ZWITTERIONIC POLYMER AND USES THEREOF

FIELD OF THE INVENTION

[0001] The present invention relates generally to zwitterionic polymers. In particular, the invention relates to addition polymers, comprising zwitterions and carbon carbon linkages and to a method of preparing the same via a base or nucleophile initiated polymerization.

BACKGROUND OF THE INVENTION

[0002] Zwitterionic polymers are macromolecules containing equal amount of both positive and negative charges in its repeating unit and are inherently charge neutral. Zwitterionic polymers gained attention in recent years because of their strong interactions with water similar to poly(ethylene glycol), which makes them useful as anti-biofouling materials for both biomedical and marine antifouling applications. They also have a highly salt loving nature (halophilic) which makes them potentially useful for oil-field applications. In addition, in some cases, they can act as poly(ionic liquid) because of the excellent ionic liquid nature of the precursor monomers.

[0003] Zwitterionic polymers are also used for robust stabilisation of nanoparticles and nanoparticle formation, and are useful in cleaning formulations, cosmetic compositions and water purification.

[0004] Traditionally, zwitterionic polymers are synthesized by free radical polymerisation (FRP) and controlled radical polymerisation (CRP) such as atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerisation techniques.

[0005] However, one issue is that these polymerisations are usually done under controlled reaction conditions such as high temperature, moisture free and under inert gases. For example, FRP and ATRP require oxygen free conditions to prevent the poisoning of the catalyst. High purity of solvents and monomers are also required to reduce premature chain end termination. Removal of the catalyst in ATRP also requires multiple purification steps with organic solvents, and which creates an issue of waste and environmental concerns.

[0006] To overcome some of these issues, more current development aims to carry out polymerisation in aqueous media. Polymerising in water offers the advantage of being environmentally friendly by reducing organic and toxic waste. This green technology can also reduce overall cost in manufacturing through the use of less stringent equipment, raw material cost as well as downstream clean-up of waste.

[0007] However, current progress using aqueous medium for polymerisation is still lacking in efficiency and yield. It was observed that monomers with ionisable pendant groups polymerise much faster in aqueous media which may result in less control over the polydispersity and final molecular weight. These polymerisations also do not go to high conversions as the solubility of the polymers drop drastically as they lengthen.

[0008] An opportunity therefore remains to develop a new class of zwitterionic polymers and methodology which address or ameliorate one or more disadvantages or shortcomings associated with existing zwitterionic polymers and their methods of manufacture, or to at least provide a useful alternative to known polymer and their method of manufacture.

SUMMARY OF THE INVENTION

[0009] The present invention relates to zwitterionic polymers. In particular, the invention relates to addition polymers, comprising zwitterions and carbon carbon linkages and to a method of preparing the same. The method comprises a base or nucleophile initiated polymerization. The inventor has found that by using a nucleophilic base initiator to initiate the polymerisation, the polymerisation of zwitterionic monomers can be performed in aqueous or polar medium with high efficiency, high monomer conversion and low polydispersity. The polymers can also have controllable molecular weight. The polymerization mechanism is “anionic” in nature and the polymers prepared by the present process can be characterized with predetermined chain end functionality. For instance, using vinyl group bearing initiators like VI, DMAEMA or VBDMA allows for polymers with terminal vinyl groups that are able to be further functionalised with, for instance, other traditional radical polymerization methods.

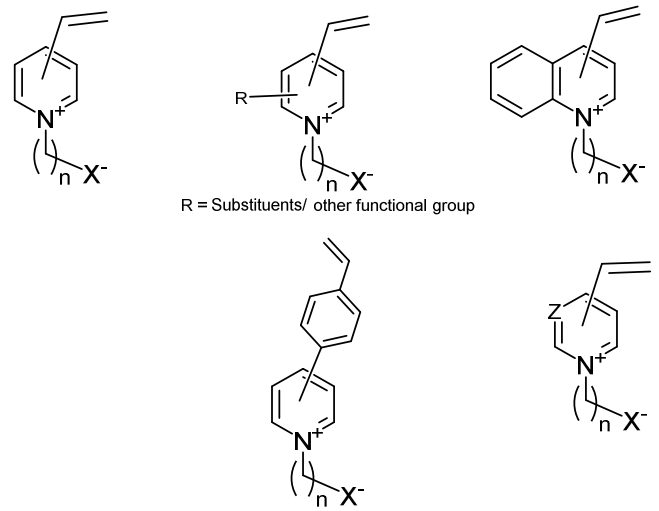
[0010] Accordingly, in an aspect, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

> initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator.

[0010a] Disclosed herein is a nucleophilic addition polymerisation process comprising the step of:

> initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator;

wherein the optionally substituted zwitterionic vinyl pyridine monomer is selected from:



Ortho- and para- vinyl substituted pyridines

wherein X^- can be sulfonate, sulphate, carboxylate, alkoxide, phosphate, phosphonate, phosphinate;

wherein Z is N; and

wherein n can be any integer from 1 to 6.

[0011] Disclosed herein is a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

[0012] In an embodiment, the present invention provides a process wherein the process is carried out at ambient temperature and under atmospheric conditions.

[0013] In a further embodiment, the present invention provides a process wherein the process is carried out in a polar medium.

[0014] In another embodiment, the present invention provides a process wherein the process is carried out in an aqueous medium.

[0015] In an aspect, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

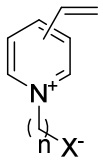
[0016] In a further aspect, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

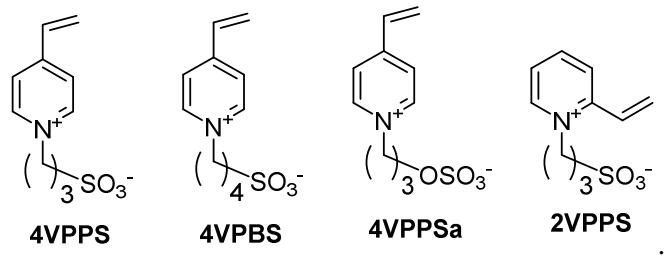
[0017] In another embodiment, the present invention provides a process wherein the optionally substituted zwitterionic vinyl pyridine monomer is a compound of formula (I):



wherein X^- can be sulfonate, sulphate, carboxylate, alkoxide, phosphate, phosphonate, phosphinate; and

wherein n can be any integer from 1 to 6.

[0018] In another embodiment, the present invention provides a process wherein the zwitterionic vinyl pyridine monomer is selected from:

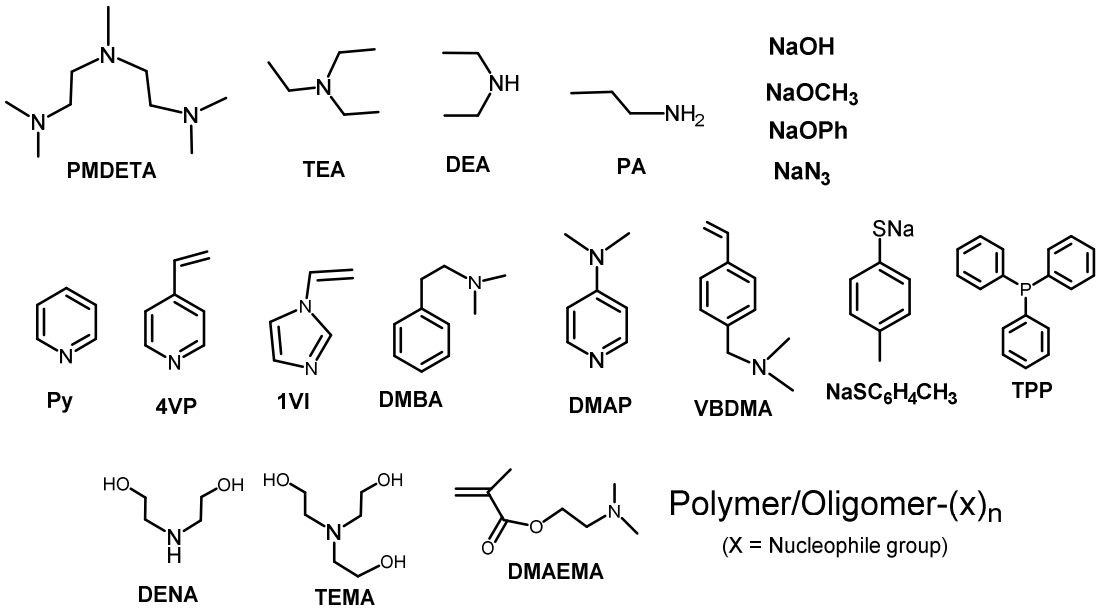


[0019] In a further embodiment, the present invention provides a process wherein the nucleophilic base initiator is selected from an inorganic alkali, amine, thiolate, phosphine, pyrrole, pyrrolidone, alkoxide, azide or phenoxide.

[0020] In an embodiment, the present invention provides a process wherein the nucleophilic base initiator is selected from optionally substituted tertiary amine, optionally substituted heteroaryl containing N or optionally substituted heterocyclyl containing N.

[0021] In another embodiment, the present invention provides a process wherein the nucleophilic base initiator is selected from a mono-amine, diamine or triamine.

[0022] In another embodiment, the present invention provides a process wherein the nucleophilic base initiator is selected from the following:



[0023] In another embodiment, the present invention provides a process wherein the aqueous medium is selected from water, brine, or a mixture thereof.

[0024] In another embodiment, the present invention provides a process wherein the aqueous medium is a mixture of water and/or brine with a polar solvent, such as

tetrahydrofuran, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, nitromethane, propylene carbonate, butanol, isopropanol, propanol, ethanol, methanol, and fluorosolvents.

[0025] In another embodiment, the present invention provides a process wherein the method is conducted in a polar medium, such as methanol, ethanol, and those known in the art as described above.

[0026] In a further embodiment, the present invention provides a process wherein the process is terminated with an electrophile.

[0027] In another embodiment, the present invention provides a process wherein the electrophile is selected from an inorganic acid.

[0028] In a further embodiment, the present invention provides a process wherein the process is free of polymerisation catalyst, such as transition metal.

[0029] In an embodiment, the present invention provides a process wherein the process produces a polymer with a polydispersity index of less than 1.8.

[0030] In another embodiment, the present invention provides a process wherein the process produces a polymer with a polydispersity index of less than 1.6.

[0031] In another embodiment, the present invention provides a process wherein the process produces a polymer with a polydispersity index of less than 1.4.

[0032] In another embodiment, the present invention provides a process wherein the optionally substituted zwitterionic vinyl pyridine monomer comprises of a plurality of optionally substituted zwitterionic vinyl pyridine monomers.

[0033] In an embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the steps of:

initiating polymerisation of a first optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer; and

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

[0034] In another embodiment, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a first optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate; and

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

[0035] In another embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the steps of:

initiating polymerisation of a first optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer;

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a second said polymer; and

polymerising a third zwitterionic monomer with the second said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

[0036] In another embodiment, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a first optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer;

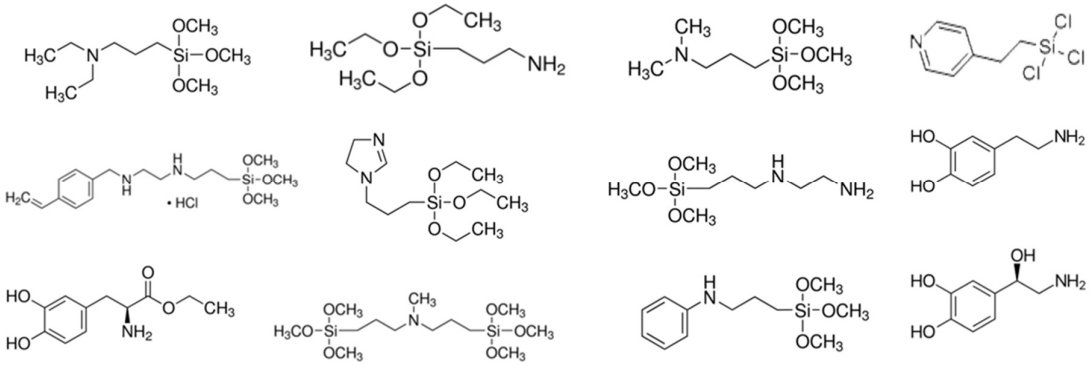
wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate; and

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a second said polymer; and

polymerising a third zwitterionic monomer with the second said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

[0037] In an embodiment, the present invention provides a process wherein the substrate is modified with a nucleophilic base initiator.

[0038] In another embodiment, the substrate can be modified with a nucleophilic base initiator selected from:



[0039] In another embodiment, the base initiator located on the surface of the substrate is selected from polydopamine or polynorepinephrine.

[0040] In another embodiment, the substrate can be modified with polydopamine or polynorepinephrine.

[0041] In this regard, the present invention provides an embodiment wherein the substrate may be modified with a nucleophilic base initiator by applying, dip coating, spin coating, spraying, brushing or gas phase deposition.

[0042] Disclosed herein is a polymer produced by a process as mentioned herein.

[0043] In a further aspect, the present invention provides a polymer comprising

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone.

[0043a] Disclosed herein is a polymer comprising

iii. a carbon-carbon backbone; and

iv. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone is derived from optionally substituted zwitterionic vinyl pyridine monomer.

[0044] In a still further aspect, the present invention provides a surface provided with a polymer, wherein the polymer comprises

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently or ionically coupled to the carbon-carbon backbone as polymer chain end functionality.

[0044a] Disclosed herein is a surface provided with a polymer, wherein the polymer comprises

iii. a carbon-carbon backbone; and

iv. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone is derived from optionally substituted zwitterionic vinyl pyridine monomer.

[0045] In a further embodiment, a polymer or surface as mentioned herein has a carbon-carbon backbone which may be derived from optionally substituted zwitterionic vinyl pyridine monomer.

[0046] In another embodiment, the present invention provides a polymer or surface wherein the polymer is characterised by a polydispersity index of less than 1.8.

[0047] In another embodiment, the present invention provides a polymer or surface wherein the polymer is characterised by a polydispersity index of less than 1.6.

[0048] In another embodiment, the present invention provides a polymer or surface wherein the polymer is characterised by a polydispersity index of less than 1.4.

[0049] In another embodiment, the present invention provides a use of the polymer or modified surface as mentioned herein for anti-biofouling, anti-bacterial, anti-dirt pick up, low friction, chromatography, or adhesive applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0050] Figure 1 illustrates ^{1}H NMR spectrum of 4VPBS.

[0051] Figure 2 illustrates ^{1}H NMR spectrum of 4VPPSa.

[0052] Figure 3 illustrates ^{1}H NMR spectra (in 0.5M NaCl/D_2O) of a) 4VPPS monomer and poly(4VPPS) synthesized by b) FRP and c) by base initiated polymerization.

[0053] Figure 4 illustrates ^{1}H NMR spectra (in 0.5M NaCl/D_2O) of a) poly(4VPBS), P11 and b) poly(4VPPSa), P12, both synthesized using TEA.

[0054] Figure 5 illustrates overlay GPC chromatogram of poly(2VPPS)s synthesized by FRP (P13) and base initiated polymerisation using TEA in water (P15), NaOH in water (P16) and TEA in MeOH (P20).

[0055] Figure 6 illustrates plausible mechanism of the base initiated polymerisation of 4VPPS.

[0056] Figure 7 illustrates UV-Vis spectra (in 0.5M brine) of a) 4VPPS before polymerization b) P10 after 1h of polymerization (using NaOH) c) P10 after 1h of polymerization and quenching with HCl, d) P5 after 1h of polymerization (using DMAP) and e) P5 after 1h of polymerization and quenching with HCl.

[0057] Figure 8 illustrates kinetic plots of base initiated polymerizations of a) 4VPPS using TEA, b) 2VPPS using NaOH and c) the evolution of molecular weight and PDI with the monomer conversion of 2VPPS polymerization using NaOH.

[0058] Figure 9 illustrates ^{1}HNMR spectra and end group correlation of poly(4VPPS)s and poly(2VPPS)s initiated by different nucleophile initiators.

[0059] Figure 10 illustrates schematics of chain extension of poly(2VPPS) to diblock copolymer poly(2VPPS)-*b*-poly(4VPBS).

[0060] Figure 11 illustrates overlay GPC chromatogram of a) poly(2VPPS) and b) poly(2VPPS)-*b*-poly(4VPBS).

[0061] Figure 12 illustrates ^{1}H NMR spectra of a) poly(2VPPS) and b) poly(2VPPS)-*b*-poly(4VPBS).

DETAILED DESCRIPTION OF THE INVENTION

[0062] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by those of ordinary skill in the art to which the invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, preferred methods and materials are described. For the purposes of the present invention, the following terms are defined below.

[0063] As used herein, the term "addition polymerisation" has the common meaning as would be understood by those skilled in the art. Polymerisation comprises of coupling vinyl monomers to give carbon carbon linkages that form part of the polymer's backbone. When the polymerisation is initiated with nucleophilic reagents, it may be known as anionic polymerisation.

[0064] The term "polymer backbone" of the polymer as used herein refers to the main structure of the polymer on which the substituents may be attached. The main structure of the polymer may be linear or branched.

[0065] The term "living polymer" is meant a polymer chain derived from monomers that have been polymerised by a living polymerisation technique. Those skilled in the art will appreciate that "living polymerisation" is a form of addition polymerisation whereby chain growth propagates with essentially no chain transfer and essentially no termination that give rise to dead polymer chains. By a "dead polymer chain" is meant one that can not undergo further addition of monomers. Characteristics and properties of a living polymerisation generally include (i) the molecular weight of the polymer increases with conversion, (ii) there is a narrow distribution of polymer chain lengths (i.e. they are of similar molecular weight), and (iii) additional monomers can be added to the polymer chain to create block co-polymer structures.

[0066] The term "zwitterionic" with reference to a molecule or polymer as used herein refers to a neutral species with both positive and negative electrical charges. In some cases multiple positive and negative charges may be present. A zwitterionic molecule would have at least a positive and a negative electrical charge present. A zwitterionic polymer would have at least a positive and a negative electrical charge present, but more preferentially multiple positive and negative electrical charges present. The positive and negative electrical charges may be on the same monomer or may be on different monomers.

[0067] The term "nucleophilic" species and "nucleophile" refers to an electron-rich molecule which can react with an electron-deficient molecule, wherein the reaction results in a covalent bond formation. The electron-rich molecule donates an electron pair to the electron-deficient molecule and can be molecules with at least a lone pair of electrons, at least one π bond, or a negatively charged species. A nucleophile is attracted to a positive or slightly positive part of another molecule or ion. For example, amines contain an active lone pair of electrons on the very electronegative nitrogen atom. It is these electrons which are attracted to positive parts of other molecules or ions. The person skilled in the art would appreciate that this does not only involve amines but other nucleophiles such as NaOH, NaOPh, NaN_3, R-SNa and PPh_3 are also able to initiate the polymerization.

[0068] The term "electrophilic" species and "electrophile" refers to an electron-deficient molecule which can react with an electron-rich molecule, wherein the reaction results in a covalent bond formation. The electron-deficient molecule accepts an electron pair from the electron-rich molecule which can be molecules with at least a lone pair of electrons, at least one π bond, or a negatively charged species.

[0069] The term "base" refers to a nucleophile which donates an electron pair towards a hydrogen ion or a proton. In this regard, the "base" forms a bond to a proton.

[0070] The term "vinyl pyridine monomer" as used herein refers to a monomer with a functional group $–CH=CH_2$ which is conjugated with pyridine that can be used to form a polymer.

[0071] The term "nucleophilic base initiator" as used herein refers to any species which are nucleophilic or basic in nature and reacts with a monomer to form an intermediate species capable of linking successively with other monomers to form a polymer.

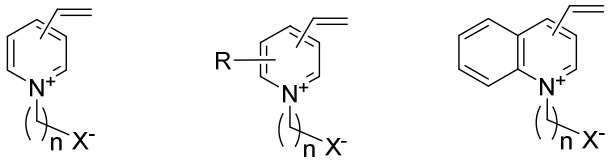
[0072] The term "ambient temperature and under atmospheric conditions" as used herein refers to the temperature, humidity and air pressure of the surrounding area or environment. Preferentially, it refers to the temperature, humidity and air pressure which are prevailing at that time on that day.

[0073] In this specification "optionally substituted" is taken to mean that a group may or may not be further substituted or fused (so as to form a condensed polycyclic group) with one or more groups selected from hydroxyl, acyl, alkyl, alkoxy, alkenyl, alkenyloxy, alkynyl, alkynyloxy, amino, aminoacyl, thio, arylalkyl, arylalkoxy, aryl, aryloxy, carboxyl, acylamino, cyano, halogen, nitro, phosphono, sulfo, phosphorylamino, phosphinyl, heteroaryl, heteroarylalkyl, heteroaryloxy, heterocyclyl, heterocyclylalkyl, heterocyclyloxy, oxyacyl, oxime, oxime ether, hydrazone, oxyacyloxy, oxyacylamino, oxysulfonylamino, acyloxy, aminoacyloxy, trihalomethyl, trialkylsilyl, pentafluoroethyl, trifluoromethoxy, difluoromethoxy, trifluoromethanethio, trifluoroethenyl, mono- and di-alkylamino, mono-and di-(substituted alkyl)amino, mono- and di-arylamino, mono- and di-heteroarylamino, mono- and di-heterocyclyl amino, and unsymmetric di-substituted amines having different substituents selected from alkyl, aryl, heteroaryl and heterocyclyl, and the like, and may also include a bond to a solid support material, (for example, substituted onto a polymer resin). For instance, an "optionally substituted amino" group may include amino acid and peptide residues.

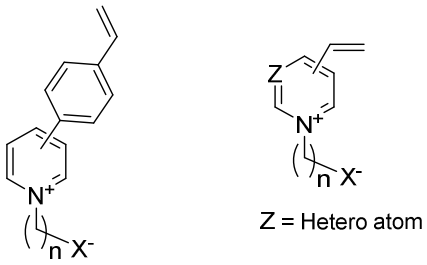
[0074] The term “residue” refers to a single molecular unit within a polymer. Accordingly, the residue differs from the monomer in that the residue is refers to the monomer within the polymer. In this sense, the monomer is chemically modified such that it can be incorporated into the polymer. For example, the monomer may loss a hydrogen and/or hydroxyl group to form a residue. As used herein, the residue of a monomer is chemically modified such that the hybridization of the vinyl carbon changes from sp2 to sp3. A residue of a nucleophilic base initiator is chemically modified such that the base initiator gains a charge or losses a hydrogen.

[0075] In an embodiment, the vinyl monomers are optionally substituted zwitterionic betaines. In another embodiment, the vinyl monomers are optionally substituted sulfobetaines or sulfabetaines. In another embodiment, the vinyl monomers are optionally substituted vinyl pyridines.

[0076] In an embodiment, the vinyl monomers are optionally substituted vinyl pyridines selected from the following:



R = Substituents/ other functional group



Z = Hetero atom

Ortho- and para- vinyl substituted pyridines

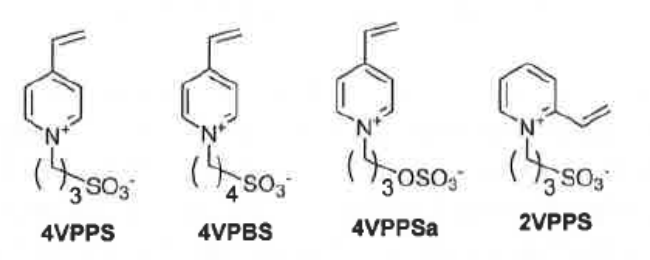
wherein X^- can be sulfonate, sulphate, carboxylate, alkoxide, phosphate, phosphonate, phosphinate; and

wherein n can be any integer from 1 to 6.

[0077] In an embodiment, X^- is selected from sulfonate, sulphate, carboxylate, alkoxide, phosphate or phosphonate. In another embodiment, X^- is selected from sulfonate, sulphate, carboxylate or alkoxide. In some embodiments, X^- is sulfonate. In some embodiments, X^- is sulphate. In another embodiment, X^- is carboxylate. In another embodiment, X^- is alkoxide. In another embodiment, X^- is phosphate. In another embodiment, X^- is phosphonate. In another embodiment, X^- is phosphinate.

[0078] In some embodiments, n is an integer from 1 to 5. In other embodiments, n is an integer from 1 to 4. In other embodiments, n is an integer from 1 to 3.

[0079] In another embodiment, the vinyl pyridine monomers can be selected from the following:



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[0080] In another embodiment, optionally substituted may be on the vinyl, pyridinyl or the alkyl linker. In an embodiment, the vinyl monomer is a vinyl pyridine, optionally substituted on the vinyl. In another embodiment, the vinyl is optionally substituted with one or more groups selected from hydroxyl, alkyl, alkoxy, arylalkyl, arylalkoxy, halogen, heterocyclylalkyl, trihalomethyl, trialkylsilyl, or pentafluoroethyl.

[0081] In an embodiment, the vinyl monomer is a vinyl pyridine, optionally substituted on the pyridine. In another embodiment, the pyridine is optionally substituted with one or more groups selected from hydroxyl, alkyl, alkoxy, arylalkyl, arylalkoxy, aryl, aryloxy, halogen, nitro, phophono, sulfo, phosphinyl, heteroarylalkyl or heterocyclylalkyl.

[0082] In an embodiment, the vinyl monomer is a vinyl pyridine, optionally substituted on the alkyl linker. In another embodiment, the alkyl linker is optionally substituted with one or more groups selected from hydroxyl, acyl, alkyl, alkoxy, amino, aminoacyl, thio, arylalkyl, arylalkoxy, aryl, aryloxy, carboxyl, acylamino, cyano, halogen, nitro, phosphono, sulfo, phosphorylamino, phosphinyl, heteroaryl, heteroarylalkyl, heteroaryloxy, heterocyclyl, heterocyclylalkyl or heterocyclyloxy.

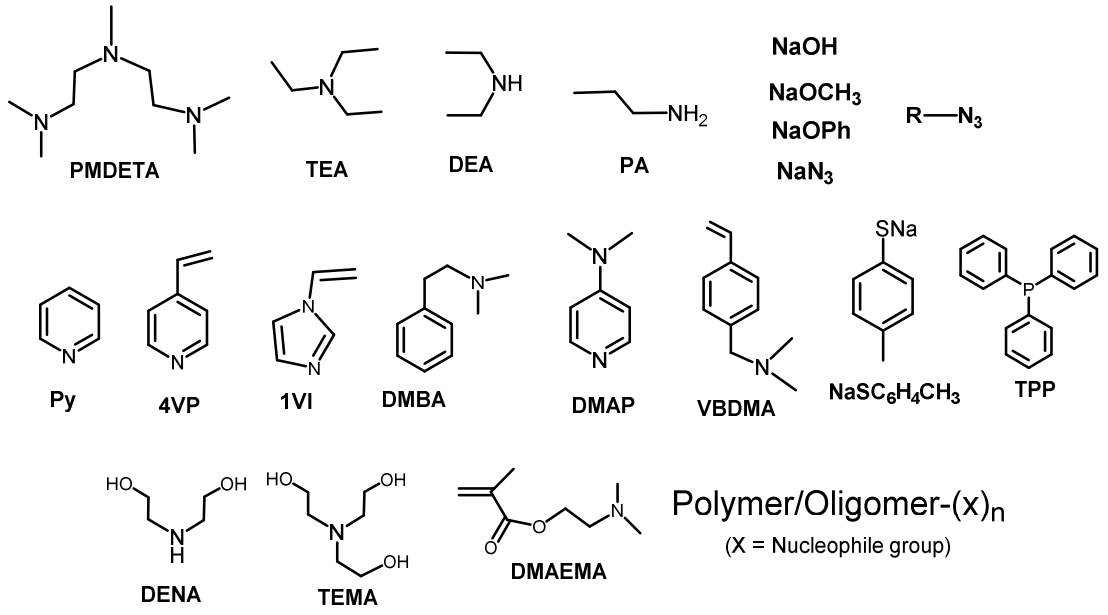
[0083] In an embodiment, the base initiators are nucleophiles. In another embodiment, the base initiators can be hydroxide or alkoxide. In another embodiment, the base initiators can be selected from aliphatic, aromatic or cyclic amines. In another embodiment, the base initiators can be primary aliphatic amines. In another embodiment, the base initiators can be secondary aliphatic amines. In another embodiment, the base initiators can be tertiary aliphatic amines. In another embodiment, the base initiators can be aromatic amines. In another embodiment, the base initiator can be tertiary amine, heteroaryl containing N or heterocyclyl containing N. In another embodiment, the base initiators can be monoamine, diamine or triamine. In another embodiment, the base initiator is a tertiary amine.

[0084] "Heteroaryl" refers to a monovalent aromatic heterocyclic group which fulfils the Hückel criteria for aromaticity (ie. contains $4n + 2$ π electrons) and preferably has from 2 to 10 carbon atoms and 1 to 4 heteroatoms selected from oxygen, nitrogen, selenium, and sulfur within the ring (and includes oxides of sulfur, selenium and nitrogen). Such heteroaryl groups can have a single ring (eg. pyridyl, pyrrolyl or N-oxides thereof or furyl) or multiple condensed rings (eg. indolizinyl, benzoimidazolyl, coumarinyl, quinolinyl, isoquinolinyl or benzothienyl). It will be understood that where, for instance, R_2 or R' is an optionally substituted heteroaryl which has one or more ring heteroatoms, the heteroaryl group can be connected to the core molecule of the compounds of the present invention, through a C-C or C-heteroatom bond, in particular a C-N bond.

[0085] "Heterocyclyl" refers to a monovalent saturated or unsaturated group having a single ring or multiple condensed rings, preferably from 1 to 8 carbon atoms and from 1 to 4 hetero atoms selected from nitrogen, sulfur, oxygen, selenium or phosphorous within the ring. The most preferred heteroatom is nitrogen. It will be understood that where, for instance, R_2 or R' is an optionally substituted heterocyclyl which has one or more ring heteroatoms, the heterocyclyl group can be connected to the core molecule of the compounds of the present invention, through a C-C or C-heteroatom bond, in particular a C-N bond.

[0086] In another embodiment, the base initiators can have a pK_b of more than about 0.2. In another embodiment, the pK_b is more than about 0.3. In another embodiment, the pK_b is more than about 0.5. In another embodiment, the pK_b is more than about 1. In another embodiment, the pK_b is more than about 2. In another embodiment, the pK_b is more than about 4. In another embodiment, the pK_b is more than about 6. In another embodiment, the pK_b is more than about 8. In another embodiment, the pK_b is more than about 10.

[0087] In another embodiment, the base initiators can be selected from the following:



[0088] In another embodiment, the base initiator is selected from PMDETA, TEA, DMAP, NaOH, DMBA, TEMA or DMAEMA. In some embodiments, the base initiator is selected from PMDETA, TEA, VBDMA or NaOH.

[0089] In an embodiment, the process is carried out at ambient temperature and under atmospheric conditions. An advantage of the present invention is that the polymerisation can be performed at ambient temperature. Current polymerisation reactions require high temperatures. Such high temperature can be a safety issue. In this regard, being able to perform polymerisation at ambient temperature allows for more versatile use and applications. As external control of temperature is not required, the polymerisation is also cheaper to perform and can be done in any environment. In another embodiment, the process is carried out at ambient temperature. "Ambient temperature" refers to the immediate temperature surrounding an area or environment. Accordingly, "ambient temperature" may also be referred to as room temperature. In an embodiment, the ambient temperature is about 1 ºC to about 40 ºC. In another embodiment, the ambient temperature is about 10 ºC to about 35 ºC. In another embodiment, the ambient temperature is about 15 ºC to about 30 ºC. In another embodiment, the ambient temperature is about 20 ºC to about 30 ºC.

[0090] In a further embodiment the method may be performed below 1°C using, for instance, polar medium such as methanol.

[0091] Accordingly, in an embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature.

[0092] In a further aspect, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature;

[0093] wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

[0094] Another advantage of the present invention is that the polymerisation can be performed under atmospheric conditions. Current polymerisation reactions require high pressures for good control over the reaction. This limits the reaction size/volume. By being able to perform the reaction under atmospheric conditions and/or pressure, the limitation of reaction size/volume is eliminated. Further, such polymerisation would also be less costly and safer to perform. In another embodiment, the process is carried out under atmospheric conditions. As used herein, "atmospheric conditions" refers to the state of the immediate environment in terms of pressure. In this regard, the polymerisation is not subjected to additional external pressure

[0095] Accordingly, in an embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions.

[0096] In a further aspect, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

[0097] A further advantage of the present invention is that the polymerisation can be performed in an aqueous medium. Current polymerisation reactions require the use of organic solvents. These organic solvents can also be hazardous, toxic and/or flammable. Such use cannot be considered to be clean and/or green. By using an aqueous medium, the use of organic solvents is eliminated or reduced. Less hazardous waste is also created which is beneficial to the environment and health of personnel handling the waste.

[0098] The term 'aqueous medium' used herein refers to a water based solvent or solvent system, and which comprises of mainly water. Such solvents can be either polar or non-polar, and/or either protic or aprotic. Solvent systems refer to combinations of solvents which resulting in a final single phase. Both 'solvents' and 'solvent systems' can include, and is not limited to, pentane, cyclopentane, hexane, cyclohexane, benzene, toluene, dioxane, chloroform, diethylether, dichloromethane, tetrahydrofuran, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, nitromethane, propylene carbonate, formic acid, butanol, isopropanol, propanol, ethanol, methanol, acetic acid, ethylene glycol, diethylene glycol, fluoro-solvents or water. Water based solvent or solvent systems can also include dissolved ions, salts and molecules such as amino acids, proteins, sugars and phospholipids. Such salts may be, but not limited to, sodium chloride, potassium chloride, ammonium acetate, magnesium acetate, magnesium chloride, magnesium sulfate, potassium acetate, potassium chloride, sodium acetate, sodium citrate, zinc chloride, HEPES sodium, calcium chloride, ferric nitrate, sodium bicarbonate, potassium phosphate and sodium phosphate. As such, biological fluids, physiological solutions and culture medium also falls within this definition.

[0099] Accordingly, in an embodiment, the aqueous medium is water. In another embodiment, the aqueous medium is brine. In another embodiment, the aqueous medium is a mixture of water and brine. In another embodiment, the aqueous medium is predominately water and/or brine.

[0100] Accordingly, in an embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

[0101] In a further aspect, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

[0102] A further advantage of the present invention is that the polymerisation can be performed without the use of a catalyst. In this regard, the polymerisation is free of a polymerisation catalyst, such as a transition metal. As mentioned above, removal of the catalyst in polymerisation reactions requires multiple purification steps with organic solvents. This creates an issue of waste and environmental concerns. There is also a difficulty of totally removing the catalyst from the polymer. This creates an issue of toxicity, especially in healthcare applications. In the present invention, such issues are reduced and/or eliminated.

[0103] Accordingly, in an embodiment, the present invention provides a nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium;

wherein the polymerisation process is free of a polymerisation catalyst.

[0104] In a further aspect, the present invention provides a surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate; and wherein the polymerisation process is free of a polymerisation catalyst.

[0105] In an embodiment, the electrophile is an inorganic acid selected from H_2SO_4, HCl, HBr, HF, HI, HNO_3, H_3PO_4, H_3BO_3 or $HClO_4$. In another embodiment, the electrophile is an inorganic acid selected from H_2SO_4, HCl, HBr, HI, HNO_3, H_3PO_4, or $HClO_4$. In another embodiment, the electrophile is an inorganic acid selected from H_2SO_4, HCl, HBr or HNO_3. In another embodiment, the electrophile is an inorganic acid selected from H_2SO_4, HCl or HNO_3. In another embodiment, the electrophile is HCl.

[0106] Advantageously, because the polymerisation can be performed in ambient temperature, under atmospheric conditions and/or in aqueous medium, the polymerisation can be performed in situ, at the site of reaction. For example, the polymerisation can be performed on a surface using a grafting approach. In this approach, the polymer can be allowed to grow on a surface through the addition of monomers.

[0107] In an embodiment, the substrate is located with a nucleophilic base initiator. In another embodiment, the substrate is modified with a nucleophilic base initiator. In another embodiment, the substrate is modified to attach the nucleophilic base initiator covalently. In another embodiment, the substrate is modified to attach the nucleophilic base initiator non-covalently.

[0108] In an embodiment, the present invention provides a polymer comprising

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone may be derived from optionally substituted zwitterionic vinyl pyridine monomer.

[0109] In another embodiment, the present invention provides a surface provided with a polymer, wherein the polymer comprises

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone may be derived from optionally substituted zwitterionic vinyl pyridine monomer.

[0110] In an embodiment, the polymer as described herein has a polydispersity index of less than 1.8. In another embodiment, the polymer has a polydispersity index of less than 1.7. In another embodiment, the polymer has a polydispersity index of less than 1.6. In another embodiment, the polymer has a polydispersity index of less than 1.5. In another embodiment, the polymer has a polydispersity index of less than 1.4. In another embodiment, the polymer has a polydispersity index of less than 1.3. In another embodiment, the polymer has a polydispersity index of less than 1.2. In another embodiment, the polymer has a polydispersity index of less than 1.1. In another embodiment, the polymer has a polydispersity index of less than 1.05. In another embodiment, the polymer has a polydispersity index of about 1.1.

[0111] In an embodiment, the polymer has a molecular weight of about 1000 to about 6000. In another embodiment, the polymer has a molecular weight of about 1500 to about 5500. In another embodiment, the polymer has a molecular weight of about 2000 to about 5000. In another embodiment, the polymer has a molecular weight of about 2500 to about 4500. In another embodiment, the polymer has a molecular weight of about 3000 to about 4000. In another embodiment, the polymer has a molecular weight of about 1500. In another embodiment, the polymer has a molecular weight of about 2000. In another embodiment, the polymer has a molecular weight of about 2500. In another embodiment, the polymer has a molecular weight of about 3000. In another embodiment, the polymer has a molecular weight of about 3500. In another embodiment, the polymer has a molecular weight of about 4000. In another embodiment, the polymer has a molecular weight of about 4500. In another embodiment, the polymer has a molecular weight of about 5000. In another embodiment,

the polymer has a molecular weight of about 6000.

[0112] In an embodiment, the polymer has a molecular weight of up to about 20,000. Molecular weight can be determined, for instance, by end group analysis using ^{1}H NMR.

[0113] In an embodiment, the present invention provides a process wherein the optionally substituted zwitterionic vinyl pyridine monomer comprises of a plurality of optionally substituted zwitterionic vinyl pyridine monomers. The monomers may be provided simultaneously or sequentially and in any order, and the monomer may be provided separately or as a fixed combination. In this regard, a subsequent (second and/or third) monomer may be provided to the polymerisation reaction after the previous (first) monomer has been depleted. The monitoring of the polymerisation reaction is known to the skilled person and can be performed using, for example, NMR.

[0114] In an embodiment, the subsequent monomer is provided when the previous monomer conversion is more than about 50%. In another embodiment, the previous monomer conversion is more than about 60%. In another embodiment, the previous monomer conversion is more than about 70%. In another embodiment, the previous monomer conversion is more than about 80%. In another embodiment, the previous monomer conversion is more than about 85%. In another embodiment, the previous monomer conversion is more than about 90%. In another embodiment, the previous monomer conversion is more than about 95%. In another embodiment, the previous monomer conversion is more than about 96%. In another embodiment, the previous monomer conversion is more than about 97%. In another embodiment, the previous monomer conversion is more than about 98%. In another embodiment, the previous monomer conversion is more than about 99%. In another embodiment, the previous monomer conversion is more than about 99.5%.

[0115] In an embodiment, the subsequent monomer is provided at about 0.5 h after the previous monomer. In another embodiment, the subsequent monomer is provided at about 0.75 h. In another embodiment, the subsequent monomer is provided at about 1 h. In another embodiment, the subsequent monomer is provided at about 1.5 h. In another embodiment, the subsequent monomer is provided at about 2 h. In another embodiment, the subsequent monomer is provided at about 3 h. In another embodiment, the subsequent monomer is provided at about 4 h. In another embodiment, the subsequent monomer is provided at about 6 h. In another embodiment, the subsequent monomer is provided at about 10 h. In another

embodiment, the subsequent monomer is provided at about 24 h. In another embodiment, the subsequent monomer is provided at about 36 h. In another embodiment, the subsequent monomer is provided at about 48 h.

[0116] Those skilled in the art will appreciate that the invention described herein in susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within the spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

[0117] Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

[0118] The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

[0119] In order that the invention may be readily understood and put into practical effect, particular preferred embodiments will now be described by way of the following non-limiting examples.

EXAMPLES

Materials and Characterisations

[0120] All chemicals, except VBDMS (Acros), were purchased from Aldrich. and were used as such. 1H and 13C NMR spectra were recorded on a 400 MHz Bruker UltraShield AVANCE 400SB spectrometer. Residual solvent peaks were used as internal standard. NMR spctra were processed (phase and baseline correction) by Bruker Topspin sofware. The aqueous GPC system was equipped with a Delta 600 HPLC pump, a 600 controller, a 717 plus autosampler, a 2487 dual absorbance detector and a 2414 refractive-index detector, all from Waters. The following GPC columns were arranged in series: Ultrahydragel guard, and Ultrahydragel 120 (7.8 mm ID × 300 mm) and an Ultrahydragel Linear (7.8 mm ID × 300 mm). The eluent (0.1 M NaNO3 in deionized water) flow rate was 0.7 mL/min and the columns were maintained at 40 ºC. The results were obtained using PEO/PEG calibrations. UV-visible spectra were recorded on SHIMADZU UV-2700 spectrophotometer.

Synthesis of 4-vinylpyridine propanesulfonate (4VPPS)

[0121] 4-Vinylpyridine (4.695 g, 44.6 mmol) was added by syringe dropwise to a solution of 1,3-propane sultone (PS, 6.0 g, 1.1×44.6 mmol) and 1,3-dinitrobenzene (DNB, 25 mg) in dry THF (25 ml) placed on an ice bath. The stirring was continued for an hour. Then the light pink precipitate was separated by centrifuging the solution. The decanted cloudy solution was then transferred to a dry round bottom flask and heated at 65 ºC on an oil bath for 24 hrs. The precipitated solid was thoroughly washed with dry THF several times (6 × 20 ml) and finally the product was collected by centrifugation. A white fine powder product was obtained after drying in high vacuum oven at room temperature. Yield 7.5 g (74 %). Insoluble in THF, $CHCl_3$, ACN and DMF, partially soluble in MeOH and water and fully soluble in 0.5 M aqueous solution of NaCl, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol. ^{1}H NMR (400 MHz, 0.5 M NaCl/D_2O): δH (ppm)= 2.37-2.41 (2H, m, aliphatic CC*H*$_2$C), 2.94 (2H, t, aliphatic C*H*$_2$S), 4.65 (2H, t, aliphatic N+C*H*$_2$), 5.92 (1H, d, vinyl C*H*$_2$), 6.41 (1H, d, vinyl C*H*$_2$), 6.92 (1H, m, vinyl C*H*), 7.99 (2H, d, aromatic 2×C*H*), 8.68 (2H, d, aromatic 2×C*H*). ^{13}C NMR (400 MHz, 0.5 M NaCl in D_2O) δC (ppm)= 26.07, 47.10, 59.04, 124.80, 127.33, 132.07, 144.15, 153.99. Calcd. $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16; S, 14.11; Found C, 52.45; H, 6.00; N, 6.05; S, 13.79 %. HRMS (*m/z*) (M+H)+: calcd. for $C_{10}H_{13}NO_3S$ 228.0689, found 228.0695.

Synthesis of 2-vinylpyridine propanesulfonate (2VPPS)

[0122] This was also synthesized by the modified literature method.[1] 2-Vinylpyridine (4.695 g, 44.6 mmol) was added by syringe dropwise to a solution of 1,3-propane sultone (PS, 6.0 g, 1.1×44.6 mmol) and 1,3-dinitrobenzene (DNB, 23 mg) in dry THF (25 ml) placed on an ice bath. Then the clear yellowish solution was brought to room temperature then heated at 75 ºC on an oil bath for 70 hrs. The precipitated product was thoroughly washed with dry THF several times (6 × 20 ml) and finally the solid product was collected by centrifugation. A white fine powder product was obtained after drying in high vacuum oven at room temperature. Yield 5.5 g (55 %). Insoluble in THF, $CHCl_3$, ACN and DMF but soluble in MeOH and water. ^{1}H NMR (400 MHz, D_2O): δH (ppm)= 2.23-2.27 (2H, m, aliphatic CC*H*$_2$C), 2.90 (2H, t, aliphatic C*H*$_2$S), 4.66 (2H, t, aliphatic N+C*H*$_2$), 6.02 (1H, d, vinyl C*H*$_2$), 6.25 (1H, d, vinyl C*H*$_2$), 7.11 (1H, m, vinyl C*H*), 7.79 (1H, t, aromatic C*H*), 8.08 (1H, d, aromatic C*H*), 8.34 (1H, t, aromatic C*H*), 8.63 (1H, d, aromatic C*H*). ^{13}C NMR (400 MHz, D_2O) δC (ppm) = 27.47, 49.60, 59.07, 129.05, 129.14, 129.39, 132.71, 147.27, 148.08, 155.30. Calcd. $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16; S, 14.11; Found C, 52.62; H, 5.75; N, 6.04; S, 14.08.

Synthesis of 4-vinylpyridine butanesulfonate (4VPBS)

[0123] 4-Vinylpyridine (3.405 g, 3.49 ml, 32.39 mmol) was added by syringe to a solution of 1,4-butane sultone (BS, 4.85 g, 1.1× 32.39 mmol) and 1,3-dinitrobenzene (DNB, 22 mg) in dry THF (25 ml) placed on a ice bath. The clear yellowish solution was brought to room temperature and then heated at 75 ºC on an oil bath for 48 hrs. The precipitated product was thoroughly washed with dry THF several times (6 × 20 ml) and finally collected by centrifugation. A pale yellow fine powder product was obtained after drying in high vacuum oven at room temperature. Yield 3.25 g (41.6 %). Insoluble in THF, $CHCl_3$, EtOH and DMF, produce cloudy solution in MeOH and soluble in water, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol. ^{1}H NMR (400 MHz, D_2O): δH (ppm)= 1.67 (2H, m, aliphatic CC*H*$_2$C), 2.03 (2H, m, aliphatic CC*H*$_2$C C*H*$_2$S), 2.2.85 (2H, t, aliphatic C*H*$_2$S), 4.46 (2H, t, aliphatic N+C*H*$_2$), 5.85 (1H, d, vinyl C*H*$_2$), 6.32 (1H, d, vinyl C*H*$_2$), 6.79-6.86 (1H, m, vinyl C*H*), 7.90 (2H, d, aromatic C*H*), 8.60 (2H, d, aromatic C*H*). ^{13}C NMR (400 MHz, in D_2O) δC (ppm) = 22.18, 30.53, 51.28, 61.64, 124.21, 125.97, 128.34, 133.36, 145.30, 155.09. Calcd. $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80; S, 13.29; O, 19.89 %; Found C, 54.96; H, 6.27; N, 5.80; S, 13.23%.

Synthesis of 4-vinylpyridine propanesulfate (4VPPSa)

[0124] 4-Vinylpyridine (1.383 g, 1.42 ml, 13.16 mmol) was added by syringe dropwise to a solution of 1,3-propanediol cyclic sulfate (PSa, 2.0 g, 1.1 × 13.16 mmol) and 2,4-dinitrobenzene (DNB, 10 mg) in dry THF (15 ml) placed on a ice bath. The stirring was continued for an hour. The light pink precipitate was separated by centrifuging the solution. The decanted cloudy solution was then transferred to a dry round bottom flask and heated at 65 ºC on an oil bath for 26 hrs. The precipitated product was thoroughly washed with dry THF several times (6 × 20 ml) and finally solid product was collected by centrifugation. A white fine powder product was obtained after drying in high vacuum oven at room temperature. Yield 3.25 g (100 %). Insoluble in THF, $CHCl_3$, EtOH MeOH and DMF but fully soluble in water, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol. ^{1}H NMR (400 MHz, D_2O): δH (ppm)= 2.29 (2H, m, aliphatic CC*H*$_2$C), 3.99 (2H, t, aliphatic C*H*$_2$O), 4.57 (2H, t, aliphatic N+C*H*$_2$), 5.84 (1H, d, vinyl C*H*$_2$), 6.33 (1H, d, vinyl C*H*$_2$), 6.80-6.97 (1H, m, vinyl C*H*), 7.91 (2H, d, aromatic 2×C*H*), 8.61 (2H, d, aromatic 2×C*H*). ^{13}C NMR (400 MHz, D_2O) δC (ppm)= 30.88, 59.28, 66.55, 124.20, 125.91, 128.43, 133.35, 145.60, 155.23. Calcd. $C_{10}H_{13}NO_4S$: C, 49.37; H, 5.39; N, 5.76; S, 13.18; O, 26.31 %; Found C, 49.71; H, 5.40; N, 5.70; S, 13.11 %.

Typical polymerization procedures

Example 1: (Comparative Example) Free radical polymerization (FRP) of 4-vinylpyridine propanesulfonate (4VPPS) (P1)

[0125] 4-Vinylpyridine propanesulfonate, 4VPPS (0.3 g, 1.32 mmol), 4,4′-azobis(4-cyanovaleric acid), ABCV (7.3 mg, 0.026 mmol) and DMF (50 µl, as internal standard) were dissolved in 0.5M NaCl/water (1.5 ml) and purged with N_2 for 15 min. The mixture was heated on an oil bath at 70 ºC under N_2 for required time. Time to time aliquot was collected for NMR analysis. Finally the polymer was precipitated out from water, washed with acetone and then dried in vacuum oven at 50 ºC.

Example 2: DMAP-initiated polymerization of 4-vinylpyridine propanesulfonate (2VPPS) (P5)

[0126] 4-Vinylpyridine propanesulfonate, 4VPPS (0.3 g, 1.32 mmol) and DMF (50 µl, as internal standard) were dissolved in 0.5M NaCl/water (1.0 ml) in a glass vial. DMAP stock solution (0.1N) in water (264 µl, ~3.23 mg, 0.026 mmol) was then added to the monomer solution and the polymerization was carried out atroom temperature (23 ºC) and under air for required time. Time to time aliquot (100 µl) was collected, quenched immediately with

1N HCl (100 µl) and was used for NMR (to determine monomer conversion) analysis. Finally the reaction was quenched with HCl and the polymer was precipitated out from water, washed with acetone and then dried in vacuum oven at 50 ºC.

[0127] For end group analysis by NMR, the HCl quenched reaction mixture dialized using MWCO 2K dialysis tubing aginst 0.5M NaCl/water followed by deionized water. The sticky solid polymer obtained was then washed with acetone and dried in vacuum oven at 50 ºC to yield white powder.

Example 3: VBDMA-initiated polymerization of 2-vinylpyridine propanesulfonate (2VPPS) (P19)

[0128] 2-Vinylpyridine propanesulfonate, 2VPPS (0.3 g, 1.32 mmol) and DMF (50 µl, as internal standard) were dissolved in water (1.0 ml) in a glass vial. VBDMA stock solution in MeOH (100 µl, 10.64 mg, 0.026 mmol) was then added to the monomer solution and the polymerization was carried out at room temperature (23 ºC) and under air for required time. Time to time aliquot (100 µl) was collected, quenched immediately with 1N HCl (100 µl) and was used for NMR (to determine monomer conversion) analysis. Finally the reaction was quenched with HCl and the polymer was precipitated out from methanol and then dried in vacuum oven at 50 ºC to yield white powder. The product was used for GPC (aqueous) analysis and end group analysis by NMR.

Example 4: DMAP-initiated polymerization of 2-vinylpyridine propanesulfonate (2VPPS) followed by chain extension reaction to yield diblock copolymer

[0129] 2-Vinylpyridine propanesulfonate, 2VPPS (0.2 g, 0.88 mmol) and DMF (50 µl, as internal standard) were dissolved in water (1.0 ml) in a glass vial. DMAP stock solution (0.2N) in water (220 µl, 5.37 mg, 0.044 mmol) was then added to the monomer solution. Target DP = 20. The polymerization was carried out at room temperature (23 ºC) and under air for two hours. 2VPPS conversion >99%. Then 4VPBS (0.11 g, 0.44 mmol) solution in water (0.5 ml) was added to it and the polymerization was continued for two more hours. 4VPBS conversion >99%. Finally the reaction was quenched with HCl, the polymer was precipitated out from methanol and then dried in vacuum oven at 50 ºC to yield light pink powder. The product was characterized by aqueous GPC and ^{1}H NMR spectroscopy.

Example 5: Typical TEA-initiated polymerization of 4-vinylpyridine propanesulfonate (4VPPS) for kinetics investigation

[0130] 4-Vinylpyridine propanesulfonate, 4VPPS (0.3 g, 1.32 mmol) and DMF (50 µl, as internal standard) were dissolved in water (1.5 ml) in a glass vial. Triethylamine stock solution (0.1N) in water (264 µl, ~2.67 mg, 0.0264 mmol) was then added to the monomer solution and the polymerization was carried out at room temperature (23 ºC) and under air for required time. Monomer : TEA = 50:1. Time to time aliquot (100 µl) was collected, quenched immediately with 1N HCl (100 µl) and was used for NMR (to determine monomer conversion) analysis.

Example 6: Typical NaOH-initiated polymerization of 2-vinylpyridine propanesulfonate (2VPPS) for kinetics investigation

[0131] 2-Vinylpyridine propanesulfonate, 2VPPS (0.3 g, 1.32 mmol) and DMF (50 µl, as internal standard) were dissolved in water (1.5 ml) in a glass vial. NaOH stock solution (0.1N) in water (264 µl, ~1.06 mg, 0.0264 mmol) was then added to the monomer solution and the polymerization was carried out at room temperature (23 ºC) and under air for required time. Time to time aliquot (100 µl) was collected, quenched immediately with 1N HCl (100 µl) and was used for NMR (to determine monomer conversion) and GPC analysis.

[0132] Table 1. Polymerisation of zwitterionic monomers and 4VP (as comparative study)

Polymer code	Monomer	Initiator/ base[a]	Solvent, temperature (ºC) and atmosphere	Monomer conversion (%) with time[c]			
				5 min	1 h	6h	23h
P1	4VPPS	ABCVA (FRP)	0.5M NaCl/water, 70 ºC, N_2	8.0	98.8	98.9	>99
P2	4VPPS	PMDETA	0.5M NaCl/water, 23 ºC, Air	3.0	49.2	77.4	96.6
P3	4VPPS	None	0.5M NaCl/water, 23 ºC, Air	Nil	Nil	Nil	Nil[d]
P4	4VPPS	TEA	0.5M NaCl/water, 23 ºC, Air	Neg	66.1	93.3	94.8
P5	4VPPS	DMAP	0.5M NaCl/water, 23 ºC, Air	NA	91.3	>99[e]	--
P6	4VPPS	VBDMA[b]	0.5M NaCl/water, 23 ºC, Air	NA	91.7	96.6	--
P7	4VPPS	DEA	0.5M NaCl/water, 23 ºC, Air	NA	15.3	23.8	38.0
P8	4VPPS	PA	0.5M NaCl/water, 23 ºC, Air	NA	41.7	51.9	52.0
P9	4VP	DMAP	MeOH, 23 ºC, Air	NA	Nil	Nil	Nil
P10	4VPPS	NaOH	0.5M NaCl/water, 23 ºC, Air	8.2	91.8	> 99	--
P11	4VPBS	TEA	Water, 23 ºC, Air	3.0	39.7	85.3	96.0
P12	4VPPSa	TEA	Water, 23 ºC, Air	7.7	29.5	83.4	97.8

DMF was used as internal standard and bases were used as aqueous solution (0.1N); NA = not available, Neg = negligible, Nil = no polymerization. [a] Monomer to initiator molar ratio = 50:1; ABCVA = 4,4'-azobis(4-cyanovaleric acid), FRP = free radical polymerization; PMDETA = *N,N,N',N",N"*-pentamethyldiethylenetriamine, TEA = triethylamine, DMAP = 4-(dimethylamino)pyridine, VBDMA = *N*-(4-vinylbenzyl)-*N,N*-dimethylamine, DEA = *N,N*-diethylamine and PA = propylamine; [b] 4VPPS: VBDMA = 20:1; [c] determined by ^{1}HNMR spectroscopy; [d] no polymerization observed in 7days. [e] $M_{n,NMR}$ of resultant polymer = 18200 Da.

Table 2. Polymerisation of 2VP based zwitterionic monomers.

Polymer code	Monomer	Initiator/ Nuclophile[a]	Solvent, Temperature (°C), atmosphere	Monomer conversion with time[c]			$M_{n,GPC}$, Da and (PDI) of final precipitated polymer[d]
				1 h	6h	23h	
P13	2VPPS	ABCVA (FRP)	Water, 70 °C, N_2 (solution polymerization)	30.0	65.5	83.1	11290 (1.4)
P14	2VPPS	PMDETA	Water, 23 °C, Air (solution polymerization)	27.9	94.1	98.3	2400 (1.19)
P15	2VPPS	TEA	Water, 23 °C, Air (solution polymerization)	9.3	56.1	84.3	2240 (1.28)
P16	2VPPS	NaOH	Water, 23 °C, Air (solution polymerization)	94.6	> 99[e]	--	3860 (1.15)
P17	2VPPS	DMAP	Water, 23 °C, Air (solution polymerization)	96.4	97.8[e]	--	3050 (1.2) 13200[f]
P18	2VPPS	DMAP[b]	Water, 23 °C, Air (solution polymerization)	96.8	>99[e]	--	2620 (1.16) 6800[f]
P19	2VPPS	VBDMA[b]	Water, 23 °C, Air (solution polymerization)	>99[e]	--	--	2244 (1.2) 6800[f]
P20	2VPPS	TEA	MeOH, 23 °C, Air (precipitation polymerization)	74.6[e]	--	--	5960 (1.58)
P21	2VPPS	VI	Water, 23 °C, Air (solution polymerization)	7.0	20.5	91.2	3000 (1.27)
P22	2VPPS	NaOMe[b,g]	MeOH, 23 °C, Air (precipitation polymerization)	>99[i]	--	--	5530 (1.49)
P23	2VPPS	Ph_3P[b,h]	MeOH, 23 °C, Air (precipitation polymerization)	>99[i]	--	--	3900 (1.9)
P24	2VPPS	NaOPh[b]	Water, 23 °C, Air (solution polymerization)	19.7	75.7	98	3170 (1.25)
P25	2VPPS	$NaSC_6H_4CH_3$[b]	Water, 23 °C, Air (solution polymerization)	>99	--	--	1500 (1.22) 4610[f]
P26	2VPPS	Ph_3P[b,h]	Water/MeOH (1:1), 23 °C, Air (precipitation polymerization)	>99[i]	--	--	2100 (1.63)
P27	2VPPS	NaN_3[b]	Water, 23 °C, Air (solution polymerization)	--	7.0	92.7	3100 (1.28)

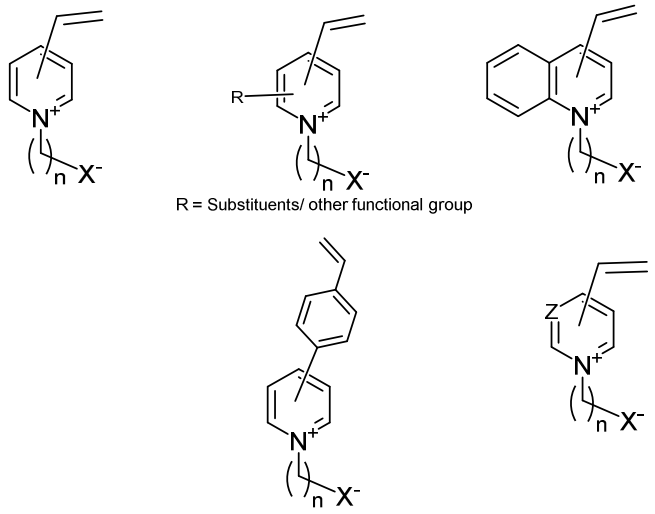
DMF was used as internal standard and bases are used as aqueous solution (0.1N); [a] Monomer : initiator/ base = 50:1 (by mole); ABCVA = 4,4'-azobis(4-cyanovaleric acid), FRP = free radical polymerization, PMDETA = N,N,N',N",N"-pentamethyldiethylenetriamine, TEA = triethylamine, DMAP = 4-(dimethylamino)pyridine and VBDMA = *N*-(4-vinylbenzyl)-*N,N*-dimethylamine; [b] monomer : nucleophile = 20:1 (by mole); [c] determined by ^{1}HNMR spectroscopy; [d] determined in aqueous GPC; [e] reaction stopped at this time; [f] $M_{n,NMR}$ values in Da; [g] added as freshly prepared MeOH solution; [h] added as THF solution; [i] immediate precipitation, conversion after 5 min.

THE CLAIMS DEFINING THE INVENTION

1. A nucleophilic addition polymerisation process comprising the step of:

initiating polymerisation of a optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator;

wherein the optionally substituted zwitterionic vinyl pyridine monomer is selected from:



wherein X^- can be sulfonate, sulphate, carboxylate, alkoxide, phosphate, phosphonate, phosphinate;

wherein Z is N; and

wherein n can be any integer from 1 to 6.

2. A surface initiated nucleophilic addition polymerisation process comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

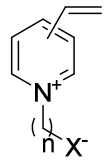
contacting a optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate.

3. A process according to claims 1 or 2, wherein the process is carried out at ambient temperature and under atmospheric conditions.

4. A process according to any one of claims 1 to 3, wherein the process is carried out in an aqueous or polar medium.

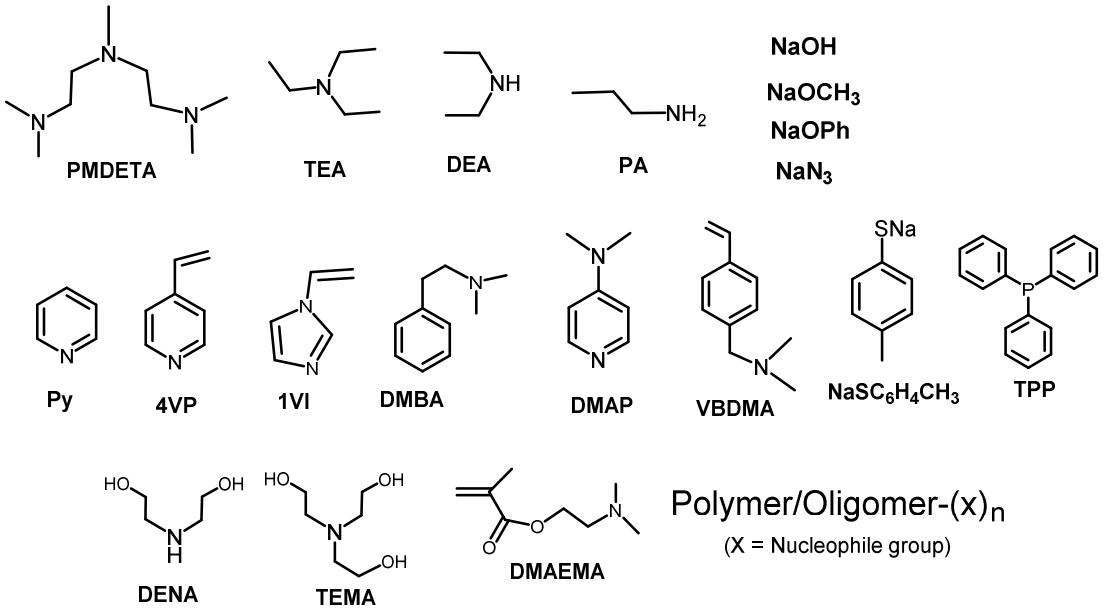
5. A process according to any one of claims 1 to 4, wherein the optionally substituted zwitterionic vinyl pyridine monomer is a compound of formula (I):



wherein X^- can be sulfonate, sulphate, carboxylate, alkoxide, phosphate, phosphonate, phosphinate; and
wherein n can be any integer from 1 to 6.

6. A process according to any one of claims 1 to 5, wherein the nucleophilic base initiator is selected from an inorganic alkali, amine, thiolate, phosphine, pyrrole, pyrrolidone or phenoxide.

7. A process according to any one of claims 1 to 5, wherein the nucleophilic base initiator is selected from the following:



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8. A process according to any one of claims 4 to 7, wherein the aqueous medium is selected from water, brine, or a mixture thereof.

9. A process according to any one of claims 1 to 8, wherein the process is terminated with an electrophile, wherein the electrophile is an inorganic acid.

10. A process according to any one of claims 1 to 9, wherein the process produces a polymer with a polydispersity index of less than 1.6.

11. A process according to any one of claims 1 to 10, wherein the optionally substituted zwitterionic vinyl pyridine monomer comprises of a plurality of optionally substituted zwitterionic vinyl pyridine monomers.

12. A nucleophilic addition polymerisation process according to claim 1 comprising the steps of:

initiating polymerisation of a first optionally substituted zwitterionic vinyl pyridine monomer with a nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer; and

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

13. A surface initiated nucleophilic addition polymerisation process according to claim 2 comprising the steps of:

providing a substrate having a surface on which is located a nucleophilic base initiator; and

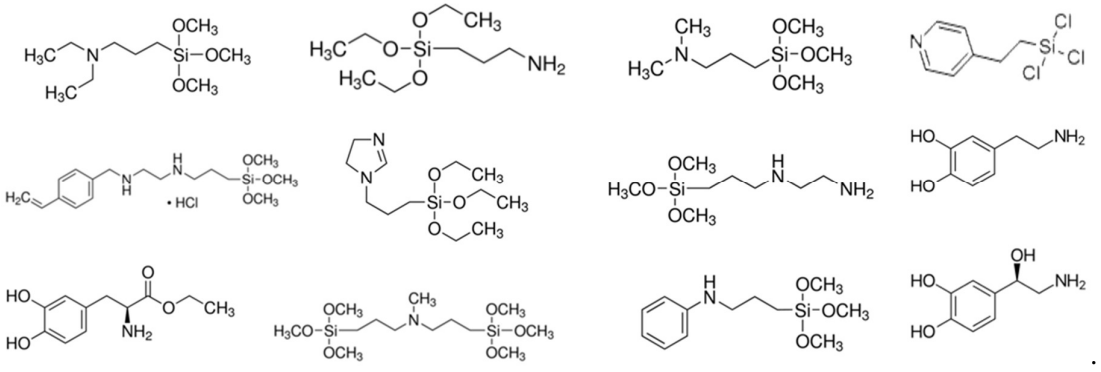
contacting a first optionally substituted zwitterionic vinyl pyridine monomer with the nucleophilic base initiator at ambient temperature and under atmospheric conditions in an aqueous or polar medium to form a first said polymer;

wherein the nucleophilic base initiator initiates addition polymerisation of the optionally substituted zwitterionic vinyl pyridine monomer to form a polymer on the surface of the substrate; and

polymerising a second zwitterionic monomer with the first said polymer at ambient temperature and under atmospheric conditions in an aqueous or polar medium.

14. A process according to claim 2, wherein the substrate is modified with a nucleophilic base initiator.

15. A process according to claim 2, wherein the substrate is modified with a nucleophilic base initiator selected from polydopamine, polynorepinephrine or



16. A process according to claims 14 or 15, wherein the substrate is modified with a nucleophilic base initiator by applying, dip coating, spin coating, spraying, brushing or gas phase deposition.

17. A polymer produced by a process according to any one of claims 1 to 16.

18. A polymer comprising

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone is derived from optionally substituted zwitterionic vinyl pyridine monomer.

19. A surface provided with a polymer, wherein the polymer comprises

i. a carbon-carbon backbone; and

ii. a residue of a nucleophilic base initiator covalently coupled to the carbon-carbon backbone;

wherein the carbon-carbon backbone is derived from optionally substituted zwitterionic vinyl pyridine monomer.

20. A polymer or surface according to claims 18 or 19, wherein the polymer is characterised by a polydispersity index of less than 1.6.

21. Use of the polymer or modified surface according to any one of claims 17 to 20 for anti-biofouling, anti-bacterial, anti-dirt pick up, low friction, chromatography, or adhesive applications.