

Proceeding Paper

Synthesis and Structural Characterization of Novel Urethane-Dimethacrylate Monomer with Two Quaternary Ammonium Groups [†]

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[†] Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: <https://asec2023.sciforum.net/>.

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

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



Citation: Drejka, P.; Chrószcz-Porębska, M.; Barszczewska-Rybarek, I. Synthesis and Structural Characterization of Novel Urethane-Dimethacrylate Monomer with Two Quaternary Ammonium Groups. *Eng. Proc.* **2023**, *56*, 285. <https://doi.org/10.3390/ASEC2023-15348>

Academic Editor: Elisabeta Szerb

Published: 26 October 2023



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1. Introduction

Sugar is the most widely used food substance in everyday life. It can be found in sweets, beverages, and food additives. In the modern day, the consumption of sugar rises every year. As sugar is not indifferent to the human body, health issues also rise [1]. High consumption of sugar in combination with insufficient oral hygiene results 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 for the 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 the 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 via the chemical incorporation of monomers with quaternary ammonium groups (QA). QAs are capable of interacting with bacteria walls, which results in the disturbance of the electrostatic balance and, finally, the 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 [5–14].

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

wings with methacrylate groups at the end and a 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), and 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)

^1H and ^{13}C NMR spectra were obtained by using a 300 MHz NMR spectrometer (UNITY/INOVA, Varian, Palo Alto, CA, USA) with 512 and 40,000 scans, respectively. The spectra were recorded as solutions of CD_2Cl_2 or CDCl_3 , with TMS as the internal standard.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded via Spectrum Two in ATR (Attenuated Total Reflectance) mode (Elmer-Perkin, Waltham, MA, USA), with 16 scans at a resolution of 1 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 the transesterification (Figure 1) of MMA (0.75 mol, 75.09 g) with MDEA (0.50 mol, 59.88 g), resulting in HAMA and its by-product, i.e., methanol. The reaction was conducted in 300 mL of toluene solution. Next, 8% wt. of K_2CO_3 catalyst and a 500 ppm PTZ polymerization inhibitor were also used. The reaction mixture was heated for 2.5 h in the temperature range of 65–100 °C in a 1000 mL round-bottomed flask. The round-bottomed flask was equipped with a standard distillation kit. After 2.5 h, the mixture was cooled down and filtered. Firstly, the mixture was washed at a 2:1 ratio with distilled water, and then the trichloromethane was mixed with an aqueous phase, where the ratio of water to trichloromethane was 3:1. To remove the residual water, MgSO_4 was added to the trichloromethane solution and left overnight. Trichloromethane was evaporated under reduced pressure (30 mbar) by using a rotary evaporator. Raw HAMA was purified via vacuum distillation (10 mbar), taking the boiling fraction at 120–130 °C.

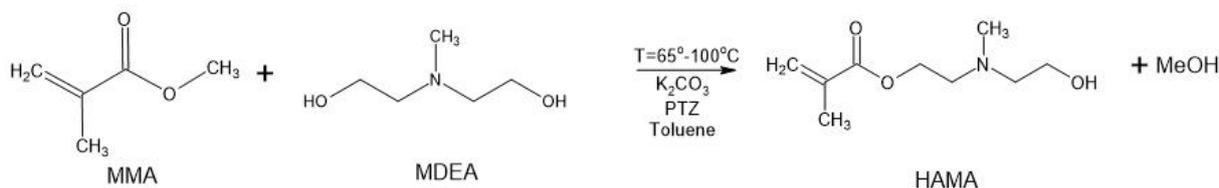


Figure 1. The transesterification of MMA with MDEA, resulting in HAMA.

2.5. Synthesis of 2-(Methacryloyloxy)ethyl-2-decylhydroxyethylmethylammonium Bromide (QAHAMA-10)

The second step of monomer synthesis was the N-alkylation of HAMA, resulting in QAHAMA-10 (Figure 2). The reaction was carried out in a 250 mL three-necked, round-bottomed flask, and the following reaction components were introduced: HAMA (0.08 mol, 15.00 g), 1-bromodecane (0.08 mol, 17.72 g), and PTZ (500 ppm). The reaction was carried out at 82 °C for 5 days, with the utilization of an oil bath and a mechanical stirrer.

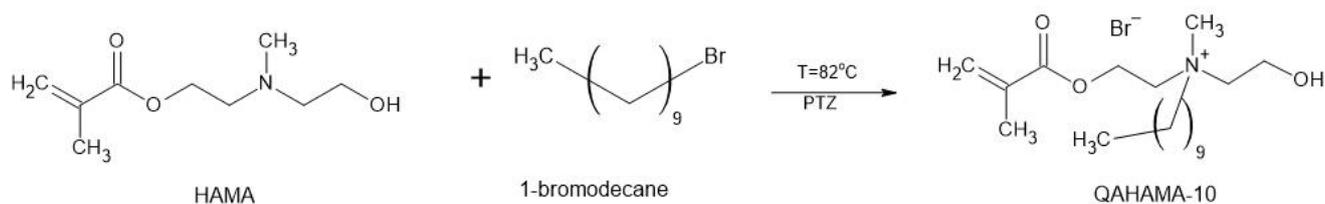


Figure 2. The HAMA N-alkylation with 1-bromodecane, resulting in QAHAMA-10.

2.6. Synthesis of Quaternary Ammonium Urethane-Dimethacrylate Monomer (QA10+TMXDI)

The addition of QAHAMA to TMXDI was conducted in a 250 mL three-necked, round-bottomed 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 h. After the last droplet was added, the reaction was continued for 5 h (Figure 3). Dichloromethane was evaporated under reduced pressure (30 mbar with a rotary evaporator). The final product, QA10+TMXDI, was a yellowish, viscous liquid.

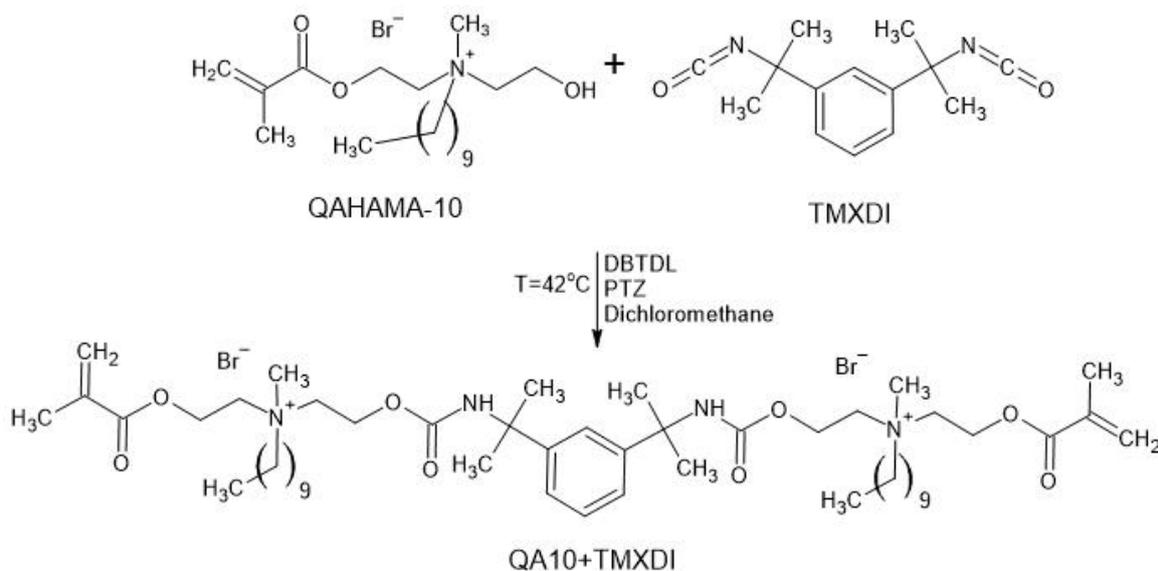


Figure 3. The addition of QAHAMA-10 to TMXDI, resulting in QA10+TMXDI.

3. Spectroscopy Analysis

3.1. ^1H NMR

In Figure 4 the ^1H 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: $-\text{CH}=\text{O}$ (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: CH_3-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.

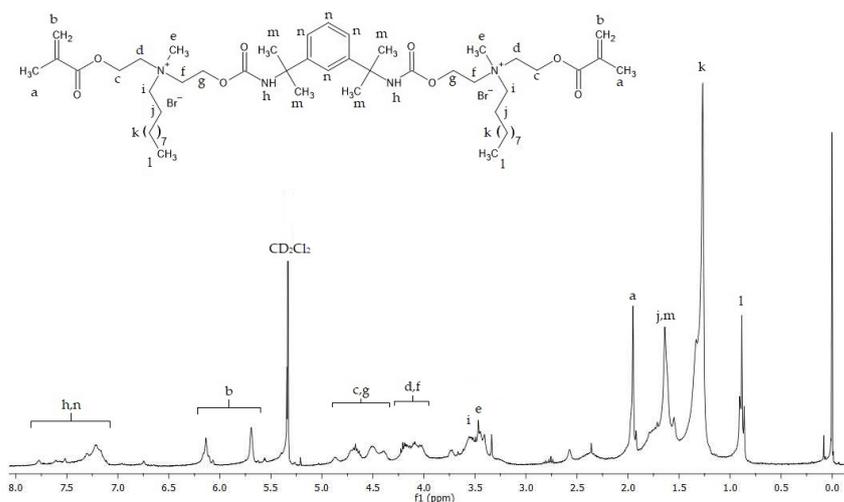


Figure 4. The ^1H NMR spectrum of the QA10+TMXDI monomer.

3.2. ^{13}C NMR

The ^{13}C NMR spectrum of QA10+TMXDI shows carbon atoms (Figure 5) of a 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 and 34 ppm, and $\text{CH}_3\text{-(CH}_2)_8\text{-CH}_2\text{-N}^+$ 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 -COO- at 169 ppm. Aromatic carbon atoms can be seen at 124 and 126 ppm for -CH= (ar), as well as at 131 ppm for >C= (ar). Other peaks come from a carbon of urethane bond: -NH-C=O at 156 ppm, as well as a methyl group neighboring the nitrogen atom $\text{CH}_3\text{-N}^+$ at 50 ppm.

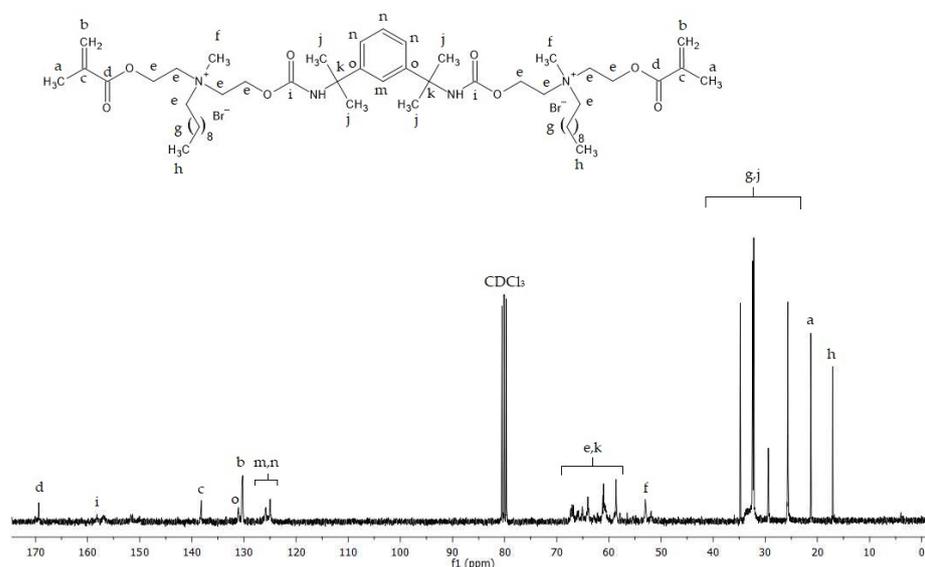


Figure 5. The ^{13}C NMR spectrum of the QA10+TMXDI monomer.

3.3. FTIR

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

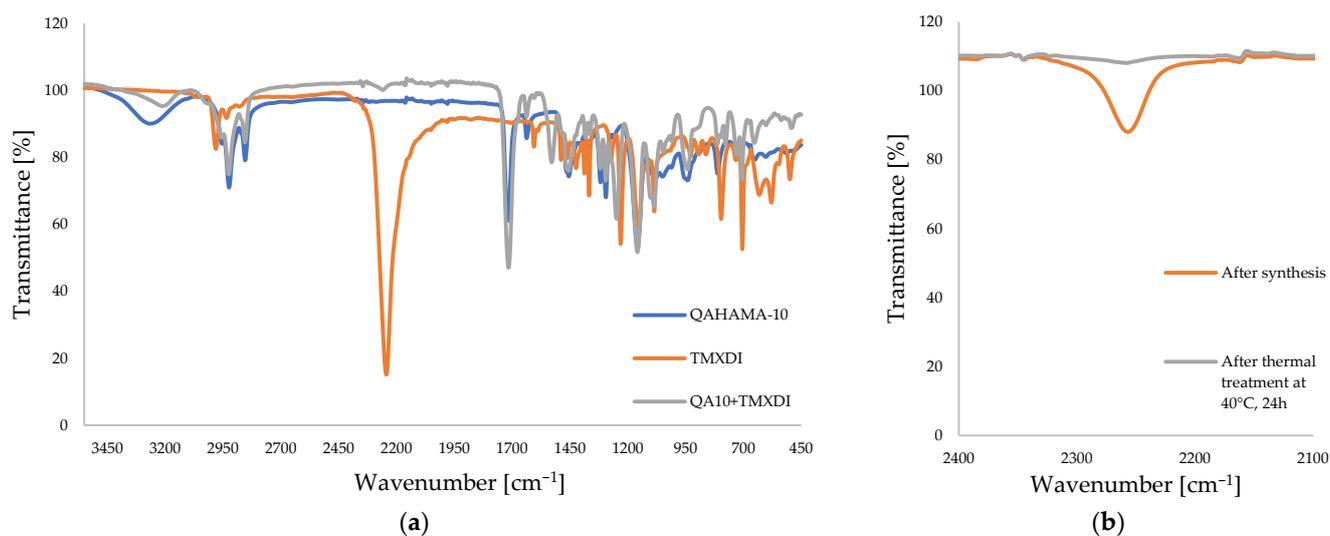


Figure 6. (a) FTIR spectra of QA10+TMXDI, TMXDI, and QA10+TMXDI monomers. (b) The FTIR spectrum of QA10+TMXDI shows the consumption of the isocyanate groups due the thermal treatment.

The addition reaction time was determined by monitoring the presence of the -NCO band at 2252 cm⁻¹. After 5 h of monomer synthesis, described in Section 2.6, this band was still observed in the FTIR spectrum. Due to that fact, the round-bottomed flask with QA10+TMXDI monomer was placed in a laboratory dryer at 40 °C for 24 h. After that time, we observed that the peak at 2252 cm⁻¹ disappeared, which confirms that the isocyanate groups were completely reacted (Figure 6b).

4. Conclusions

A 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 via FTIR, ¹H, and ¹³C 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 the copolymers of QA10-TMXDI with commercially available dimethacrylate monomers, such as Bis-GMA and UDMA.

Author Contributions: Conceptualization, I.B.-R. and P.D.; methodology, I.B.-R., P.D. and M.C.-P.; investigation, P.D.; resources, I.B.-R., M.C.-P. and P.D.; data curation, I.B.-R. and P.D.; writing—original draft preparation, I.B.-R. and P.D.; writing—review and editing, I.B.-R.; visualization, P.D.; supervision, I.B.-R.; project administration, I.B.-R. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Polish Budget Funds for Scientific Research in 2023 as core funding for research and development activities at the Silesian University of Technology—funding for young scientists, grant number: 04/040/BKM23/0258.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; the collection, analyses, or interpretation of data; the writing of the manuscript; or the decision to publish the results.

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