of a diol or triol forming a bishemiether. A separate molecule of diol or triol being required for each phenolic OH. Remaining OH groups, e.g. of the diols, are then esterified by acrylic or methacrylic acid to provide the useful binders of this invention which are devoid of active hydrogen atoms. Particularly, they are free from hydroxyl groups. The diphenols which are used, i.e., dihydroxy aromatic compounds, have at least two noncondensed aromatic nuclei joined directly or through an intervening linking group such as —O—, $—CH_2—$,

$$>C(CH_3)_2,\ >C(CF_3)_2,$$

and $—CH(CH_3)—$. The aromatic nuclei are single rings, i.e., mononuclear, and are otherwise free from substituent groups other than linking groups and the phenolic OH groups required for the reaction.

In order that polymerization of these polymethacrylates may proceed rapidly after initiation an accelerator is usually used. The preferred class of accelerators are mononuclear aromatic tertiary amine accelerators for free radical polymerization such as N,N-dimethyl-p-toluidine, N,N-dimethyl aniline, N,N-dimethyl-p-anisidine, N,N-bis(hydroxyethyl)-3,5-xylidine N,N-bis(hydroxyethyl)toluidine, and the like. Other known accelerators for free-radical polymerization are considered generally the equivalents of the preferred class in kind although possibly not as efficient.

The amounts of accelerator are adjusted, as will be evident to those skilled in the art, so that initial setting is deferred for a few minutes after mixing; usually 3 to 5 minutes for dental compositions. This provides the time for mixing, depositing in a tooth cavity and consolidating before curing or setting has advanced beyond a workable stage. Usually 0.05 to 5 weight percent of accelerator is dissolved in the binder. A preferred proportion is about 0.2 to 0.5 weight percent for aromatic tertiary amines such as dimethyl-p-toluidine. N,N-bis(hydroxy-lower-alkyl) aromatic amines are used in amounts of about 0.2 to 3 percent. In these lower alkyl is generally 2–6 carbon atoms.

It is desirable that the monomers be devoid of any peroxide compounds which may be present as a artefacts in the preparation. A treatment with reducing agent prior to use is thus desirable. If this precaution is not taken, shelf life may be very short.

Test procedures for dental materials are contained in Guide to Dental Materials, American Dental Association, 2nd and 3rd editions, Chicago and proposed Tentative Specification for Composite Resin Filling Materials, September, 1967.

The fillers employed in the compositions of the invention may include small amounts of pigments, either for visual color or fluorescent effect, glassy spherules or particles in small sizes, crystalline materials such as lithium aluminum silicates, hydroxyapatite, silica or siliceous minerals, alumina or aluminiferous materials, glasses such as borosilicate glasses. Particles should be generally smaller than 50 microns and preferably smaller than 30 microns. A commercially available lithium aluminum silicate is used in certain examples herein as providing an exemplary and generally valuable filler. As obtained particles range from submicron sizes up to 44 microns with an average of about 2 to 15 microns or in some cases larger up to about 85 to 90 microns. Other fillers may be used in somewhat different proportions and may have slightly different properties from the exact figures given. The selection of filler is not critical in the present invention.

It is preferred that the fillers be treated to promote adhesion by the binder, for example, using a conventional vinyl silane treatment or other such pretreatment well known in the art for other fillers as disclosed in the above-mentioned Bowen U.S. Pat. No. 3,066,112.

It is found that the most satisfactory workable consistency for dental filling compositions is obtained when fillers having particle sizes in the average range of about 2 to 15 microns are milled with organic binder containing about 0.5 to 2 mole percent of tertiary amine accelerator (and including any diluent which may be desired) in proportions of about 60 to about 85 percent by weight of filler and 40 to 15 percent of binder. The preferred range is 65 to 80 percent of filler depending on its specific gravity. In both cases the lower percentages are used with more viscous binders. The exact proportions may be varied depending on individual preferences, temperature requirements, etc..

It is an important advantage of the instant binders that the viscosities are sufficiently low that a diluent is not necessary. This is in contrast to the very viscous hydroxyl-group containing moisture-absorptive binders described in the above-noted Bowen patent.

The dental restorative compositions of the invention having, after hardening and exposure to moisture, moisture absorption of less than 1 percent by weight, comprise as binder a liquid polymerizable organic binder comprising 0.05 to 5 percent of accelerator for free-radical polymerization and a polycarbinol polymethacrylate or polyacrylate, substantially free from active hydrogen atoms and devoid of peroxides of the formula

$$MO(DO)_nX(OD)_nOM$$

wherein M is methacrylate or acrylate, D is alkylene of 2 to about 6 carbon atoms, n is 1 to 4 and X is the nucleus of a diphenol of at least two aromatic rings and from 12 to 24 carbon atoms.

Mixing of binder and filler may be by any convenient method and desirably with as little occlusion of air bubbles as possible. Milling or kneading by generally available procedures provides adequate blending. Ball-milling may be less desirable when a spherular filler is included. For convenience in dispensing to dentists two part systems are preferred. These may be two pastes, a paste and liquid or a liquid and solid. Catalyst is then included in one part and accelerator in the other. It is desirable to avoid inclusion of air during spatulation with catalyst before actually placing the polymerizing compositions in dental cavities. It is desired that the viscosity be not over about 10,000 centipoises. A low concentration of methacrylate groups (milliequivalents per gram of ester) is advantageous in decreasing shrinkage on polymerization although somewhat adversely affecting compressive strength. In general, therefore, the polyether methacrylate esters preferably do not have a very low molecular weight, i.e., 400 or more and upwards as compared to 100 for methyl methacrylate.

The polyether methacrylate esters which are particularly useful in dental restorative compositions of the present invention are represented by the general formula

$$MO\text{-}(DO)_nX(OD)_nOM$$

wherein M is methacrylate, D is alkylene of 2 to 6 carbon atoms, n is 1 to 4 and X is the nucleus of a diphenol