Ethyl α-Hydroxymethylacrylate, a Novel Isomeric Analog of 2-Hydroxyethyl Methacrylate (HEMA)

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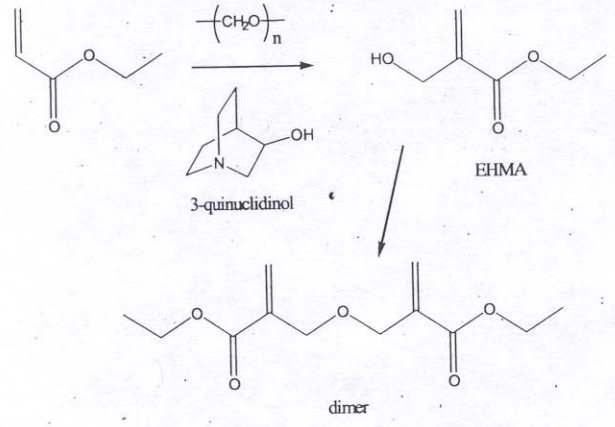
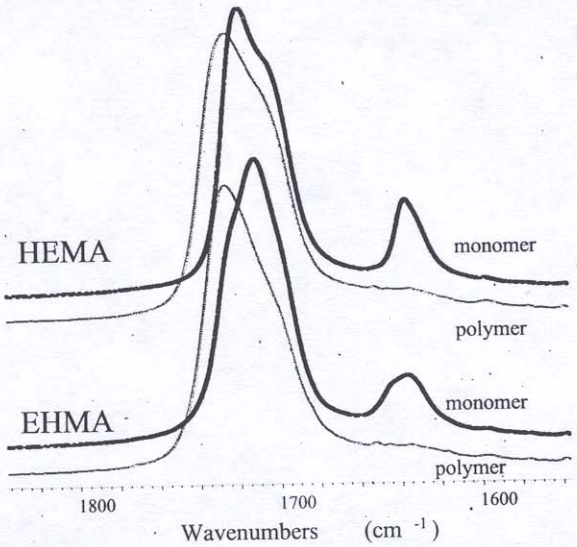
Introduction: HEMA (2-hydroxyethyl methacrylate), a hydrophilic , surface active monomer is widely used in dental adhesive systems and, in its polymeric forms, in numerous biomedical applications. Poly(HEMA) was the first synthetic hydrogel intended for use as a biomaterial. Some of the traditional uses of HEMA polymers and copolymers include soft contact lenses, vascular grafts, soft tissue substitutes, and hydrogels for controlled-release delivery systems. HEMA also has found use in the formulation of photocurable bioactive composites with remineralization potential. Recently a unique isomeric analog of HEMA, ethyl α-hydroxymethylacrylate (EHMA), was synthesized. This study describes a high yield synthetic method for the preparation of EHMA and compares the bulk polymerizability of EHMA and HEMA.

Materials and Methods: In a stoppered flask equipped for magnetic stirring was placed 10 mmol ethyl acrylate, 10 mmol paraformaldehyde, 1.25 mmol 3-quinuclidinol, 2.5 g dimethyl sulfoxide and 0.85 g of distilled water. The mixture was heated at 100 °C for 30 min and, after cooling to room temperature, extracted with dilute aqueous hydrochloric acid to remove the quinuclidinol. Vacuum distillation of the crude product yielded mass fractions of 75 % to 80 % EHMA. The purified EHMA was characterized by FTIR and $^{1}H/^{13}C$ NMR spectroscopies. As shown below, some dimer product also forms but this can be minimized by controlling the reaction conditions and removed from the product by vacuum distillation. Compared with HEMA, EHMA has decreased water solubility.



Polymerization of EHMA: Previous studies have described the polymerization of EHMA with conventional free radical initiators, e.g. benzoyl peroxide. In this study we investigated the visible light photopolymerization of EHMA alone and with Bis-GMA. Comparative photopolymerizations were conducted with HEMA. Homopolymerizations of EHMA and HEMA were con-ducted by photo-DSC (conditions: 30 °C, nitrogen purge, 150 W Xe source, irradiation intensity of 4.3 mW/cm^2). As a measure of the relative rates of reaction, the maximum heat flow values were 7.6 W/g for HEMA and 3.2 W/g for EHMA (relative uncertainty of 3 %). However, essentially identical degree of conversion values were obtained for the homopolymerizations, with HEMA at 73.5 % and EHMA at 72.6 % (relative uncertainty 3 %). Copolymerizations of Bis-GMA/HEMA and Bis-GMA/EHMA (65:35, mass ratios) in the photo-DSC under the same conditions previously described gave heat flow maxima of 15.9 W/g and 12.9 W/g, respectively. The degree of conversion in these copolymer systems was calculated as 63.4 % for Bis-GMA/HEMA and 59.9 % for Bis-GMA/EHMA. Polymer films approximately 20 μm in thickness of each monomer system were formed between glass slides by visible light irradiation for 60 s per side in a Triad unit (Dentsply) followed by postcuring at 37°C for 24 h. Triplicate FTIR measurements of degree of conver-sion were made for each type of polymer with the following results: HEMA ≈ EHMA at 97 %, Bis-GMA/HEMA, 86.2 % and Bis-GMA/EHMA, 89.9 %; standard uncertainty (s.u.) = 0.9.

Computer modeling indicated that EHMA forms a more stable intramolecular hydrogen bond compared with HEMA. This appears to be validated by analysis of the carbonyl absorption in the infrared spectra of the isomers. Three different IR wavenumber carbonyl stretching bands are possible for each monomer corresponding to free -C=O and intramolecular and intermolecular hydrogen bonded -C=O (-C=O---HO-). Second derivative IR and peak fit spectra show three bands for EHMA at (1726, 1712, and 1697) cm^{-1} (s.u. = 1 cm^{-1}). The 1726 cm^{-1} band derives from free carbonyl and the latter two, plausibly, from intramolecular and intermolecular hydrogen bonded carbonyl, respectively. HEMA has two second derivative and peak fitted bands at 1721 cm^{-1} and 1705 cm^{-1}. These bands, respectively, derive from free carbonyl and, plausibly, intermolecular hydrogen bonded carbonyl; a third band for possible intramolecular hydrogen bonded carbonyl was not clearly detected which suggests minimal bonding of this type in HEMA.



Conclusions: EHMA has decreased water solubility compared with HEMA, probably due to strong intramolecular hydrogen bonding interactions. The rates of polymerization of EHMA, either alone or as a comonomer, were somewhat less than those obtained with HEMA. However, the final conversion values of EHMA and HEMA polymers and copolymers were essentially equivalent. These results suggest that EHMA has the potential to serve as an alternative to HEMA in dental and biomedical applications. *This work supported by NIST-NIDCR IA Y1-DE-7006-0. Materials and equipment identification do not imply recommendation or endorsement by NIST or NIH.*