

CLAIMS:

1. A process for the preparation of a multimodal polyethylene comprising:
 - (i) polymerising ethylene and optionally an α -olefin comonomer in a first slurry polymerisation stage to produce a first ethylene polymer; and
 - (ii) polymerising ethylene and optionally an α -olefin comonomer, in the presence of said first ethylene polymer, in a second slurry polymerisation stage,
 wherein said first and second polymerisation stages are carried out in the presence of an unsupported metallocene catalyst, a solution of said unsupported metallocene catalyst in a solvent is employed, and each polymerisation stage produces at least 5 %wt of said multimodal polyethylene, and said multimodal polyethylene has a multimodal molecular weight distribution, a weight average molecular weight of at least 50,000 g/mol and a bulk density of at least 250 g/dm³.
2. A process as claimed in claim 1, wherein said solvent is a C₃₋₁₀ saturated alkane, preferably a C₄₋₁₀ saturated alkane which is preferably selected from hexane and cyclohexane, or an aromatic hydrocarbon, preferably toluene.
3. A process as claimed in any preceding claim, wherein the metallocene catalyst is a complex of a group 3 to 10 metal, preferably a complex of a metal ion formed by a metal which is Zr, Hf or Ti, having at least two ligands, wherein each ligand is a substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted indenyl, substituted or unsubstituted fluorenyl or substituted or unsubstituted tetrahydroindenyl.
4. A process as claimed in any preceding claim, wherein said metallocene is a compound of formula (I):



wherein

each Cp is independently a substituted or unsubstituted, preferably unsubstituted, cyclic group having a delocalised system of pi electrons, more preferably a substituted or

unsubstituted, preferably unsubstituted, cyclopentadienyl, indenyl, fluorenyl or tetrahydroindenyl;

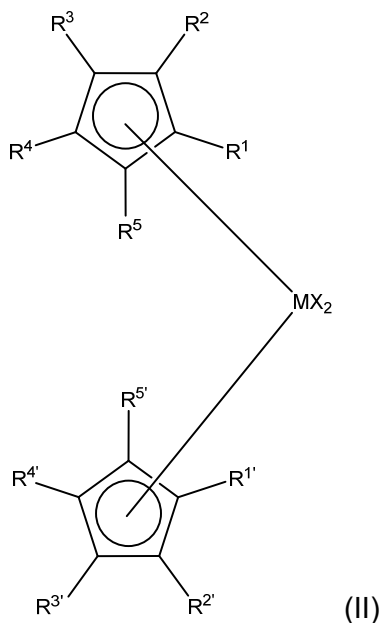
L is a bridge of 1-7 atoms, preferably a methylene, ethylene or silyl bridge;

n is 0 or 1;

M is a transition metal of Group 3 to 10, preferably Ti, Zr or Hf; and

each X is independently a sigma-ligand, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂ cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR'', -PR'', SiR''₃, -OSiR''₃, -NR''₂ or -CH₂Y wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, -NR''₂, -SR'', -PR''₃, -SiR''₃, or -OSi''₃ and wherein each R'' is independently a hydrogen or hydrocarbyl; or in the case of -NR''₂, the two substituents R'' can form a ring, together with the nitrogen atom to which they are attached.

5. A process as claimed in any preceding claim, wherein said metallocene is of formula (II):



wherein

M is a transition metal of Group 4 to 6;

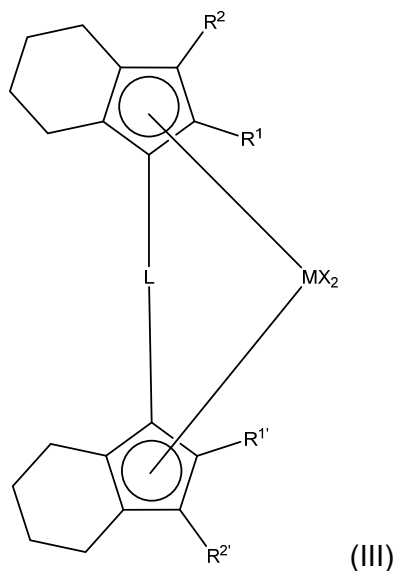
each X is independently a sigma-ligand, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂-cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR["], -PR["]₃, -SiR["]₃, -OSiR["]₃, -NR["]₂ or -CH₂-Y, wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, NR["]₂, -SR["], -PR["]₃, -SiR["]₃, or -OSiR["]₃ and wherein each R["] is independently a hydrogen or hydrocarbyl; or in the case of -NR["]₂, the two substituents R["] can form a ring, together with the nitrogen atom to which they are attached, preferably each X is independently halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryl, C₇₋₂₀ arylalkenyl or -NR["]₂;

R¹ and R^{1'} are each independently C₁₋₂₀ hydrocarbyl; and

R², R^{2'}, R³, R^{3'}, R⁴, R^{4'}, R⁵ and R^{5'} are each independently H or a C₁₋₂₀ hydrocarbyl,

or

wherein said metallocene is of formula (III):



wherein

M is a transition metal of Group 4 to 6, preferably Ti, Zr or Hf;

each X is independently a sigma-ligand, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂-cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR["], -PR["]₃, -SiR["]₃, -OSiR["]₃, -NR["]₂ or -CH₂-Y, wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, NR["]₂, -SR["], -PR["]₃, -SiR["]₃, or -OSiR["]₃ and wherein each R["] is independently a hydrogen or hydrocarbyl; or in the case

of $-NR''_2$, the two substituents R'' can form a ring, together with the nitrogen atom to which they are attached, preferably each X is independently halogen, C_{1-20} alkyl, C_{1-20} alkoxy, C_{6-20} aryl, C_{7-20} arylalkenyl or $-NR''_2$;

R^1 , $R^{1'}$, R^2 , $R^{2'}$, are each independently H or a C_{1-20} hydrocarbyl; and

L is a bridge of 1-4 C-atoms and 0-4 heteroatoms, wherein each of the bridge atoms may bear independently substituents; or a bridge of 1-3 hetero atoms, preferably a methylene, ethylene or silyl bridge.

6. A process as claimed in any preceding claim, wherein said metallocene is $(nBuCp)_2HfCl_2$, $(Ind)_2ZrCl_2$, $Et-(tetrahydroindenyl)_2ZrCl_2$ or $(nBuCp)_2ZrCl_2$.

7. A process as claimed in any preceding claim, wherein an aluminoxane cocatalyst is employed, preferably wherein:

a solution of said aluminoxane cocatalyst in a solvent, preferably a C_{3-10} saturated alkane, more preferably a C_{4-10} saturated alkane which is preferably selected from hexane and cyclohexane, or an aromatic hydrocarbon, preferably toluene, is employed; or

a mixture of an aluminoxane cocatalyst and metallocene, diluted in a C_{4-10} saturated alkane or toluene, is employed.

8. A process as claimed in any preceding claim, wherein:

said process is semi-continuous or continuous, preferably continuous;

said first and/or second slurry polymerisation is carried out in an aliphatic hydrocarbon diluent;

said first and/or said second polymerisation stage is carried out in the presence of hydrogen;

there is no reactor fouling in said first and/or said second polymerisation stage; and/or

said second polymerisation is carried out in the absence of hydrogen.

9. A process as claimed in any preceding claim, wherein said process consists of a first polymerisation stage, which preferably produces 1 to 65 %wt of said multimodal

polyethylene, and a second polymerisation stage, which preferably produces 35 to 99 %wt of said multimodal polyethylene.

10. A process as claimed in any one of claims 1 to 8, wherein said process consists of a first polymerisation stage, which preferably produces 1 to 65 %wt of said multimodal polyethylene, a second polymerisation stage, which preferably produces 35 to 99 %wt of said multimodal polyethylene, and a third polymerisation stage, preferably wherein said third polymerisation stage is carried out in slurry conditions and/or produces 0.5-30 wt% of said multimodal polyethylene.

11. A process as claimed in claim 10, comprising the sequential steps (a)-(c):
(a) polymerising ethylene and optionally an α -olefin comonomer in the first polymerisation stage to produce a lower molecular weight ethylene (LMW) polymer;
(b) polymerising ethylene and optionally an α -olefin comonomer in the second polymerisation stage to produce a first higher molecular weight ethylene polymer (HMW1);
and
(c) polymerising ethylene and optionally an α -olefin comonomer in the third polymerisation stage to produce a second higher molecular weight ethylene polymer (HMW2),
wherein the molecular weight of the components increases in the order
LMW<HMW1<HMW2,

or

comprising the sequential steps (a)-(c):
(a) polymerising ethylene and optionally an α -olefin comonomer in the first polymerisation stage to produce a lower molecular weight ethylene polymer (LMW);
(b) polymerising ethylene and optionally an α -olefin comonomer in the second polymerisation stage to produce a second higher molecular weight ethylene polymer (HMW2); and
(c) polymerising ethylene and optionally an α -olefin comonomer in the third polymerisation stage to produce a first higher molecular weight ethylene polymer (HMW1),

wherein the molecular weight of the components increases in the order
 $LMW < HMW1 < HMW2$.

12. A process as claimed in any preceding claim, wherein there is no reactor fouling in said second polymerisation stage.

13. A process as claimed in claim 10 or claim 11, wherein there is no reactor fouling in said third polymerisation stage.

14. A process as claimed in any one of claims 1 to 9 or claim 12, wherein said multimodal polyethylene has a bimodal molecular weight distribution.

15. A process as claimed in any one of claims 1 to 8, 10, 11, 13, or claim 12 when not dependent on claim 9, wherein said multimodal polyethylene has a trimodal molecular weight distribution.

16. A process as claimed in any preceding claim, wherein said multimodal polyethylene has:

a Mw of 100,000 to 250,000 g/mol

a Mn of 18,000 to 40,000 g/mol

a MWD of greater than 1 and no more than 25

a MFR₂ of 0.005 to 0.2 g/10min

a MFR₅ of 0.05 to 1 g/10min

an ash content of 0 to 800 wt ppm

a density of 920 to 980 kg/dm³

a bulk density of 250 to 400 g/dm³; and/or

less than 100 wt ppm of material of hardness more than 3 on Moh's scale.

17. A process as claimed in any preceding claim, wherein said multimodal polyethylene comprises 0.5 to 10 %wt comonomer.

18. A process as claimed in any preceding claim, wherein said multimodal polyethylene is in the form of particles.
19. A process as claimed in any preceding claim, wherein said first ethylene polymer has a MFR₂ of at least 10 g/10min, preferably 10 to 1000 g/10min.
20. A multimodal polyethylene obtained by a process as claimed in any preceding claim.
21. A metallocene multimodal polyethylene comprising:
- i) a multimodal molecular weight distribution;
 - ii) a weight average molecular weight of at least 50,000 g/mol;
 - iii) a MFR₂ of less than 0.2 g/10min;
 - iv) a MFR₅ of less than 1 g/10min;
 - v) a bulk density of at least 250 g/dm³; and
 - vi) an ash content of less than 800 ppm wt
- and preferably wherein said metallocene multimodal polyethylene contains less than 100 wt ppm of material of hardness more than 3 on Moh's scale.
22. A process for preparing a pipe comprising:
- i) preparing a multimodal polyethylene by the process claimed in any one of claims 1 to 19; and
 - ii) extruding said multimodal polyethylene to produce pipe.
23. A pipe obtained by a process as claimed in claim 22 or comprising a metallocene multimodal polyethylene as claimed in any one of claims 20 to 21.