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## POLYMERIZATION OF SILOXANES

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10 Claims

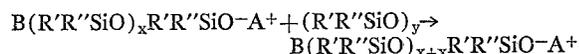
### ABSTRACT OF THE DISCLOSURE

Cyclic siloxanes are polymerized to produce organopolysiloxanes having a narrow molecular weight distribution by carrying out the polymerization reaction employing a basic catalyst and terminating the polymerization reaction at a point where the ratio of weight average molecular weight to number average molecular weight is less than 1.6.

This invention relates to a method for the polymerization of cyclic diorganosilicon compounds and is particularly concerned with the provision of diorganosilicon polymers having a narrow molecular weight distribution.

The polymerization of cyclic diorganosiloxanes in the presence of basic catalysts to produce high molecular weight linear siloxane polymers has long been known. Included among the catalysts used and proposed for this purpose are alkali metal hydroxides, quaternary ammonium hydroxides, quaternary phosphonium compounds and alkali metal silanulates.

The method by which the polymerization of cyclic siloxanes has been believed to proceed involves the stepwise addition of cyclic siloxane units to a silanolate active center, for example according to the equation



wherein R' and R'' represent the silicon-bonded organic radicals in the cyclic siloxane, x and y are integers and A and B are the cation and anion formed by the dissociation of the catalyst.

The silanolate active center may exist as the unsolvated ion pair as represented above, as a solvated ion pair or as the free ions. A dynamic equilibrium will exist between these various forms of the silanolate active center and polymerization of the cyclic siloxane will proceed at different rates from each type of center. Formation of the silanolate active center may take place in situ following the addition of the basic catalyst to the cyclic siloxane or it may be pre-formed, for example by the reaction of an alkali metal with a triorganosilanol.

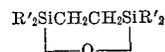
In connection with the above described polymerization mechanism, it is known that side reactions occur during the polymerization process which result in redistribution of siloxane bonds between the silanolate active centers and the polymeric product. One effect of this rearrangement is that the spectrum of the molecular weights of siloxane polymers in the product is broadened. Similar broadening of the molecular weight distribution also arises from the depolymerization reaction and transfer reactions which take place in the system in the presence of water.

Thus, the known processes for polymerizing cyclic siloxanes to the commercially desirable linear polymers lead to products which consist of siloxanes having a very wide distribution of molecular weights and which are characterized by a ratio of weight average molecular weight ( $\bar{M}_w$ ) to number average molecular weight ( $\bar{M}_n$ ) which is often considerably in excess of 2.0. To obtain products hav-

ing improved and more desirable molecular weight distributions, therefore, it has hitherto been necessary to subject the polymerization product to tedious and expensive fractionation procedures.

The object of this invention is to modify the known polymerization procedures described above to arrive at a polymeric product having a distribution of molecular weights which is significantly narrower than that obtained by conventional techniques. Polymeric organosilicon products obtained in the absence of expensive fractionation processes in which the ratio of weight average molecular weight ( $\bar{M}_w$ ) to number average molecular weight ( $\bar{M}_n$ ) is considerably less than 2.0 are also sought. Other objects and advantages of this invention are detailed in or will be apparent from the following disclosure.

According to this invention there is provided a process for the preparation of an organosilicon polymer comprising (1) polymerizing at a temperature up to 160° C. at least one cyclic organosilicon compound which is (a) a cyclic diorganopolysiloxane of the formula  $(R_2SiO)_m$  wherein each R represents a hydrogen atom, a monovalent hydrocarbon radical or monovalent halohydrocarbon radical and m is 3 or 4 or (b) a compound of the general formula



wherein each R' represents a monovalent hydrocarbon radical, a monovalent halohydrocarbon radical or a lower alkoxy radical, in the presence of a catalytic quantity of a basic catalyst and (2) terminating the polymerization prior to equilibrium and at a point where the ratio of weight average molecular weight ( $\bar{M}_w$ ) to number average molecular weight ( $\bar{M}_n$ ) is less than 1.6.

Cyclic trisiloxanes  $(R_2SiO)_3$  and cyclic tetrasiloxanes  $(R_2SiO)_4$  can be polymerized according to this invention to obtain linear organosiloxane polymers having a narrow molecular weight distribution. In general, however, it is possible to obtain a lower  $\bar{M}_w/\bar{M}_n$  ratio with the cyclic trisiloxanes and the use of such materials is therefore normally preferred.

Also operative in the process of this invention are the cyclic silethylene siloxanes which are polymerizable to organosilicon polymers in which the silicon atoms are joined through ethylene radicals and oxygen atoms.

In the general formulae of the operative cyclic starting materials each R can represent any monovalent hydrocarbon radical, for example an alkyl radical such as the methyl, ethyl, propyl, nonyl and octadecyl radicals, alkenyl radicals such as vinyl, allyl and butenyl radicals and aryl radicals such as the phenyl, tolyl and xylyl radicals. Each R can also represent a hydrogen atom or a monovalent halogenated hydrocarbon radical, for example the chloromethyl, bromophenyl and trifluoropropyl radicals. The radical R' in the cyclic silethylene siloxane can represent the same organic radicals as R and in addition can also represent a lower alkoxy radical, that is, an alkoxy radical containing from 1 to 6 carbon atoms.

Organosilicon polymers containing monovalent hydrocarbon or halohydrocarbon radicals particularly those selected from methyl, vinyl, phenyl and trifluoropropyl radicals are usually of most commercial significance and the preferred cyclic organosilicon materials for use in this invention are those containing such radicals. Preferably, also the cyclic organosilicon compound is the cyclotrisiloxane. If desired, mixtures of cyclic organosilicon compounds can be employed and also if desired R can represent different radicals in any particular cyclic material. Operative cyclic siloxanes for use in the process of this invention therefore include hexamethylcyclotrisiloxane, methylphenylcyclotrisiloxane, methy(trifluoropropyl)cyclotrisiloxane and mixtures thereof. If desired,