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<p>(21) International Application Number: PCT/GB00/00695</p> <p>(22) International Filing Date: 28 February 2000 (28.02.00)</p> <p>(30) Priority Data: 9905121.1 5 March 1999 (05.03.99) GB 9917329.6 23 July 1999 (23.07.99) GB</p> <p>(71) Applicant (for all designated States except US): DOW CORNING CORPORATION [US/US]; 2200 W. Salzburg Road, Auburn, Midland, MI 48611 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): HABIMANA, Jean de la Croi [RW/BE]; 199B Chaussee D'Ecaussinne, B-7090 Braine le Comte (BE). CHEVALIER, Pierre [FR/GB]; 5 Plymouth Road, Penarth CF64 3DA (GB). TAPPER, Tristan [GB/GB]; 17 Pentyrch Street, Cathays, Cardiff CF24 4JW (GB).</p> <p>(74) Agents: VANDAMME, Luc, J. et al.; Dow Corning Limited, Cardiff Road, Barry CF63 2YL (GB).</p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
(54) Title: USE OF AN INITIATOR FOR CONTROLLED POLYMERISATION REACTIONS		
<p>(57) Abstract</p> <p>An initiator is used for initiating controlled polymerisation reactions, the initiator comprising units of the formulae R^7_3SiO, $(R^7_2SiO_{3/2})$, and/or $(SiO_{4/2})$ and has at least one group $D-CR^8_2X$, wherein each R^7 is independently an optionally substituted hydrocarbon group, D is a divalent straight chain or branched alkylene group containing an oxygen or nitrogen heteroatom and/or substituted by a carbonyl group, each R^8 is independently an alkyl group or a hydrogen atom and X is a halogen atom. Preferably each R^7 is a methyl group and the initiator comprises two terminal $-D-CR^8_2X$ groups wherein each R^8 is a methyl group, X is bromine and D is a group $CO-NR^9R^{10}$ or a group $CO-(OR^{10})$ wherein R^9 is an alkyl group or a hydrogen atom and each R^{10} is independently a straight chain or branched alkylene group. The initiator is particularly useful for initiating controlled polymerisation of vinyl containing monomers.</p>		

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USE OF AN INITIATOR FOR CONTROLLED POLYMERISATION REACTIONS

The present invention relates to use of an initiator for controlled polymerisation reactions, in particular use
5 of an initiator for controlled polymerisation of vinyl containing monomers to produce a polymer or copolymer.

Controlled polymerisation systems are of considerable importance in macromolecular chemistry since they allow for controlled preparation of polymers having a specific desired
10 morphology. For example, by controlling the ratio of monomer to initiator concentration the molecular weight, molecular weight distribution, functionality, topology and/or dimensional structure of the resulting polymer can be controlled.

15 For many years free radical polymerisation has been a commercially important process for the preparation of high molecular weight polymers. A wide variety of monomers may be polymerised or copolymerised by free radical polymerisation under relatively simple conditions in bulk,
20 solution, emulsion, suspension or dispersion. However, a drawback of conventional free radical polymerisation is the lack of control of the morphology of the resulting polymer.

Processes for controlled radical polymerisation have been proposed. For example, WO 96/30421, WO 97/18247 and WO
25 98/01480 disclose polymerisation processes based on atom transfer radical polymerisation (ATRP) which provide for controlled radical polymerisation of styrene, (meth)acrylates, and other radically polymerisable monomers. The processes disclosed comprise the use of (i) an

initiating system which comprises an initiator having a radically transferable atom or group, for example a 1-phenylethyl halide, alkyl 2-halopropionate, p-halomethylstyrene, or α, α' -dihaloxylylene, (ii) a transition metal compound, for example Cu(I)Cl, Cu(I)Br, Ni(0), FeCl₂, or RuCl₂, and (iii) a C-, N-, O-, S-, or P-containing ligand which can co-ordinate with the transition metal, for example bipyridine or (alkoxy)₃P. In Chem. Commun., 1999 99-100 Haddleton et al disclose solid supported copper catalysts, which are alleged to be easy to remove from polymer products for reuse, and their use in atom transfer polymerisation of methyl methacrylate using ethyl-2-bromoisobutyrate as an initiator.

WO 98/01480 further discloses the preparation and use of polydimethylsiloxane (PDMS) based macroinitiators; for example, benzyl chloride end groups are introduced to PDMS having silicon bonded hydrogen atoms by a platinum catalysed hydrosilylation reaction with vinylbenzylchloride. However, this route produces two isomers, α and β , having different activities. The β isomer which represents 65% of the product is totally inactive towards initiation of controlled polymerisation reactions of vinyl monomers, and use of the α isomer results in polymers or copolymers containing unacceptably high amounts of unreacted siloxane which is difficult to remove due to slow initiation of the reaction.

We have prepared an alternative PDMS based macroinitiator by a condensation reaction which is capable of initiating a controlled polymerisation reaction of vinyl monomer and yielding a well defined polymer or copolymer, and which is more reactive than the aforementioned prior art

PDMS based macroinitiator and leaves little or no unreacted siloxane remaining in the product.

The word "comprises" where used herein is used in its widest sense to mean and to encompass the notions of
5 "includes", "comprehends" and "consists of".

According to the present invention there is provided use of an initiator for initiating controlled polymerisation reactions, the initiator having at least one group $-D-CR^8_2X'$ and comprising units of the formulae $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$,
10 $(R^7SiO_{3/2})$, and/or $(SiO_{4/2})$, wherein D is a divalent straight chain or branched alkylene group containing an oxygen or nitrogen heteroatom and/or substituted by a carbonyl group, each R^8 is independently an alkyl group or a hydrogen atom, X' is a halogen atom, and each R^7 is independently a group -
15 $D-CR^8_2X'$ or an optionally substituted hydrocarbon group.

The initiator may be a linear, branched, cyclic or resinous siloxane.

R^7 may be an alkyl group, (e.g. a methyl, ethyl, propyl or butyl, pentyl or hexyl group), a substituted alkyl group,
20 (e.g. a fluoropropyl group), an alkenyl group, (e.g. a vinyl or hexenyl group), an aryl group (e.g. a phenyl group), an aralkyl group (e.g. a benzyl group) or an alkaryl group (e.g. a tolyl group), and is preferably a C_1 - C_6 alkyl group.

Preferably, at least one group R^8 in each group $-D-$
25 CR^8_2X' is an alkyl group, i.e. X' is preferably a secondary or tertiary halogen atom, more preferably both groups R^8 in each group $-D-CR^8_2X'$ are alkyl groups, i.e. X' is more preferably a tertiary halogen atom. In a particularly preferred embodiment each R^8 is a methyl group.

30 X is preferably a bromine atom.

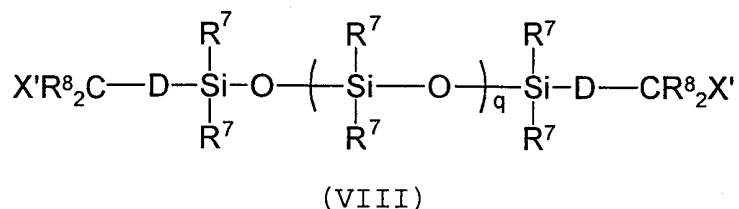
Preferred examples of divalent group D include



wherein R^9 is an alkyl group, for example a methyl group, or
 5 a hydrogen atom, each R^{10} is independently a straight chain
 or branched alkylene group, and r is an integer of from 1 to
 4.

Preferred initiators used in the present invention have
 the formula $R^7_3SiO(SiR^7_2O)_qSiR^7_3$, wherein R^7 is as defined above
 10 and q is 0 or a positive integer, for example from 10 to
 100.

Particularly preferred initiators have the general
 formula (VIII):

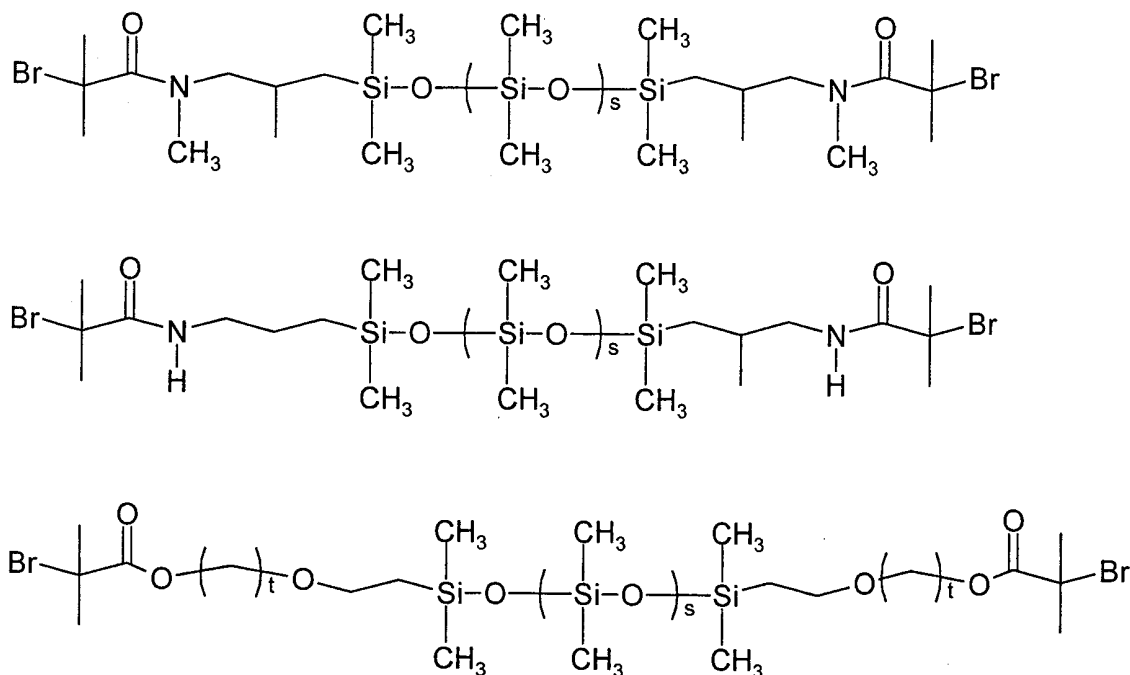


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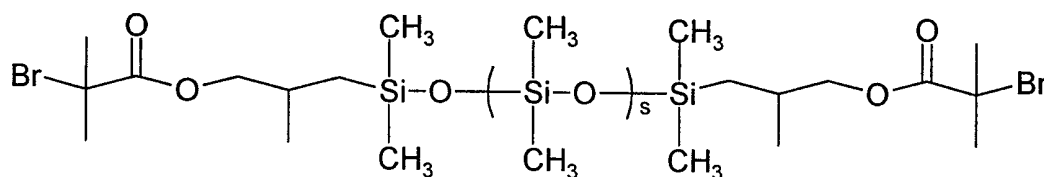
wherein R^7 , R^8 , D , X' and q are as defined above.

Examples of initiators of formula (VIII) are:

20



and



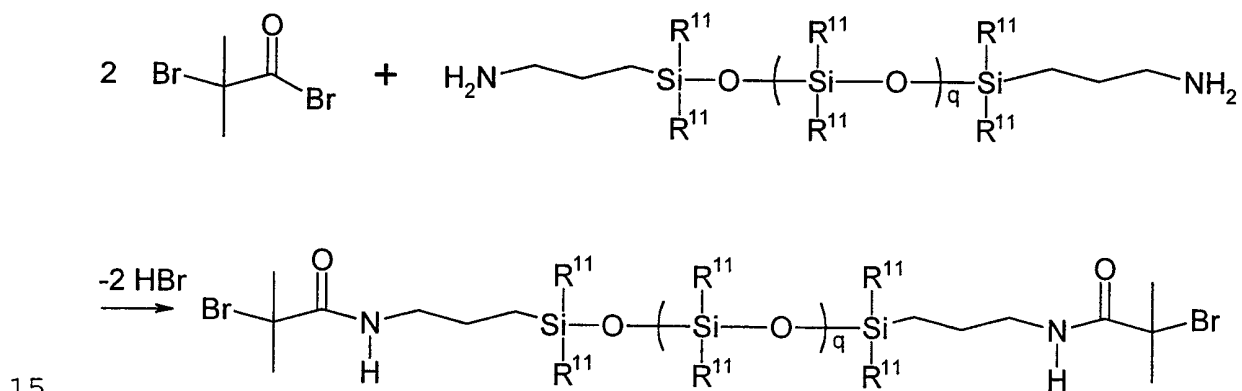
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wherein *s* is 0 or a positive integer, for example from 1 to 100, and *t* is a positive integer, for example from 1 to 10.

The initiator used in the present invention may be made by a method which comprises performing a condensation
 10 reaction between (i) a siloxane having at least one group R¹¹ and comprising units of the formulae (R¹¹₃SiO_{1/2}), (R¹¹₂SiO_{2/2}), (R¹¹SiO_{3/2}), and/or (SiO_{4/2}) wherein at least one group R¹¹ is an amino-, hydroxy- or alkoxy- group, or an amino-, hydroxy- or alkoxy-substituted alkyl group and the remaining groups
 15 R¹¹ are each independently a group R⁷ as previously defined, and (ii) a compound X'CR⁸₂-E wherein E is a group capable of

participating in a condensation reaction with the amino-, hydroxy- or alkoxy- group, or an amino-, hydroxy- or alkoxy-substituted alkyl group to form a divalent straight chain or branched alkylene group containing an oxygen or nitrogen heteroatom and/or substituted by a carbonyl group, and R⁸ and X' are as previously defined.

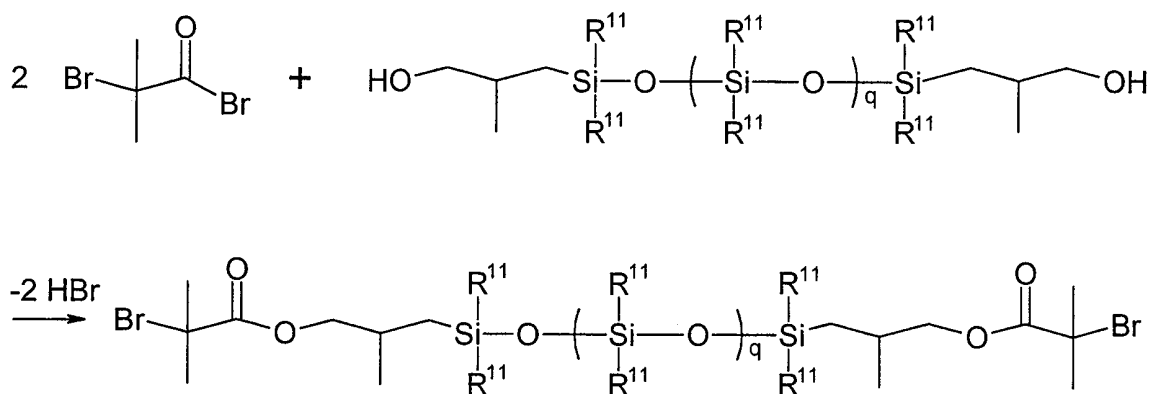
The particular reagents (i) and (ii) defined above to be used in the method of making the initiator will of course depend upon the particular initiator to be made. For example, to make an initiator in which divalent group D previously defined comprises a peptide linkage, the condensation reaction may be performed between an aminoalkyl substituted siloxane and an acyl halide:



15

By way of further example, if divalent group D is to comprise a carboxy linkage then the condensation reaction may be performed between a hydroxyalkyl substituted siloxane and an acyl halide:

20



The condensation reaction may be performed at room
 5 temperature or above, for example from 50 to 100°C.

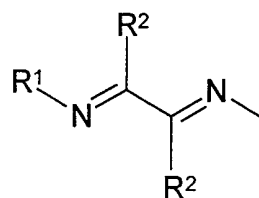
According to the present invention the initiator is
 used for initiating controlled polymerisation reactions,
 especially controlled polymerisation of vinyl containing
 monomers, such as those described in WO 96/30421, WO
 10 97/18247, WO 98/01480 and Chem. Commun., 1999 99-100
 (Haddleton et al). The present initiator is capable of
 initiating a controlled polymerisation reaction of vinyl
 monomer to yield a well defined polymer or copolymer. It is
 more reactive than the aforementioned prior art PDMS based
 15 macroinitiators and leaves little or no unreacted siloxane
 remaining in the product.

We have found that the initiator is particularly
 effective for controlled polymerisation of vinyl monomers
 when used together with a particular catalyst composition
 20 which is solid at room temperature and comprises a
 transition metal or transition metal compound having on
 average more than one ligand co-ordinated thereto, each
 ligand being supported by a support via a divalent group R,
 wherein R is an optionally substituted C₁-C₂₀ straight chain,

branched, or cyclic alkylene group, arylene, alkarylene or aralkylene group.

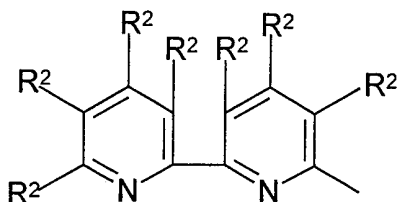
The transition metal may, for example, be selected from copper, iron, ruthenium, chromium, molybdenum, tungsten, rhodium, cobalt, rhenium, nickel, manganese, vanadium, zinc, gold and silver. Suitable transition metal compounds include those having the formula MY wherein M is a transition metal cation and Y is a counter anion. M is preferably selected from Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), and is most preferably Cu(I). Y may be, for example, Cl, Br, F, I, NO₃, PF₆, BF₄, SO₄, CN, SPh, SCN, SePh or triflate (CF₃SO₃), and is most preferably Cl or Br.

The catalyst composition comprises on average greater than one ligand co-ordinated with the transition metal or transition metal compound, and preferably has at least two co-ordinated ligands. Suitable ligands include C-, N-, O-, P-, and S- containing ligands which can co-ordinate with the transition metal or transition metal compound. WO 97/47661, WO 96/30421, WO 97/18247 and WO 98/01480 disclose many examples of suitable ligands. Preferred ligands are those which contain an organodiimine group, in particular a 1,4-diaza-1,3-butadiene of formula (I),



(I)

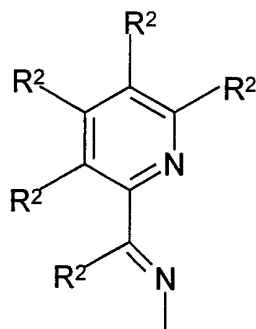
a 2,2'-bipyridine of formula (II),



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(II)

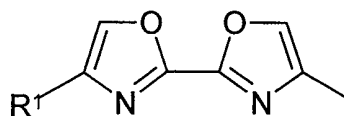
a pyridine-2-carboxaldehyde imine of formula (III),



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(III)

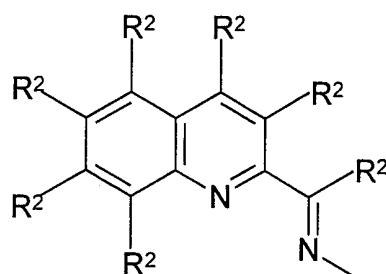
an oxazolidone of formula (IV),



15

(IV)

or a quinoline carbaldehyde of formula (V),



5

(V)

wherein each R¹ is independently a hydrogen atom, an optionally substituted C₁-C₂₀ straight chain, branched, or cyclic alkyl group, aryl, alkaryl, aralkyl group or halogen atom. Preferably, R¹ is a hydrogen atom or an unsubstituted C₁-C₁₂ alkyl group. Each R² is independently an R¹ group, a C₁-C₂₀ alkoxy group, NO₂-, CN-, or a carbonyl group.

One or more adjacent R¹ and R² groups, and R² and R² groups, may form C₅-C₈ cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclic aryl groups, for example cyclohexyl, cyclohexenyl or norbornyl groups. The 2-pyridinecarbaldehyde imine compounds of formula (III) may comprise fused rings on the pyridine group.

A preferred organodiimine containing group is of formula (III) wherein each R² is a hydrogen atom.

Divalent group R is preferably a C₁-C₆ unsubstituted straight chain or branched alkylene group, for example a propylene group, or an aralkylene or alkarylene group, for example a benzylene or tolylene group.

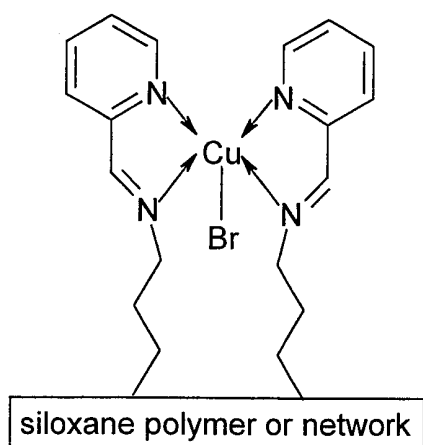
The support may be an inorganic or organic network or polymer. Suitable inorganic networks or polymers consist of

oxides of Si, Zr, Al or Ti, including mixed oxides thereof, for example a zeolite. A preferred inorganic support is a siloxane polymer or network having units of the formula $(R^3SiO_{1/2})_a(R^3SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$ wherein each R^3 is independently an alkyl group, preferably a methyl group, a hydroxyl group or alkoxy group, a , b , c and d are each independently 0 or a positive integer, and $a+b+c+d$ is an integer of at least 10. The siloxane polymers and networks may be formed by polymerisation or cross-linking of silicon-containing monomers or oligomers, for example organofunctional silanes, silicas, and organocyclosiloxanes having the formula $(R^4SiO)_e$ wherein R^4 is an alkyl group, for example a C_1 - C_6 alkyl group, most preferably a methyl group.

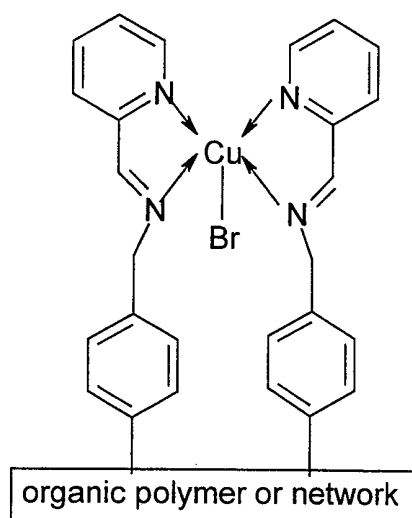
Suitable organic network or polymer supports may comprise any organic material which will render the catalyst composition solid at room temperature and will not hinder any polymerisation reaction which the catalyst composition is to catalyse. Examples of suitable organic networks or polymers include polyolefins, polyolefin halides, oxides and glycols, polymethacrylates, polyarylenes and polyesters.

The ligands may be physically or chemically attached to the support via divalent group R; however, chemical bonding of the ligands to the support via divalent group R is preferred.

Particularly preferred catalyst compositions for catalysing controlled polymerisation reactions which are initiated according to the present invention are according to formula (VI) and (VII),



(VI)

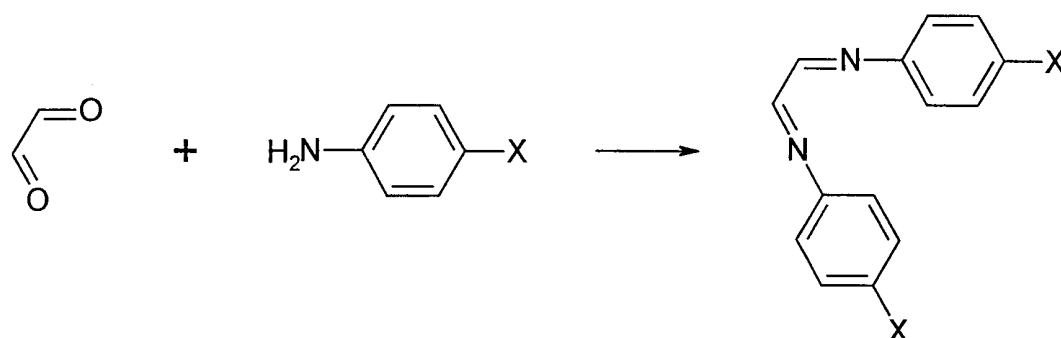


(VII)

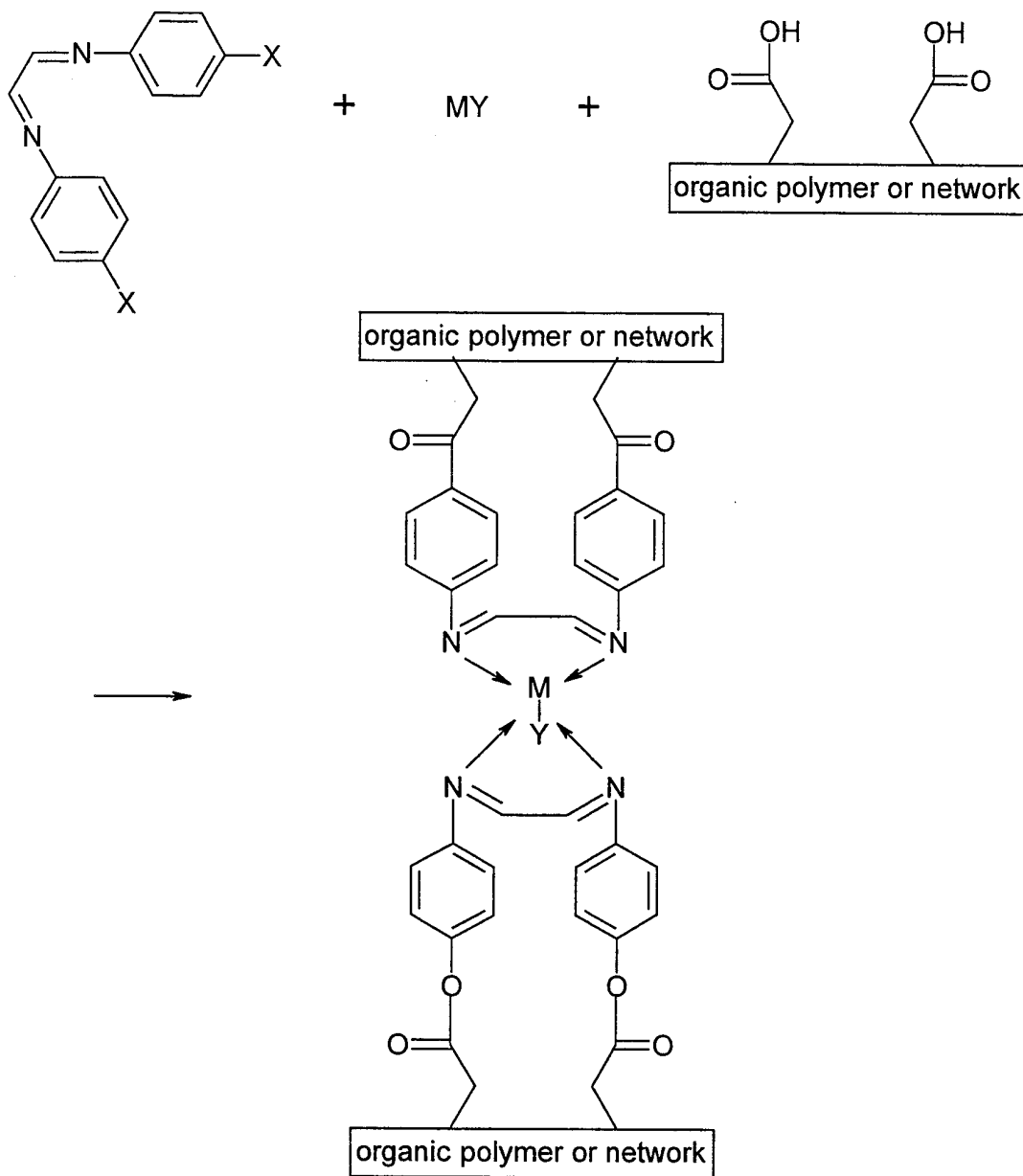
5 wherein the siloxane polymer or network has units of the formula $(R^3SiO_{1/2})_a(R^3SiO_{2/2})_b(R^3SiO_{3/2})_c(SiO_{4/2})_d$, R^3 , a , b , c and d are as defined above and n is a positive integer.

The catalyst composition may be made by conventional methods known to those persons skilled in the art. The
 10 molar ratios of reagents to be used to make the catalyst composition must be such that in the catalyst composition the transition metal or transition metal compound has on average more than one ligand co-ordinated thereto.

By way of example, organodiimine containing groups
 15 which are diazabutadienes may be prepared by reaction of glyoxal with aniline derivatives:

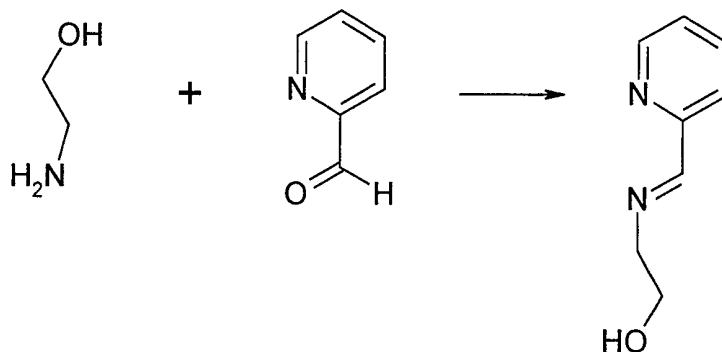


wherein X is a leaving group, for example a hydroxy or alkoxy group or a halogen atom, which diazabutadienes may
5 then react with a suitable support material and transition metal compound to form the catalyst composition, for example:



wherein n is as defined above.

By way of further example, organodiimine containing
 5 groups which are pyridine-2-carboxaldehyde imines of formula
 (III) above may be made by reaction of ethanolamine with
 pyridine-2-carboxaldehyde:



The pyridine-2-carboxaldehyde imine may then be reacted with a suitable support material Z and transition metal compound to form the catalyst composition, as illustrated
5 above.

The catalyst composition hereinabove described in detail has an advantage over the aforementioned prior art controlled polymerisation methods in that the catalyst composition is a solid at room temperature and is thus
10 recoverable from the polymer product and is reusable, and allows for a high degree of control over the polymerisation reaction. Particularly advantageous catalyst compositions are those which are a solid at room temperature but which have a melting point at a temperature lower than the
15 temperature at which the polymerisation reaction occurs. Particularly effective polymerisation reactions may be performed in this way when the catalyst composition is a fluid in the reaction mixture at the reaction temperature and thus the transition metal compound may more easily blend
20 into the reaction mixture to effect catalysis of the reaction. As the temperature of the product cools after the reaction has occurred to below the melting point of the catalyst composition the catalyst may solidify and be recovered from the reaction mixture.

The vinyl containing monomer to be polymerised may be a methacrylate, an acrylate, a styrene, methacrylonitrile or diene. Examples of vinyl containing monomers include methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and other alkyl methacrylates, and the corresponding acrylates, including organofunctional methacrylates and acrylates, including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates. Other suitable vinyl containing monomers include methacrylic acid, acrylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene, α -methylstyrene, vinyl halides, for example vinyl chloride and vinyl fluoride, acrylonitrile, methacrylonitrile, vinylidene halides of the formula $\text{CH}_2=\text{C}(\text{halogen})_2$ wherein the halogen may be Cl or F, optionally substituted butadienes of the formula $\text{CH}_2=\text{CR}^5-\text{CR}^5=\text{CH}_2$ wherein each R^5 is independently H, a C_1 - C_{10} alkyl group, Cl or F, acrylamide or derivatives thereof of the formula $\text{CH}_2=\text{CHCONR}^6_2$ and methacrylamide or derivatives thereof of the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{CONR}^6_2$ wherein R^6 is H, a C_1 - C_{10} alkyl group or Cl. Mixtures of different monomers may also be used.

Polymerisation may take place under an inert atmosphere, for example under argon or nitrogen.

The catalyst composition may be used in an amount of from 1 to 50%, preferably from 1 to 20%, more preferably from 5 to 10% by weight of the monomer.

A variety of polymers and copolymers can be produced by controlled polymerisation reactions initiated according to the present invention. A large variety of monomers may be polymerised to afford homopolymers, random or gradient
5 copolymers, periodic copolymers, block copolymers, functionalised polymers, hyperbranched and branched polymers, graft or comb polymers, and polysiloxane-organic copolymers. Polysiloxane-organic copolymers have a number of potential applications; for example, polysiloxane-
10 polyhydroxyalkyl acrylate block and graft copolymers are used in soft contact lens applications, polysiloxane-aminoacrylate copolymers are usable as antifoam and anti-dye transfer agents, and polysiloxane-aminoacrylate copolymers having a short aminoacrylate block are usable as textile
15 treating agents, polyalkoxysilylalkylacrylate-polysiloxane and polyepoxyglycidylacrylate-polysiloxane copolymers are usable as additives for epoxy resins, curable powder coatings and sealants, long alkyl methacrylate or acrylate-polysiloxane copolymers are usable as surface modifiers or
20 additives for polyolefins and polyester-polyacrylate copolymers, and the ABA methacrylate or acrylate-polysiloxane block copolymer may be usable as a plasma crosslinkable oxygen barrier coating, and phosphobetaine or sulphobetaine-polysiloxane ionomers are biocompatible, for
25 example for use in shampoos and other hair treating agents.

The present invention will now be illustrated by way of example.

Reference Example 1 - preparation of bromoisobutyrylamide end-capped polydimethylsiloxane (PDMS) macroinitiator

To a solution of 9.0g (62.9mmol) of tetramethylazasilacyclopentane in 40ml of toluene under N₂ in a 250 ml flask equipped with a magnetic stirrer, condenser and addition funnel was added dropwise 100.0g of hydroxy terminated PDMS (degree of polymerisation (Dp) = 45) in 40ml toluene at room temperature. After heating for 2 hours at 50°C volatile materials were removed under vacuum to afford 93.0g of colourless liquid. Analysis by ¹³C, ²⁹Si NMR and FTIR confirmed the liquid to be amine end-capped PDMS (Dp=45).

Then, to 30g of the amine end-capped PDMS in 50ml triethylamine in a 100ml flask equipped with a magnetic stirrer, condenser and addition funnel was added dropwise under N₂ 4.25g (18.5mmol) of bromoisobutyrylbromide in 20ml toluene at room temperature. The mixture was kept at 90°C for 1 hour with stirring prior to filtration of salts and evaporation of solvents under vacuum. The polymer was washed with toluene and water. The organic phase was dried with magnesium sulphate, filtered and volatiles removed to afford 27.8g (86% yield) of a pale yellow liquid. ¹H, ¹³C and ²⁹Si NMR characterisation of the liquid confirmed the formation of N-bromoisobutyryl, N-methylamino, 2-methyl propyl endblocked PDMS (Br(CH₃)₂CCON(CH₃)CH₂CH(CH₃)CH₂-).

Reference Example 2 - preparation of first solid supported copper catalyst

20.0g (186.7mmol) of 2-pyridine carboxyaldehyde and
5 10.7g (74.6mmol) of CuBr were mixed in 62ml of
tetrahydrofuran in a 100ml flask equipped with a magnetic
stirrer and a condenser. Insoluble material was dissolved
by addition of 33.5g (186.8mmol) of 3-aminopropyltrimethoxy-
silane. The reaction was exothermic forming a deep red
10 solution, which was allowed to cool to room temperature
prior to the addition of 0.07g (1.9mmol) of NH_4F diluted in
1.7ml water. The solution was then heated under stirring at
60°C for 24 hours. Volatile materials were evaporated under
vacuum and the resulting solid was ground, washed with ether
15 and dried in vacuo at 80°C to afford 45.5g of brown-red
powder (Cu(%m/m)=8.92%, insoluble in toluene, xylene and
acetone).

Example 1 - polymerisation of methylmethacrylate

20 5.39g (53.9mmol) of methylmethacrylate (MMA) in 11.5ml
of anhydrous p-xylene was added to 0.66g of the catalyst
prepared in Reference Example 2 above in a schlenk tube.
The mixture was deoxygenated by a single freeze-pump-thaw
cycle prior to addition of 1.0g of the macroinitiator
25 prepared in Reference Example 1 above at room temperature.
The solution was heated at 90°C for 6 hours under N_2 and
samples were taken against time for ^1H NMR analysis. The
final polymer and catalyst were separated by simple
filtration on paper. The polymer was dried under vacuum to
30 afford 3.9g of a pale yellow solid. The degree of

conversion of the monomer observed by ^1H NMR was 59%. The catalyst was washed with toluene and ether and dried in vacuo to afford 0.51g of active copper catalyst, reusable for further polymerisations. The results are given in Table 1 below and show a very good correlation between theoretical and experimental molecular weight and hence controlled polymerisation:

Time (hours)	Conversion %	Mn_{th} (g/mole)	Mn (g/mole)	PDMS %
0	0	3710	3710	100
2	10	5710	5480	68
3	27	9110	8590	43
4	42	12160	11470	32
5	52	14130	14090	26
6	59	15450	15200	24

Mn = number average molecular weight

10 Mn_{th} = theoretical number average molecular weight

Example 2 - polymerisation of MMA using recycled catalyst

4.01g (40.1mmol) of MMA in 8.6ml of anhydrous p-xylene was added to 0.49g of copper catalyst recycled from Example 1 above in a schlenk tube. The mixture was deoxygenated by a single freeze-pump-thaw cycle prior to addition of 0.744g of the macroinitiator prepared in Reference Example 1 above. The solution was heated at 90°C for 24 hours under N_2 and samples were taken against time for ^1H NMR analysis. The results are given in Table 2 below and show a good correlation between theoretical and experimental molecular weight and hence controlled polymerisation:

Time (hours)	Conversion %	Mn _{th} (g/mole)	Mn (g/mole)	PDMS %
0	0	3710	3710	100
4	9	5510	5350	70
6	13	6310	5990	62
24	84	20500	18700	20

Reference Example 3 - preparation of bromoisobutyrate end-capped PDMS macroinitiator

5 51g PDMS having $-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_2-\text{o}-(\text{CH}_2)_3\text{CH}_2\text{OH}$ terminal units and a number average molecular weight of 2084 (0.049 mole of OH) and 5.43g (0.053mol) of triethylamine were placed into a 100ml flask equipped with a magnetic stirrer a condenser and an addition funnel containing 20ml of toluene.

10 12.37g (0.053 mole) of bromobutyratebromide was added dropwise at room temperature and the reaction was allowed to react overnight at room temperature prior to filtration of salts and evaporation of solvents. The polymer was washed with toluene and water. The organic phase was dried with

15 magnesium sulphate, filtrated and volatiles removed under reduced pressure. The ^1H NMR spectrum confirms the total disappearance of the carbinol function ($\delta=3.56\text{ppm}$) and the appearance of $-\text{Si}(\text{CH}_3)_2-(\text{CH}_2)_2-\text{o}-(\text{CH}_2)_3\text{CH}_2\text{OCOC}(\text{CH}_3)_2\text{Br}$ at 4.19ppm.

20

Reference Example 4 - preparation of second solid supported copper catalyst

100.4g (560.0mmol) of 3-aminopropyltrimethoxysilane and 63.0g (558.2mmol) of 2-pyridine carboxyaldehyde were mixed

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in a 1l flask equipped with a magnetic stirrer and a condenser. After stirring for 10 minutes 26.8g (186.8mmol) of CuBr, 170.4g (1119.4mmol) tetramethoxysilane, 45.2g (2511.1mmol) water and 0.6g (16.2mmol) NH_4F were

5 successively added to the flask. A strong exotherm was observed affording an homogenous dark solution at room temperature. After 48 hours the solution gelled to a soft gel. The solids were aged for one week before removing volatiles by evaporation under vacuum. The resulting solid

10 was ground, washed with ether and dried in vacuo at 80°C for 8 hours to afford 202.5g of a brown-red powder.

Example 3 - polymerisation of MMA

190g (1.9mol) of MMA in 300ml of anhydrous p-xylene was

15 added to 10g of the catalyst prepared in Reference Example 4 above (previously extracted with p-xylene for 6 hours in a soxhlet) in a 500ml schlenk tube. The mixture was deoxygenated by a single freeze-pump-thaw cycle and heated at 90°C prior to addition of 10g of the macroinitiator

20 prepared in Reference Example 3 above. The reaction was continued for 30 hours at 90°C. Samples were taken against time for ^1H NMR analysis. During polymerisation the solution became very viscous but remained clear and the catalyst remains visible in the polymer solution. After

25 polymerisation the solid catalyst was filtered out. The degree of conversion of the monomer observed by ^1H NMR was 44%, and the M_n as measured by ^1H NMR was 20,900. The catalyst was extracted with p-xylene in a soxhlet for 6 hours, reusable for further polymerisations. GPC analysis

30 of the polymer showed a narrower molecular weight

distribution ($Mn_{th}/Mn = 1.29$) compared to the starting polysiloxane macroinitiator ($Mn_{th}/Mn = 1.5$).

Example 4 - polymerisation of MMA using recycled catalyst

5 30g (0.3mol) of MMA in 30ml of anhydrous p-xylene was added to 2.3g of the catalyst collected from Example 3 above (previously extracted with p-xylene for 6 hours in a soxhlet) in a 100ml schlenk tube. The mixture was deoxygenated by a single freeze-pump-thaw cycle and heated
10 at 90°C prior to addition of 3g of the macroinitiator prepared in Reference Example 3 above. The reaction was continued for 44 hours at 90°C. Samples were taken against time for ¹H NMR analysis. During polymerisation the solution becomes very viscous but remains clear and the
15 catalyst remains visible in the polymer solution. After polymerisation the solid catalyst was filtered out. The results are shown in Table 3 below and show an excellent correlation between theoretical and experimental molecular weight and hence controlled polymerisation.:

20

Time (hours)	Conversion %	Mn_{th} (g/mole)	Mn (g/mole)	PDMS %
0	0	2400	2400	100
28	22	7800	7800	30.7
44	33.5	10400	10400	23

Reference Example 5 - preparation of third solid supported copper catalyst

25 5g (0.01 mole -NH₂) of aminomethylpolystyrene and 1.2g (0.012 mole) of pyridinecarboxyaldehyde were added to a

100ml flask containing 50ml diethylether at room temperature and allowed to react overnight under nitrogen. After the reaction, a yellow powder was collected, washed with dichloromethane and toluene and dried at 65°C for 2 hours.

5 4.5g of the powder was mixed with 1.02g of CuBr in 50ml of acetone and agitated until all the powder turned black. The reaction was continued under acetone reflux for 3 hours. After the reaction, the powder was washed with water and extracted with methanol in a soxhlet for 7 hours. Solid

10 state ¹³C NMR confirmed the presence of imine groups and the absence of amine groups.

Example 5 - polymerisation of MMA

20ml of anhydrous p-xylene and 10g (1.9mole) of MMA

15 were added to a 100ml schlenk tube containing 5.3g of copper catalyst prepared according to Reference Example 5 above. The mixture was deoxygenated by a single freeze-pump-thaw cycle and then heated at 90°C prior to addition of 1.01g of PDMS macroinitiator prepared in Reference Example 3 above.

20 The reaction was continued for 5 hours at 90°C and sampled against time. During polymerisation the solution became very viscous but remained clear. The catalyst particles are visible in the polymer solution. After 5 hours of polymerisation, ¹H NMR studies measured 33% monomer

25 conversion and Mn=7100.

Example 6 - polymerisation of MMA

47.4g (0.47mol) of MMA in 50ml of anhydrous p-xylene was added to 19.4g of copper catalyst prepared according to

30 Reference Example 4 above in a 250ml schlenk tube. The

mixture was deoxygenated by a single freeze-pump-thaw cycle and heated at 90°C prior to addition of 5.0g of the macroinitiator prepared according to Reference Example 3 above. The reaction was continued for 4 hours at 90°C under N₂. Samples were taken against time for H¹ NMR analysis. During polymerisation the solution becomes very viscous and the catalyst remains visible in the polymer solution. The results are shown in Table 4 below and show a very good correlation between theoretical and experimental molecular weight and hence controlled polymerisation.:

Time (mins)	Conversion %	Mn _{th} (g/mole)	Mn (g/mole)	PDMS %
0	0	960	960	100
32	0	960	960	100
60	21	2850	2960	32.3
123	65	6811	7760	12.6
182	84	8522	9360	10.3
237	95	9512	10760	8.9

Reference Example 6 - preparation of PDMS macroinitiator having pendant bromoisobutyrate groups.

A 500 ml 3-neck reaction flask equipped with a dropping funnel, a thermometer and a magnetic stirrer was charged with 80.5 g of dimethylethoxy end-blocked dimethylmethyl(aminopropyl)siloxane having a degree of polymerisation of 100 and containing 0.018 mole NH₂, and 100 ml of p-xylene. After homogenisation, 3.35 ml (0.024 mole) of triethylamine was added and 5.53 g (0.024 mole) of bromoisobutyryl bromide were injected slowly at room temperature.

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The reaction was allowed to proceed for 3 hours at 50° C under agitation. After reaction, p-xylene was evaporated prior the addition of 300 ml of n-hexane to precipitate the triethylammonium salt. This step was followed by filtration
5 and evaporation of hexane. The product was a clear yellow and very viscous polymer. The disappearance of amine functionality was confirmed by ¹H NMR spectroscopy, the peak of CH₂CH₂NH₂ shifts from 3.99 ppm to 3.30 ppm and a new signal corresponding to -NH-COC(CH₃)₂Br appears at 6.99 ppm.
10 The bromination yield =100 % although some terminal ethoxy groups are hydrolysed.

Reference Example 7 - preparation of fourth solid supported copper catalyst

15 A 2000 ml 3-neck reaction flask equipped with a dropping funnel, a thermometer and a reflux condenser was charged with 246 g (1.37 mole) of aminopropyltrimethoxy-silane and 300 ml of p-xylene. Then, 75 g (4.16 mole) of water was added over 60 minutes whilst distilling off
20 methanol. After methanol removal, p-xylene is stripped off under reduced pressure to yield a white brittle solid. 84 g of the solid and 300 ml of p-xylene were then charged into a 1000 ml reaction flask and 70 g (1.0 mole) of 2-pyridine carboxyaldehyde was added slowly with cooling. After
25 addition of the 2-pyridine carboxyaldehyde, 57 g of CuBr was added under strong agitation keeping the temperature below 30°C. The agitation was maintained until the total disappearance of the green colour characteristic of free Cu(I). After the reaction, the solid was separated from the

solvent, washed with toluene and used without further extraction. Theoretical CuBr w/w % = 29.

Example 7 - polymerisation of MMA

5 A 250 ml Schlenk reaction flask was charged with 2.65 g
(0.76 mole) of catalyst prepared in Reference Example 7
above and 4.85 g(1.2 mmole)of the macroinitiator prepared in
Reference Example 6 above. The contents of the flask were
vacuum dried at 80°C to remove oxygen and then covered by a
10 nitrogen blanket. 28 g of MMA was then added under
nitrogen. The mixture was deoxygenated by three freeze-thaw
pump cycles in liquid nitrogen. The flask was then rapidly
heated in an oil bath to the reaction temperature of 90°C.
During the polymerisation reaction the viscosity increases
15 and the solid particles of the catalyst remain in the
polymer solution as a suspension. After polymerisation, the
polymer solution is filtered, the residual monomer
evaporated and the polymer analysed by ¹H NMR and/or by SEC
to determine the average number molecular weight and the
20 polydispersity. Based on a 100% monomer conversion and a
total macroinitiator conversion, the theoretical degree of
polymerisation is 233. From ¹H NMR calculation, the
experimental degree of polymerisation is 113 after 4 hours.

25 Reference Example 8 - preparation of bromoisobutyrylamide
functional MT resin macroinitiator

To a solution of 100.0g (1.45 mol) of MeSiO_{3/2} resin
containing 3.6 wt% of OH functionality in 200 ml of toluene
under N₂ in a 500 ml flask equipped with a magnetic stirrer,
30 condenser and addition funnel, was added dropwise 32.2g

(225.2 mmol, in excess) of tetramethylazasilacyclopentane in 50 ml toluene at room temperature. After heating for 1 hour at 60°C volatile materials were removed under vacuum to afford 114.0g of colourless liquid. Analysis by ¹³C, ²⁹Si NMR and FTIR confirmed the liquid to be an amine functional MT resin containing 4.75 wt% of -NMeH functionality.

Then, to 112.7g of the amine functional MT resin in 200ml triethylamine in a 500ml flask equipped with a magnetic stirrer, condenser and addition funnel was added dropwise under N₂ 50.0g (217.5 mmol, in excess) of bromoisobutyrylbromide in 150ml toluene at room temperature. The mixture was kept at 60°C for 2 hours with stirring prior to filtration of salts and evaporation of solvents under vacuum. The functionalised MT resin was washed with toluene and water. The organic phase was dried with magnesium sulphate, filtered and volatiles were removed to afford 108.2g of a yellow viscous liquid. ¹H, ¹³C and ²⁹Si NMR characterisation of the liquid confirmed the formation of N-bromoisobutyryl, N-methylamino, 2-methylpropyl functional MT resin (Br(CH₃)₂CCON(CH₃)CH₂CH(CH₃)CH₂-) containing 9.89 wt% of Br.

Reference Example 9 - preparation of fifth solid supported copper catalyst

A 500 ml 3-neck reaction flask equipped with a dropping funnel, a thermometer and a reflux condenser was charged with 50g (279.3 mmole) of aminopropyltrimethoxy silane and 200 ml of p-xylene. 18g (1.25 moles) of water was added over a period of 60 minutes whilst distilling off methanol. After methanol removal, p-xylene was removed under reduced

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pressure to yield a white solid. 200ml of toluene was then added to the solid, and the flask equipped with Dean & Stark apparatus. Water was azeotropically distilled from the reaction by heating at 120°C for 4 hours. Toluene was removed under reduced pressure to yield a white brittle solid, which was extracted for 4 hours with p-xylene in a Soxhlet extractor, followed by drying in a vacuum oven for 4 hours at 120°C.

10g of the white solid and 50 ml of p-xylene were charged into a 250ml reaction flask and 8.6g (69.9 mmole) of 2-pyridine carboxyaldehyde was added slowly and left overnight to react. An orange solid was recovered by filtration and washed with p-xylene.

8.6g of the orange solid, 3.5g CuBr (24.5 mmole), and 30ml of p-xylene were added to a 100ml flask and heated at 80°C for 4 hours. After cooling, the solvent was colourless, and absent of green colour characteristic of free CuBr. The reaction product was filtered to obtain a black solid which was extracted for 4 hours with p-xylene in a Soxhlet extractor and dried in a vacuum oven at 50°C for 6 hours. (Theoretical CuBr% (w/w) = 35).

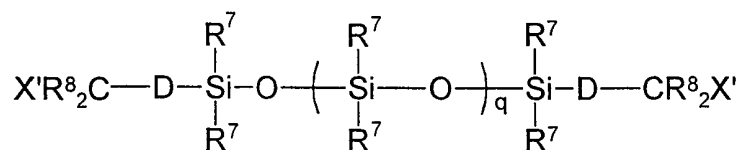
Example 8 - polymerisation of MMA

2.7g (1.17 mmole) of macroinitiator prepared in Reference Example 8 and 3.55g of catalyst prepared in Reference Example 9 were weighed into a Schlenk vessel and deoxygenated by exposure to a vacuum for 30 minutes. 23.6g (0.236 mole) of distilled methymethacrylate was added under nitrogen and degassed by three freeze-pump-thaw cycles. The solution was heated at 90°C for 195 minutes and samples

removed. During polymerisation the solution became highly viscous, which prevented the removal of samples. After 195 minutes of polymerisation, 77% monomer conversion was measured by ^1H NMR.

CLAIMS

1. Use of an initiator for initiating controlled polymerisation reactions, the initiator having at least one group $-D-CR^8_2X'$ and comprising units of the formulae $(R^7_3SiO_{1/2})$, $(R^7_2SiO_{2/2})$, $(R^7SiO_{3/2})$, and/or $(SiO_{4/2})$, wherein D is a divalent straight chain or branched alkylene group containing an oxygen or nitrogen heteroatom and/or substituted by a carbonyl group, each R^8 is independently an alkyl group or a hydrogen atom, X' is a halogen atom, and each R^7 is independently a group $-D-CR^8_2X'$ or an optionally substituted hydrocarbon group.
2. Use according to Claim 1 wherein at least one group R^8 in each group $-D-CR^8_2X'$ is an alkyl group.
3. Use according to Claim 2 wherein both groups R^8 in each group $-D-CR^8_2X'$ are alkyl groups.
4. Use according to any one of Claims 1 to 3 wherein the initiator has the formula $R^7_3SiO(SiR^7_2O)_qSiR^7_3$, wherein R^7 is as defined above and q is 0 or a positive integer.
5. Use according to Claim 4 wherein the initiator has the formula (VIII):



(VIII)

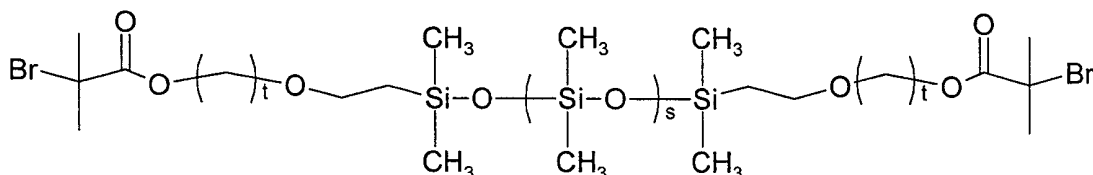
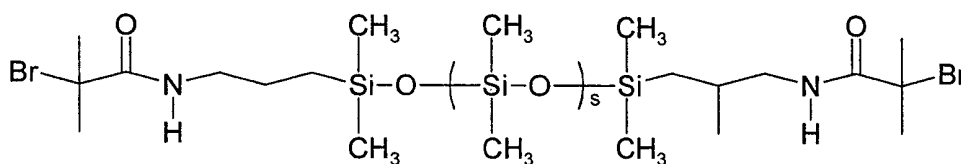
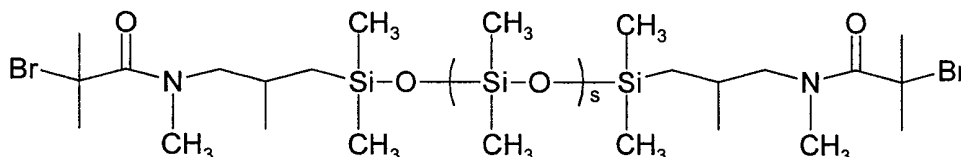
wherein R^7 , R^8 , X' , D and q are as previously defined.

6. Use according to any preceding Claim wherein each R^7 is a C_1 - C_6 alkyl group and D is selected from the groups:

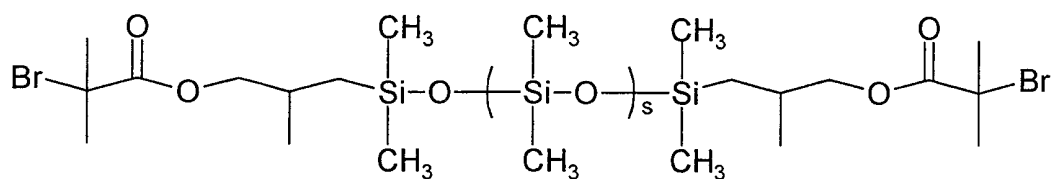


wherein R^9 is an alkyl group or a hydrogen atom, each R^{10} is independently a straight chain or branched alkylene group, and r is an integer of from 1 to 4.

7. Use according to Claim 6 wherein the initiator is selected from



and



wherein s is from 40 to 45 and t is 4.

8. Use according to any preceding Claim for initiating controlled polymerisation of vinyl containing monomers.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00695

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08F4/00 C08F2/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 870 774 A (DOW CORNING) 14 October 1998 (1998-10-14) examples claims	1-8
A	WO 98 01480 A (UNIV CARNEGIE MELLON) 15 January 1998 (1998-01-15) cited in the application claims 1,26 examples 23,24	1-8
P,A	DE 198 38 241 A (HALLENSLEBEN MANFRED LUDWIG ;WURM HELLMUTH (DE); BOETTCHER HENRIK) 24 February 2000 (2000-02-24) claims 8,9	1-8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 321 108 A (KUNZLER JAY ET AL) 14 June 1994 (1994-06-14) claims -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00695

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
EP 0870774	A	14-10-1998	US 5789516 A JP 10279643 A	04-08-1998 20-10-1998
WO 9801480	A	15-01-1998	US 5789487 A AU 3585997 A BR 9710273 A CA 2259995 A CN 1228789 A EP 0914352 A US 5945491 A	04-08-1998 02-02-1998 10-08-1999 15-01-1998 15-09-1999 12-05-1999 31-08-1999
DE 19838241	A	24-02-2000	WO 0011043 A	02-03-2000
US 5321108	A	14-06-1994	AU 669058 B AU 6167094 A BR 9405839 A CA 2154660 A CN 1117739 A DE 69407573 D DE 69407573 T EP 0683799 A ES 2114181 T HK 1008746 A JP 8506841 T MX 9401067 A SG 47856 A WO 9418253 A US 5387662 A US 5539016 A	23-05-1996 29-08-1994 05-12-1995 18-08-1994 28-02-1996 05-02-1998 16-04-1998 29-11-1995 16-05-1998 14-05-1999 23-07-1996 31-08-1994 17-04-1998 18-08-1994 07-02-1995 23-07-1996