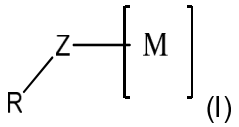
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

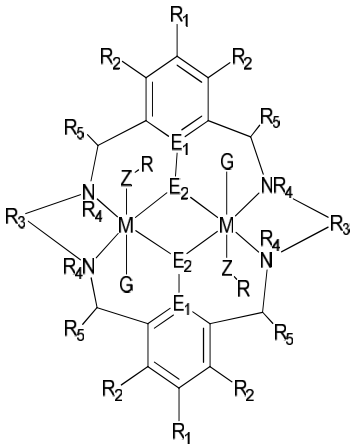
1. A method for producing a block copolymer, using a single catalytic system, wherein the single catalytic system comprises a catalyst of formula (I):



(I)

wherein:

the catalyst of formula (I) is a catalyst having the following structure:



wherein

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, a thioether group, a sulfoxide group, a sulfinate group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

Z is absent or selected from -E-, -EX(E)-, or -EX(E)E-;

X is C or S;

Each E is independently selected from O, S or NR^Z, wherein R^Z is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl;

R is hydrogen, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl, alkylheteroaryl, silyl or a polymer; and when Z is absent, R may additionally be selected from halide, phosphinate, azide or nitro;

each G is independently absent or a neutral or anionic donor ligand which is a Lewis base;

M is Zn(II), Cr(II), Co(II), Mn(II), Mg(II), Fe(II), Ti(II), Cr(III)-Z-R, Co(III)-Z-R, Mn (III)-Z-R, Fe(III)-Z-R, Ca(II), Ge(II), Al(III)-Z-R, Ti(III)-Z-R, V(III)-Z-R, Ge(IV)-(-Z-R)$_2$ or Ti(IV)-(-Z-R)$_2$;

the method comprising the steps of:

a) forming a first block by polymerising a first monomer or combination of monomers, wherein the first monomer or combination of monomers is selected from the groups (i) to (iii):

Group (i): a lactide and/or a lactone,
Group (ii): an epoxide and an anhydride, or
Group (iii): an epoxide and carbon dioxide,

b) optionally contacting the catalyst of formula (I) with a compound [Y] which is capable converting the group -Z-R, wherein Z is absent or a group selected from -E-X(E)- or -E-X(E)E-, to a group -Z-R wherein Z is -E-;

c) forming a second block by polymerising a second monomer or combination of monomers, wherein the second monomer or combination of monomers is selected from a different group (i) to (iii) to that selected for the first monomer or combination of monomers:

Group (i): a lactide and/or a lactone,
Group (ii): an epoxide and an anhydride, or
Group (iii): an epoxide and carbon dioxide,

wherein when the first monomer or combination of monomers is Group (i), Z is -E-; and

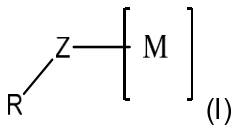
wherein when the first monomer or combination of monomers is group (ii) or Group (iii), and the second monomer or combination of monomers is Group (i), step b) is performed after step a).

2. The method according to claim 1, wherein the first monomer or combination of monomers is Group (i), and Z-R is -E-R, the second monomer or combination of monomers is Group (ii) or Group (iii) and the second monomer or combination of monomers is added to the reaction after step a) has been performed.

3. The method according to claim 1, wherein the first monomer or combination of monomers is Group (ii) or Group (iii), the second monomer or combination of monomers is Group (i), and step b) is performed after step a) and before step c).

4. The method according to claim 3, wherein the second monomer or combination of monomers is added to the reaction with the first monomer or combination of monomers, or after step a) has been performed.

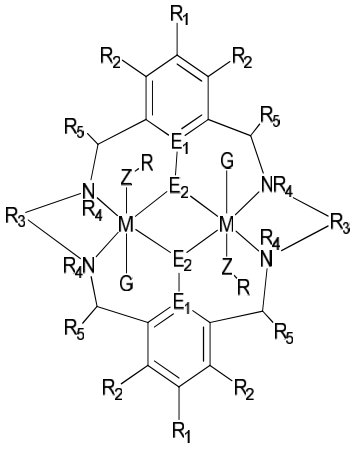
5. A method for producing a block copolymer, said block copolymer having a first and second block, using a single catalytic system, wherein the single catalytic system comprises a catalyst of formula (I):



(I)

Wherein:

the catalyst of formula (I) is a catalyst having the following structure:



wherein

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, a thioether group, a sulfoxide group, a sulfinate group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

Z is absent or selected from -E-, -EX(E)-, or -EX(E)E-;

X is C or S;

Each E is independently selected from O, S or NR^Z, wherein R^Z is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl;

R is hydrogen, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl, alkylheteroaryl, silyl or a polymer; and

when Z is absent, R may additionally be selected from halide, phosphinate, azide or nitro;

each G is independently absent or a neutral or anionic donor ligand which is a Lewis base;

M is Zn(II), Cr(II), Co(II), Mn(II), Mg(II), Fe(II), Ti(II), Cr(III)-Z-R, Co(III)-Z-R, Mn (III)-Z-R, Fe(III)-Z-R, Ca(II), Ge(II), Al(III)-Z-R, Ti(III)-Z-R, V(III)-Z-R, Ge(IV)-(-Z-R)$_2$ or Ti(IV)-(-Z-R)$_2$;the method comprising the steps of:

a) providing a mixture comprising:

i. an epoxide;

ii. a first monomer or combination of monomers, wherein the first monomer or combination of monomers is selected from a group (i) to (iii):

Monomer (i): a lactide and/or a lactone,
Monomer (ii): an anhydride, or
Monomer (iii): carbon dioxide, and

iii. a second monomer or combination of monomers, wherein the second monomer or combinations of monomers is selected from a different group (i) to (iii) to that selected for the first monomer or combination of monomers:

Monomer (i): a lactide and/or a lactone,
Monomer (ii): an anhydride, or
Monomer (iii): carbon dioxide; and

b) contacting the mixture with the single catalytic system;

wherein the rate of insertion of the first monomer or combination of monomers into the bond between the metal complex [M] and the ligand -Z-R is faster than the rate of insertion of the second monomer or combination of monomers into the bond between the metal complex [M] and the ligand -Z-R;

wherein when the first monomer or combination of monomers is Group (i), either -Z-R is -E-R, or the mixture comprises a compound [Y], and

wherein when the second monomer or combination of monomers is Group (i), the mixture comprises a compound [Y].

6. The method according to claim 5, wherein the mixture further comprises a third monomer or combination of monomers, wherein the third monomer or combination of monomers is selected from a group which is different from the first and second monomers or combination of monomers:

Monomer (i): a lactide and/or a lactone,
Monomer (ii): an anhydride, or
Monomer (iii): carbon dioxide;

wherein the rate of insertion of the first and second monomers are as claimed in claim 5, and wherein the rate of insertion of the third monomer or combination of monomers into the bond between the metal complex [M] and the ligand -Z-R is slower than the rate of insertion of the first and second monomers or combination of monomers into the bond between the metal complex [M] and the ligand -Z-R; and

wherein when the third monomer or combination of monomers is Monomer (i), the reaction mixture comprises a compound [Y].

7. The method according to any one of the preceding claims, wherein the compound [Y] is a compound having a three, four or five membered saturated ring and at least one heteroatom selected from O, S or N.

8. The method according to claim 7, wherein the compound [Y] is an epoxide, an aziridine, an episulfide, an oxetane, a thietane, an azetidine, a saturated furan, a saturated thiophene, a pyrrolidine or a saturated four-membered carbon ring where two adjacent carbon atoms are replaced by -Y-C(Y)-, wherein each Y is independently selected from O, S or NR^Y, and wherein R^Y is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl.

9. The method according to claim 8, wherein the compound [Y] is an epoxide.

10. The method according to any one of the preceding claims, wherein each E is O.

11. The method according to any one of the preceding claims, wherein M is selected from Zn(II), Mg(II), Co(II), Co(III)-Z-R, Cr(II), Cr(III)-Z-R, Mn(II), Mn(III)-Z-R, Al(III)-Z-R, Fe(II), and Fe(III)-Z-R.

12. The method according to any one of the preceding claims, wherein M is Zn(II) or Mg(II).

13. The method according to any one of the preceding claims, wherein E_1 is C and E_2 is O.

14. The method according to any one of the preceding claims, wherein R_1 is hydrogen, halide, an amine, an ether group, a thioether group, or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic.

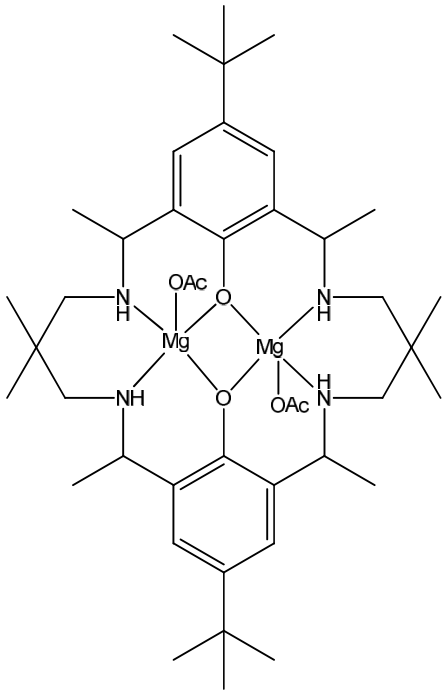
15. The method according to any one of the preceding claims, wherein R_2 is hydrogen or optionally substituted alkyl, heteroalkyl, aryl or heteroaryl.

16. The method according to any one of the preceding claims, wherein R_4 is hydrogen or optionally substituted alkyl, heteroalkyl, aryl or heteroaryl.

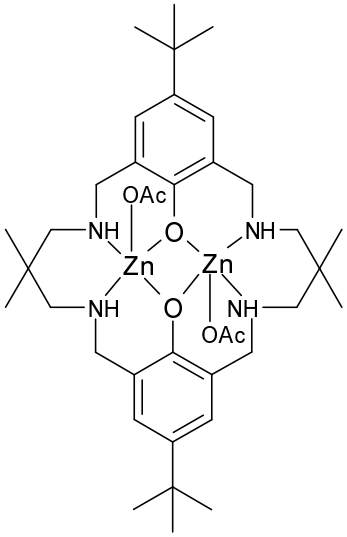
17. The method according to any one of the preceding claims, wherein R_5 is hydrogen or optionally substituted alkyl, heteroalkyl, aryl or heteroaryl.

18. The method according to any one of the preceding claims, wherein R_3 is optionally substituted alkylene, heteroalkylene, arylene or cycloalkylene.

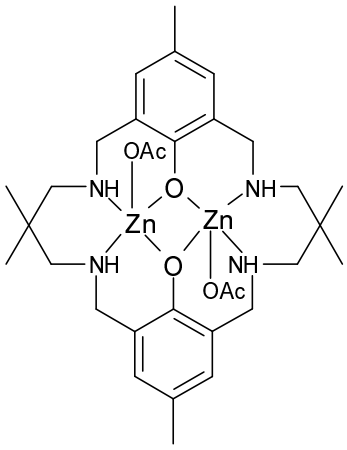
19. The method according to any one of the preceding claims, wherein the catalyst is selected from:



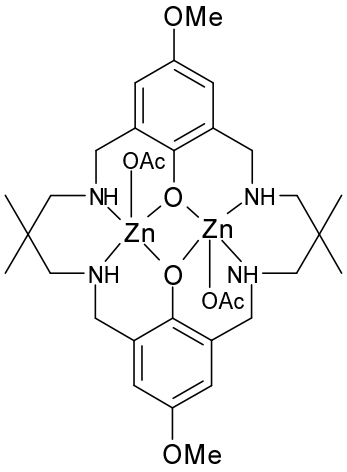
$[L^4Mg_2(OAc)_2]$,



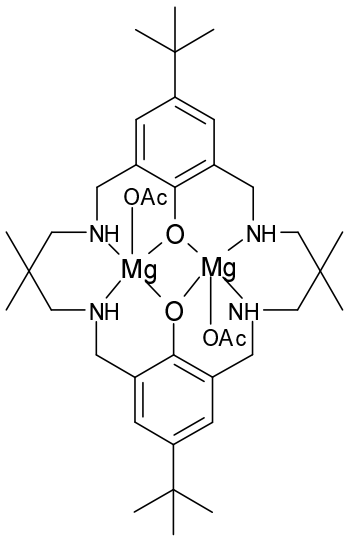
$[L^1Zn_2(OAc)_2]$



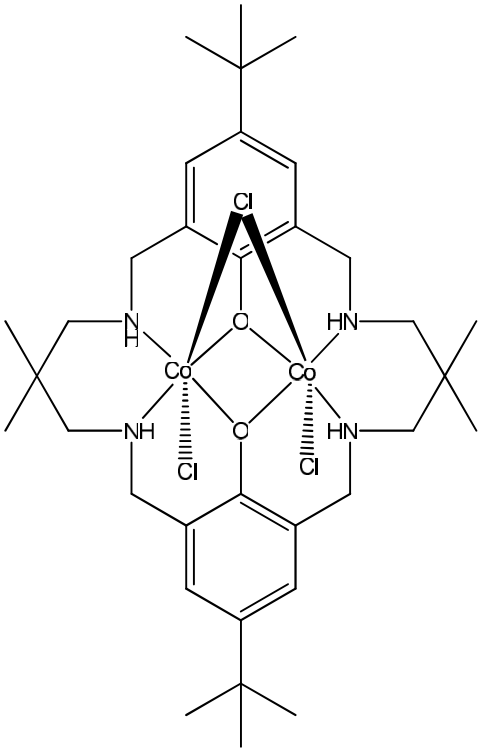
$[L^2Zn_2(OAc)_2]$



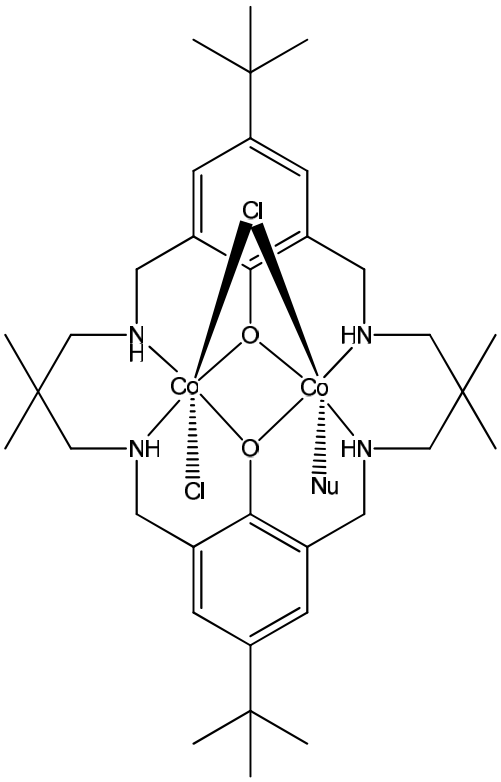
$[L^3Zn_2(OAc)_2]$



$[L^1Mg_2(OAc)_2]$



$[L^1Co_2Cl_3]^-[B\text{-}H]^+$



$[L^1Co_2Cl_2Nu]$

$[B\text{-}H]^+$ represents any counterion, for example,
B may be NEt_3, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), etc

Nu = N-methylimidazole
= pyridine
= dimethylaminopyridine

,

$[L^1Mg_2Cl_2(methylimidazole)]$,

$[L_1Mg_2Cl_2(dimethylaminopyridine)]$,

$[L_1Mg_2Br_2(dimethylaminopyridine)]$,

$[L^1Zn_2(F_3CCOO)_2]$,

$[L^1Zn_2(OOCC(CH_3)_3)_2]$,

$[L^1Zn_2(OC_6H_5)_2]$,

$[L^1Fe_2Cl_4]$,

$[L^1Co_2(OAc)_3]$,

$[L^1Zn_2(adamantyl\ carbonate)_2]$,

$[L^1Zn_2(pentafluorobenzoate)_2]$,

$[L^1Zn_2(diphenylphosphinate)_2]$,

$[L^1Zn_2(bis(4\text{-}methoxy)phenyl\ phosphinate)_2]$,

$[L^1Zn_2(hexanoate)_2]$,

$[L^1Zn_2(octanoate)_2]$,

$[L^1Zn_2(dodecanoate)_2]$,

$[L^1Mg_2(F_3CCOO)_2]$,
$[L^1Mg_2Br_2]$,
$[L^1Zn_2(C_6F_5)_2]$,
$[L^1Zn_2(C_6H_5)_2]$ and
$[L^1Zn_2(OiPr)_2]$.

20. The method according to any one of the preceding claims, wherein the catalyst system comprises a chain transfer agent.

21. A block copolymer produced by the method according to any one of claims 1-20.