Claims

1. Method for the preparation of a synthetic rubber blend,
the method comprising the step of
polymerizing at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers,
in the presence of one or more polymerization initiators and, optionally, a polar agent in an organic solvent,

wherein the step of polymerizing the at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, comprises

(i) a first stage of providing the solvent, a first portion of the at least one conjugated diene monomer and a first portion of the one or more polymerization initiator and, optionally, a first portion of the one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, and, optionally, a first portion of the polar agent; and polymerizing the at least one conjugated diene monomer and, optionally, the one or more alpha olefin monomers up to a conversion rate of at least 95 % to give a mixture comprising a living high molecular weight polydiene polymer or copolymer;

and optionally adding to and reacting with the living high molecular weight polydiene polymer or copolymer a coupling agent to obtain a mixture comprising a living and coupled polymer;

(ii) a second stage of adding to the mixture of stage (i) a second portion of a polymerization initiator
as well as a second portion of the at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, as well as, optionally, a polar agent;
and polymerizing to obtain a blend comprising a high molecular weight polydiene (A), and a low molecular weight polydiene (B), wherein the high molecular weight polydiene (A) has a weight average molecular weight (Mw) of from 500 -3000 kg/mol and wherein the low molecular weight polydiene (B) has a weight average molecular weight (Mw) of from 0,5 – 100 kg/mol; and

optionally (iii) a third stage of adding to the blend obtained in stage (ii) at least one chain end modifying compound to obtain a blend comprising a chain end modified high molecular weight polydiene (A), and a chain-end modified low molecular weight polydiene (B).

2. The method according to claim 1, wherein the step of polymerizing the at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, comprises said third stage (iii).

3. The method according to claim 1 or claim 2, wherein the polymerization initiator comprises an organolithium compound, preferably an organolithium compound selected from methyllithium, ethyllithium, n-butyllithium, s-butyllithium, t-butyllithium, t-octyllithium, isopropyllithium, phenyllithium, cyclohexyllithium, 2-butyllithium, 4-phenylbutyllithium, t-butyldimethylsilyloxypropyllithium, dialkylaminopropyllithium, N-morpholinopropyllithium, sodium biphenylide, sodium naphthalenide, potassium naphthalenide, 1,3-bis(1-(phenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-ethylphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-methylphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-propylphenyl)1-lithiohexyl)benzene,1,3-bis(1-(4-(tert-butyl)phenyl)1-lithiohexyl)-benzene, 1,3-bis(1-(4-(diethylamino)phenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-(dimethylamino)phenyl)1-lithiohexyl)benzene,1,3-bis(1-(4-ethoxyphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-(dimethoxy)phenyl)1-lithiohexyl)benzene, (((dimethylamino)dimethylsilyl)methyl)lithium, (((diethylamino)dimethylsilyl)methyl)lithium, (((dibutylamino)dimethylsilyl)methyl)lithium, (((dihexylamino)dimethylsilyl)methyl)lithium, (((dioctylamino)dimethylsilyl)methyl)lithium, (((dibenzylamino)dimethylsilyl)methyl)lithium, ((dimethyl(piperidin-1-yl)silyl)methyl)lithium, ((dimethyl(morpholino)silyl)methyl)lithium, ((dimethyl(4-methylpiperazin-1-yl)silyl)methyl)lithium, ((dimethyl(4-ethylpiperazin-1-yl)silyl)methyl)lithium, and ((dimethyl(4-benzylpiperazin-1-yl)silyl)methyl)lithium or a combination of any two or more of these organolithium compounds;

and/or wherein the polar agent comprises an ether compound, preferably selected from the group consisting of: diethyl ether, di-n-butyl ether, ethylene glycol diethyl ether, ethylene glycol dibutylether, diethylene glycol dimethyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutylether, alkyltetrahydrofurylethers, such as, methyltetrahydrofurylether, ethyltetrahydro-furylether, propyltetrahydrofurylether, butyltetrahydrofurylether, hexyltetrahydro-

furylether, octyltetrahydrofurylether, tetrahydrofuran, 2,2-(bistetrahydro-furfuryl)propane, bistetrahydrofurfurylformal, methyl ether of tetrahydrofurfuryl alcohol, ethyl ether of tetrahydrofurfuryl alcohol, butyl ether of tetrahydrofurfuryl alcohol, α-methoxytetrahydrofuran, dimethoxybenzene, and dimethoxyethane; and/or a tertiary amine compound, preferably selected from the group consisting of: butyl ether of triethylamine, pyridine, N,N,N',N'-tetramethyl ethylenediamine, dipiperidinoethane, methyl ether of N,N-diethylethanolamine, ethyl ether of N,N-diethylethanolamine, and N,N-diethylethanolamine, oligomeric oxolanyl alkanes, preferably N,N,N',N'-tetramethyl ethylenediamine and 2,2-(bistetrahydro-furfuryl)propane; or a combination of any two or more of these ether and amine compounds;

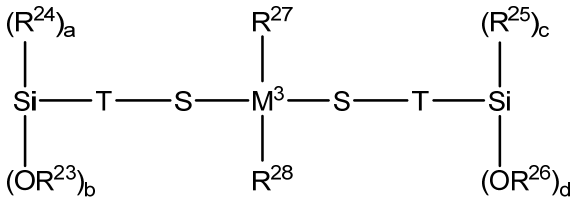
and/or wherein the solvent is selected from the group consisting of cyclohexane, butane, butane, hexane and heptane, and mixtures thereof.

4. The method according to any of claims 1 to 3, wherein the chain end modifying compounds are represented by any one of the following Formulas 7, 8, 9, 10, 11, 12, 13, 14, 15 and 16 and Lewis base adducts thereof:

(R30)e Si (OR29)f

Formula 7

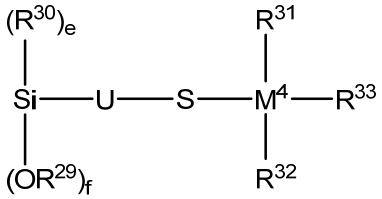
wherein Si is a silicon atom;
R^{29} is independently selected from (C_1-C_4) alkyl, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
R^{30} is independently selected from (C_1-C_{18}) alkyl, (C_1-C_{18}) alkoxy, (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and R^{34}-$(C_2H_4O)_g$-O-, wherein R^{34} is selected from (C_5-C_{23}) alkyl, (C_5-C_{23}) alkoxy, (C_6-C_{18}) aryl and (C_7-C_{25}) alkylaryl and e is selected from 0, 1 and 2; f is selected from 1, 2, 3 and 4; and e+f=4;



Formula 8

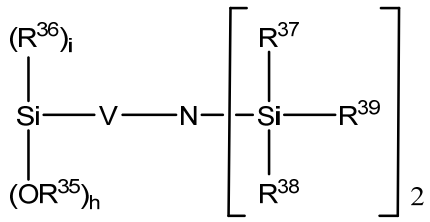
wherein M^3 is a silicon atom or a tin atom;
T is at least divalent and is selected from (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and (C_1-C_{18}) alkyl,

wherein each group is optionally substituted with one or more groups selected from di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino, tris(C_1-C_7 hydrocarbyl)silyl, (C_7-C_{18}) alkylaryl and (C_6-C_{18}) aryl;
R^{23} and R^{26} are each independently selected from (C_1-C_4) alkyl;
R^{24}, R^{25}, R^{27} and R^{28} are each independently selected from (C_1-C_{18}) alkyl, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
a and c are each independently selected from 0, 1 and 2; b and d are each independently selected from 1, 2 and 3; a+b=3; and c+d=3;

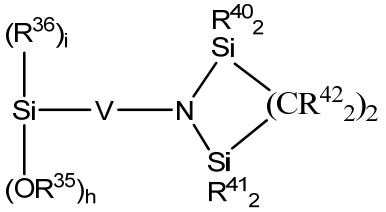


Formula 9

wherein M^4 is a silicon atom or a tin atom;
U is at least divalent and is selected from (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and (C_1-C_{18}) alkyl, wherein each group is optionally substituted with one or more groups selected from di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino, tris(C_1-C_7 hydrocarbyl)silyl, (C_7-C_{18}) alkylaryl and (C_6-C_{18}) aryl;
R^{29} is independently selected from (C_1-C_4) alkyl, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
R^{31}, R^{32} and R^{33} are each independently selected from (C_1-C_{18}) alkyl, (C_1-C_{18}) alkoxy, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
R^{30} is independently selected from (C_1-C_{18}) alkyl, (C_1-C_{18}) alkoxy, (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and R^{34}-$(C_2H_4O)_g$-O-, wherein R^{34} is selected from (C_5-C_{23}) alkyl, (C_5-C_{23}) alkoxy, (C_6-C_{18}) aryl and (C_7-C_{25}) alkylaryl and g is selected from 4, 5 and 6;
e is selected from 0, 1 and 2; f is selected from 1, 2 and 3; and e+f=3;



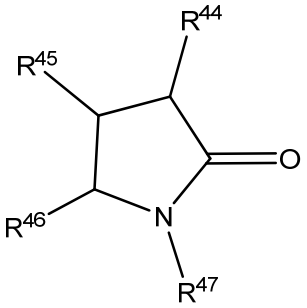
Formula 10



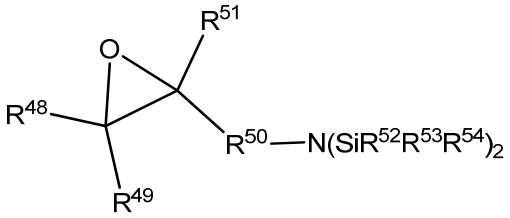
Formula 11

wherein V is at least divalent and is selected from (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and (C_1-C_{18}) alkyl, wherein each group is optionally substituted with one or more groups selected

from di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino, tris(C_1-C_7 hydrocarbyl)silyl, (C_7-C_{18}) alkylaryl and (C_6-C_{18}) aryl;
R^{35} is independently selected from (C_1-C_4) alkyl, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
R^{37}, R^{38}, R^{39}, R^{40}, R^{41} and R^{42} are each independently selected from (C_1-C_{18}) alkyl, (C_1-C_{18}) alkoxy, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
R^{36} is independently selected from (C_1-C_{18}) alkyl, (C_1-C_{18}) alkoxy, (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and R^{43}-$(C_2H_4O)_j$-O-, wherein R^{43} is selected from (C_5-C_{23}) alkyl, (C_5-C_{23}) alkoxy, (C_6-C_{18}) aryl and (C_7-C_{25}) alkylaryl; and j is selected from the 4, 5 and 6;
i is selected from 0, 1 and 2; h is selected from 1, 2 and 3; and i+h=3;

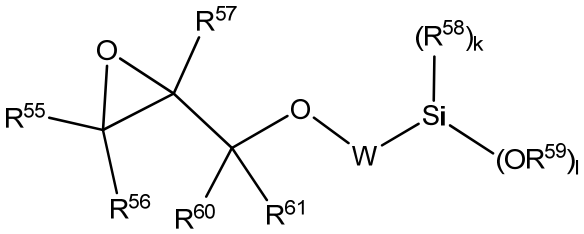


Formula 12

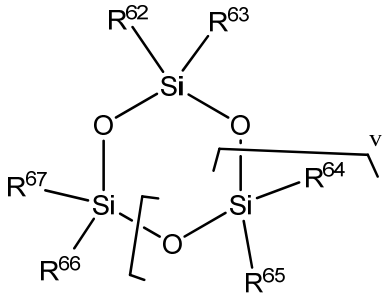


Formula 13,

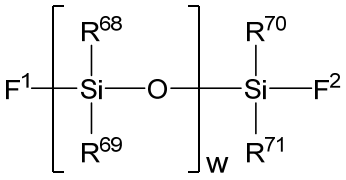
wherein R^{44}, R^{45}, R^{46}, R^{47}, R^{48}, R^{49}, R^{51}, R^{52}, R^{53} and R^{54} are each independently selected from hydrogen, (C_1-C_{16}) alkyl, (C_6-C_{16}) aryl and (C_7-C_{16}) alkylaryl; and
R^{50} is at least divalent and is selected from (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and (C_1-C_{18}) alkyl, wherein each group is optionally substituted with one or more groups selected from di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino, tris(C_1-C_7 hydrocarbyl)silyl, (C_7-C_{18}) alkylaryl and (C_6-C_{18}) aryl.



Formula 14



Formula 15,



Formula 16

In Formulas 14, 15 and 16, R^{55}, R^{56}, R^{57}, R^{58}, R^{60}, R^{61}, R^{62}, R^{63}, R^{64}, R^{65}, R^{66}, R^{67}, R^{68}, R^{69}, R^{70} and R^{71} are each independently selected from hydrogen, (C_1-C_{16}) alkyl, (C_6-C_{16}) aryl and (C_7-C_{16}) alkylaryl;
R^{59} is selected from (C_1-C_4) alkyl, (C_6-C_{18}) aryl and (C_7-C_{18}) alkylaryl;
W is at least divalent and is selected from (C_6-C_{18}) aryl, (C_7-C_{18}) alkylaryl and (C_1-C_{18}) alkyl, wherein each group is optionally substituted with one or more groups selected from di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino, tris(C_1-C_7 hydrocarbyl)silyl, (C_7-C_{18}) alkylaryl and (C_6-C_{18}) aryl;
k is selected from 0, 1 and 2; l is selected from 1, 2 and 3; k+l=3; and v is selected from 1 to 20;
F^1 and F^2 are independently selected from hydrogen, hydroxy, chlorine, bromine, iodine, -$SiR^{52}R^{53}R^{54}$, wherein R^{52}, R^{53}, R^{54} are the same or different and are as defined for Formulas 12 and 13, vinyl, (C_6-C_{16}) aryl, (C_7-C_{16}) alkylaryl and (C_1-C_{16}) alkyl, wherein each hydrocarbyl group is optionally substituted with one or more groups selected from hydroxyl, di(C_1-C_7 hydrocarbyl)amino, bis(tri(C_1-C_{12} alkyl)silyl)amino and an epoxy group.

5. The method according to any of claims 1-4, wherein the coupling agent is selected from the group consisting of tin halides and
silicon halides, preferably including: $SnCl_4$, $(R_1)_3SnCl$, $(R_1)_2SnCl_2$, R_1SnCl_3, $SiCl_4$, R_1SiCl_3, $(R_1)_2SiCl_2$, $(R_1)_3SiCl$, Cl_3Si-$SiCl_3$, Cl_3Si-O-$SiCl_3$, Cl_3Sn-$SnCl_3$ and Cl_3Sn-O-$SnCl_3$ wherein R_1 is a hydrocarbyl group, preferably an alkyl group; and tin alkoxides and silicon alkoxides, preferably including: $Sn(OMe)_4$, $Si(OMe)_4$, $Sn(OEt)_4$ and $Si(OEt)_4$; wherein the coupling agent is most preferably selected from the group consisting of: $SnCl_4$, $SiCl_4$, $Sn(OMe)_4$ and $Si(OMe)_4$.

6. The method according to any of claims 1 to 5, wherein the conjugated diene monomer is selected from 1,3-butadiene, 1,2-buadiene, 2-alkyl-1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 2-methyl-2,4-pentadiene, cyclopentadiene, 2,4-hexadiene and/or 1,3-cyclooctadiene, preferably 1,3-butadiene, and/or 2-methyl-1,3-butadiene; and/or wherein the one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, are selected from vinyl aromatic monomers and from vinyl silanes; the vinyl aromatic momomers comprising styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2,4-dimethylstyrene, 2,4,6-trimethylstyrene, α-methylstyrene, stilbene, 2,4-diisopropylstyrene,4-tert-butylstyrene, vinyl benzyl dimethylamine, (4-vinylbenzyl)dimethyl aminoethyl ether, N,N-dimethylaminoethyl styrene, N,N-bis-(trialkylsilyl)aminostyrene, tert-butoxystyrene, vinylpyridine, and/or

divinylbenzene, and vinyl silanes comprising vinyl silyl-piperazine monomers, aminovinylsilanes and /or combinations of these monomers.

7. The method according to any of the preceding claims, wherein the first and/or the second stage of the step of polymerizing the at least one conjugated diene monomer and, optionally, the one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, is carried out at a temperature of from 10 to 100°C; and/or wherein the conversion rate in the first stage (i) of the at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, is more than 95 %, preferably more than 98% and most preferred more than 99%.

8. The method according to any of the preceding claims, wherein the ratio of the first and of the second portion of the at least one conjugated diene monomer and, optionally, one or more alpha olefin monomers, including aromatic vinyl and vinyl silane monomers, based on the total amount of conjugated diene monomer, alpha olefin monomers provided in the first and in the second stage is as follows:

1st portion monomer is of 0.93 – 0.5; and
2nd portion monomer is of 0.07 – 0.5;

and wherein the ratio of the first and of the second portion of the polymerization initiator based on the total amount of initiator moles provided in the first and in the second stage is:

1st portion initiator is of from 0.033 – 86.9 mole % of total initiator
2nd portion initiator is of from 99.967-13.1 mole % of total initiator

9. The method according to any of the preceding claims, wherein the method comprises a fourth stage (iv) of adding and reacting a polymer chain terminating agent and one or more antioxidants and removing the solvent from the blend obtained in stage (ii) or stage (iii).

10. Synthetic rubber blend obtainable according to the method of any of claims 1 to 9.

11. Synthetic rubber blend according to claim 10, wherein the blend comprises

(a) 50-93 parts by weight of a high molecular weight polydiene (A) having a weight average molecular weight (Mw) of from 500 -3000 kg/mol;

and

(b) 7-50 Parts by weight of a low molecular weight polydiene (B) having a weight average molecular weight (Mw) of from 0,5 – 100 kg/mol.

12. Synthetic rubber blend according to any of claims 10 to 11, wherein the blend has a single glass transition temperature, and/or wherein the blend has a molecular weight distribution Mw/Mn of from 3 to 150, and/or wherein the Mooney viscosity of the blend is in the range of from 30 to 100.

13. Rubber composition comprising the blend of any of claims 10 to 12.

14. Rubber composition of claim 13, further comprising filler and/or further comprising one or more additional rubber selected from the group consisting of styrene butadiene rubber, butadiene rubber, synthetic isoprene rubber and natural rubber.

15. Method for the preparation of a cross-linked rubber composition, the method comprising the step of adding one or more vulcanizing agent to the synthetic rubber blend according to any of claims 10 to 12 or to the rubber composition according to any of claims 13 or 14 and cross-linking the composition.

16. Cured rubber composition obtainable according to the method of claim 15.

17. Article, comprising a cured rubber composition according to claim 16, wherein the article is a tire, a tire tread, a tire side wall, a conveyer belt, a seal or a hose.