

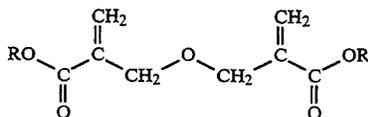
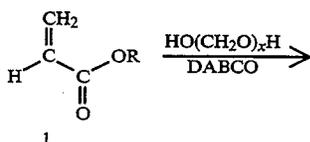
# MULTIFUNCTIONAL ACRYLATES AND THE SYNTHESIS THEREOF

## TECHNICAL FIELD

This invention relates to acrylate compounds, and more particularly to multifunctional acrylate monomers that undergo ambient free radical polymerization.

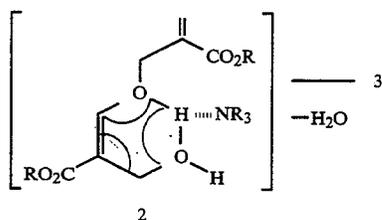
## BACKGROUND ART

Novel difunctional and multifunctional vinyl monomers with a propensity for intra-intramolecular addition polymerization (cyclopolymerization) have been conveniently synthesized from conventional acrylates or diacrylates and paraformaldehyde under neat conditions using 1,4-diazabicyclo[2,2,2]octane (DABCO) as the catalyst



R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, etc.

The mechanism for the formation of oxy-bismethacrylates such as 3 from monoacrylates such as 1 (and presumably the oligomeric monomers derived from diacrylates as well) appears to involve an unusual base catalyzed self etherification of the intermediate  $\alpha$ -hydroxymethyl acrylate 2



Recently the scope of this interesting reaction was extended to the synthesis of difunctional and oligomeric multifunctional fluorinated monomers from the corresponding mono- and difunctional fluorinated acrylates. In contrast to the solventless conditions used in the transformation of conventional hydrocarbon acrylates, the highly fluorinated starting monomers required the use of a solvent such as dimethyl sulfoxide (DMSO) to achieve their successful conversion to difunctional and oligomeric monomers.

The serendipitous discovery that the DABCO-catalyzed reaction of an acrylate ester and formaldehyde would proceed beyond the initial  $\alpha$ -hydroxymethyl acrylate intermediate to a 1,6-diene has uncovered a rich vein of new monomers. The monomers are essentially ether-fused dimethacrylates with the ester groups located externally. This ester functionality can be varied to significantly alter the properties of the monomers

and their corresponding polymers. The 1,6-diene configuration in the monomer gives access to an intramolecular cyclization pathway for polymerization. Depending on the polymerization conditions, linear polymer can be formed exclusively via cyclopolymerization or crosslinked polymer can be obtained by a combination of the 1,6-cycloaddition and 1,2-addition polymerization modes.

In addition to the difunctional 1,6-diene monomers, multifunctional oligomers capable of several discrete cyclopolymerizations per chain, thereby yielding highly crosslinked polymers, have been synthesized and evaluated. All these new monomers share several properties that make them attractive prospects for use in dental resins. By virtue of the cyclopolymerization process, high degrees of conversion can be achieved while yielding relatively high modulus polymeric materials. An efficient cyclopolymerization process also offers a route to significantly reduced levels of polymerization shrinkage compared with conventional dimethacrylate polymerizations.

Those aware with these and other developments recognize the need to extend and establish the bounds of this new avenue of chemistry and evaluate novel monomers and their applications.

## DISCLOSURE OF THE INVENTION

The present invention provides a process for converting a hydrophobic siloxane diacrylate and a hydrophilic polyethylene glycol diacrylate to their respective multifunctional oligomers. Bis(4-acryloxybutyl)-tetramethyldisiloxane, prepared from the corresponding diol, is converted to relatively low viscosity, multifunctional oligomers with the use of DMSO. The hydrophilic monomer, polyethylene glycol 400 diacrylate, formed more viscous, water soluble oligomeric products without the need for a solvent. Characterization of these oligomers by infrared spectroscopy and <sup>1</sup>H NMR supports the assigned structures. Because of the predominant 1,6-arrangement of double bonds in these oligomers, they have a propensity to undergo cyclopolymerization as well as the usual crosslinking associated with the free radical polymerization of multifunctional monomers and oligomers. These novel oligomeric monomers have potential use in dental composites, sealants, adhesives, dentures, biomedical prostheses, cements, contact lenses, drug delivery systems, coatings and caulks.

An object of the present invention is the provision of an improved process for synthesizing multifunctional acrylate monomers having a predominant 1,6-arrangement of double bonds.

A still further object of the present invention is the provision of a process for synthesizing multifunctional acrylates having a propensity to undergo cyclopolymerization.

These and other attributes of the invention will become more clear upon a thorough study of the following description of the best mode for carrying out the invention, particularly when reviewed in conjunction with the examples.

### Best Mode for Carrying Out the Invention

The following examples are illustrative of the best mode for carrying out the invention. They are obviously not to be construed as limitative of the invention