Claims

1. A method for preparing a zwitterionic co-polymer comprising the steps of:

a) providing a solution of at least one ethylenically unsaturated polymerizable zwitterionic monomer dissolved in a solvent;

b) combining said solution of zwitterionic monomer with at least one co-monomer being selected from cationic, anionic and non-ionic ethylenically unsaturated monomers;

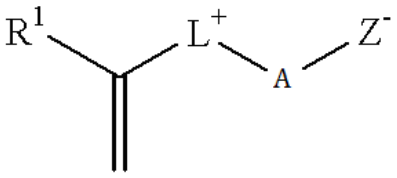
c) polymerizing the zwitterionic monomer and said at least one co-monomer in the presence of said solvent to form a solution or dispersion of co-polymer; and,

d) replacing at least part of said solvent with a further solvent in which said co-polymer shows sufficient solubility to form a solution of said co-polymer in that further solvent,

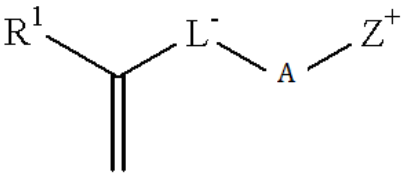
wherein step b) and step c) may be performed sequentially or concurrently.

2. A method according to claim 1 for preparing a zwitterionic co-polymer comprising the steps of:

a) providing a solution in a first solvent of at least one zwitterionic monomer, said zwitterionic monomer being selected from monomers of Formula A, monomers of Formula B or mixtures thereof;



Formula A

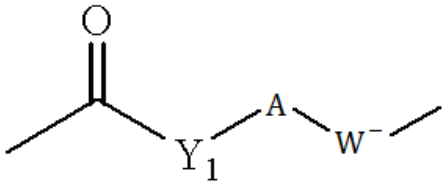


Formula B

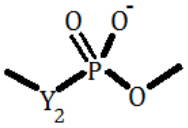
wherein: R^1 is hydrogen or methyl;

L^+ is an aliphatic, alicyclic or aromatic divalent group comprising up to 40 carbon atoms and a cation selected from N+, P+ and S+;

L^- is a group of formula

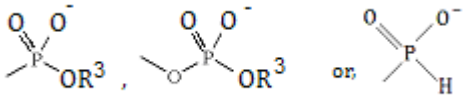


A is an alkyl, alkenyl, alkynyl, aryl or aralkyl group having up to 16 carbon atoms,

W^- is  ;

Y_1 and Y_2 are independently selected from O or NR^2;

Z^- is CO_2^-, or SO_3^- or



Z^+ is $—N^+R^4R^5R^6$, $—P^+R^4R^5R^6$ or $—S^+R^4R^5$, and,

R^2, R^3, R^4, R^5 and R^6 are independently selected from hydrogen, C_6-C_{20} aryl, C_7-C_{20} aralkyl and C_1-C_{20} alkyl;

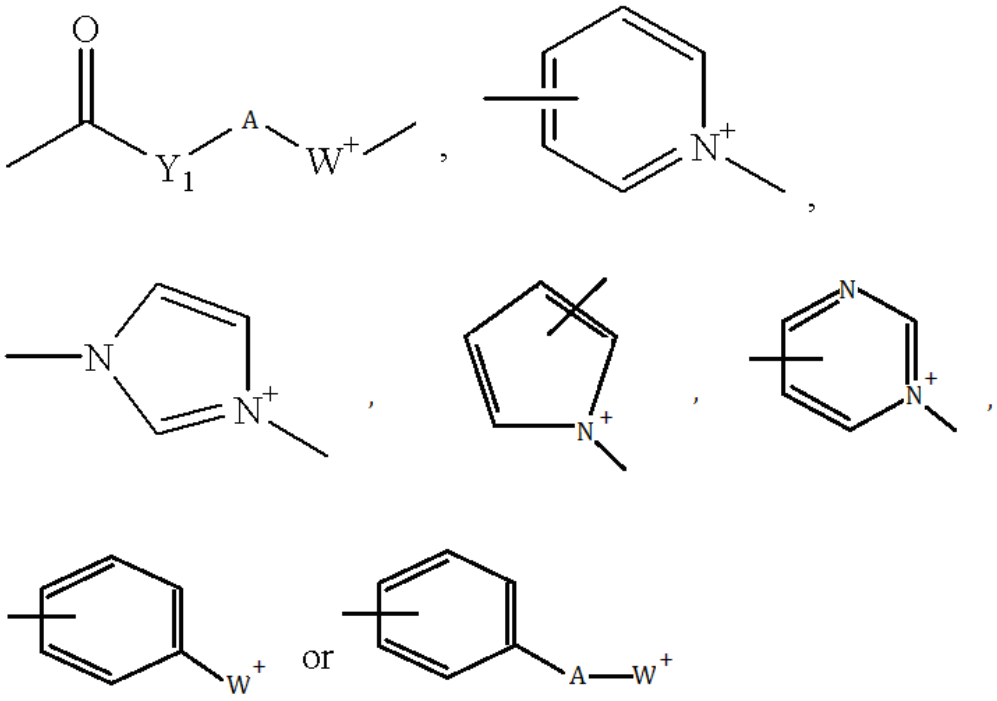
b) combining said solution of zwitterionic monomer with at least one co-monomer and optionally an amount of a second solvent, wherein said at least one co-monomer is selected from cationic, anionic and non-ionic ethylenically unsaturated monomers;

c) polymerizing the zwitterionic monomer and said at least one co-monomer to form a dispersion of co-polymer in said first and second solvents; and,

d) replacing at least part of said first and second solvents with a third solvent in which said co-polymer is soluble, thereby forming a solution of said co-polymer,

wherein step b) and step c) may be performed sequentially or concurrently.

3. The method according to claim 2, wherein in Formula A, L^+ is a group of formula



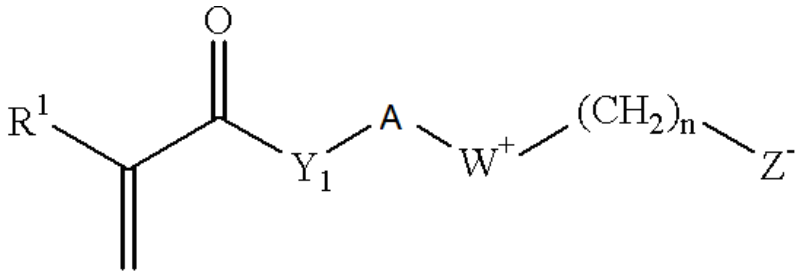
in which: A is an alkyl, alkenyl, alkynyl, aryl or aralkyl group having up to 16 carbon atoms, and,

W^+ is $—S^+R^7—$, $—N^+R^8R^9—$, or $—P^+R^8R^9—$,

wherein: R^7, R^8 and R^9 are independently selected from hydrogen, C_1-C_{20} alkyl, C_6-C_{20} aryl and C_7-C_{20} aralkyl, and preferably are independently selected from C_1-C_6 alkyl.

4. A method according to any one of claims 1 to 3 for preparing a zwitterionic co-polymer comprising the steps of:

a) providing a solution in a first alcoholic solvent of zwitterionic monomer as defined in Formula I:



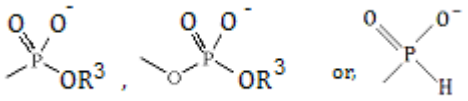
Formula I

wherein: R^1 is hydrogen or methyl;

Y_1 is selected from O and NR^2;

A is a linear or branched alkyl group having from 1 to 16, preferably from 1 to 10 carbon atoms;

Z^- is CO_2^-, or SO_3^- or



W^+ is $—S^+R^7—$, $—N^+R^8R^9—$, or $—P^+R^8R^9—$;

n is an integer of from 1 to 5; and

R^2, R^3, R^7, R^8, and R^9 are independently selected from hydrogen and $C_1 – C_{20}$ alkyl, C_6-C_{20} aryl and C_7-C_{20} aralkyl, and preferably are independently selected from C_1-C_6 alkyl;

b) feeding said solution of zwitterionic monomer into a second alcoholic solvent into which solvent is separately fed at least one co-monomer, said at least one co-monomer being selected from cationic, anionic and non-ionic ethylenically unsaturated monomers;

c) polymerizing the zwitterionic monomer and said at least one co-monomer to form a dispersion of co-polymer in said first and second alcoholic solvents; and,

d) replacing at least a part of said first and second alcoholic solvents with a third solvent in which said co-polymer is soluble, thereby forming a solution of said co-polymer,

wherein step b) and step c) may be performed sequentially or concurrently.

5. The method according to claim 4, wherein in Formula I:

Y_1 is O;

W^+ is —$N^+R^8R^9$—; and,

Z^- is SO_3^-.

6. The method according to any one of claims 1 to 5, wherein said ethylenically unsaturated co-monomer comprises at least 50 mol%, based on the total number of moles of co-monomer, of non-zwitterionic monomer selected from: (meth)acrylonitrile; alkyl (meth)acrylate esters; (meth)acrylic acids; vinyl esters; and, vinyl monomers;

preferably wherein said ethylenically unsaturated co-monomer comprises at least 50 mol%, based on the total number of moles of co-monomer, of non-zwitterionic monomers selected from C_1 to C_{14}, preferably C_2 to C_{12} alkyl esters of (meth)acrylic acid.

7. The method according to any one of claims 1 to 6, wherein the molar amount of zwitterionic monomer to be polymerized is in the range from 2 to 80 mol.%, preferably from 5 to 60 mol.% and more preferably from 10 to 50 mol.%, based on the total number of moles of zwitterionic monomer and said at least one co-monomer.

8. The method according to any one of claims 1 to 7, wherein said polymerization step c) is performed at a temperature of from 30°C to 200°C for a period of from 1 to 24 hours, and is preferably performed at a temperature of from 40°C to 150°C for a period of from 3 to 6 hours.

9. The method according to any one of claims 1 to 8, wherein said step c) is a free radical addition polymerization initiated by free radical initiator, said free radical initiator being initially included in one or more of said solution of zwitterionic monomer, said second solvent and said co-monomer feed.

10. The method according to any one of claims 2 to 9, wherein said first solvent and / or said second solvent independently comprise, by weight of each said solvent:

from 70 to 100 wt.% of one or more C_1 to C_4 alkanols;

from 0 to 30 wt.% organic co-solvent; and,

from 0 to 20 wt.% water.

11. The method according to any one of claims 2 to 10, wherein the third solvent has a boiling point which is higher than the boiling point of each of the first and second solvents and wherein, in step d), the first and second solvents are removed by distillation from the co-polymer dispersion.

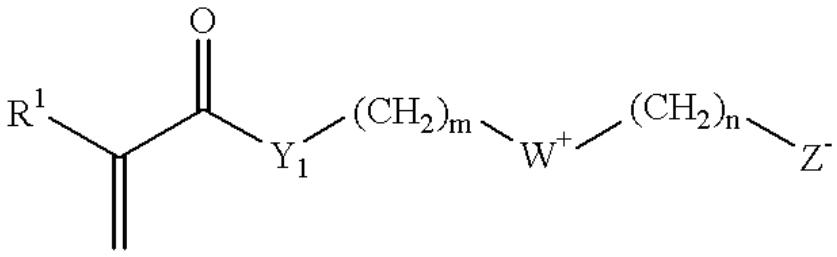
12. The method according any of claims 2 to 11, wherein said third solvent comprises, by weight of said solvent:

from 70 to 100 wt.% of benzene and / or one or more liquid alkyl benzenes in which the or each alkyl substituent on the benzene ring contains from 1 to 12, preferably 1 to 4 carbon atoms; and,

from 0 to 30 wt.% organic co-solvent.

13. The method according to claim 1 or claim 2 for preparing a zwitterionic co-polymer, said method comprising the steps of:

a) i) providing zwitterionic monomer as defined in Formula Ia;



Formula Ia

wherein: R_1 is hydrogen or methyl;

Y is O;

W^+ is —$N^+R^8R^9$— in which R^8 and R^9 are independently selected from hydrogen and C_1-C_4 alkyl;

m is 2 or 3;

n is an integer of from 1 to 5; and

Z^- is SO_3^-;

a) ii) dissolving said zwitterionic monomer in a first alcoholic solvent at a temperature in the range of from 30°C to 120°C;

b) maintaining said solution of zwitterionic monomer at a temperature in the range of from 30°C to 120°C and feeding said solution into a second alcoholic solvent, into which solvent is separately fed at least one co-monomer, said at least one co-monomer being selected from non-ionic ethylenically unsaturated monomers;

c) polymerizing the zwitterionic monomer and said at least one co-monomer to form a dispersion of co-polymer in said first and second alcoholic solvents; and,

d) distilling said first and second alcoholic solvents from the co-polymer dispersion and replacing said first and second alcoholic solvents with a third solvent in which said co-polymer is soluble, thereby forming a solution of said co-polymer,

said method being further characterized in that

said first alcoholic solvent is the same or different from said second alcoholic solvent, and said first and second alcoholic solvents comprise, by weight of each said solvent, from 70 to 100 wt.% of one or more C_1 to C_4 alkanols, from 0 to 30 wt.% of organic co-solvent and from 0 to 20 wt.% water; and,

said third solvent has a boiling point which is higher than the boiling point of each of the first and second alcoholic solvents.

14. A fouling resistant coating composition comprising a zwitterionic co-polymer prepared in accordance with the method as defined in any one of claims 1 to 13.