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Thermal radical polymerization of Bis(methacrylamide)s

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Abstract

Methacrylamides monomers for dental applications were synthesized using a one-step procedure starting from methacrylic anhydride and the respective diamine: *N,N'*-(propane-1,3-diyl)-bis(*N*-ethyl-2-methylacrylamide) (**1**), *N,N'*-(butane-1,4-diyl)-bis(2-methacrylamide) (**2**), *N,N'*-(octane-1,8-diyl)-bis(2-methylacrylamide) (**3**) and *N,N'*-(1,4-phenylene)-bis(2-methylacrylamide) (**4**). The structures were confirmed by ¹H NMR, ¹³C NMR, FTIR-ATR and UHPLC-QTOF-MS. Thermal polymerization kinetics was investigated by modulated DSC for monomers (**2**), (**3**) and (**4**) using heating rates of 1, 2, 3 and 5 °C min⁻¹. All IR spectra showed the C=C axial deformation at 1610 cm⁻¹, in ¹H NMR spectra the olefinic hydrogens were observed at 5.3 and 5.8 ppm and in ¹³C NMR, the vinylic carbons at 120 and 140 ppm. The exact m/z values were: 267.2068, 225.1595, 281.2222 and 245.1283 for monomers (**1**), (**2**), (**3**) and (**4**), respectively. The activation energy was: -182.7; -165.8 and -156.7 kJ mol⁻¹ for monomers (**2**), (**3**) and (**4**), respectively. Monomers are promising candidates for use as hydrolytic stable adhesive systems for dental applications.

Keywords: adhesives, monomers, kinetics, differential scanning calorimetry (DSC), synthesis.

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1. Introduction

Dental hard tissues (enamel and dentin) achieve a strong bond with restorative polymers by means of dental adhesives. These dental adhesives are compounds of hydrophilic and hydrophobic monomers, photoinitiators and solvents^[1]. Crosslinking dimethacrylates and acrylates are the most commonly monomers used in adhesives due to improvement of polymerization reactivity and material properties^[2-4]. The long-term durability of adhesive/dentin interface depends on the functional monomers and polymer chain integrity^[5,6]. However, the methacrylate monomers present low hydrolytic stability mainly in acid environments as in single-bottle adhesive^[7-9].

In this respect, methacrylamides and acrylamides were synthesized due to the hydrolytic stable amide group instead of an ester group, and also to their similarity to the amino acids as collagen fibrils that could facilitate hydrogen bond between collagen and amide groups^[9-15]. Bis(acrylamide)s and bis(methacrylamide)s have been synthesized via acryloyl chloride or methacryloyl chloride with diamines resulting sometimes in solid monomers, with a very low solubility in organic solvents and difficult purification^[16-22]. In this context, suitable liquid bis-(acrylamide)s *N,N'*-diethyl-1,3-bis(acrylamido)propane (DEAAP), *N,N'*-dimethyl-1,3-bis(acrylamido)propane (DMAAP), and *N,N'*-dimethyl-1,6-bis(acrylamido)hexane (DMAAH) were

synthesized as substitute to methacrylates commonly used in adhesive systems such as TEGDMA (triethylene glycol dimethacrylate) or HEMA (2-hydroxyethyl methacrylate) and improving hydrolytic stability of dental adhesives^[16,23,24].

Monomers with reactivity, obtained with good yields and synthesized by one-step synthetic route are important to development of simplified dental adhesives. Thus, the aim of this study is the synthesis of hydrolytically stable bis(methacrylamide) monomers for dental applications by one-step synthetic route and the investigation their kinetic thermal polymerization by DSC using Kissinger methodology^[23].

2. Materials and Methods

2.1 Materials

N,N'-diethyl-1,3-propanediamine, methacrylic anhydride and 4-(dimethylamino)pyridine were purchased from Sigma-Aldrich and used without any further purification. 1,8-diaminooctane, 1,4-diaminobutane and *p*-phenylenediamine were purchased from Alfa Aesar and also used without any further purification. Triethylamine and solvents as dichloromethane, tetrahydrofuran, hexane and ethyl acetate were purchased from local suppliers. Dichloromethane was dried by refluxing with calcium hydride and further

distillation under N₂ atmosphere. Column chromatography was performed using Silica gel Si 70 – 230 Mesh (supplied by Sigma Aldrich) as stationary phase.

2.2 Monomer synthesis

Synthesis of *N,N'*-(propane-1,3-diyl)-bis(*N*-ethyl-2-methylacrylamide) (**1**)

To a solution of *N,N'*-diethyl-1,3-propanediamine (0.5 g; 3.84 mmol), triethylamine (1.5 eq.) and 4-(dimethylamino)pyridine (5 mol%) in 12 mL of anhydrous dichloromethane, a solution of methacrylic anhydride (1.5 eq.) in 12 mL of anhydrous dichloromethane was added dropwise in an ice bath. After 16 hours at room temperature, 6 mL of water was added and the solution was extracted with dichloromethane (3 x 5 mL). After drying the organic phase with anhydrous Na₂SO₄, the solvent was removed in rotatory evaporator. The crude product was purified by column chromatography, eluting with hexane:ethyl acetate (70:30) to give monomer (**1**) as yellow viscous oil. Yield: 50 %. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.10 (s, 2H); 5.01 (s, 2H), 3.51 – 3.25 (m, 8H); 1.97 (m, 6H); 1.85 (m, 2H); 1.15 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.5 (2); 141.1 (2); 114.3 (2); 114.3 (2); 43.1 (2); 41.4 (2); 27.6 (2); 20.6 (2); 14.3 (2).

Synthesis of *N,N'*-(butane-1,4-diyl)-bis(2-methylacrylamide) (**2**)

A solution of methacrylic anhydride (2.1 eq.) of dry dichloromethane (10 mL) was added dropwise to a solution of 1,4-diaminobutane (0.510 g; 57.72 mmol) and triethylamine (2.1 eq.) in dry dichloromethane (30 mL) in an ice bath. After stirring 16 hours at room temperature, water (10 mL) was added to the reaction and the aqueous phase was extracted with dichloromethane (3 x 10 mL). After drying the organic phase with anhydrous Na₂SO₄ the solvent was evaporated. The crude product was purified by precipitation in hexane to afford monomer (**2**) as a white solid. Yield: 61 %. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.27 (s, 2H); 5.69 (s, 2H); 5.32 (s, 2H); 3.34 (q, *J* = 6.2 Hz, 4H); 1.96 (s, 6H); 1.60 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.7 (2); 140 (2); 119.4 (2); 39.2 (2); 26.9 (2); 18.7 (2). Mp: 127.4 °C.

Synthesis of *N,N'*-(octane-1,8-diyl)-bis(2-methylacrylamide) (**3**)

A solution of methacrylic anhydride (2.5 eq.) in dry dichloromethane (10 mL) was added dropwise to a solution of 1,8-diaminooctane (0.510 g; 3.46 mmol) and triethylamine (3.5 eq.) in 30 mL of dry dichloromethane in an ice bath. After stirring 16 hours at room temperature, water (10 mL) was added to the reaction and the aqueous phase was extracted with dichloromethane (3 x 10 mL). After drying the organic phase in anhydrous Na₂SO₄ the solvent was removed in rotatory evaporator. The crude product was purified by precipitation in hexane to afford monomer (**3**) as a white solid. Yield: 48 %. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.05 (s, 2H); 5.67 (s, 2H); 5.30 (s, 2H); 3.28 (q, *J* = 6.8 Hz, 4H); 1.96 (s, 6H); 1.53 (qt, *J* = 6.8 Hz, 4H); 1.32 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.5 (2); 140.3 (2); 119.1 (2); 39.7 (2); 29.5 (2); 29.1 (2); 26.8 (2); 18.7 (2). Mp: 109.2 °C.

Synthesis of *N,N'*-(1,4-phenylene)-bis(2-methylacrylamide) (**4**)

To a solution of *p*-phenylenediamine (0.515 g; 4.62 mmol) and triethylamine (3.5 eq.) in 30 mL of anhydrous dichloromethane, was added dropwise a solution of methacrylic anhydride (3.5 eq.) in anhydrous dichloromethane (10 mL) in an ice bath for 30 minutes. After stirring 16 hours at room temperature, water (15 mL) was added and the solution was extracted with tetrahydrofuran (3 x 10 mL). The organic phase was dried under anhydrous Na₂SO₄ and the solvent was removed in rotatory evaporator. The crude product was purified by precipitation in hexane to afford the monomer (**4**) as a white solid. Yield: 31 %. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 9.73 (s, 2H); 7.61 (s, 4H); 5.79 (s, 2H); 5.49 (s, 2H); 1.95 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 166.5 (2); 140.4 (2); 134.7 (2); 120.4 (4); 119.7 (2); 18.8 (2). Mp: 246.5 °C.

2.3 Monomer characterization

2.3.1 Nuclear Magnetic Resonance (NMR)

NMR measurements were recorded on a Bio Spin GmbH (Bruker Biospin, Rheinstetten, Germany), ¹H: 400 MHz, ¹³C: 100 MHz, in CDCl₃ using tetramethylsilane (TMS) as standard or DMSO-*d*₆. The multiplicities were attributed as: *s* = singlet; *d* = doublet; *t* = triplet; *q* = quartet; *qt* = quintuplet; *dd* = double doublet; *ddd* = double double doublet; *m* = multiplet. The hydrogen assignments were attributed based on relative integral and coupling constant (*J*) in Hertz (Hz).

2.3.2 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR measurements were performed in the Bruker Alpha FTIR Spectrometer (Bruker Optics, Ettlingen, Germany). The monomers were dispensed over a diamond crystal of Attenuated Total Reflectance (ATR) accessory. A total of 64 scans were collected from 400 cm⁻¹ to 4000 cm⁻¹ at 4 cm⁻¹ resolution.

2.3.3 Ultra-High Liquid Chromatography Quadrupole Time of Flight Mass Spectrometry (UHPLC-QTOF-MS)

High-resolution mass spectra were obtained with a Q-TOF Micro instrument (Impact II, Bruker,) in electrospray ionization positive (ES⁺) mode. A Q-TOF system was used to separate the analytes of interest. Shim-pack XR-ODS III column (50 mm X 2 mm X 1.6 μm) was used to separate the analytes in isocratic mode with the mobile phase 40 % acetonitrile (0.1 % formic acid); 60 % water (0.1 % formic acid) (LC, Nexera x2, Shimadzu, Tokyo, Japan). The flow rate was 0.4 mL min⁻¹ and column temperature was 35 °C. The optimal MS parameters were as following: capillary voltage 4500 V, source temperature 200 °C, end plate offset voltage 500 V, mass range (*m/z*) of 60-800 and calibration with sodium formate.

2.3.4 Thermal polymerization kinetics

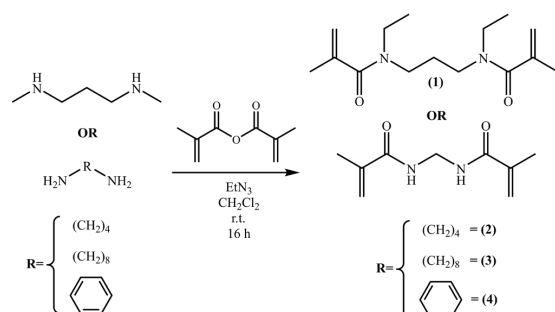
The polymerization kinetics of monomers (**2**), (**3**) and (**4**) were investigated using modulated differential scanning calorimetry technique (MDSC, Q2000, TA Instruments). Three samples were analyzed with temperature range of 0–300 °C using an aluminum pan, at different heating rates

(1, 2, 3 and 5 °C min⁻¹), with 100 s of period, amplitude of ± 1.0 °C, under nitrogen atmosphere with flow rate of 50 mL min⁻¹ and with sample weight about 2.0 mg. The maximum temperature peak obtained from nonreverse curve was used to determine the activation energy of the polymerization according to Kissinger methodology^[24].

3. Results and Discussions

3.1 Synthesis and characterization of monomers

Bis(methacrylamide)s were prepared in one-step reaction between methacrylic anhydride and diamines as showed in Scheme 1.



Scheme 1. Bis(methacrylamide)s synthesis.

The following monomers were synthesized with yields higher than 30 %: *N,N'*-(propane-1,3-diyl) bis(*N*-ethyl-2-methylacrylamide) (**1**), *N,N'*-(butane-1,4-diyl) bis(2-methylacrylamide) (**2**), *N,N'*-(octane-1,8-diyl) bis(2-methylacrylamide) (**3**) and *N,N'*-(1,4 phenylene) bis(2-methylacrylamide) (**4**). As expected, monomer (**1**) having an ethyl substituent at nitrogen atom (*N,N*-dialkylamide) was liquid, while monomers (**2**), (**3**) and (**4**) were white solids. The C=C double bond axial deformation of monomers was detectable in the IR spectrum at 1610 cm⁻¹, while C=O stretching appeared at 1660 cm⁻¹, N-H at 3300 cm⁻¹ and C-N at 1520 cm⁻¹, confirming the synthesis of monomers (Figure S1, Supplementary Material). The signals of olefinic hydrogens of the compounds were detected by ¹H NMR at 5.3 and 5.8 ppm, while the sp²-hybridized C-atoms of the acrylamide double bonds were observed at 120 and 140 ppm in the ¹³C NMR spectra. Complete assignments of the monomers structures were given in Figure S2 (Supplementary Material). The signals of olefinic hydrogens of the compounds were detected by ¹H NMR at 5.3 and 5.8 ppm, while the sp²-hybridized C-atoms of the acrylamide double bonds were observed at 120 and 140 ppm in the ¹³C NMR spectra. Complete assignments of the monomers structures were given in Figure S2 (Supplementary Material). The exact m/z value of each monomer was determined by UHPLC-QTOF-MS, and the structure confirmed by comparison with theoretical isotopic profile, Table 1 and Figure S3 (Supplementary Material). Error values lower than 1.2 ppm (corresponding to a 20 mDa) and mSigma values ranged from 3.4 to 17.2 for the synthesized monomers were obtained. According to the manufacturer the err value below 5 ppm and mSigma below 20 is considered acceptable results.

Table 1. Exact m/z value for the synthesized monomers.

Monomer	Molecular Structure	m/z (g/mol)	err (ppm)
(1)		267.2068	0.2
(2)		225.1595	1.2
(3)		281.2222	0.6
(4)		245.1283	0.6

3.2 Thermal polymerization of the monomers

Differential scanning calorimetry (DSC) is the most used thermal analysis technique in material sciences because of its ability to provide detailed information about both the physical and energetic properties of a substance and/or formulation. However, conventional DSC was not used in this study due to shortcomings with respect to weak transitions and overlapping events, which could be solved by the use of the more sophisticated modulated DSC (mDSC). In Figure 1 is showed the reverse, nonreverse and total heat flow of monomer (**2**) at a heating rate of 5 °C min⁻¹. Total heat flow presented an endothermic event (related to monomer melting) followed by an exothermic event corresponding to the thermal polymerization. Using modulated DSC both events could be well separated, allowing the determination of the melting peak in the reverse heat flow and the polymerization enthalpy in the nonreverse heat flow (Table 2).

Unexpectedly, no exothermic event corresponding to the thermal polymerization was observed in DSC for the monomer (**1**) *N,N'*-(propane-1,3-diyl)bis(*N*-ethyl-2-methylacrylamide) in the investigated temperature range. To verify the monomer photochemical polymerization 1 mol % of camphorquinone

(CQ) and 1 mol % of ethyl 4-dimethylaminobenzoate (EDAB) were added and was investigated by PhotoDSC^[23] (see Supplementary Material for experimental conditions). Even after 600 s of photopolymerization the polymerization not occurred. It is known from the literature that *N*-disubstituted methacrylamides show a very low reactivity in radical homopolymerization, which can be explained on the basis of steric effects of the substituents of the amide group^[25]. This behavior was not observed neither for *N,N*-disubstituted bis(acrylamide) nor for *N*-substituted bis(methacrylamide) that were commonly used in hydrolytically stable dental adhesive formulations^[16]. Monomers (**2**), (**3**) and (**4**) are *N*-substituted bis(methacrylamide) and polymerized by radical thermal auto initiation (Table 2).

Different chemical structure of monomers resulted in activation energy (E_a) between -156.7 kJ mol⁻¹ for monomer (**4**) to -182.7 kJ mol⁻¹ for monomer (**2**). The presence of phenyl ring in monomer (**4**) makes the double bond more electron-deficient and more susceptible to polymerize (lower activation energy). The more flexible structure of monomer (**3**) also favors the polymerization reaction and the E_a is lower than monomer (**2**). No glass transition temperature could be observed in the second heating curve.

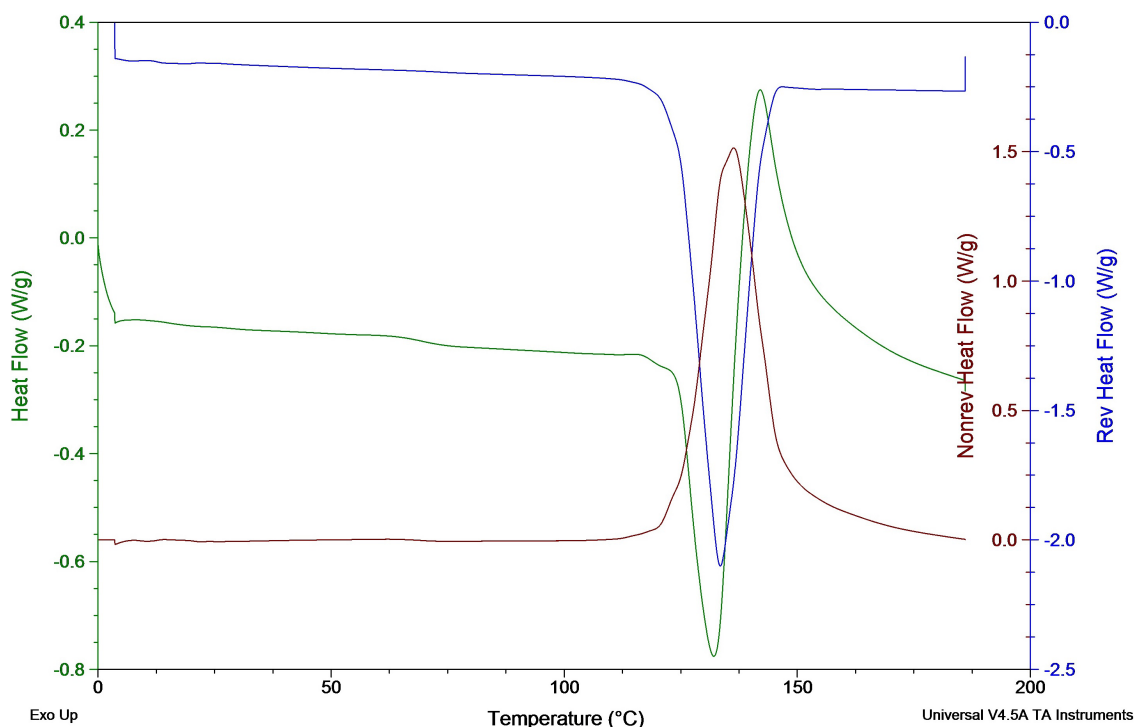


Figure 1. MDSC curves of monomer (**2**) at a heating rate of 5 °C min⁻¹ with 100 s of period, amplitude of ± 1.0 °C.

Table 2. Results of thermal kinetics, temperature maximum (T_{max}) according with heating rate, activation energy (E_a – kJ mol⁻¹) and correlation constant (R^2) of monomers (M).

M	T_{max} (°C)				E_a kJ mol ⁻¹	R^2
	1 °C min ⁻¹	2 °C min ⁻¹	3 °C min ⁻¹	5 °C min ⁻¹		
(2)	119.31	121.5	122.5	129.4	182.7	0.83
(3)	114.2	113.2	118.0	122.6	165.8	0.72
(4)	259.0	273.0	268.3	260.4	156.7	0.64

4. Conclusions

The synthetic route used in this study resulted in solid and liquid monomers with yields higher than 30 %. Moreover, the monomer (**1**) showed appropriate color and viscosity to dental adhesive application, but during characterization did not polymerized due to steric effects. The investigation of the thermal polymerization of monomers (**2**), (**3**) and (**4**) was obtained only by mDSC due to separation of cure and melting peaks and the monomer 4 showed the higher reactivity.

5. Acknowledgements

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Supplementary Material

Supplementary material accompanies this paper.

Figure S1. IR spectra of monomers **(1)**, **(2)**, **(3)** and **(4)**.

Figure S2. ¹H NMR and ¹³C NMR of monomers **(1)**, **(2)**, **(3)** and **(4)**.

Figure S3. Mass spectra of monomers **(1)**, **(2)**, **(3)** and **(4)** and theoretical isotopic profile.

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