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(54) NOVEL FLUOROALKYLSUBSTITUTED CYCLOTRISILOXANES, THEIR USE FOR PREPARATION OF NEW POLYMERS AND NOVEL POLYMERS

FLUORALKYLSUBSTITUIERTE TRICYCLOSILOXANE, IHRE ANWENDUNG ZUR HERSTELLUNG NEUER POLYMERE UND NEUE POLYMERE

NOUVEAUX TRICYCLOSILOXANES A SUBSTITUTION FLUOROALKYLE, UTILISATION DE CES TRICYCLOSILXANES POUR LA PRODUCTION DE NOUVEAUX POLYMERES ET NOUVEAUX POLYMERES AINSI OBTENUS

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WO-A1-97/20851
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Description

[0001] . This invention concerns new fluoroalkylsubstituted cyclotrisiloxanes, new homopolymers and block copolymers derived from said cyclotrisiloxanes, and their preparation.

BACKGROUND OF THE INVENTION

[0002] The only commercially available fluoroalkylsiloxane is poly(trifluoropropylmethylsiloxane). It is prepared via anionic or cationic ring opening polymerization of cyclotri(trifluoropropylmethylsiloxane). Crystalline fluoroalkylmethylpolysiloxane has been obtained from the monomer of pure cisisomer. [1,2] Precursor of cyclotri(trifluoropropylmethylsiloxane) is trifluoropropylmethyldichlorosilane, prepared usually by platinum (H_2PtCl_6) catalyzed hydrosilation reaction between methyldichlorosilane and 3,3,3-trifluoropropene. [3] The reaction has also been applied to the preparation of bis(trifluoropropyl)dichlorosilane using dichlorosilane instead of methyldichlorosilane. Unlike non-fluorinated alkenes (ethene, propene) which give good yields between 60 and 79 %[4], 3,3,3-trifluoropropene gives only low yields, 26...36 % in preparation of disubstituted silicon. [5] Bis (1H, 1H, 2H-perfluorohexyl)dichlorosiloxane has been obtained in 42% overall yield via a two step process, where both $Co_2(CO)_8$ and platinium cyclovinylmethylsiloxane complex were used for the hydrosilylation reaction between dichlorosilane and 1H, 1H, 2H-perfluorohexane. [6] High yields have been obtained via, UV-light catalyzed radical reaction. [7,8,9]

[0003] 3-(Pentafluorophenyl)ethylmethyldichlorosilane has been prepared in 70 % yield from methyldichlorosilane and pentafluorostyrene. [10] Cyclics having both dimethylsiloxy and 3-(pentafluorophenyl)ethylmethylsiloxane units were prepared by Matsui et al [11] via hydrosilation reaction between pentafluorostyrene and cyclics containing dimethylsiloxy and methylsiloxy units. Polymerization of these cyclics was catalyzed by tetramethylammonium hydroxide, polymer M_w/M_n = 38,000/21,000 g/mol. See Scheme 1.

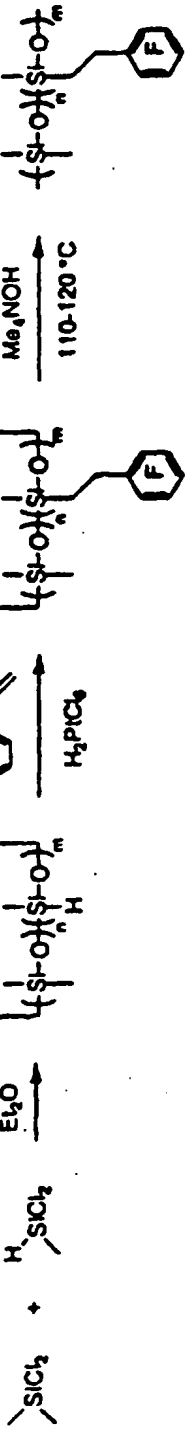
[0004] Matsui also prepared hetero cyclics of dimethyldichlorosilane and 3,3,3-trifluoropropylmethyldichlorosilane or 1H,1H,2H,2H-perfluorodecylmethyldichlorosilane via co-hydrolysis in ether. Polymerization was carried out as in the previous case.

[0005] The European patent publication EP 0563902 by Dow Corning [12] describes a method for preparation of block co-copolymers from D_3 and D_3-type cyclic monomers having 1H,1H,2H,2H-perfluoroalkylmethylsiloxane groups and/or vinylmethylsiloxane groups. See Scheme 2.

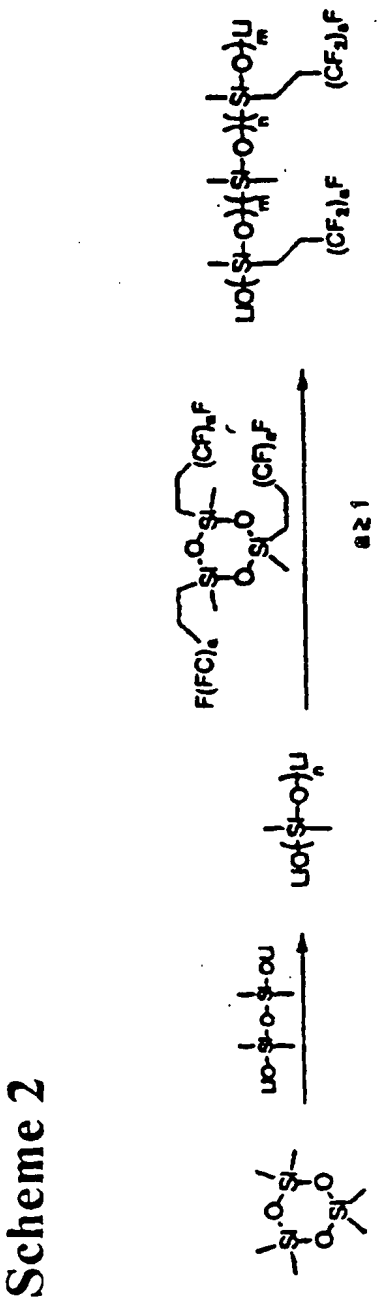
[0006] US patent 4,814,418 [13] describes a similar procedure, but instead of sequential addition of monomers, they add them simultaneously, resulting a non-block copolymer. The patent covers the use of cyclic trimers of $\{[F(CF_2)_aC_2H_4](CH_3)SiO\}_3$ and $\{[H(CF_2)_aC_2H_4](CH_3)SiO\}_3$ (a = 1...16) with or without D_x (x = 3...6) and/or D_x^{McVi} (x = 3...6, Vi = alkenyl group). The patent also claims higher molecular weight polymers by use of a phase transfer catalyst/initiator combination instead of initiator alone. Phase transfer catalyst is a quaternary ammonium or phosphonium salt and can be presented by the formulas $R_4N^+X^-$ or $F_4P^+X^-$, where R is alkyl, cycloalkyl or phenyl group and X^- is Cl^- or Br^-.

[0007] The document US3,070,617 discloses two cyclic bistrifluoropropyl siloxanes, namely $[(CF_3CH_2CH_2)_2SiO]_3$ and $[(CF_3CH_2CH_2)_2SiO]_4$. These compounds are useful as intermediates in the preparation of copolymers of bistrifluoropropylsiloxane with other siloxanes, such as trifluoropropylmethylsiloxane or diphenylsiloxane.

Scheme 1



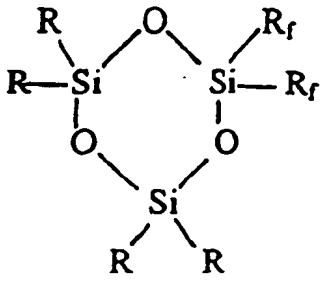
Scheme 2



OBJECTS AND SUMMARY OF THE INVENTION

[0008] The aim of this invention is to provide novel fluoroalkylsubstituted cyclotrisiloxanes and novel polymers made thereof, either homopolymers made by anionic or cationic polymerization, or block copolymers made by anionic polymerization of said fluoroalkylsubstituted cyclotrisiloxanes.

[0009] Thus, according to one aspect, this invention concerns novel fluoroalkyl substituted cyclotrisiloxane of the formula (Ia)

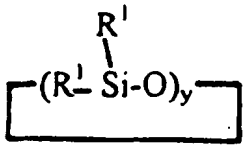


(Ia)

wherein R is a lower alkyl of 1 to 4 carbon atoms and R_f has the formula $(CH_2)_2$-$(CR'_2)_n$-CR'_3, wherein all or some of the R' substituents are F, the remaining R' substituents being H, and n is an integer varying from 0 to 8.

[0010] According to another aspect, this invention concerns a method for the preparation of a homopolymer, wherein said compound of formula (Ia) is subjected to anionic or cationic polymerisation in bulk or in a suitable solvent to give said homopolymer.

[0011] According to a further aspect, the invention concerns a method for the preparation of a block copolymer or random copolymer, wherein the compounds of formula (Ia), and a cyclosiloxane of formula (II),



(II)

wherein y is 3, 4 or 5 and all or some of the R^1 substituents are alkyl of 1 to 4 carbon atoms, vinyl or phenyl, or wherein one R^1 is R_f as defined before and the remaining R^1 substituents are alkyl of 1 to 4 C-atoms, vinyl or phenyl, are subjected to anionic or cationic polymerisation to give said block or random copolymer.

[0012] The invention concerns also the novel homopolymers, block copolymers and random copolymers.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The most preferable compounds of formula Ia and Ib are those where each of the R' substituents in $(CH_2)_2$-$(CR'_2)_n$-CR'_3 (R_f) is F.

[0014] The polymerization can be carried out either in bulk or in a suitable solvent.

[0015] The cationic polymerization is preferably initiated by trifluoromethane sulfonic acid (triflic acid).

[0016] The anionic polymerization is preferably initiated by a lithium containing base, for example dilithium diphenylsilanolate or dilithium tetramethyldisiloxanolate.

[0017] The compounds Ia, Ib and II can be polymerized in any order with respect to each other. They can also be mixed with each other before the initiation of the polymerization.

[0018] The invention will be described more in detail in The Experimental section in the following non-limiting examples.

Experimental

Spectroscopic Analysis

[0019] ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. Forty percent w/v solutions in acetone-d_6 were used to obtain the spectra. ^{13}C and ^{19}F NMR spectra were obtained with broad band proton decoupling. An inverse gate decoupling pulse sequence with a 60 sec delay was used to acquire ^{29}Si NMR spectra. Tetramethylsilane (TMS) was used as an internal standard for ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectra, and $CFCl_3$ for ^{19}F spectra. IR spectra of neat films on NaCl plates were recorded on a Perkin Elmer Spectrum 2000 FT-IR spectrometer.

EXAMPLE 1

Preparation of 1,1-bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane

a) Bis(1'H,1'H,2'H,2'H-perfluorooctyl)dichlorosilane

[0020] Dichlorosilane (5.2 mL, 63 mmol), 1H,1H,2H-perfluoro-1-octene (27.7 mL, 126 mmol), 3 drops of 10 % H_2PtCl_6 in THF/MeOH solution and 100 µL Pt/divinyltetramethyldisiloxane complex in toluene were placed into Ace pressure tube for 24 h. Distillation gave 13.0 g desired product, bp 96 °C/0.2 mm. Yield 27.5 %. ^{1}H NMR δ: 1.66(m, 4H), 2.47 (m, 4H). ^{13}C NMR δ: 11.04, 25.61 (t, J = 24 Hz), 106-123(m). ^{19}F NMR δ: -122.55(m, 4F), -119.46(br s, 4F), -119.09 (br s, 4F), - 118.07(br s, 4F), -111.89(p, 4F, J = 15 Hz), -77.63(t, 6F, J = 10 Hz). ^{29}Si NMR δ: 32.63. IR ν: 2956, 2910, 2877, 1444, 1410, 1364, 1319, 1296, 1237, 1202, 1146, 1121, 1073, 1019, 902, 812, 708, 649, 566, 533 cm^{-1}.

b) 1,1-Bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane

[0021] Bis(1'H,1'H,2'H,2'H-Perfluorooctyl)dichlorosilane from step a) (20.0 g, 25 mmol) in 15 mL Et_2O and tetramethyldisiloxanediol [14] (4.19 g, 25 mmol) in 15 mL Et_2O were simultaneously dropped into solution of Et_3N (8.0 mL, 57 mmol) and 100 mL Et_2O in 1 h. After filtration the solution was washed with water, dried over $MgSO_4$ and solvents were removed by evaporation. Fractional distillation gave 11.33 g (50.7 % yield), bp 113 °C/0.2 mm, mp 56 °C. The reaction was carried out at room temperature. ^{1}H NMR δ: 0.21(s, 12H), 1.01(m, 4H), 2.29(m, 4H). ^{13}C NMR δ: 0.68, 5.98, 25.51(t, J_{C-F} = 23 Hz), 106-123(m). ^{19}F NMR δ: -127.05(s, 4F), -124.21(s, 4F), -123.56(s, 4F), -122.53 (s, 4F), -117.00(t, 4F, J = 16 Hz), -82.16(t, 6F, J = 10 Hz). ^{29}Si NMR δ: -13.35(1Si), -7.08(2Si). IR ν: 2969, 2947, 2913, 1445, 1367, 1316, 1260, 1247, 1212, 1185, 1145, 1067, 1020, 808, 735, 691, 648, 605, 566, 528 cm^{-1}.

EXAMPLE 2

Anionic polymerization of 1,1-bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane.

Initiator for anionic polymerization:

[0022] Dilithium diphenylsilanolate was prepared by treatment of diphenylsilanediol with *n*-butyl lithium in THF. Styrene was used as an indicator.[2] Tetramethyldisiloxanediol can be used instead of diphenylsilanediol in order to enhance initiator's solubility in low temperature polymerizations.

[0023] Monomer (1,1-bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane) (2.0 g, 2.3 mmol), initiator (159 µL, 40 µmol) were allowed to react in 0.6 mL THF at RT for 2.5 h. Polymer was endcapped with trimethylchlorosilane and precipitated three times from $CFCl_3$ with hexanes/acetone solution. After drying under vacuum, 1.95 g (98 % yield) was obtained. T_g = -64 °C. ^{1}H NMR δ: 0.19(m, 12H), 0.94(m, 4H), 2.23(m, 4H). ^{13}C NMR δ: 1.10, 6.02, 25.67(t, J = 23 Hz), 102-125(m). ^{19}F NMR δ: 126.45(4F), -123.34(4F), -122.99(4F), - 121.96(4F), -116.29(4F), -81.47 (6F). ^{29}Si NMR δ: -26.35, -26.21, -25.85, -25.80, - 25.76, -20.84, -20.337, -20.25, -20.02, -19.97, -19.77, -19.62, -19.60, -19.54, -19.45, -19.21, -18.84. IR ν: 2966, 2912, 1444, 1423, 1420, 1363, 1352, 1317, 1296, 1264, 1240, 1210, 1197, 1167, 1146, 1119, 1104, 1073, 1018, 950, 905, 844, 807, 747, 738, 707, 651, 566, 532 cm^{-1}.

EXAMPLE 3

Cationic polymerization of 1,1-bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane

[0024] Monomer (1,1-bis(1'H,1'H,2'H,2'H-perfluorooctyl)-3,3,5,5-tetramethylcyclotrisiloxane) (2.0 g, 2.3 mmol) and $CFCl_3$ (1 mL) were sealed into 10 mL test tube equipped with magnetic stir bar and rubber septum. System was cooled to -9 °C and 2 µL of solution consisting of 50 µL triflic acid in 2 mL toluene was injected. Polymerization was allowed to proceed for 1 hour, after which polymer was precipitated as above yielding 1.7 g (85 %). Polymer properties were as above.

EXAMPLE 4

Hexakis(1'H,1'H,2'H,2'H-perfluorooctyl)cyclotrisiloxane.

[0025] A solution of bis(1,1,2,2-tetrahydroperfluorooctyl)dichlorosilane, (10.6 g, 13.4 mmol) and 25 mL dry $CHCl_3$ were placed in a 50 mL rb flask equipped with a 10 mL dropping funnel. DMSO, (2, 10g, 26.9 mmol) in 6 mL $CHCl_3$

was dropped into the solution in 30 min at rt, and the reaction was allowed to proceed for 5 h. The flask was then cooled to 0°C, and the upper layer was decanted out. [15,16] The lower layer was washed once with 30 mL $CHCl_3$. The ^{29}Si NMR showed 81% D_3 and 19% D_4-type monomer composition of the crude reaction product: It was distilled through a short path distillation apparatus. Hexakis(1'H,1'H,2'H,2'H-perfluorooctyl)-cyclotrisiloxane (6.00g, yield 61%), bp 200°C/0.01 mm was collected. ^1H NMR δ: 1.19 (m, 8H), 2.37 (m, 8H). ^{13}C NMR δ: 6.51, 25.84(t, J_{C-F} = 24 Hz), 107.61-122.55(m). ^{19}F NMR δ: -126.16(s, 8F), -123.02(s, 8F), -122.64(s, 8F), -121.61(s, 8F), -115.95(t, 8H, J = 13 Hz), -81.31(t, 12F, J = 11 Hz). ^{29}Si NMR δ: -10.27(s, 3Si). IR v: 2981, 2950, 2913, 2871, 1443, 1422, 1353, 1318, 1298, 1238, 1192, 1144, 1074, 1012, 952, 909, 897, 811, 777, 747, 727, 708, 651, 566, 528 cm^{-1}.

EXAMPLE 5

Poly[bis(1'H,1'H,2'H,2'H-perfluorooctyl)siloxane-co-dimethylsiloxane].

[0026] Hexakis(1'H,1'H,2'H,2'H-perfluorooctyl)cyclotrisiloxane (0.78 g, 0.35 mmol), octamethylcyclotetrasiloxane (1.05 g, 3.6 mmol) and triflic acid (40 μL, 0.24 mmol) were placed into a test tube equipped with a Teflon covered magnetic stirring bar and a rubber septum. The system was heated to 100 °C and allowed to react for 7 h. The tube and its contents were cooled to RT. Hexamethyldisilazane (100 μL, 0.47 mmol) was added to neutralize the acid. The crude polymer solution was cloudy. It was washed twice with acetone, perfluorohexane, toluene and methanol, and dried in vacuum for 6 h. In this way, clear, colorless material, M_w/M_n = 20,010/13,190, T_g = -123 °C, 0.50 g (27 %) was obtained. ^1H NMR δ: 0.11 (s, 24 H), 1.01 (m, 1.33 H), 2.25 (m, 1.33 H). ^{13}C NMR δ: 1.35, 5.96, 25.41 (m), 106.78-121.76 (m). ^{19}F NMR δ: -126.37 (2 F), -123.17 (2 F), -122.98 (2 F), -121.96 (2 F), -116.12 (2 F),-81.29 (3 F). ^{29}Si NMR δ: -26.66 (6.5 Si), -24.82 (4.5 Si), -24.18 (10.0 Si), -23.52 (5.4 Si), -21.99 (100.0 Si), -21.74 (7.9 Si), -21.56 (8.3 Si), -21.14 (7.7 Si), -20.67 (2.6 Si), -20.38 (6.4 Si), -20.18 (9.2 Si), -19.31 (3.4 Si), -18.71 (7.4 Si), -18.30 (1.4 Si), -4.76 (1.9 Si). IR v: 2964, 2908, 1262, 1240, 1210, 1146, 1096, 1020, 865, 802, 746, 707. TGA (in N_2): Polymer is stable to 250 °C, 90% is left at 345 °C. At 430 °C, 50% of the material is left. Above 500 °C, 32% residue remains.

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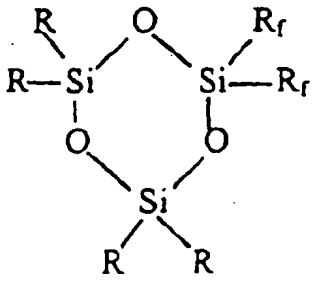
Claims

1. A fluoroalkyl substituted cyclotrisiloxane of the formula (Ia)



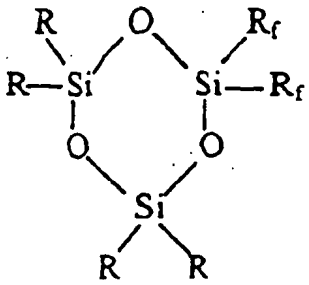
(Ia)

wherein R is a lower alkyl of 1 to 4 carbon atoms and R_f has the formula $(CH_2)_2$-$(CR'_2)_n$-CR'_3, wherein all or some of the R' substituents are F, the remaining R' substituents being H, and n is an integer varying from 0 to 8.

2. The compound according to claim 1 wherein each of the R'-substituents is F.

3. The compound according to claim 1 wherein each of the R'-substituents is F, R is methyl and n is 5.

4. A method for the preparation of a homopolymer wherein a compound of formula (Ia)



(Ia)

wherein R is a lower alkyl of 1 to 4 carbon atoms and R_f has the formula $(CH_2)_2$-$(CR'_2)_n$-CR'_3, wherein all or some of the R' substituents are F, the remaining R' substituents being H, and n is an integer varying from 0 to 8.
is subjected to anionic or cationic polymerisation in bulk or a suitable solvent to give said homopolymer.

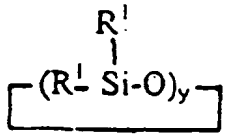
5. The method according to claim 4 wherein the polymerization is a cationic polymerization initiated by trifluoromethane sulfonic acid (triflic acid).

6. The method according to claim 4 wherein the polymerization is an anionic polymerization initiated by a lithium containing base.

7. The method according to claim 6, wherein the lithium containing base is dilithium diphenylsilanolate or dilithium tetramethyldisiloxanolate.

8. A homopolymer as prepared by any of the claims 4 to 7.

9. A method for the preparation of a block copolymer or random copolymer, wherein the compounds of formula (Ia), and a cyclosiloxane of formula (II),



(II)

wherein y is 3, 4 or 5 and all or some of the R^1 substituents are alkyl of 1 to 4 carbon atoms, vinyl or phenyl, or wherein one R^1 is R_f as defined before and the remaining R' substituents are alkyl of 1 to 4 C-atoms, vinyl or phenyl, are subjected to anionic or cationic polymerisation to give said block or random copolymer.

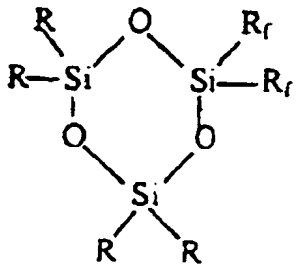
10. The method according to claim 9 wherein the anionic polymerization is initiated by a lithium containing base.

11. The method according to claim 10, wherein the lithium containing base is dilithium diphenylsilanolate or dilithium tetramethyldisiloxanolate.

12. A block copolymer or random copolymer as prepared by any of the claims 9 to 11.

Revendications

1. Cyclotrisiloxane portant un substituant fluoroalkyle, de formule (Ia)



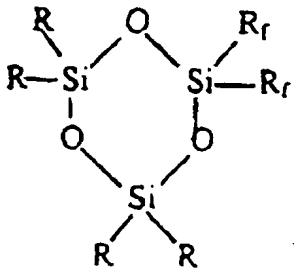
(Ia)

dans lequel R est un groupe alkyle inférieur comportant de 1 à 4 atomes de carbone et R_f répond à la formule $(CH_2)_2$-$(CR'_2)_n$-CR'_3, dans laquelle tous les substituants R' ou certains d'entre eux représentent F, les substituants R' restant représentent H, et n est un nombre entier dont la valeur varie entre 0 et 8.

2. Composé selon la revendication 1, dans lequel chacun des substituants R' représente F.

3. Composé selon la revendication 1, dans lequel chacun des substituants R' représente F, R représente un groupe méthyle et n vaut 5.

4. Procédé de préparation d'un homopolymère dans lequel un composé de formule (Ia)



(Ia)

dans lequel R est un groupe alkyle inférieur comportant de 1 à 4 atomes de carbone et R_f répond à la formule $(CH_2)_2$-$(CR'_2)_n$-CR'_3, dans laquelle tous les substituants R' ou certains d'entre eux représentent F, les substituants R' restant représentent H, et n est un nombre entier dont la valeur varie entre 0 et 8,
est soumis à une polymérisation anionique ou cationique dans la masse ou dans un solvant approprié pour donner ledit homopolymère.

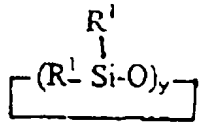
5. Procédé selon la revendication 4, dans lequel la polymérisation est une polymérisation cationique amorcée par de l'acide trifluorométhanesulfonique (acide triflique).

6. Procédé selon la revendication 4, dans lequel la polymérisation est une polymérisation anionique amorcée par une base contenant du lithium.

7. Procédé selon la revendication 6, dans lequel la base contenant du lithium est le diphénylsilanolate dilithié ou le tétraméthyldisiloxanolate dilithié.

8. Homopolymère préparé par un procédé selon l'une quelconque des revendications 4 à 7.

9. Procédé de préparation d'un copolymère séquencé ou d'un copolymère statistique, dans lequel des composés de formules (Ia), et un cyclosiloxane de formule (II)



(II)

dans laquelle y vaut 3, 4 ou 5 et tous les substituants R^1 ou certains d'entre eux représentent un groupe alkyle comportant de 1 à 4 atomes de carbone, un groupe vinyle ou phényle, ou dans laquelle un des R^1 représente R_f tel que défini précédemment et les substituants R^1 restants représentent un groupe alkyle comportant de 1 à 4 atomes de carbone, un groupe vinyle ou phényle,
sont soumis à une polymérisation anionique ou cationique pour donner ledit copolymère séquencé ou statistique.

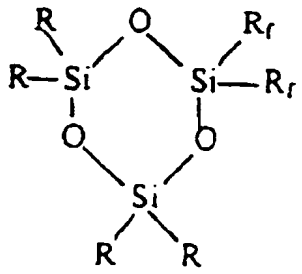
10. Procédé selon la revendication 9, dans lequel la polymérisation anionique est amorcée par une base contenant du lithium.

11. Procédé selon la revendication 10, dans lequel la base contenant du lithium est le diphénylsilanolate dilithié ou le tétraméthyldisiloxanolate dilithié.

12. Copolymère séquencé ou copolymère statistique, préparé par un procédé selon l'une quelconque des revendications 9 à 11.

Patentansprüche

1. Fluoralkyl-substituierte Cyclotrisiloxane der Formel (Ia)



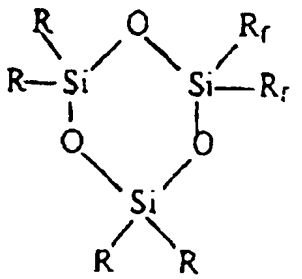
(Ia)

worin R Niedrigalkyl mit 1 bis 4 Kohlenstoffatomen bedeutet und R_f die Formel $(CH_2)_2$-$(CR'_2)_n$-CR'_3 besitzt, worin alle oder einige der R'-Substituenten F bedeuten, die restlichen R'-Substituenten H bedeuten und n eine ganze Zahl, variierend von 0 bis 8, ist.

2. Verbindung nach Anspruch 1, worin jeder der R'-Substituenten F bedeutet.

3. Verbindung nach Anspruch 1, worin jeder der R'-Substituenten F bedeutet, R Methyl bedeutet und n 5 bedeutet.

4. Verbindung zur Herstellung eines Homopolymers, wobei eine Verbindung der Formel (Ia)



(Ia)

worin R Niedrigalkyl mit 1 bis 4 Kohlenstoffatomen bedeutet, und R_f die Formel $(CH_2)_2$-$(CR'_2)_n$-CR'_3 besitzt, worin alle oder einige der R'-Substituenten F bedeuten, die restlichen R'-Substituenten H bedeuten und n eine ganze Zahl, variierend von 0 bis 8 bedeutet,
einer anionischen oder kationischen Polymerisation in Masse oder in einem geeigneten Lösungsmittel unter Bildung des Homopolymeren unterworfen wird.

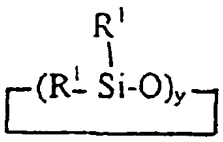
5. Verfahren nach Anspruch 4, wobei die Polymerisation eine kationische Polymerisation ist, die durch Trifluormethansulfonsäure (triflic acid) initiiert wird.

6. Verfahren nach Anspruch 4, wobei die Polymerisation eine anionische Polymerisation ist, die durch eine Lithium-enthaltende Base initiiert wird.

7. Verfahren nach Anspruch 6, wobei die Lithium-enthaltende Base Dilithiumdiphenylsilanolat oder Dilithiumtetramethyldisiloxanolat ist.

8. Homopolymer, hergestellt nach einem der Ansprüche 4 bis 7.

9. Verfahren zur Herstellung eines Blockcopolymeren oder Randomcopolymeren, wobei die Verbindungen der Formel (Ia) und ein Cyclosiloxan der Formel (II)



(II)

worin y 3, 4 oder 5 bedeutet und alle R^1-Substituenten Alkyl mit 1 bis 4 Kohlenstoffatomen, Vinyl oder Phenyl bedeuten oder worin R^1 die gleiche Bedeutung wie R_f zuvor definiert besitzt, und die restlichen R^1-Substituenten Alkyl mit 1 bis 4 Kohlenstoffatomen, Vinyl oder Phenyl bedeuten,
einer anionischen oder kationischen Polymerisation unter Bildung eines Block- oder Randomcopolymeren unterworfen werden.

10. Verfahren nach Anspruch 9, wobei die anionische Polymerisation durch eine Lithium-enthaltende Base initiiert wird.

11. Verfahren nach Anspruch 10, wobei die Lithium-enthaltende Base Dilithiumdiphenylsilanolat oder Dilithiumtetramethyldisiloxanolat ist.

12. Blockcopolymer oder Randomcopolymer, hergestellt nach einem der Ansprüche 9 bis 11.