

# Synthesis and Structural Characterization of Novel Urethane-Dimethacrylate Monomer with Two Quaternary Ammonium Groups <sup>†</sup>

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**Abstract:** Composite restorative materials with dimethacrylate matrices are commonly used as dental fillings. They have good usable properties, however, lack antibacterial activity. It may promote secondary caries. A solution to that problem can be the application of monomers with micro-biologically active quaternary ammonium groups. This research aimed at the synthesis of a new urethane-dimethacrylate monomer having the 1,3-bis(2-isocyanatopropan-2-yl)benzene (TMXDI) core, and two arms having quaternary ammonium group with the decyl substituent. The structure of obtained monomer was confirmed by FTIR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies.

**Keywords:** urethane-dimethacrylate; photocurable dental resins; quaternary ammonium groups

## 1. Introduction

Sugar is a food substance the most widely used in everyday life. It can be found in sweets, beverages, and food additives. In modern-day, the consumption of sugar rises every year. As sugar isn't indifferent to the human body, health issues rise as well [1]. High consumption of sugar in combination with insufficient oral hygiene result in large-scale tooth decay. The WHO reported in 2022, that oral diseases mostly affect people living in middle-income countries, where the right diet and hygiene are not the most important concern. It is estimated that worldwide 2 billion adult people suffer from caries and 514 million children are also afflicted by tooth decay of primary teeth [2].

The dental practice treatment of caries is based on affected tissue removal and cavity filling with a dental composite restorative material (DCRM). DCRMs consist of inorganic fillers, responsible for the right mechanical properties, and polymeric matrices, which are responsible for physicochemical properties and support properties of fillers. Commercially available matrices are poly(dimethacrylate)s, which possess satisfying usable properties. However, they lack antibacterial activity [3]. This may promote secondary caries formation. This problem can be solved by providing DCRM with antibacterial activity. For example, matrices can be modified by chemical incorporation of monomers with quaternary ammonium groups (QA). QAs are capable of interacting with bacteria walls, which results in the disturbance of electrostatic balance and finally death of bacteria [4]. These days, dimethacrylates with QA are particularly extensively researched. They possess great potential as components of DCRM matrices due to their antibacterial activity and a high degree of conversion of methacrylate groups [5-11].

The main goal of this work was the development of the synthesis route and structural characterization of a novel urethane-dimethacrylate monomer having the TMXDI core

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and two wings with methacrylate groups at the end and QA group in the middle, whose nitrogen atom was substituted with an alkyl chain of ten carbon atoms.

## 2. Materials and Methods

### 2.1. Materials

Methyl methacrylate (MMA), *N*-methyldiethanolamine (MDEA), 1-bromodecane were purchased from Acros Organics (Geel, Belgium). Phenothiazine (PTZ), dibutyltin dilaurate, and tetramethylsilane (TMS) were purchased from Sigma-Aldrich (Burlington, MA, USA). 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Potassium carbonate and magnesium sulfate were purchased from Chempur (Piekary Śląskie, Poland). Toluene, trichloromethane, and dichloromethane were purchased from Stanlab (Lublin, Poland).

### 2.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

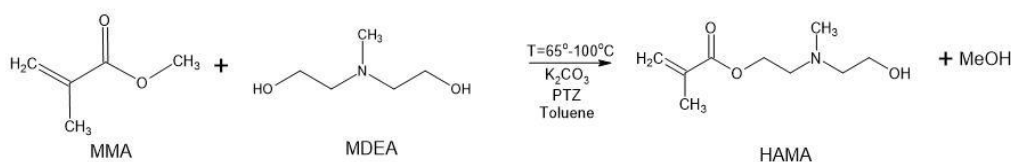
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with a 300 MHz NMR spectrometer (UNITY/INOVA, Varian, Palo Alto, CA, USA) with 512 and 40 000 scans, respectively. Spectra were recorded as solutions of  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  with TMS as the internal standard.

### 2.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded with Spectrum Two with ATR (Attenuated Total Reflectance) mode (Elmer-Perkin, Waltham, MA, USA) with 16 scans at resolution  $1\text{ cm}^{-1}$ .

### 2.4. Synthesis of *N,N*-(2-hydroxyethyl)methylaminoethyl methacrylate (HAMA)

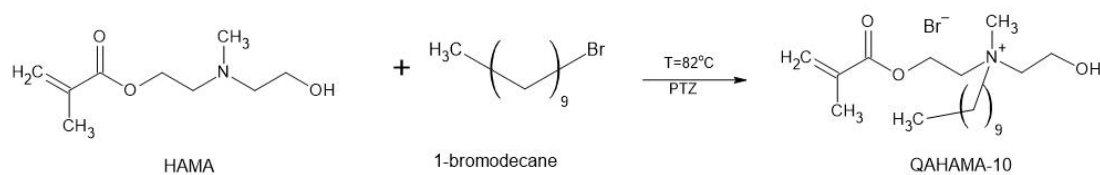
The novel dimethacrylate monomer was obtained in a three-step process, according to the procedure described in the literature [7]. The first step of synthesis was transesterification (Fig.1) of MMA (0,75 mol, 75,09 g) with MDEA (0,50 mol, 59,88 g) resulting in HAMA and by-product, methanol. The reaction was conducted in 300 ml of toluene solution. 8% wt. of  $\text{K}_2\text{CO}_3$  catalyst and 500 ppm PTZ polymerization inhibitor were also used. The reaction mixture was heated for 2,5 hours in the temperature range of  $65\text{--}100^\circ\text{C}$  in a 1000 ml round-bottom flask. Round-bottom flask was equipped with a standard distillation kit. After 2,5 hours mixture was cooled down and filtered. First the mixture was washed in a 2:1 ratio with distilled water and then the trichloromethane was mixed with aqueous phase, where ration of water to trichloromethane was 3:1. To remove the residual water,  $\text{MgSO}_4$  was added to the trichloromethane solution and left overnight. Trichloromethane was evaporated under reduced pressure (30 mbar) with a rotary evaporator. Raw HAMA was purified by vacuum distillation (10 mbar), taking boiling fraction at  $120\text{--}130^\circ\text{C}$ .



**Figure 1.** The transesterification of MMA with MDEA resulting in HAMA.

### 2.5. Synthesis of 2-(methacryloyloxy)ethyl-2-decylhydroxyethylmethylammonium bromide (QAHAMA-10)

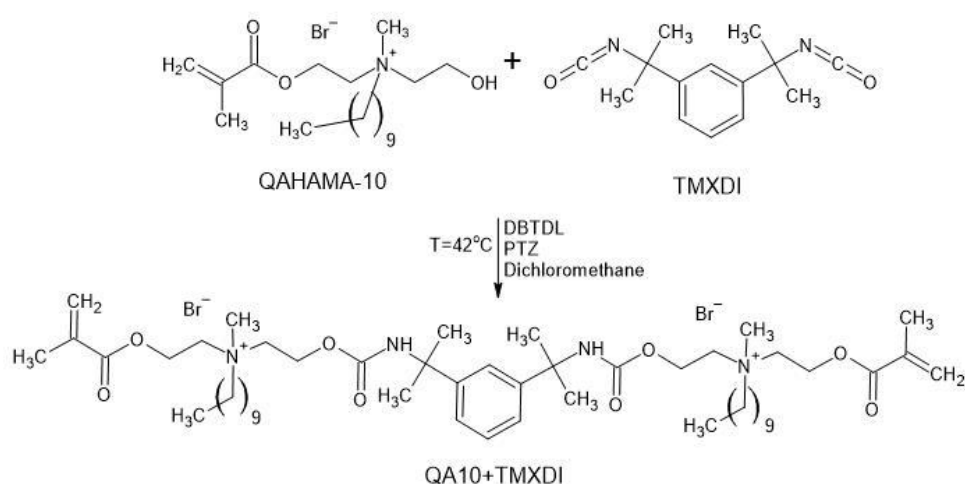
The second step of monomer synthesis was N-alkylation of HAMA resulting in QAHAMA-10 (Fig.2). The reaction was carried out in a 250 ml three-neck round-bottom flask and the reaction components were introduced: HAMA (0,08 mol, 15,00 g), 1-bromodecane (0,08 mol, 17,72 g), PTZ (500 ppm). The reaction was carried out at  $82^\circ\text{C}$ , for 5 days, with utilization of oil bath and mechanical stirrer.



**Figure 2.** The HAMA N-alkylation with 1-bromodecane resulting in QAHAMA-10.

### 2.6. Synthesis of quaternary ammonium urethane-dimethacrylate monomer (QA10+TMXDI)

Addition of QAHAMA to TMXDI was conducted in a 250 ml three-neck round-bottom flask equipped with a thermometer and reflux condenser. The mixture of 50% wt. solution of QAHAMA (0,050 mol, 20,42 g) in dichloromethane with 0,03% wt. of DBTDL catalyst and 500 ppm PTZ was heated with an oil bath to the boiling point of dichloromethane. Then 50% wt. solution of TMXDI (0,025 mol, 6,10 g) in dichloromethane was slowly dropped for 1 hour. After the last droplet was added, the reaction was continued for 5 hours (Fig.3). Dichloromethane was evaporated under reduced pressure (30 mbar with a rotary evaporator). The final product, QA10+TMXDI, was a yellowish, viscous liquid.

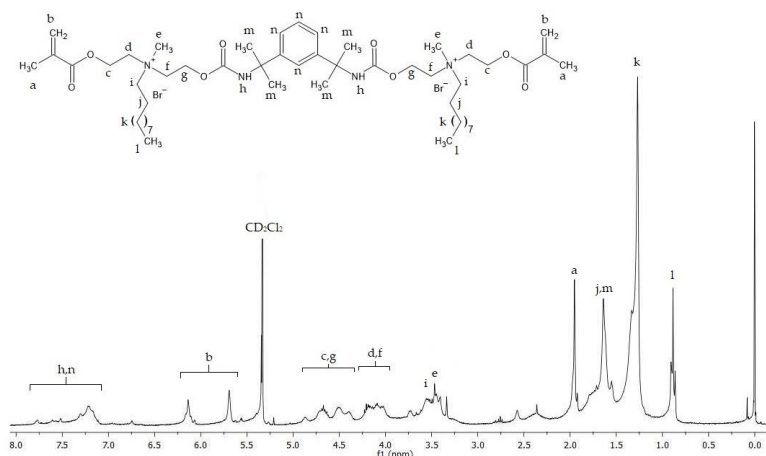


**Figure 3.** The addition of QAHAMA-10 to TMXDI resulting QA10+TMXDI.

## 3. Spectroscopy analysis

### 3.1. <sup>1</sup>H NMR

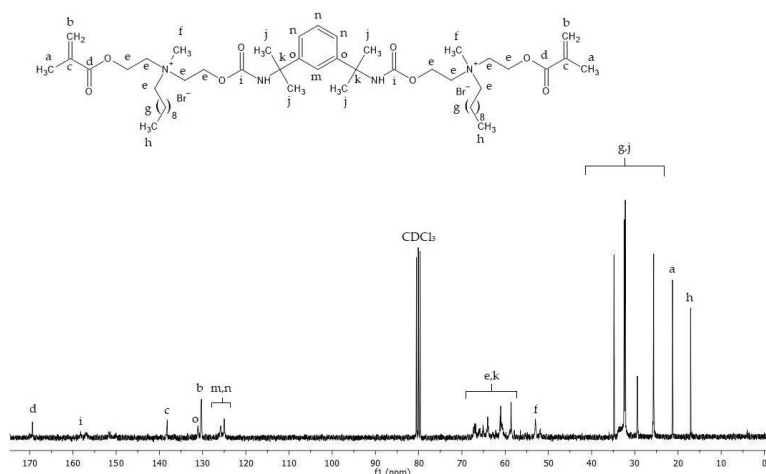
In Figure 4 the <sup>1</sup>H NMR spectrum of QA10+TMXDI is shown. Protons of the decyl substituent are visible:  $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$  at 0,86-0,91 ppm,  $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$  in the range 1,25-1,32 ppm,  $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$  overlapping with  $-\text{NH}-\text{C}(\text{CH}_3)_2-$  at 1,55-1,71 ppm,  $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$  at 3,59 ppm. Peaks of protons, that comes from methacrylate groups are also present:  $\text{CH}_3-\text{C}=\text{C}$  at 1,94 ppm and  $\text{CH}_2=\text{C}$  at 5,69 and 6,14 ppm. Urethane bond protons and aromatic protons:  $-\text{CH}_2-$  (ar) and  $-\text{NH}-\text{C}=\text{O}$  overlap and can be found in the range 7,10-7,61 ppm. Other noticeable peaks are:  $\text{CH}_3-\text{N}^+$  at 3,50 ppm,  $-\text{CH}_2-\text{N}^+$  at 3,99-4,21 ppm and also  $-\text{CH}_2-\text{O}-$  in the range 4,30-4,60 ppm.



**Figure 4.**  $^1\text{H}$  NMR spectrum of the QA10+TMXDI monomer.

### 3.2. $^{13}\text{C}$ NMR

$^{13}\text{C}$  NMR spectrum of QA10+TMXDI shows carbon atoms (Fig.5) of n-alkyl substituent:  $\text{CH}_3\text{-(CH}_2)_8\text{-CH}_2\text{-N}^+$  at 17 ppm,  $\text{CH}_3\text{-(CH}_2)_8\text{-CH}_2\text{-N}^+$  grouped with  $\text{-NH-C(CH}_3)_2\text{-}$  between 25-34 ppm,  $\text{CH}_3\text{-(CH}_2)_8\text{-CH}_2\text{-N}^+$  grouped with carbons of  $\text{-CH}_2\text{-N}^+$ ,  $\text{-CH}_2\text{-O-}$  and  $\text{-NH-C(CH}_3)_2\text{-}$  at 58-66 ppm. Carbon atoms of methacrylate groups are visible:  $\text{CH}_3\text{-C=}$  at 21 ppm,  $\text{CH}_2\text{=}$  at 130 ppm,  $\text{CH}_2\text{=C<}$  at 138 ppm, and  $\text{-COO-}$  at 169 ppm. Aromatic carbon atoms can be seen: at 124 and 126 of  $\text{-CH= (ar)}$  and also  $\text{>C= (ar)}$  at 131 ppm. Other peaks come from a carbon of urethane bond:  $\text{-NH-C=O}$  at 156 ppm and of methyl group neighboring to nitrogen atom:  $\text{CH}_3\text{-N}^+$  at 50 ppm.



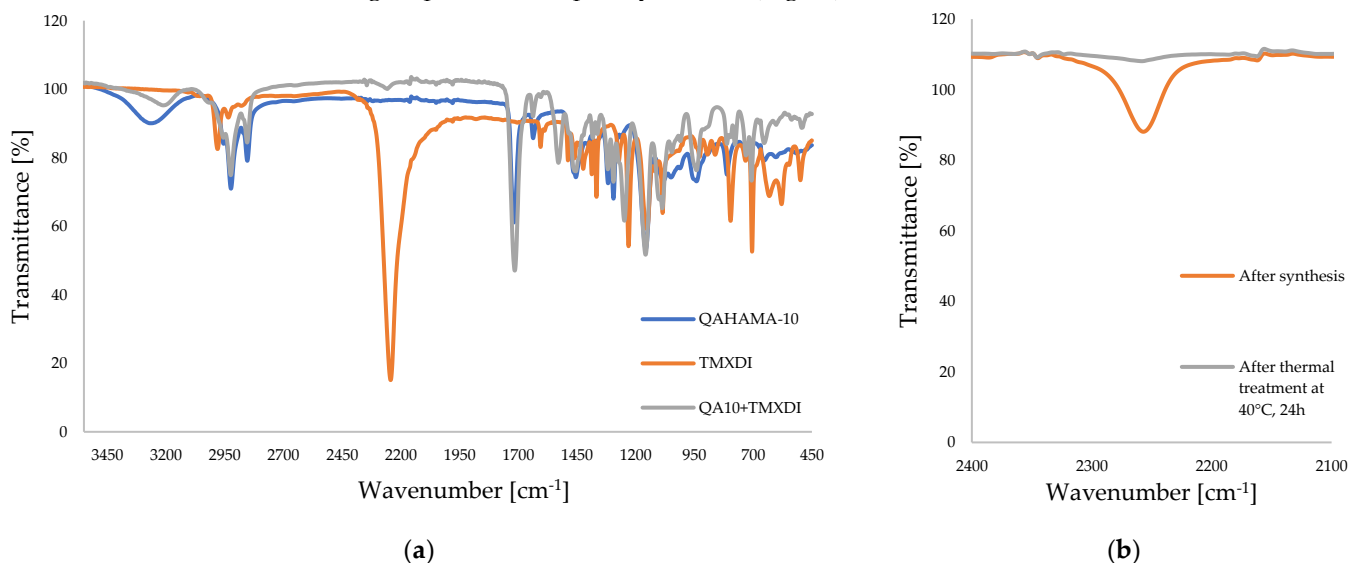
**Figure 5.**  $^{13}\text{C}$  NMR spectrum of the QA10+TMXDI monomer.

### 3.3. FTIR

FTIR spectra of QAHAMA-10, TMXDI, and QA10+TMXDI final monomer are presented in Figure 6a. The most noticeable change is the disappearance of peak  $2252\text{ cm}^{-1}$ , which comes from the TMXDI isocyanate groups, in the final monomer. This confirms the total addition of QAHAMA-10 to TMXDI.

The addition reaction time was determined by monitoring the presence of the  $\text{-NCO}$  band at  $2252\text{ cm}^{-1}$ . After 5 hours of monomer synthesis, described in 2.8, this band was still observed in the FTIR spectrum. Due to that fact, the round-bottom flask with QA10+TMXDI monomer was placed in a laboratory dryer at  $40^\circ\text{C}$  for 24 hours. After that

time it was observed that the peak at  $2252\text{ cm}^{-1}$  disappeared, which confirms, that isocyanate groups were completely reacted (Fig.6b).



**Figure 6.** (a) FTIR spectrum of QA10+TMXDI monomer (b) The FTIR spectrum of QA10+TMXDI showing consumption of the isocyanate groups due the thermal treatment.

#### 4. Conclusions

Novel QA10+TMXDI monomer can be efficiently obtained from 2-(methacryloyloxy)ethyl-2-decylhydroxyethylmethylammonium bromide and 1,3-bis(2-isocyanatopropan-2-yl)benzene. Its structure was confirmed by FTIR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR.

Due to the satisfying results of the QA10+TMXDI synthesis, this monomer will be further researched. Future studies will include determining its physicochemical properties as well as the physicochemical, biocidal and mechanical properties of copolymers of QA10-TMXDI with commercially available dimethacrylate monomers, such as Bis-GMA and UDMA.

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