formed (gel content, gel %) was obtained by extracting the soluble part (sol fraction, sol %) from the cured polymer with acetone. The polymer was grinded in an agata mortar and suspended in acetone (ratio of polymer to acetone, 1 : 10 w/w) at room temperature, with constant stirring of 300 rpm during 12 h. This procedure was repeated once. The solid was filtered and dried at constant weight, thus obtaining the gel fraction for each experiment. Sol and gel fractions were characterized by FTIR. All the reaction systems were homogeneous before and after the polymerization.

**BAET and BACET as Crosslinking Agents for Acrylic Monomers.** BAET and BACET were tested as crosslinking agents for acrylic acid (AA) and methacrylic acid (MA) using weight ratios of crosslinking agent to acrylic monomer of 1 : 1, 1 : 2 and 1 : 10. The crosslinking monomer was added to a test tube containing a solution of the initiator in acetone. Once dissolved, the acetone was removed at reduced pressure and room temperature. After that, the acrylic monomer was added. The tube was sealed and degassed at room temperature. Then, it was filled with argon, degassed again, and heated at 80°C during 10 min. Finally, it was heated at 90°C for 1 h. After this time, amber solids were obtained in all cases. For each experiment, 2 wt % of BPO was used respect the total weight of the mixture. Gel content was obtained following the procedure described for the BAET and BACET homopolymers. Extracted polymers were characterized by FTIR.

#### Silanization of Silica Particles

Nanosized silica particles were prepared according to the next procedure. Concentrated nitric acid (0.8 g) and 7.0 mL of TEOS were added to 8.0 mL of deionized water under vigorous stirring, for 15 min. Then, the solution was transferred to a baker glass, sealed, and held at 40°C for 24 h. The gel obtained was ground and immersed in a 1M nitric acid solution for 6 h. This solution was renewed every 2 h. After that, the gel was washed three times by immersion in deionized water for 24 h. Then, the gel was dried in a water bath to evaporate the residual nitric acid, immersed again in deionized water overnight, and dried at 110°C for 2 h. The dried material was crushed to obtain a 300-mesh size, dried at 300°C at a rate of 100°C/h and held at this temperature for 3 h. Finally, the material was crushed to obtain a -400-mesh size.

The silica particles were silanized with 3-(trimethoxysilyl)propyl methacrylate (MPS), following the method of Chen and Brauer.<sup>17</sup> To a one necked round-bottomed flask equipped with a magnetic stir bar, silica (5 g), MPS (0.44 g), and cyclohexane (100 mL) were added and stirred at room temperature for 30 min and then at 60°C for another 30 min. The reaction vessel was then placed in a rotary evaporator at 60°C for removing the solvent. The powder was then heated at 95°C for 1 h and finally dried at 60°C in a vacuum oven for 24 h. The amount of silane in grams to obtain a minimum coverage of the silica nanoparticles is given by the following equation<sup>18</sup>:

$$X = \left(\frac{A}{\omega}\right)f$$

where  $A$  is the surface area of the silica particles (623 m<sup>2</sup>/g),  $\omega$  is the surface coverage per gram of silane MPS (2525 m<sup>2</sup>/g), and  $f$  is the amount of silica.

#### Preparation of the Composites

The organic resin matrix was prepared by mixing BACET and TEGDMA monomers in the ratio of 50/50 by wt %. The mixture was heated at 40°C to accelerate the solubility of the BACET monomer. Then, a 5 wt % of initiator (BPO) was added to the monomers mixture at room temperature. Composite resins were prepared by mixing the organic matrix with the silanized filler in the ratio of 45/55 by wt %. A similar formulation

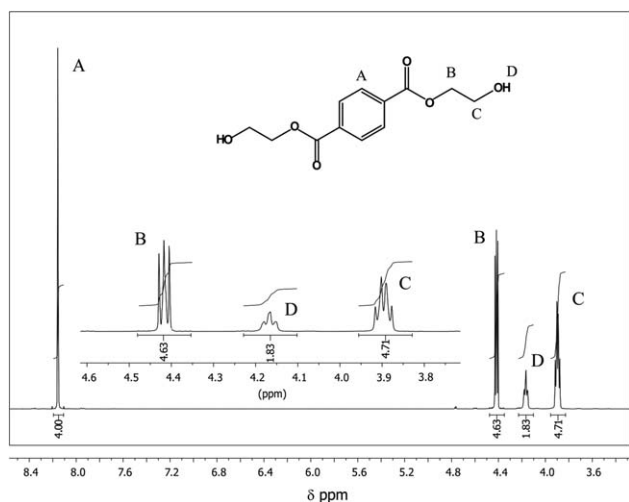


Figure 1.  $^1\text{H-NMR}$  spectrum for the BHET monomer.

containing Bis-GMA/TEGDMA (50/50 by wt %) was used as a control. Both of the formulated resins were polymerized in an oven at  $90^\circ\text{C}$  for 1 h. The composites were heat cured because visible light polymerization of the BACET resin formed a non-homogeneous composite.

#### Measurement of Double Bond Conversion

The double bond conversion of the composite resins was determined by infrared spectroscopy (FTIR). Samples were pulverized into a fine powder. Ten milligrams of the composite were thoroughly mixed with 100 mg of potassium bromide. This mixture was placed into the pelleting device and then compressed in a press to obtain a pellet about 0.5 mm thickness. The pellet was then placed into a standard sample holder. FTIR spectra of the uncured and cured samples were obtained in absorbance over the  $4000\text{--}300\text{ cm}^{-1}$  region with a resolution of  $4\text{ cm}^{-1}$  and a total of 32 scans per spectrum. For each spectrum, it was determined the height of the aliphatic  $\text{C}=\text{C}$  peak absorption at  $1638\text{ cm}^{-1}$  and the aromatic  $\text{C}=\text{C}$  peak absorption at  $1585\text{ cm}^{-1}$ . The aromatic  $\text{C}=\text{C}$  vibration was used as an

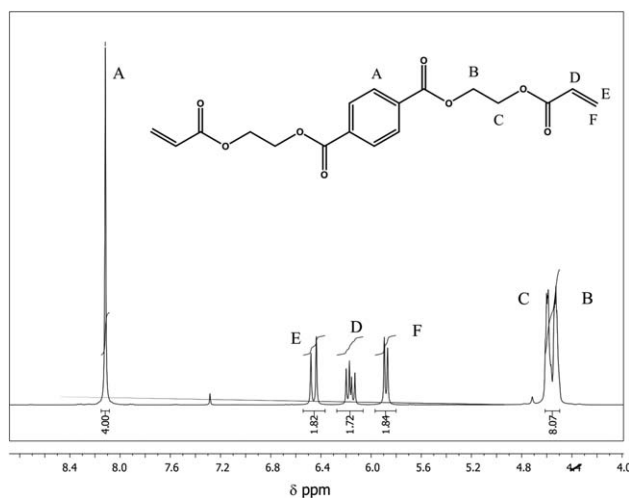


Figure 2.  $^1\text{H-NMR}$  spectrum for the BAET monomer.

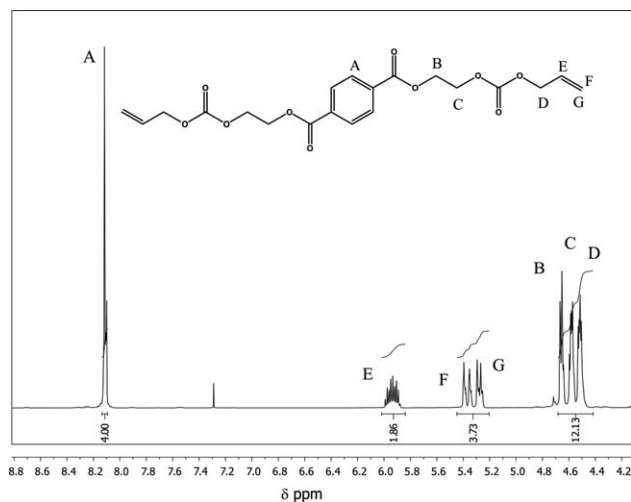


Figure 3.  $^1\text{H-NMR}$  spectrum for the BACET monomer.

internal reference. The double bond conversion was determined according to the following equation:

$$\text{Double bond conversion (\%)} = 100 \left[ 1 - \frac{\left( \frac{A_{1638}}{A_{1585}} \right)_{\text{polymer}}}{\left( \frac{A_{1638}}{A_{1585}} \right)_{\text{monomer}}} \right]$$

#### Water Sorption and Solubility

Sorption and solubility tests were determined according to the method described in the ISO International Standard No. 4049 for polymer-based restorative materials.<sup>19</sup> Specimen discs were prepared by filling a stainless steel mold (15 mm in diameter and 1 mm in thickness) with the unpolymerized composite. The samples were polymerized in an oven at  $90^\circ\text{C}$  for 1 h. After that, the specimen was removed from the mold and all the flashes and irregularities were removed by holding the specimen against 1000 grit abrasive paper. Three specimens were prepared for each sample.

Specimens were transferred to a desiccator. After 22 h, they were weighted to an accuracy of 0.1 mg. This cycle was repeated until a constant mass,  $m_1$ , was obtained (mass loss of each specimen was  $<0.1\text{ mg}$  in a 24 h period). Then, specimens were immersed in deionized water for 7 days. After that, they were

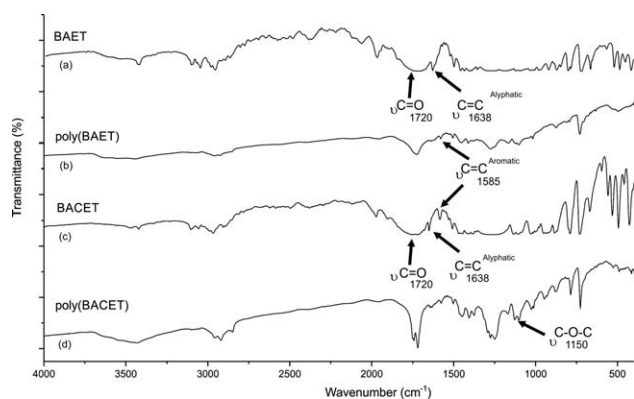
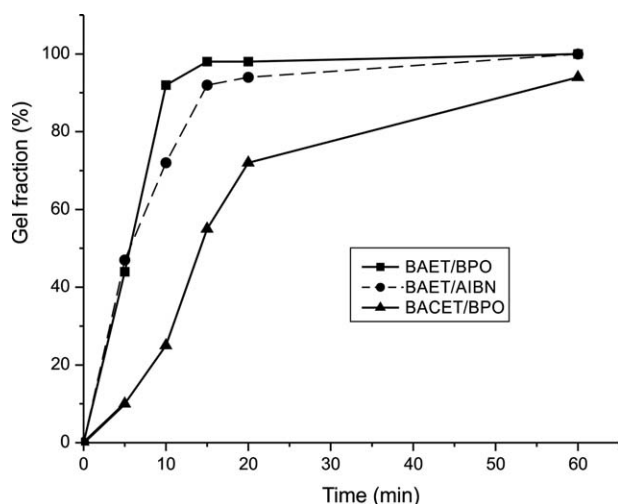


Figure 4. FTIR spectra of the BAET and BACET monomers (a and c) and their respective homopolymers (b and d).





**Figure 5.** Sol-gel conversion curves as a function of time for the homopolymerization of BAET and BACET using AIBN and BPO as initiators.

weighted and the mass was recorded as  $m_2$ . Finally, the specimens were reconditioned to constant mass in a desiccator using the cycle described previously; this new constant mass was recorded at  $m_3$ .

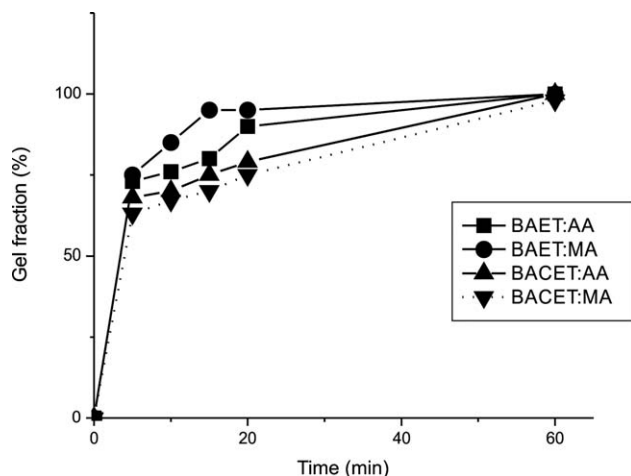
Water sorption ( $W_{sp}$ ) and solubility ( $W_{sl}$ ) for each specimen was calculated using the following equations:

$$W_{sp} = \frac{m_2 - m_1}{V} \quad W_{sl} = \frac{m_1 - m_3}{V}$$

where  $m_1$  is the conditioned mass in micrograms prior to immersion in water,  $m_2$  is the mass of the specimen, in micrograms, after immersion in water for 7 days,  $m_3$  represents the mass of the reconditioned specimen in micrograms and  $V$  is the calculated volume of the specimen in cubic millimeters.

### Flexural Properties

Flexural strength was measured in accordance with the International Standard Organization (ISO) Specification No. 4049,<sup>19</sup> while flexural modulus was measured in accordance to the American National Standard Institute/American Dental Association



**Figure 6.** Sol-gel conversion curves for the copolymers obtained from BAET with the acrylic monomers, and BACET with the acrylic monomers using the weight ratios 1 : 1 as a function of time.

**Table I.** Gel % for the Different Monomer Reacting Mixtures After 1 h of Polymerization

Crosslinking monomer : acrylic monomer ratio	BAET : AA Gel (%)	BAET : MA Gel (%)	BACET : AA Gel (%)	BACET : MA Gel (%)
1 : 1	100	81	100	95
1 : 2	98	100	100	98
1 : 10	75	100	78	100

(ANSI/ADA) Specification No. 27.<sup>20</sup> Bar-specimens were prepared by filling the uncured samples into a stainless steel mold (25 mm x 2 mm x 2 mm). The samples were heat polymerized into an oven at 90°C for 1 h. Three specimen bars were prepared and stored in distilled water at  $37 \pm 1^\circ\text{C}$  in dark for 24 h. A three-point bending test was carried out to evaluate the flexural properties of the cured samples, with an Instron 4465 universal testing machine, at a crosshead speed of 1.00 mm/min until fracture occurred. Flexural strength ( $\sigma$ ) and flexural modulus ( $E$ ), both in MPa were calculated using the following equations:

$$\sigma = \frac{3Fl}{2bh^2} \quad E = \frac{F_1 l^3}{4bh^3 d}$$

where  $F_1$  represents the load in Newton exerted on the specimen,  $F$  is the maximum load in Newton exerted on the specimen at the point fracture,  $l$  is the distance in mm between the supports,  $h$  is the height of the specimen in mm measured immediately prior to testing,  $b$  is the width of the specimen in mm measured immediately prior to testing, and  $d$  is the deflection corresponding to the load  $F_1$ .

### Statistical Analysis

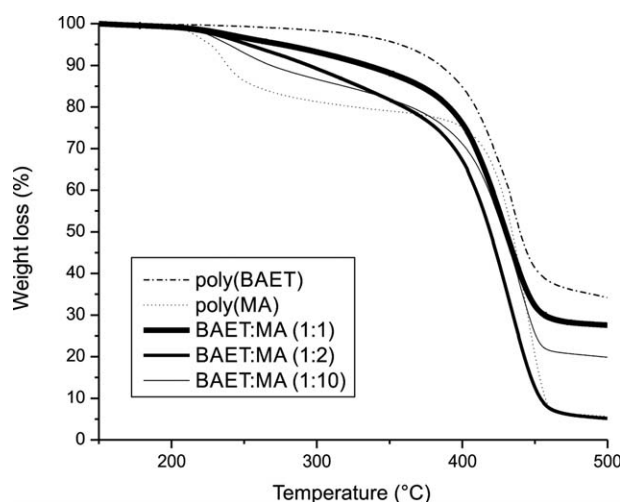
Double bond conversion, water sorption, solubility, flexural strength, and flexural modulus results were analyzed using one way analysis of variance ANOVA. Statistical differences were considered if  $P < 0.05$ .

## RESULTS AND DISCUSSION

PET depolymerization was carried out according to a modification of the method reported for Xi et al.<sup>21</sup> For the depolymerization of chips measuring  $3 \times 3$  mm, the optimal conditions

**Table II.** Weight Loss Percentage at 300°C for the Polymers and the Copolymers Synthesized

Crosslinking monomer : acrylic monomer ratio	BAET : AA Gel (%)	BAET : MA Gel (%)	BACET : AA Gel (%)	BACET : MA Gel (%)
1 : 0 (Poly(BAET) or Poly(BACET))	0	0	0	0
1 : 1	11	7	20	16
1 : 2	16	11	15	14
1 : 10	15	14	20	19
0 : 1 [Poly (AA) or poly(MA)]	25	19	25	19



**Figure 7.** TGA thermograms of the homopolymers derived from BAET and MA monomers, poly(BAET) and poly(MA) respectively, and of the copolymers obtained from them. Weight ratios indicated in parentheses.

used by Xi were weight ratios of 5 and 1% for the mixture EG/PET and catalyst/PET, respectively, and 3 h of reaction time to obtain a BHET yield of 86%. In this work, we observed a slightly higher yield, 89% after 2 h of depolymerization, using double EG and catalyst concentrations, for irregular PET particles ranging from 1 to 2.8 mm. It has been reported that for PET hydrolysis in alkaline conditions, the smaller the particle size the higher the rate and the degree of PET degradation, because smaller particles have increased surface area available for the reaction.<sup>7</sup> We observed faster conversions, about 45 min for smaller particle sizes, ranging from 0.1 to 1 mm. However, the conversion degree to BHET diminished to 70%. This could be attributed to the formation of hydrolysis by-products<sup>22</sup> due to the presence of adsorbed water in the PET pellets, because higher surfaces areas would tend to adsorb more water. Figure 1 shows the <sup>1</sup>H-NMR spectrum for the BHET and the corresponding peaks assignment. As can be seen, the product was obtained spectroscopically pure.

Figure 2 shows the <sup>1</sup>H-NMR spectrum and the assignment of peaks for BAET. Peaks D, E, and F confirm the presence of the acrylic moiety, besides, it can be seen that the monomer is spectroscopically pure through the integration of the signals corresponding to the four aromatic protons A and the eight aliphatic protons C and B. The <sup>1</sup>H-NMR spectrum for BACET can be seen in Figure 3. Peaks E, F, and G show the presence of the 6 protons corresponding to the allylic groups, while peaks B, C, and D integer for the 12 aliphatic protons.

Figure 4 shows the FTIR spectra corresponding to the BAET (a) and BACET (c) monomers and their homopolymers, poly(BAET) and poly(BACET) after 20 and 60 min of polymerization, respectively (b and d). Similar common signals can be observed: signals at 1585 cm<sup>-1</sup> correspond to the νC=C bonds of the aromatic groups, the peaks at about 1720 and 1150 cm<sup>-1</sup> are assigned to the stretching vibration of νC=O groups and the bending vibration of the νC—O—C bonds, respectively. Besides, the bis allyl carbonate monomer, BACET, and its polymer show in 1750 the signal assigned to the stretching νC=O of the carbonate group. The peaks at 1638 cm<sup>-1</sup> in Figure 4(a,c) are attributed to the stretching νC=C of the acrylic and allylic groups, respectively. In Figure 4(b,d) a noticeable decrease in these bands can be seen, which evidences a very high double bond conversion of the monomers to their respective homopolymers, specially for BAET.

In Figure 5, the variation of gel fraction as a function of time is observed. The polymerization of BAET with both BPO and AIBN showed similar conversion times, over 90% before 20 min of polymerization, while BACET reached a conversion nearby 80%. The noticeable sol-gel differences between the BAET and BACET, specially during the first minutes of homopolymerization is attributed to the higher reactivity of the acrylic moieties compared with the allylic groups.<sup>23</sup>

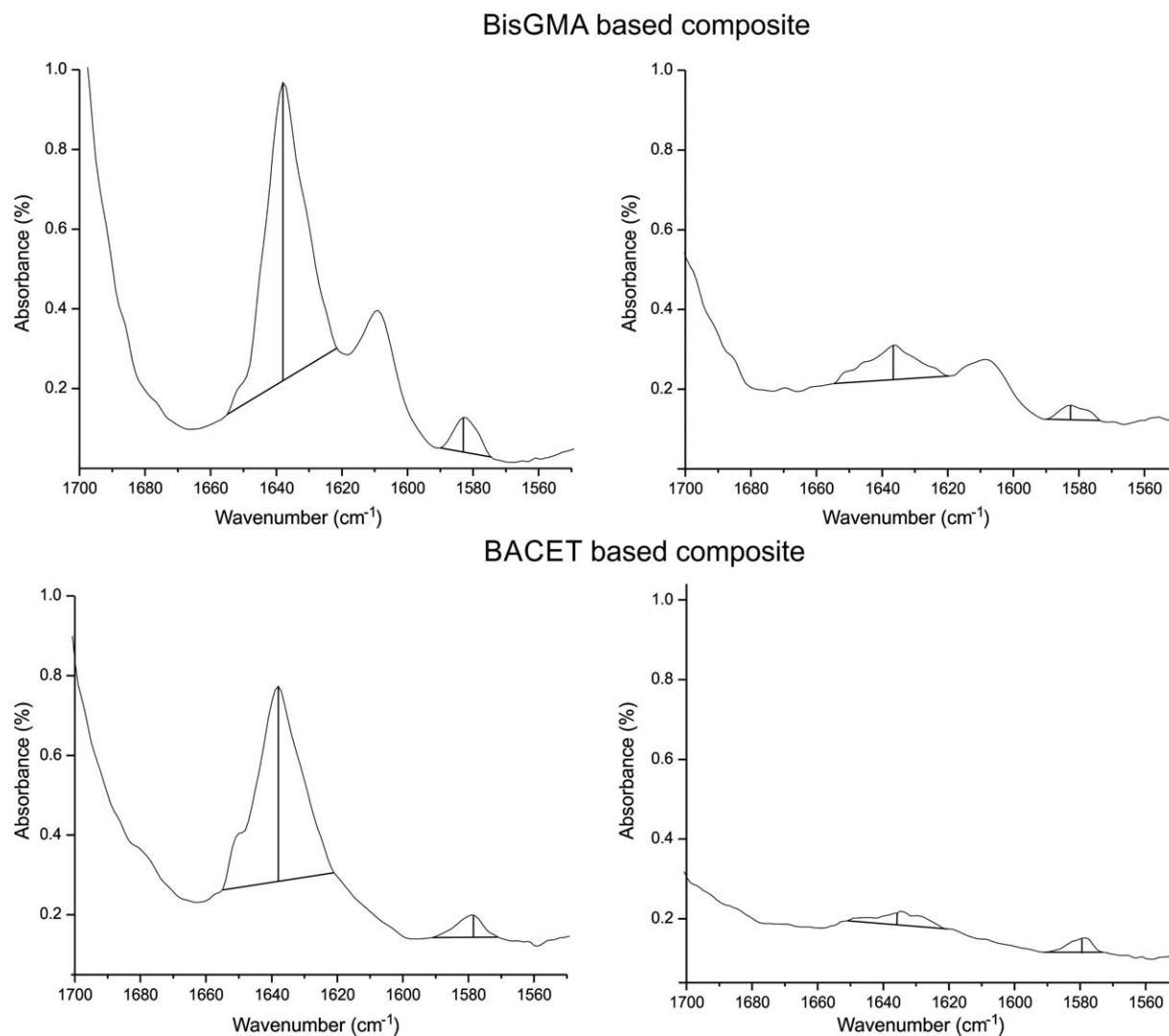
This different reactivity can be also observed during the first minutes of the polymerizations with acrylic and methacrylic acids using 1 : 1 ratio (Figure 6). It can be seen that from 0 to 5 min the gel fraction increased quickly up to 75% for the BAET mixtures, while gel fractions were lower in the case of BACET. However, after 1 h of polymerization reaction, gel fractions were similar for all the cases. Table I summarizes the gel percentages obtained for each one of the different copolymerizations. As can be seen, gel percentages close to 100% were obtained for most of the experiments after 1 h reaction time.

Regarding their thermal stability, Table II shows the weight loss at 300°C for the polymers and the copolymers synthesized. For all of the copolymers obtained, we observed that their thermal stability lay between that of the corresponding homopolymers, being the weight loss of the copolymers closer to the AA or MA homopolymers than to the poly(BAET) or poly(BACET) homopolymers, specially for the BACET copolymers. Figure 7 shows a representative set of thermograms, corresponding to the BAET : MA reacting mixture. Poly(BAET) showed thermal stability up to approximately 350°C, while poly(methacrylic acid), poly(MA), started its decomposition around 210°C. As can be seen, the three copolymer networks

**Table III.** Flexural Properties, Degree of Conversion, Water Sorption, and Solubility of the Materials Tested [Mean (Standard Deviation)] *n* = 3

Composite	Flexural strength (MPa)	Flexural modulus (MPa)	Degree of conversion (%)	Water sorption (μg/mm <sup>3</sup> )	Water solubility (μg/mm <sup>3</sup> )
Control resin	48.64 (6.8) <sup>a</sup>	4665.67 (289.03) <sup>a</sup>	70.11 (2.93) <sup>b</sup>	51.96 (3.39) <sup>a</sup>	6.52 (1.85) <sup>a</sup>
BACET resin	46.30 (2.6) <sup>a</sup>	3140.00 (390.52) <sup>b</sup>	87.98 (0.99) <sup>a</sup>	51.84 (1.76) <sup>a</sup>	8.28 (2.28) <sup>a</sup>

Common corresponding letters (a and b) in a given column indicate no significant difference.



**Figure 8.** FTIR spectra of the BisGMA (top) and BACET (bottom) based composites before (left) and after (right) polymerization.

had similar decomposition tendencies and were relatively close to each other up to 240°C, approximately. In general, the higher the proportion of crosslinking agent the higher the stability. This behavior can be due to the phenylene ring in BACET and BAET, as has been observed for the copolymerizations between MMA with divinylbenzene and styrene with bisphenol A dimethacrylate.<sup>24</sup> It is hypothesized that the rigidity of the aromatic ring prevents the movement of the fragments against bond scission.<sup>25</sup>

Good thermal stabilities have also been observed for copolymers formed from trimethacrylate and aromatic diacrylic monomers,<sup>26,27</sup> which could be also due, in part, to the aromatic character of the acrylic monomer. Thus, it is possible that the copolymers where BACET and BAET might be used show an improvement in their thermal stabilities, especially if high double bond conversions are obtained.

Another possible application for the synthesized monomers could be as Bis-GMA substitutes in external dental curing resins. BACET and BAET show structural resemblance with Bis-GMA,

whose aromatic backbone structure provides superior toughness to resin composites. Nevertheless, due to its high viscosity, it is necessary to use a diluent, usually TEGDMA. BACET was found to be slightly miscible in TEGDMA, only 10% at room temperature, while it dissolved up to 100% of its weight of BACET, when the mixture was heated at 42°C, melting point of BACET. Thus, only this one could be tested in a composite resin containing silica as the inorganic phase and TEGDMA as diluent. Double bond conversion, solubility, water sorption, and flexural properties of this resin were measured and compared against a similar formulation containing Bis-GMA instead of BACET (Table III).

In regards to flexural properties, flexural strength was found statistically similar for both formulations. Nevertheless, in spite of its higher degree of conversion, flexural modulus for the BACET formulation was lower. Therefore, this has lower rigidity and increased toughness compared with the Bis-GMA composite and is able to absorb better the shrinkage stress created during the polymerization.<sup>26,28</sup> The lower flexural modulus could be attributed to the following differences between the two monomers: (1) the Bis-GMA monomer units have

two hydroxyl groups, which can form strong hydrogen bonds and increase the rigidity of the polymer network; (2) the bisphenylene moiety in Bis-GMA is much more rigid than the terephthalate moiety in BACET; and (3) it is possible that the allyl carbonate group bring about slighter barriers to bond rotations<sup>27,29,30</sup> than the methacrylate group in Bis-GMA.

The differences on stiffness between the two monomers could also explain the noticeable differences on their degrees of conversion. Figure 8 shows the FTIR spectra for the composites evaluated before and after the curing process. This technique has proved to provide adequate double bond conversion values.<sup>31</sup> From these spectra, it can be seen that the peak at  $1638\text{ cm}^{-1}$  decreases in intensity once the polymerization process was carried out, this decrease is more noticeably for the BACET resin than for the Bis-GMA composite, Table III shows that double bond conversion for BACET composite is almost 20% higher than Bis-GMA composite. Although allylic radicals are more stable than acrylic radicals,<sup>23</sup> it seems that the flexibility of the BACET monomer favors higher degrees of double bond conversion, as has been reported for monomers with long flexible chains, where vitrification does not occur and final conversions of double bonds may reach 100%.<sup>27,32,33</sup> The high degree of conversion for the BACET is desirable because the higher the degree of conversion the lower of monomer that can be released to the oral environment, lowering its toxicity.

In the case of water sorption and solubility, values measured for the resin prepared from BACET were not statistically different than the corresponding values from the Bis-GMA resin. Studies have shown that water is absorbed predominantly within the matrix resin and is mainly affected by the structure and the amount of this phase.<sup>34–36</sup> Solubility is mainly influenced by monomer structure and degree of conversion, among other factors. Considering that the double bond conversion of the BACET monomer is higher than for the Bis-GMA, it would be expected that the water sorption and solubility of the former were lower than for the later. However, similarities could be explained based on the structural heterogeneity of polymers networks because the more densely crosslinked the network the more heterogeneous its structure.<sup>37,38</sup> Thus, the space created between the polymers chains is larger and can accommodate a larger quantity of water.<sup>39</sup> Other factors that favor water adsorption such as a higher flexibility in BACET and the presence of OH in Bis-GMA possibly also contribute to this similar behavior.

## CONCLUSIONS

Two novel bisacrylic (BAET) and bisallylcarbonate (BACET) monomers obtained from post-industrial PET were synthesized. Both of them were tested as crosslinking agents for AA and MA using thermal copolymerizations. Sol-gel conversions higher than 75% were obtained in all cases after 1 h of reaction at  $90^{\circ}\text{C}$ . It was found that the copolymers showed higher thermal stabilities than the acrylic homopolymers. Although BAET was more reactive than BACET, only the latter was able to be used in a dental composite as Bis-GMA substitute. A heat cured composite resin prepared by using BACET, TEGDMA and silanized silica showed similar water sorption, solubility, and flexural strength, but lower flexural modulus and higher degree of conversion, compared with a similar resin prepared using

Bis-GMA. This work presents new paths for potential applications of PET derived depolymerization monomers such as crosslinking agents with enhanced thermal stability and Bis-GMA substitutes for external dental composite resins.

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