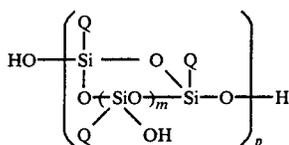


POLYOL TERMINATED SILICONES AND DERIVATIVES THEREOF

BACKGROUND OF THE INVENTION

Silicones (polyorganosiloxanes) having acrylic, epoxy, photoinitiating or other organic functional groups bound to silicon atoms by various linkages are well known. Recently, there have been described silicones with cluster acrylic functionality, that is multiple acrylic groups spatially concentrated near each other. Thus, in U.S. Pat. No. 4,387,240 there are described low molecular weight oligomers having a high methacrylate density which may be represented by the formula:

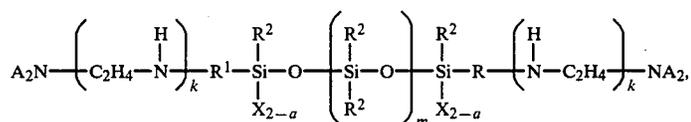


Where m is 1, 2 or 3; p is 2-10 and Q is methacryloxypropyl or similar groups. These oligomers are used as binders in dental filling compositions to give hard abrasion resistant cured fillings. Also, in U.S. Pat. No. 4,424,328 there are described branched low molecular weight siloxane compounds with 3 or 4 of the branches terminated with methacryloxypropyl groups. These compounds are used in the preparation of hard contact lenses.

In copending applications, U.S. Ser. Nos. 623,759, now U.S. Pat. No. 4,575,546, 623,760, now U.S. Pat. No. 4,575,545 and 723,791, filed June 22, 1984, now abandoned, it is disclosed that good elastomeric properties and much more rapid cure times are obtained by block silicones of the formula (AB)_nC where A is a relatively short polymer segment containing at least 3 siloxane repeat units having acrylic functionality, B is a longer segment containing no acrylic functionality and C is A or a triorganosilyl group such as methacryloxypropyldimethylsilyl. See also U.S. Pat. No. 4,504,629.

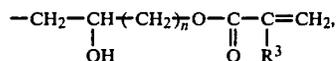
In Au20051/83 there are disclosed reaction products of silicone carbinols, diisocyanates and hydroxy functional ethylenically unsaturated compounds such as hydroxyethyl methacrylate. This reference suggests, does not exemplify the use of triisocyanates and/or polyacrylic hydroxyl compounds such as pentaerithritol di- or tri-acrylate. Such products are disclosed as useful for contact lenses where high oxygen permeability is desired. It is well known, however, that urethane linkages have poor high temperature resistance and the oxygen permeability of the silicone portion of the molecule would be expected to further erode the high temperature stability of the urethane linkage.

In U.S. Pat. No. 4,293,397 there are disclosed silicones of the general formula:



where R¹ is a divalent hydrocarbon group, R² is a monovalent hydrocarbon group, X is a hydroxy group or a hydrolyzable group, k is 0 or a positive integer not

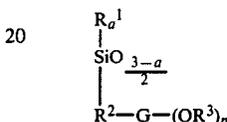
exceeding 4, m is a positive integer from 50 to 10,000, a is 0, 1 or 2 and at least two of the groups denoted by A in the molecule are each a acryloxy-containing group represented by the formula.



R³ being a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms and n being a integer from 1 to 10, the remainder of A being each a hydrogen atom.

DESCRIPTION OF THE INVENTION

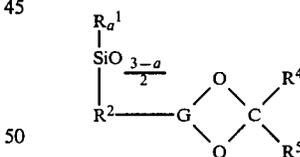
The present invention pertains to novel silicone polymers, that is polyorganosiloxanes, which include at least one group of the formula:



where R¹ is an organo group; R² is alkylene or alkenylene; G is a n+1 valent hydrocarbon, oxyhydrocarbon or poly(oxyhydrocarbon) radical in which some or all of the hydrogen atoms may optionally be substituted by halogen atoms; R³ is H or an organic functional group, particularly polymerizable groups, polymerization accelerating groups or polymerization initiating groups; n is an integer of 2 or more provided that when n is 2 and one of R³ is H, the other R³ group is also H; and a is 0, 1 or 2.

In the preferred polymers of the invention, a poly dihydrocarbyl siloxane is capped with groups of the above formula where R¹ is methyl, a is 2, R² is alkylene and the R³ groups are the same or different groups selected from groups having (meth)acrylic or epoxy functionality, N-tosylcarbonyl, H, or optionally substituted styryl groups.

A further aspect of the invention are useful intermediate compounds having groups defined by the formula



where R⁴ and R⁵ are H or a mono valent hydrocarbon group.

Examples of polymerizable groups R³ are H; (meth)aryl; (meth)acryloxyethylcarbonyl; styryl, particularly p-vinylphenyl, p-isopropenylphenyl and p-(1-propenyl)phenyl, any of which may optionally be sub-

stituted in the meta positions with alkyl or alkoxy groups; cinnamyl; alkenyl, such as vinyl or allyl; mer-