



Synthesis and photopolymerization of novel, highly reactive phosphonated-urea-methacrylates for dental materials



Ayşe Altın^a, Burcin Akgün^a, Özlem Büyükgümüş^a, Zeynep Saraylı Bilgici^a, Sesil Agopcan^a, Didar Asik^b, Havva Yagci Acar^c, Duygu Avcı^{a,*}

^a Department of Chemistry, Bogazici University, 34342 Bebek, Istanbul, Turkey

^b Department of Molecular Biology and Genetics, Koc University, Rumelifeneri Yolu, Sariyer, Istanbul, Turkey

^c Department of Chemistry, Koc University, Rumelifeneri Yolu, Sariyer, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 23 January 2013

Received in revised form 30 June 2013

Accepted 2 July 2013

Available online 16 July 2013

Keywords:

Synthesis

Photopolymerization

Dental composites

Reactive diluents

Phosphonates

ABSTRACT

An urea methacrylate (**1**) and two phosphonated methacrylates (**2–3**) were synthesized from 2-isocyanoethyl methacrylate (IEM) and benzyl amine (**1**), diethyl aminomethylphosphonate (**2**) and diethyl amino(phenyl)methylphosphonate (**3**). Their photopolymerization rates are notably higher than commercial monomers, despite the presence of only one double bond. Their polymerization rates follow the order **1** ~ **2** > **3** ~ triethylene glycol dimethacrylate (TEGDMA) > 2-hydroxyethyl methacrylate (HEMA). A tendency toward high crosslinking density during thermal bulk polymerizations, low oxygen sensitivity and high conversions with benzophenone during photopolymerization indicated the importance of hydrogen abstraction/chain transfer reactions. It was found that the addition of the monomers to HEMA significantly increased its polymerization rate, proving their utility as replacements for TEGDMA as reactive diluents for 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyl)oxy] phenyl] propane (Bis-GMA). Copolymer systems containing **2** and **3** showed improved T_g values compared to Bis-GMA/TEGDMA systems.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Acrylates and methacrylates are the most commonly used monomers in photoinitiated polymerizations due to their high reactivities and the excellent properties (especially optical and mechanical) of their resultant polymers, which find use as dental restorative materials, biomaterials, coatings, adhesives and in photolithography [1–5]. Extensive research has been performed to investigate the relationship between the structure of potential monomers and their reactivity to enhance the polymerization process and final materials [6–17].

Among the hydrogen bonding monomers investigated by Janzen and Berchtold, monomers containing urea were found to be the most reactive [14,15]. For example, the photopolymerization rate of ethyl urea ethyl acrylate (25.2 mol ls^{-1}) was higher than that of ethyl O-urethane-N-ethyl acrylate (16.1 mol ls^{-1}) and ethyl ester ethyl acrylate (4.4 mol ls^{-1}) [14]. Benzyl urea ethyl methacrylate was found to be the most reactive of any of the urethane, carbonate, cyclic carbonate, ester, or hydroxyl monomers studied by Berchtold et al. [15] The high reactivities were explained by a hydrogen bonding-induced pre-organization

that brings double bonds close to each other, enhancing propagation. Alternatively, a reduction in termination rate may also be involved in, or be the sole cause of, the observed reactivity.

The monomer 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (Bis-GMA) is the most commonly used precursor for dental composite materials due to its high mechanical strength, low volatility and low polymerization shrinkage [3,18,19]. However, its high viscosity requires dilution with a low viscosity monomer, such as triethylene glycol dimethacrylate (TEGDMA), to improve both the double bond conversion and its ease of handling. Although the double bond conversion is increased by the addition of TEGDMA, increased volume shrinkage and shrinkage-associated stress decreases the bond strength between the tooth tissue and composite, initiating bacterial leakage and decreasing the lifetime of the dental composite. When Bis-GMA is copolymerized with TEGDMA, a final conversion of 50–75% is obtained depending on the monomer composition and photopolymerization conditions. These low conversions are due to the formation of a highly crosslinked polymer in the early stages of polymerization that restricts mobility within the system, decreasing both the propagation and termination rates. Therefore, in recent years, various highly reactive mono-(meth)acrylates have been investigated as alternatives to TEGDMA. With the use of such

* Corresponding author. Tel.: +90 2123596816; fax: +90 2122872467.

E-mail address: avcid@boun.edu.tr (D. Avcı).

monomers, similar levels of crosslinking density are attained at much higher conversions because these reactive monomer are less prone to affect crosslinking than TEGDMA.

We propose that urea-containing monomers may be suitable for this purpose. To test this hypothesis, we designed two new urea-containing monomers functionalized with phosphonate groups for improved biocompatibility and binding properties. A previously reported [15], structurally similar monomer was also investigated to test the correlation between the monomer structure and photopolymerization reactivity. Both homopolymerizations and copolymerizations with commercial dental monomers were investigated.

2. Experimental

2.1. Materials

Diethyl amino(phenyl)methylphosphonate and diethyl aminomethylphosphonate were prepared according to literature procedures [20,21]. Chloroform was dried over activated molecular sieves (4 Å). Diethyl phosphite, 2-isocyanatoethyl methacrylate (IEM), Al(OTf)₃, benzaldehyde, diethyl phthalimidomethylphosphonate, hydrazine hydrate, 2-hydroxyethyl methacrylate (HEMA), triethylene glycol dimethacrylate (TEGDMA), hexyl acrylate (HA), 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyloxy) phenyl] propane (Bis-GMA), 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-dimethoxy-2-phenyl acetophenone (DMPA), benzophenone (BP) and all other reagents and solvents were obtained from Aldrich Chemical Co. and used as received.

2.2. Characterization

¹H, ¹³C and ³¹P NMR spectra were obtained on Varian Gemini (400 MHz) spectrometer. IR spectra were obtained on a Nicolet 6700 FTIR spectrometer. Elemental analyses were obtained on a Thermo Electron SpA FlashEA 1112 elemental analyzer (CHNS separation column, PTFE; 2 m; 6 × 5 mm). Photopolymerizations were performed using a TA Instruments Q100 differential photocalorimeter (DPC). Dynamic mechanical analysis (DMA) was performed on a Perkin Elmer Pyris Diamond DMA.

2.3. Synthesis of monomers

2.3.1. General procedure for the synthesis of monomers 1–3

To an ice-cold solution of the desired amine (2.8 mmol) in 10.2 mL of dry chloroform under a stream of nitrogen, 2-isocyanatoethyl methacrylate (2.9 mmol, 0.41 mL) was added dropwise. The solution was stirred at room temperature overnight under nitrogen and then extracted with 1 wt% NaOH (3 × 42 mL), 1 wt% HCl (3 × 42 mL), and brine (3 × 42 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to leave the crude product.

2.3.1.1. Monomer 1. The crude product was recrystallized from diethyl ether and dried under vacuum. The pure product was obtained as a white solid in 75% yield (mp = 70 °C).

¹H NMR (400 MHz, CDCl₃, δ): 1.82 (s, 3H, CH₃), 3.33 (t, 2H, OCH₂CH₂), 4.07 (t, 2H, OCH₂CH₂), 4.21 (s, 2H, CH₂–Ar), 5.12, 5.26 (bs, 2H, NH), 5.46, 5.98 (s, 2H, C=CH₂), and 7.16–7.24 (m, 5H, Ar–H).

¹³C NMR (400 Mz, CDCl₃, δ): 18.34 (CH₃), 39.58 (OCH₂CH₂), 44.47 (NH–CH₂), 64.08 (OCH₂CH₂), 125.96 (CH₂=C), 135.96 (CH₂=C), 127.30, 127.36, 128.60, 139.10 (Ar–C), 158.21 (HN–C=O), and 167.53 (O–C=O) ppm.

FTIR (ATR): 3321 (N–H), 3060, 3062 (Ar–H), 2960, 2928, 2890 (C–H), 1711 (C=O), 1628 (C=C), and 1587 (N–H) cm⁻¹.

2.3.1.2. Monomer 2. The pure product was obtained as a colorless viscous liquid in 77% yield.

¹H NMR (400 MHz, CDCl₃, δ): 1.25 (t, 6H, OCH₂CH₃), 1.87 (s, 3H, CH₃), 3.43 (t, 2H, OCH₂CH₂), 3.60 (m, 2H, CH₂–P), 4.02 (m, 4H, OCH₂CH₃), 4.13 (t, 2H, OCH₂CH₂), 5.80, 6.43 (s, 2H, C=CH₂), 6.05, 6.25 (bs, 2H, NH) ppm.

¹³C NMR (400 MHz, CDCl₃, δ): 15.36 (OCH₂CH₃), 17.17 (CH₃), 33.21, 34.95 (CH₂–P), 38.15 (OCH₂CH₂), 61.60 (OCH₂CH₃), 63.31 (OCH₂CH₂), 124.76 (CH₂=C), 135.14 (CH₂=C), 157.59 (HN–C=O), and 166.28 (O–C=O) ppm.

FTIR (ATR): 3349 (N–H), 2983, 2929, 2901 (C–H), 1716, 1686 (C=O), 1644 (C=C), 1561 (N–H), 1215 (P=O), 1019, 948 (P–O–Et) cm⁻¹.

³¹P NMR (CDCl₃): 24.44 ppm.

2.3.1.3. Monomer 3. The crude product was recrystallized from diethyl ether and washed with hexane. The pure product was obtained as a white solid in 70% yield (mp = 72 °C).

¹H NMR (400 MHz, CDCl₃, δ): 1.01, 1.29 (t, 6H, OCH₂CH₃), 1.78 (s, 3H, CH₃), 3.35 (m, 2H, OCH₂CH₂), 3.59, 3.77, 4.01 (m and t, 4H, OCH₂CH₃), 4.15 (m, 2H, OCH₂CH₂), 5.36, 5.91 (s, 2H, C=CH₂), 5.41 (dd, 1H, CH–P), 5.99 and 7.09 (t and dd, 2H, NH), 7.20–7.41 (m, 5H, Ar–H) ppm.

¹³C NMR (400 MHz, CDCl₃, δ): 16.16 (OCH₂CH₃), 18.05 (CH₃), 38.73 (OCH₂CH₂), 49.87, 51.51 (CH–P), 63.18 (OCH₂CH₃), 64.01 (OCH₂CH₂), 125.44 (CH₂=C), 136.03 (CH₂=C), 127.81, 127.99, 128.34, 135.96 (Ar–C), 157.77 (HN–C=O), and 167.13 (O–C=O) ppm.

FTIR (ATR): 3379, 3317 (N–H), 3060, 3032 (Ar–H), 2987, 2929, 2907 (C–H), 1722, 1684 (C=O), 1638 (C=C), 1545 (N–H), 1216 (P=O), 1014, 980 (P–O–Et) cm⁻¹.

³¹P NMR (CDCl₃): 23.22 ppm.

ELEM. ANAL., Calcd. for C₁₈H₂₇N₂O₆P: C, 54.27%; H, 6.83%; N, 7.03%; O, 24.10%; P, 7.77%. Found: C, 54.54%; H, 7.31%; N, 7.31%.

2.4. Photopolymerization

Photopolymerizations were conducted using a DSC equipped with a mercury arc lamp. The samples (3–4 mg) containing 2.0 mol% initiator were irradiated for 10 min at either 40 °C or 72 °C with an incident light intensity of 20 mW/cm² and a nitrogen flow of 20 mL min⁻¹. Polymerization rates were calculated using the following formula:

$$\text{Rate} = \frac{(Q/s)M}{n\Delta H_p m}$$

where Q/s is the heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule, ΔH_p the heat released per mole of double bonds reacted, and m is the mass of monomer in the sample. The value used for the ΔH_p of a methacrylate double bond was 13.12 kcal/mol [22].

2.5. Calculation of dipole moments

Boltzmann-averaged dipole moments were calculated with PM3 for all the monomers. In this procedure, all possible rotations around single bonds were considered for a given acrylate to generate all the conformations corresponding to stationary points. Minimization, followed by the calculation of the Boltzmann-averaged dipole moments for all the conformations, was carried out with PM3 in the Spartan '06 program [23]. The unique structures were

Download English Version:

<https://daneshyari.com/en/article/5210029>

Download Persian Version:

<https://daneshyari.com/article/5210029>

[Daneshyari.com](https://daneshyari.com)