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(54) IMPROVEMENTS IN POLYSILOXANES

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polysiloxanes and in particular to a block copolymer having excellent solvent resistance, as well as desirable processability and more particularly the present invention relates to a block copolymer composed of alkylperfluoroalkylethylenesiloxy blocks and diphenylsiloxy blocks which block copolymer has desirable processability properties and excellent solvent resistance.

Dimethylpolysiloxane polymers which are cured with peroxide curing catalysts to produce heat vulcanizable silicone rubber elastomers are well known in the art. Such heat vulcanizable elastomers have the desired low and high temperature stability that is well known of silicone elastomers. However, one difficulty in the production of such elastomers is that the diorganopolysiloxane gums that are utilized have viscosities of 1,000,000 to 200,000,000 centipoise at 25°C. Such materials with the incorporation of the necessary amounts of filler in them tend to be very viscous, as can be appreciated, and very tacky. Accordingly, such polymers are very difficult to process because of their tackiness on standard processing equipment in the preparation of such compositions prior to curing them at elevated temperatures.

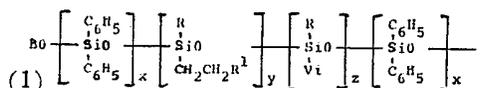
There have been many attempts to alleviate the processing problems in the treating of such uncured heat vulcanizable silicone rubber compositions. One approach to the problem is to utilize process aids. Another approach is that disclosed in Bostick, U.S. Patent 3,337,497 which is to form a block copolymer having diphenyl siloxy blocks in the copolymer along

with dimethylsiloxy blocks. The advantages of having such diphenylsiloxy block is that such blocks depending on the number of siloxy units in the block are crystalline at temperatures up to 200°C and above. Accordingly, they impart to the diorganopolysiloxane block copolymer a certain amount of stiffness which prevents the polymer from being tacky and accordingly facilitates the processing of heat vulcanizable silicone rubber compositions in the uncured state. However, such polymers while being processable in the uncured state do not have as high a solvent resistance in hydrocarbon fluids as would be desired.

Solvent resistant heat vulcanizable silicone rubber compositions having fluorinated substituent groups in the polymer are well known—see, for instance, U.S. Patent 2,979,519 of Pierce et al and U.S. Patent 3,179,619 of Brown.

However, one disadvantage of such polymers which are utilized to produce heat vulcanizable silicone rubber compositions, such as that disclosed in the above patents, is that the fluorinated gums are even more tacky than dimethylpolysiloxane gums and thus are extremely difficult to process even at temperatures below room temperature. To alleviate this problem, certain process aids have been developed for fluorosilicone polymers. However, these process aids have not completely alleviated the problem. Further, the Bostick, U.S. Patent 3,337,497, specifically discloses that this block copolymer be free of halogen hydrocarbon substituent groups. Accordingly, little, if any, attempt, has been made up to the present time to produce such block copolymers with fluorinated substituent groups.

Accordingly, the present invention provides a solvent resistant block copolymer having excellent processability properties in the uncured state which is a copolymer of the formula,

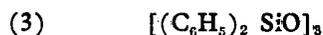


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wherein R is an alkyl radical of 1 to 3 carbon atoms, R¹ is a perfluoroalkyl radical of 1 to 8 carbon atoms, Vi is vinyl, B is selected from lithium and hydrogen, x varies from 20 to 400, y varies from 700 to 6000 and z varies from 0 to 100. The above block copolymer is produced by reacting in the anhydrous state a trimer of the formula,



in the desired molar proportions in the presence of a solvent promoter selected from tetrahydrofuran, dioxane, dimethylformamide, dimethylsulfoxide tetramethyl urea and a catalyst which is a dilithium compound and then after the fluorinated block is formed to add a trimer of the formula,



and complete the reaction.

At this point, there may optionally be added along with the fluorinated trimer a methylvinyl trimer to add various amounts of methylvinylsiloxo units in the fluorinated block to facilitate the curing of the final block copolymer with a peroxide catalyst.

In the preferred embodiment, the reaction is carried out in two stages where in the first stage the reactants are heated at a temperature of 55 to 85°C for a period of time varying from 0.5 to 4 hours and in the second reaction period the solvent promoter is stripped off and there is added to the reactants the diphenyl trimer in a high boiling solvent and the reaction is completed at a temperature varying anywhere between 85 to 180°C for an additional period of time varying from 1 to 8 hours. The high boiling solvent may be such solvents as dichlorobenzene, and the dimethoxyether of ethylene glycol and diphenylether. When the reaction is completed the dilithium compound is neutralized with any well known neutralizing agent for lithium, but is preferably neutralized with compounds such as water, acetic acid, or an aliphatic alcohol. The solvent promoter or high boiling solvent is then stripped off to yield the block copolymer. The catalyst is utilized at a concentration of 0.7 to 8.0 millimoles per mole of trimer reactants and more preferably utilized at a concentration of 1.1 to 6.0 millimoles per mole of trimer reactants. Further, it is only necessary that the solvent promoter be in sufficient quantities in the initial part of the reaction so as to dissolve the trimer reactants and more preferably it is utilized in considerable excess since it facilitates the promotion of the reaction. As can be understood in the reaction, the fluorinated trimer is first added to the solvent promoter in the presence of a catalyst and allowed to react to form a fluorinated block and then the diphenylsiloxo trimer is added

to form the terminal blocks on the block copolymer.

Once the block copolymer is prepared it may then be taken and mixed with the well known ingredients utilized in heat vulcanizable silicone rubber compositions, to produce a solvent resistant elastomer. With the diphenylsiloxo blocks in the block copolymer, the polymer with the filler mixed in and any process aids, pigments, flame retardants and other additives has stiffening properties in the composition such that it is not very tacky. Thus, the entire uncured composition has good processability properties.

In formula (1) of the block copolymer, R may be any alkyl radical of 1 to 3 carbon atoms, but it is most preferably methyl; R¹ is a perfluoroalkyl radical of 1 to 8 carbon atoms and is preferably CF₃; x varies from 20 to 400 as indicated above, but preferably varies from 100 to 200. Generally, the two diphenylsiloxo blocks are approximately of the same siloxo unit length. It is only necessary that the diphenylsiloxo block be at least 20 units long to give the block copolymer the proper crystallinity, specifically, to give the block the desired crystallinity up to a temperature of 283°C, which is the temperature at which the fluorosilicone may degrade due to heat.

Within the above ranges for y, as indicated, y may vary from 700 to 6000, but preferably varies from 1000 to 2500; B in the above formula may be lithium or is preferably hydrogen as a result of the neutralization of the catalyst during the process of producing the block copolymer.

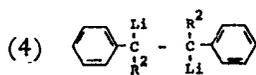
It should be noted at this instance that the presence of the hydroxy groups at the end of the block copolymer do not create a problem when the material is used to produce heat vulcanizable silicone rubber compositions since such hydroxy groups are present at a very small weight percent. Normally, the block copolymers of the instant invention as prepared with the foregoing process will have a viscosity of 10,000,000 to 200,000,000 centipoise at 25°C.

The presence of the perfluoroethylenesiloxo units imparts to the block copolymer the proper solvent resistance and the diphenylsiloxo units because they maintain their crystalline form up to temperatures of 283°C and imparts a stiffening effect to the block copolymer such that it facilitates the processing of the block copolymer.

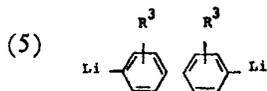
The process for producing the present block copolymer is simple and economical, but it must be followed carefully if a high yield of the present block copolymer is to be obtained.

Accordingly, the basic reaction for producing the block copolymer of the present case comprises taking a tricyclicsiloxane of formula (2), where R and R¹ are as previously defined and

dissolve in it an excess of a solvent promoter. The solvent promoter is critical to the present invention and is preferably selected from tetrahydrofuran, dioxane, dimethylformamide, dimethylsulfoxide, trimethyl urea, and compounds of an equivalent solvent promoter nature. Optionally, at this point there may be added minor amounts of a trimethyltrivinylcyclic trisiloxane so as to introduce methylvinylsiloxo units in the polymer to facilitate the curing of the final polymer with a peroxide to produce a heat cured elastomer. Preferably, sufficient cyclictrisiloxane is added so that z can vary from 1 to 100. It must be understood that insofar as such methylvinylsiloxo units are concerned they may be interspersed with the fluorinated siloxy blocks or form a separate block depending on whether the vinyl trimer is added after the block is formed or concurrently with the addition of the fluorinated trimer to reaction vessel. To this mixture there is added the necessary catalyst which can be any dilithium compound and is specifically a dilithium aromatic-containing compound. Specific types of dilithium compounds which can be utilized as catalysts in the present invention are compounds of the formula,



and compounds of the formula,



where R² and R³ are selected from hydrogen and lower alkyl radicals of 1 to 8 carbon atoms and are preferably hydrogen, or methyl.

The reaction solution composed of the fluorinated tricyclicsiloxane, solvent promoter and catalyst are then preferably heated at the reflux temperature of the solvent promoter which is generally in the range of 55°C to 85°C. This reaction temperature range is not critical. The elevated temperature above room temperature desirably promotes the reaction and higher temperatures could be utilized, however, some of the solvent promoters specified above do have a reflux temperature above the range indicated above and it is necessary initially that the temperature not exceed 85°C. With these ingredients and the heating of the mixture the fluorosilicone block is built up. The amount of trimer that is utilized is controlled by the amount of alkylperfluoroalkylethylenesiloxo units it is desired to have in the basic block in the block copolymer. This reaction is usually carried out generally anywhere from 0.5 to 4 hours. Usually a reaction time of from 0.5 to 1 hour is sufficient for the formation of an alkylperfluoroalkylethylenesiloxo block of the desired size.

At the end of that time there is then added to the reaction mixture a diphenylsiloxocyclictrisiloxane of formula (3) and the reaction is allowed to proceed in the above temperature range until the diphenylsiloxo blocks have been built up to form the block copolymer of formula (1) above. This generally takes place at an additional reaction time of anywhere from 1 to 8 hours.

It must be appreciated that during the reaction the whole system must be maintained as free of water as possible, that is, in an anhydrous state. The presence of even appreciable amounts of water will poison and neutralize the catalyst that is used as a chain propagator in the above-described process.

It must also be appreciated that only cyclictrisiloxanes should be utilized in the present reaction since they result in a high yield of polymer, that is, a yield of block copolymer in the 90 to 100% area from the above reactants. Other cyclicsiloxanes will produce a much lower yield of the desired block copolymer or will not react at all under the described conditions.

Again, the amount of diphenylcyclictrisiloxanes that are utilized in the reaction mixture will depend and is controlled by the amount or the size of the diphenylsiloxo blocks that is desired. The dilithium compound catalyst concentration may vary anywhere from 0.02 to 4.0 millimoles per mole of trimer reactants and preferably varies from 0.04 to 3.0 millimoles per mole of trimer reactants. Too little dilithium compound catalyst will not act as sufficiently as a chain propagator for the siloxy blocks to be formed and too much dilithium catalyst will result in side reactions and the formation of other copolymers other than the desired block copolymer and will result in low viscosity copolymer. After the reaction time has terminated then there may be added a neutralizing agent to the reaction solution to neutralize the lithium chain propagator ions in the block copolymer that is formed.

Such neutralizing agents may be any well known neutralizing agents for lithium ions and are most desirably acetic acid, water or aliphatic alcohols. After the utilization of the catalyst the solvent promoter may be distilled off to yield the desired ordered block copolymer of formula (1) having a viscosity of anywhere from 10,000,000 to 200,000,000 centipoise at 25°C. As such, the block copolymer will generally have anywhere from a 5 to 40 mole percent diphenylsiloxo content with the rest of the substituent groups being alkylperfluoroalkylethylenesiloxo units to give the copolymer the proper solvent resistance.

To carry out the process in two steps, the initial part of the process is carried out as described above, that is, with one of the solvent promoters indicated above, by carrying out the

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initial part of the reaction to form the alkyl-perfluoroalkylethylenesiloxy blocks by heating the reaction mixture at a temperature of 55 to 85°C for 0.5 to 4 hours. At the end of that period and after the fluorinated siloxy block has been formed, it is preferred to utilize a higher boiling solvent, that is, a solvent having a reflux temperature of anywhere from 85 to 180°C. Examples of such solvents being dichlorobenzene and the dimethoxy ether of ethylene glycol and diphenyl ether. The second solvent may be added to the reaction mixture with the diphenyl trimer of formula (3) and the solvent promoter is stripped off. The reaction mixture is then heated at temperatures of anywhere between 85 to 180°C or as higher as possible within that temperature range guided by the reflux temperature of the higher boiling solvent for a period of time of anywhere from 1 to 8 hours to complete the polymerization. The amounts of the higher boiling solvent that is utilized is generally within the same range as the initial solvent promoter. Both solvents are utilized in sufficient quantities to dissolve the reactant trimers and preferably are present in excess since this tends to accelerate the reaction of the formation of the block copolymer.

The advantage of using a high boiling solvent in the second reaction period is that it facilitates the formation of an ordered diphenylsiloxy block. Although desired block copolymers are formed without this two solvent procedure, the diphenylsiloxy blocks are formed in a faster period of time when the higher boiling solvent is utilized in the second step of the reaction.

Finally, the reaction is terminated as previously stated by neutralization of the dilithium compound and then stripping off the higher boiling solvent to yield the desired ordered block copolymer of formula (1) of the present invention.

The block copolymer of the present case can be utilized in well known procedures to produce heat vulcanizable silicon rubber compositions. Thus, the block copolymer may be mixed with the appropriate amounts of reinforcing or extended fillers. Examples of reinforcing fillers are fumed silica and precipitated silica which may be untreated or treated with cyclicsiloxanes, silazanes or other well known filler treating agents. Or they may be incorporated into it an extending filler alone or with the reinforcing filler. Examples of such extending fillers being diatomaceous earth and lithopone. Well known process aids for heat vulcanizable silicone rubber compositions can be utilized with the present block copolymers. In addition, flame retardant agents such as, platinum; heat stabilizing additives such as, iron oxide; compression set additives, as well as other well known additives for heat vulcanizable silicone rubber compositions can all

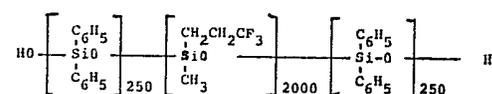
be added to the uncured composition. The composition is then cured by incorporating into it the desired amounts of well known peroxide curing agents. Examples of such peroxide curing agents are dicumyl peroxide and benzoyl peroxide. The resulting mixture is then taken and formed into the necessary fabricated part that it is desired to utilize the composition and cured at elevated temperatures which may be in the range of anywhere from 100 to 300°C to produce a silicone elastomer with excellent solvent resistance.

As an example of the general preparation of such heat vulcanizable silicone rubber compositions in which the present ordered block copolymer may be utilized in—see, for instance, the patent of DeZuba et al, U.S. Patent 3,896,123.

The following examples are given for the purpose of illustrating the present invention, but are not intended to define the limits or scope of the present ordered block copolymers and the process for making them. All parts in the present specification are by weight.

EXAMPLE 1.

To dry tetrahydrofuran there is added 4 moles of anhydrous 3,3,3 - trifluoropropylmethylcycloctrisiloxane, the tetrahydrofuran being utilized in great excess to completely dissolve the fluorinated cyclicsiloxanes. The resulting mixture is then heated to 55°C and 1.25 millimole of dilithio stilbene catalyst is then added. After a period of 3 hours there is formed fluorosiloxy blocks of about 2000 siloxy units long. To this mixture there is then added an anhydrous solution of 1 mole of hexaphenylcycloctrisiloxane dissolved in tetrahydrofuran where there is sufficient tetrahydrofuran to completely dissolve the cycloctrisiloxane. The reaction mixture is then allowed to react for 2 hours again at 55°C. At the end of this period, the tetrahydrofuran is stripped slowly off from the reaction mixture in a period of time of about 1 hour. At the end of this time the batch temperature was 85°C, but some tetrahydrofuran was still refluxing. After two hours under these conditions, the remaining tetrahydrofuran was stripped from the reaction. Then 2 drops of acetic acid are added to deactivate the catalyst. For the purpose of determining the structure of the polymer, the polymer is swelled in ethyl acetate and precipitated from ethyl acetate into methanol. No unreacted diphenyl trimer was found. The block copolymer that is formed was white in color and has the following formula,



This copolymer had a concentration of 80 mole percent of methyltrifluoropropylsiloxo units. For comparison purposes a random block copolymer is formed. Thus, there is reacted in a typical solvent, toluene, 0.8 moles of



with 0.2 moles of pure diphenylsilane diol at a 160°C temperature using 800 ppm of stannous octoate catalyst for a period of time varying from 1 to 4 hours. Utilizing this procedure there is formed a clear random copolymer which had a concentration of 80 mole percent of methyltrifluoropropylsiloxo units.

The ordered block copolymer of the formula above and the random block copolymer of the formula above are then taken and per 100 parts of the polymer there is added to each polymer 40 parts of octamethylcyclotetrasiloxane treated fumed silica and 3 parts of benzoyl powder and the resulting mixture is then cured for 20 minutes at 300°F. The samples are cooled in the mold and then post cured for 1 hour at 400°F. The solvent swell for each rubber sample is then measured in toluene at room temperature for 24 hours. The results of the solvent swell test is as follows:

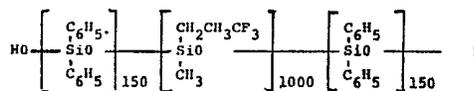
Sample	V% Solvent Swell
Block copolymer	39
Random copolymer	139

The above data indicates that for substantially the same methyltrifluoropropylsiloxo content the ordered block copolymer of the present case has substantially superior solvent resistance to hydrocarbon fluids. In addition, the uncured polymer is found to be considerably easier to handle and mix with the other ingredients than the random copolymer which did not have in it diphenylsiloxo crystalline blocks in the copolymer.

EXAMPLE 2.

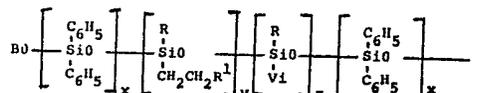
In an anhydrous system and to an excess of tetrahydrofuran there is added 5 moles of anhydrous 3,3,3-trifluoropropylmethylcyclo-trisiloxane and 2.41 millimoles of dilithio-stilbene dissolved in tetrahydrofuran is added. The resulting mixture is heated to reflux at 55°C for a period of time of about 3 hours. At the end of that time it is found that the dilithio fluorinated terminated block has 1000 siloxy units in it. Then there is added to the mixture an anhydrous solution of 1-1/2 moles of hexaphenylcyclotrisiloxane dissolved in an excess amount of dichlorobenzene. The resulting mixture is then heated at 95°C to strip off the tetrahydrofuran and then heated at a temperature of 150°C for 3 hours. At the end of that time, the dichlorobenzene is

stripped off in about 1/2 hour and 2 drops of acetic acid is added to deactivate the polymer. The ordered block copolymer that is formed has the structural formula,



WHAT WE CLAIM IS:—

1. A solvent resistant block copolymer of the formula,

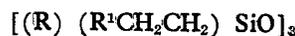


where R is an alkyl radical of 1 to 3 carbon atoms, R¹ is a perfluoroalkyl radical of 1 to 8 carbon atoms, Vi is vinyl, B is lithium or hydrogen, z is from 0 to 100, x is from 20 to 400 and y is from 700 to 6000.

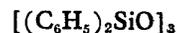
2. A copolymer as claimed in Claim 1 wherein R is methyl and R¹ is CF₃ and B is hydrogen.

3. A copolymer as claimed in Claim 1 or Claim 2 wherein x varies from 100 to 200 and y varies from 1000 to 2500.

4. A process for producing a solvent resistant block copolymer comprising reacting in an anhydrous system a trimer of the



in the presence of a solvent promoter selected from tetrahydrofuran, dioxane, dimethylformamide, dimethylsulfoxide, tetramethyl urea, and a catalyst which is a dilithium compound and then adding a trimer of the formula,



and completing the reaction.

5. A process as claimed in Claim 4 wherein the reaction is carried out in two reaction stages wherein the first reaction stage comprises reacting the fluorosilicone trimer at a temperature in the range of 55°C to 85°C for a period of time varying from 0.5 to 4 hours and in a second stage adding the diphenyl trimer and completing the reaction at a temperature in the range of 85 to 180°C for a period of time varying from 1 to 8 hours.

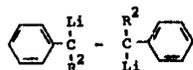
6. A process as claimed in Claim 5 wherein in said second reaction period the solvent promoter is removed and there is added a high boiling solvent to complete the polymerization in said second reaction period.

7. A process as claimed in Claim 6 wherein said high boiling solvent is selected from dichlorobenzene and the dimethoxyether of

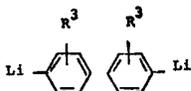
diethylene glycol and diphenylether.

8. A process as claimed in any one of Claims 5 to 7 further comprising after said second reaction period neutralizing said catalyst with a neutralizing agent selected from water, acetic acid, and an aliphatic alcohol and stripping off the solvent.

9. A process as claimed in any one of Claims 4 to 8 wherein the catalyst is selected from compounds of the formula,



and compounds of the formula,



- 15 where R² and R³ are each hydrogen or a lower alkyl radical of 1 to 8 carbon atoms.

10. A process as claimed in any one of Claims 4 to 9 wherein the catalyst is utilized at a concentration of 0.7 to 8.0 millimoles, per mole of trimer reactants.

- 20 11. A process as claimed in any one of

Claims 4 to 10 wherein the promoter solvent utilized is at least of sufficient quantity to dissolve the reactants.

12. A process as claimed in any one of Claims 4 to 11 wherein a cyclictrisiloxane of the formula,



where R is an alkyl radical of 1 to 8 carbon atoms and Vi is vinyl is also reacted with the trimer and solvent promoter.

13. A solvent resistant block copolymer as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples.

14. A process for producing a solvent resistant block copolymer as claimed in Claim 4 substantially as hereinbefore described in any one of the Examples.

15. A solvent resistant block copolymer when produced by a process as claimed in any one of Claims 4 to 12 and 14.

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