POLYMERIZABLE COMPOUNDS CONTAINING ACID AND ACID DERIVATIVES, MIXTURES CONTAINING THE SAME, AND USE THEREOF

The invention concerns polymerizable compounds containing acid groups or acid-group derivatives, mixtures containing the same, and the use thereof.

Compounds of this type adhere to various substrates, especially biological substrates. The compounds can be employed or added for general purposes, but especially in the dental and medical fields as constituents of polymerizable bonding agents, adhesive fillers, and adhesive cement and for similar mixtures.

Polymerizable mixtures based on monomeric compounds provided with one or more unsaturated groups constitute a basis for a number of plastics, with compounds having methacrylate groups being especially important in the dental and medical fields. Mixtures of this type constitute for instance the basis of acrylic-based filling and sealing materials.

These polymerizable mixtures cannot, however, generally establish any chemical bond with other materials, especially biological substrates, even when the substrates themselves contain sufficient unpolymerized polymerizable groups.

A more secure bond can accordingly be attained only through the use of highly retentive surfaces, by means that is of strictly mechanical bonding—by etching the surface of biological or inorganic materials. This drawback can, however, be eliminated by using bonding agents, substrates that is that can react chemically with biological or inorganic material as well as containing a polymerizable group.

A series of such bonding agents is known—the organosilanes with vinyl or methacryl groups for example. They are however, restricted in their adhesiveness to silicon dioxide, to glasses and ceramics that contain silicon dioxides, and to metal oxides or non-precious metals that form them. They exhibit no adhesion to biological substrates, especially dental and osseous substrates, but tend rather to have a separating action.

A series of polymerizable bonding agents with other adhesive groups, like 2-N-allylamino-4,6-dichloro-1,3,5-triazine (U.S. Pat. No. 4,203,220), combinations of hydroxymethacrylic esters with dialdehydes (Eur. Pat. No. 0 141 324), or epoxymethacrylates, have been discovered for substrates of this type. They react with the collagen or collagen-like constituents of the substrates.

There are also a number of polymerizable compounds that react with the apatite compounds in the dental and osseous tissues. These bonding-promotion compounds include acid groups or reactive acid-group derivative. Examples of such polymerizable compounds are unsaturated organic esters of phosphoric or phosphonic acids (German AS No. 2 711 234 & German OS No. 3 150 285), unsaturated organic esters of monofluorophosphoric acid (U.S. Pat. No. 3,997,504), unsaturated organic esters of phosphoric acids that contain either chlorine or bromine bonded directly to the phosphorus (Eur. Pat. No. 0 058 483), and unsaturated organic esters of phosphoric acid in the form of pyrophosphates (anhydrides) (German OS No. 3 048 410).

Also known are polymerizable carboxylic acids and reactive derivatives of carboxylic acids that exhibit satisfactory adhesion to the dental tissue. These include 4-methacryloyloxyethyltrimellitic acid and its anhydride (M. Takeyama et al., I. Jap. Soc. f. Dent. App. a. Mat. 19, 170 [1978]) and bis-2-methacryloylethyl pyromellitate. Their application, however, is very limited. Solutions in acetone or methyl methacrylate are employed.

In dimethacrylate systems like mixtures that include bis-GMA, separation and other problems like spontaneous polymerization or failure to cure occur, and the admixtures must remain less than 5% (V. P. Thompson, IADR Symposium 1985, Publ. 1103).

The aforesaid polymerizable compounds do make it possible in many cases to obtain more or less powerful adhesion on the part of acrylic-based filling and sealing materials to the dental and osseous tissues. Success, however, also depends extensively on how thick a coating of the bonding agent is applied, on how many adhesive groups enter into reaction with the biological substrate, and on how many polymerizable groups enter into reaction with the copolymerizing material.

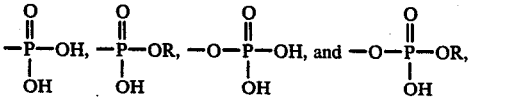
The object of the invention is to discover compounds that contain several polymerizable groups and several adhesive groups bonded to chemically very stable molecular backbones. This object is attained in accordance with the invention by means of oligomeric or prepolymeric organic compounds that contain several polymerizable unsaturated groups as well as several acid radicals, their salts, or their reactive derivative radicals.

It has been discovered that such compounds can be obtained by preparing oligomer or polymeric backbones in the form of homo- or co-oligomers or homo- or co-polymers that contain the desired acid groups or acid-derivative groups and/or functional groups that the desired acid groups or acid-derivative groups can be grafted to.

The compounds in accordance with the invention contain in a practical way three or more polymerizable unsaturated groups and three or more acid radicals, their salts or their reactive derivatives, whereby, depending on the substrate that the compounds are to adhere to and on the polymerizable system that they are contained in or that they are to polymerize with, a choice can be made as to whether there are to be more acid groups or more polymerizable groups or whether the same number of groups is to be present.

Appropriate polymerizable unsaturated groups are all alkenyl, alkenoxy, cycloalkenyl, aralkenyl, and alkenaryl radicals, in practical terms however, acryl, methacryl, vinyl, and styryl radicals, and of these in especially practical terms the acryl and methacryl radicals that constitute the polymerizable groups of many monomers in dental materials.

Especially appropriate acid groups in the compounds in accordance with the invention are in principle all those that exhibit adhesiveness to oxidic, mineral, ceramic, vitreous, metallic, or biological substrates. It is practical however, to employ carboxylic-acid radicals, the radicals



of phosphoric acids wherein R is alkyl, aryl, or vinyl for example, the radicals —SO_2H, SO_3H, or —O—SO_3H of sulfuric acids, and the radicals