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ORGANOSILOXANE BLOCK COPOLYMERS

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This invention relates to a new and improved organopolysiloxane copolymer, and more specifically to a method for making same. This method for making organopolysiloxane copolymers satisfies the need for a single method of producing a wide range of specific block copolymers of organopolysiloxanes.

Generally the prior art taught organopolysiloxane copolymers which were made by methods which produced random copolymers. The random copolymers, although made from monomers which each had at least one desirable property, would not have properties intermediate to the two homopolymers. An example would be to copolymerize monomer A which normally gave a hard and brittle film with monomer B that normally would give a soft and flexible film. The object of such copolymerization was to produce a copolymer with properties intermediate to the homopolymers A and B, for example, to give a copolymer giving a hard and flexible film. However, it was found the copolymer would generally be brittle or would still be soft, and the desired intermediate properties would not be obtained. Some improvements might be realized such as the hard and brittle polymer might be more flexible, but only marginally so.

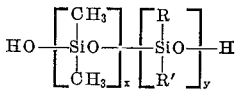
Prior art in the field of organic polymers shows that, if a regular order of monomers in the polymer or copolymer chain occurs, the final polymer or copolymer has entirely new properties in contrast to the random order copolymers. Although the same monomers and percentages of monomers make up the composition of the random order copolymer and the regular order copolymer, the final polymers in each case differ widely in properties. Also in homopolymers where all bonding between monomers is head to tail, for instance, instead of some head to tail, some head to head and some tail to tail without any order, the final homopolymer has new properties. Much of the time it is difficult, expensive and sometimes impossible to produce the desired regular order of monomers in the polymer chains because it is the nature of the specific monomers involved in such a polymerization to react to produce random order copolymers.

The development of silicon-containing block copolymers has furthered the art in producing improved properties with less difficulty, less expense and a better chance of forming an order in the copolymer chain resulting in improved properties. Still the silicon-containing block copolymers have not achieved the theoretically ultimate siloxane polymer. Many of the building blocks which would be desirable in a siloxane polymer cannot be used because the blocks are not soluble in one another, resulting in a two phase system of unusable product.

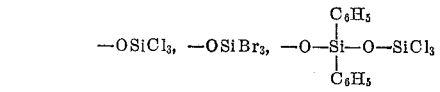
It is an object of this invention to provide a method for making new organopolysiloxane block copolymers. Novel regular order block copolymers which can be cured under ordinary conditions to either resins or rubbers are also sought. Another object is a new and improved organopolysiloxane block copolymer. A further object is a method of copolymerizing siloxanes whereby previously incompatible silicon-containing segments are made compatible and useful polymers result.

This invention relates to a method for producing a silicon-containing block copolymer consisting essentially

of (A) reacting (1) 5 to 99 mol percent of an organopolysiloxane of the general formula



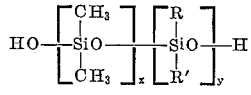
wherein each R and each R′ is selected from the group consisting of methyl, ethyl, phenyl and vinyl radicals, x is an integer of from 5 to 400 inclusive, y is an integer of from 0 to 40 inclusive, there being no more than 10 mole percent organosiloxane units other than methyl-containing siloxane units in the polymer, the siloxane containing an average of from 1.9 to 2.0 organo groups per silicon atom, having a viscosity range of from 25 to 1,000,000 centipoises at 25° C. and an amount of a suitable organic solvent from that portion necessary for the final solids concentration which is an amount of from 5 to 60 perment by weight and (2) an amount of at least one of the following molecules per hydroxyl group of (1) a silicon-containing compound of the general formula Y—SiX_3 wherein Y is selected from the group consisting of halogen atoms,



and —$SiCl_3$ and X is a halogen atom and containing an amount of a suitable organic solvent from that portion necessary for the final solids concentration which is an amount of from 5 to 60 percent by weight, in the presence of an acid acceptor and the above reaction continues until complete, (B) adding from 1 to 95 mole percent (3) of a silicon-containing compound selected from the group consisting of (a) a silane of the general formula R″SiX_3 wherein R″ is selected from the group consisting of aryl, alkaryl and halogenoaryl radicals, and X is a halogen atom, (b) a hydrolysis product of (a), and (c) mixtures thereof; (c) hydrolyzing at a temperature of from 25° to 175° C. in water containing enough hydrogen halide to have a solution of from 0.01 to 30 percent by weight, (p) the organopolysiloxane-organic phase is separated from the aqueous phase, the organic phase is neutralized and azeotroped dry, (E) the dried organopolysiloxane solution is made compatible by adding a silicon-bonded hydroxyl condensation catalyst, refluxing and then neutralizing, (F) the above composition is concentrated by driving off the solvent by conventional means and adding a curing catalyst and then curing.

It is important that the addition of the reactants be kept in the designated order to produce the desired copolymer. More significant is producing a higher degree of functionality at the ends of the polymer block having an average of from 1.9 to 2.0 inclusive, preferred 1.98 to 2.0 inclusive, organic groups per silicon atom. A critical order is the reaction of the polymer block having an average of from 1.9 to 2.0 inclusive organic groups per silicon atom with a silicon-containing material having four or more halogen atoms per molecule. The omission of the above reaction step or the change in the order of additions of reactants will not allow this invention to operate within the specified limits.

The organosiloxane having an average of from 1.9 to 2.0 inclusive Si—C linkages per silicon atom is of the general formula



wherein each R and each R′ is selected from the group consisting of methyl, ethyl, phenyl and vinyl radicals. Small amounts of other organosiloxane units can be pres-