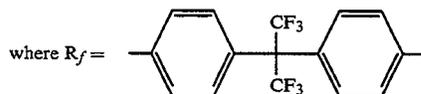
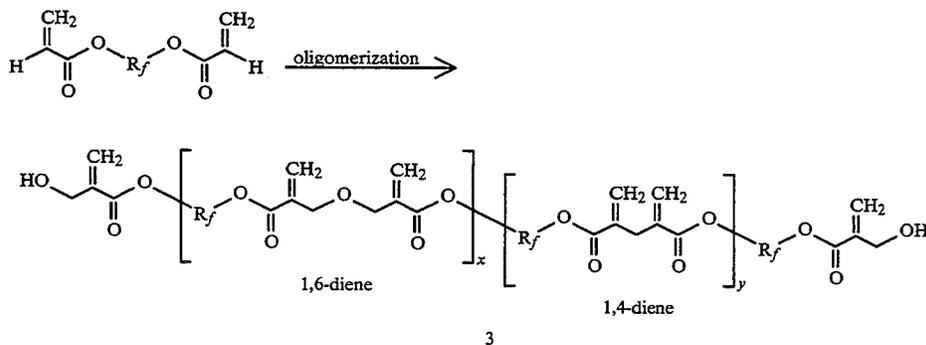


all aid in moderating the effects of polymerization contraction. The siloxane oligomers, which combine large bulk, comparatively low viscosity, high flexibility and cyclopolymerizability, offer a facile means of achieving low shrinking, hydrophobic, tough polymer structures suitable for use in a variety of dental, medical and industrial applications.

#### Synthesis of Multifunctional Fluorinated Oligomeric Monomers.

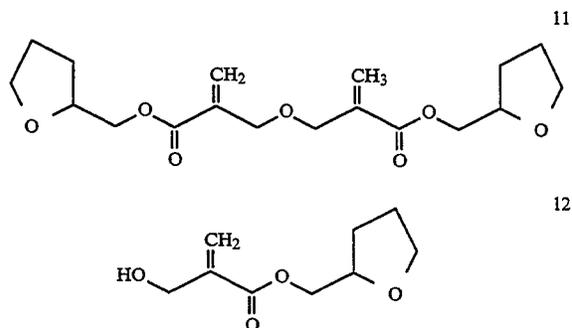
The combination of hydrocarbon acrylate esters with paraformaldehyde in the presence of DABCO yields the cyclopolymerizable 1,6-diene as the main product. Depending on the ester functionality, the reaction can also produce a 1,4-diene condensation product in concentrations ranging from 0 to approximately 15%. The 1,4-diene configuration in this product would require that a high energy four-membered ring form if cyclopolymerization were to take place through a head-to-tail intramolecular addition, thereby discounting this polymerization pathway. The use of fluorinated acrylate esters derived from  $-(CF_2)_n-CH_2OH$  type alcohols in the aldehyde insertion reaction was found to result in predominantly 1,4-diene products due to the electronegativity of the ester group. The synthesis of predominantly fluorinated 1,6-dienes was successful when acrylates derived from fluoro alcohols,  $R_fOH$ , with  $R_f = -CH_2CH_2(CF_2)_n$  were employed; however, these types of fluorinated acrylates or alcohols are extremely scarce. Therefore, in an attempt to prepare 1,6-dienes from readily available fluorinated starting materials, the diacrylate of hexafluorobisphenol A was synthesized and subjected to the standard aldehyde insertion-condensation reaction conditions.



Surprisingly, the result was a nonviscous multifunctional oligomer 3 which had internal diene linkages in a 2.1 to 1 ratio favoring the 1,4- over the 1,6-diene. The oligomer had an average of approximately five repeat units per oligomer chain. This type of fluorinated oligomer would be expected to provide a highly crosslinked, hydrophobic matrix; however, it would not be expected to undergo a high degree of cyclopolymerization. However, the combination of low viscosity and relatively high molecular weight in a resin also favors reduced polymerization shrinkage, especially in highly filled composites.

#### Synthesis of water soluble monomers

Since the ester groups can be varied in the cyclopolymerizable monomers, the functionality can be tailored to fit specific application needs. Preparation of cyclopolymerizable monomers which would be water soluble or water compatible for use as crosslinkable modifying agents for dental and medical adhesives, hybrid glass ionomer cement-composites, polymeric calcium phosphate cements, fluoride and drug release vehicles and contact lenses was undertaken. One approach to this problem involved the use of tetrahydrofurfuryl acrylate in the aldehyde insertion reaction. The major product 11 was obtained in 56% yield.



While the difunctional product 11 was significantly more polar in nature than other cyclopolymerizable monomers prepared previously, it was not water soluble. Because of its highly polar nature and facile polymerizability, it is expected to be useful as an adhesion

promoting bonding agent. The  $\alpha$ -hydroxymethyl intermediate 12 was also isolated from the reaction mixture and this product was quite water soluble and, though not able to cyclopolymerize, is a functional monomer capable of conversion to difunctional and multifunctional monomers and oligomers.

Alternatively, the synthesis of a cyclopolymerizable, difunctional HEMA type derivative was sought. Direct attempts to use 2-hydroxyethyl acrylate (HEA) in the aldehyde insertion reaction were unsuccessful due to complications attributed to the hydroxyl group. Therefore, the alcohol was first protected as the tetrahydropyranyl derivative 13 which was then converted to the 1,6-diene product 14.