From WO 2019 196999 A1, which is incorporated by reference in its entirety, as if fully set forth herein, an alternative oxygen-tolerant method for forming surface polymers is disclosed. The catalyst/ligand complex described in WO 2019 196999 A1 is halogen free in so far as the catalyst/ligand complex formed is not complexed with a halogen anion. An advantage of this method is that the complex formed between the transition metal and the ligand is inactive (i.e., not available for initiating polymerization of the monomer) and stable (oxygen-insensitive), but the system can be activated "on demand", thus, initiating polymerization and propagation of the surface polymers.

To fully exploit the potential of the surface-polymer technology, there is a need for an efficient way of forming surface polymers, both on a small, R&D, scale, and on a large, high-volume manufacturing, scale.

Summary

In an aspect, there is provided a reaction composition for surface polymer formation comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator;

at least one solvent; and

at least one polymerization control agent;

wherein the at least one polymerization control agent is at least one pH control agent for controlling pH of the reaction composition during surface polymer formation, and wherein the at least one pH control agent maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand.

In another aspect, there is provided a method for forming surface polymers comprising:

bringing at least a portion of a polymerization initiator-modified substrate into contact with a reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent;

controlling the surface polymerization by means of pH of the reaction composition by adding at least one polymerization control agent, at least once during, or prior to, the

surface polymer formation, to adjust the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand,

wherein the at least one polymerization control agent is:

(i) at least one pH control agent, or

(ii) at least one pH control agent and at least one oxygen control agent

In another aspect, there is provided a method for forming surface polymers comprising:

providing a reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent;

wherein the reaction composition is held in a reaction composition container;

bringing at least a portion of a first polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container thereby forming surface polymers on said first substrate;

withdrawing said first substrate from the reaction composition in the reaction composition container;

subsequent to the withdrawing said first substrate, bringing at least a portion of a second polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container, thereby forming surface polymers on said second substrate; and

withdrawing said second substrate from the reaction composition in the reaction composition container;

wherein the pH and/or the molecular oxygen concentration in the reaction composition is controlled by adding at least one polymerization control agent, at least once during, or prior to, the surface polymer formation, wherein the polymerization control agent is at least one pH control agent that maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand, and/or at least one oxygen control agent that maintains the molecular oxygen concentration in the reaction composition below a partial pressure of 25 hPa as measured by an O_2-selective sensor and converted to dissolved molecular oxygen concentration using Henry's law.

In another aspect, there is provided a system for forming surface polymers on a substrate, the system comprising:

a reaction composition container containing a reaction composition, said reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent; and

at least one polymerization control agent, wherein the at least one polymerization control agent is at least one pH control agent that maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand, and/or at least one oxygen control agent that maintains the molecular oxygen concentration in the reaction composition below a partial pressure of 25 hPa as measured by an O_2-selective sensor and converted to dissolved molecular oxygen concentration using Henry's law; and

a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time;

wherein the controlled time is sufficient for surface polymers to be formed on the portion of the polymerization initiator-modified substrate.

In accordance with an example of the disclosure there is provided a reaction composition for surface polymer formation comprising: at least one monomer; at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex; at least one catalyst activator; at least one solvent; and at least one polymerization control agent. Furthermore, the at least one polymerization control agent may be at least one pH control agent for controlling the pH of the reaction composition during surface polymer formation. Furthermore, the at least one polymerization control agent may comprise at least one pH control agent for controlling pH in the reaction composition during surface polymer formation and at least one oxygen control agent for controlling the molecular oxygen concentration in the reaction composition during surface polymer formation. Furthermore, the at least one pH control agent may maintain the pH of the reaction composition above a pK_aH value of the formed between at least one catalyst and at least one ligand. Furthermore, the at least one pH control agent may maintain the pH of the reaction composition above the pK_aH_1 value of the formed between the at least one catalyst and the at least one ligand. Furthermore, the at least one pH control agent may maintain the pH of the reaction composition above the pK_aH_2 value of the complex formed between the at least one catalyst and the at least one ligand. Furthermore, the at least one pH control agent may maintain the pH of the reaction composition between the pK_aH_1 and pK_aH_2 of the complex formed between the at least one catalyst and the at least one ligand. The at least one pH control agent may maintain the pH of the reaction composition above

6, and in some examples from 8 to 12. The at least one pH control agent may be a buffer. The at least one pH control agent may be an acid or a base. The at least one polymerization control agent may be at least one oxygen control agent for controlling the molecular oxygen concentration in the reaction composition. The at least one oxygen control

agent may maintain the molecular oxygen concentration in the reaction composition, corresponding to a partial pressure below or at 25 hPa. The at least one oxygen control agent may comprise an oxygen scavenger. The reaction composition for surface polymer formation may comprise a pH control agent, or an oxygen control agent, or a pH control agent and an oxygen control agent.

In particular, the reaction composition may comprise a solvent, a monomer, a catalyst; a ligand, where the catalyst and ligand form a complex; and a polymerization control agent being a pH control agent; or a pH control agent and an oxygen control agent.

In accordance an example of the disclosure there is provided a method for forming surface polymers comprising: bringing at least a portion of a polymerization initiator-modified substrate into contact with a reaction composition comprising at least one monomer; at least one ligand; at least one catalyst, wherein the at least one ligand and at least one catalyst form a complex; at least one catalyst activator; and at least one solvent; controlling the surface polymerization by means of pH and/or molecular oxygen concentration of the reaction composition; and optionally adding at least one polymerization control agent to adjust the pH of and/or the molecular oxygen concentration of the reaction composition. Furthermore, the at least one polymerization control agent may be added at least once during or prior to the surface polymer formation. The at least one polymerization control agent may be (i) at least one control agent, (ii) at least one oxygen control agent, or (iii) at least one pH control agent and at least one oxygen control agent. The at least one polymerization control agent may function as pH control agent and oxygen control agent.

In accordance with an example of the disclosure, a method for forming surface polymers is provided, the method comprising: providing a reaction composition comprising at least one monomer; a least one ligand; at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex; at least one catalyst activator; and at least one solvent, wherein the reaction composition is held in a reaction composition container; bringing at least a portion of a first polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container thereby forming surface polymers on said first substrate; withdrawing said first substrate from the reaction composition in the reaction composition container; subsequent to the withdrawing said first substrate, bringing at least a portion of a second polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container thereby forming surface polymers on said second substrate; withdrawing said second substrate from the reaction composition in the reaction composition container; wherein the pH and/or the molecular oxygen concentration in the reaction composition may be controlled by means of optionally

at least one polymerization control agent. The reaction composition may be modified during the surface polymer formation by addition of further components of the reaction composition, and/or by removal of bulk polymer byproducts. The pH of the reaction composition and/or molecular oxygen concentration in the reaction composition may be controlled by measuring pH and/or molecular oxygen concentration during the surface polymer formation in combination with supplying at least one polymerization control agent. A plurality of substrates may be subjected to surface polymer formation in the reaction composition container in a consecutive manner. The pH of the reaction composition may be adjusted to control the kinetics of the surface polymer formation.

In accordance with an example of the disclosure a system for forming surface polymers on a substrate is provided. The system may comprise: a reaction composition container containing a reaction composition, wherein the reaction composition may comprise at least one monomer, at least one ligand, at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex, at least one catalyst activator, and at least one solvent; and a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time; and wherein the controlled time is sufficient to enable surface polymers to be formed on a portion of the polymerization initiator-modified substrate. In accordance with at least some examples, the substrate displacement device may comprise any one of: a conveyor system; a programmable mechanical arm; or a roll-to-roll mechanism. In some examples the system may further comprise: one or more sensors, each sensor configured to measure a different value of a characteristic of the reaction composition; one or more dispensers configured to dispense one or more polymerization control agents and/or one or more components of the reaction composition into the reaction composition; and a control unit operatively connected to the one or more sensors; wherein the control unit may be configured to output a control signal to the one or more dispensers for dispensing the polymerization control agent and/or one or more components of the reaction composition into the reaction composition. In accordance with some examples the control unit is configured to output the control signal periodically to the dispenser, causing the dispenser to periodically dispense the polymerization control agent and/or the component of the reaction composition into the reaction composition. In accordance with some examples the control unit may be configured to output the control signal in dependence on receipt of a sensor signal indicative of a change in a value of a characteristic of the reaction composition. In some examples the control unit may be configured to output the control signal in dependence on receipt of a sensor signal indicative of the measured value of the characteristic of the reaction composition not complying with a predetermined threshold value of the characteristic of the

reaction composition. The predetermined threshold value may be a pH value and/or molecular oxygen concentration. The output control signal may cause pH control agent and/or oxygen control agent to be dispensed into the reaction composition. In accordance with some examples, the component of the reaction composition may comprise any one or more of: at least one monomer, at least one ligand, at least one catalyst, at least one catalyst activator, and at least one solvent. In some examples the system may further comprise a polymerization initiator container containing a polymerization initiator agent, wherein the substrate displacement device is configured to bring the portion of the substrate for attachment of polymerization initiators into contact with the polymerization initiator agent to form polymerization initiators on the substrate surface, prior to bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition. The system may comprise a cleaning container, the cleaning container containing a cleaning agent, and wherein: the substrate displacement device may be configured to bring the portion of the polymerization initiator-modified substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition; or, the substrate displacement device may be configured to bring the portion of substrate into contact with the cleaning agent prior to or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator. Some examples may comprise an annealing container containing an annealing agent, wherein the substrate displacement device may be configured to bring the portion of the substrate into contact with the annealing agent prior to, or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator or prior to, or subsequent to, bringing the portion of the substrate into contact with the reaction composition.

In accordance with a further example of the disclosure, a system for forming surface polymers on a substrate is provided. The system may comprise: a reaction composition container; a cleaning container; a polymerization initiator container; and a substrate displacement device. The system may further comprise an annealing container and/or a drying container. In accordance with some examples, the cleaning container's function may comprise one or more of etching; thermal cleaning; and removal of surface contaminants, by-products, and residual process chemicals. The system may be for forming surface polymers with stable kinetics according to the methods disclosed herein.

At least some examples of the present disclosure provide a solution to the aforementioned prior art problems by providing reaction compositions and methods with a controlled formation of surface polymers, in particular polymer brushes. It has surprisingly been found that controlling certain reaction conditions during the surface polymer formation

Claims

1. A reaction composition for surface polymer formation comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator;

at least one solvent; and

at least one polymerization control agent;

wherein the at least one polymerization control agent is at least one pH control agent for controlling pH of the reaction composition during surface polymer formation, and wherein the at least one pH control agent maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand.

2. A reaction composition according to claim 1, wherein the at least one pH control agent is a buffer, or wherein the at least one pH control agent is an acid or a base.

3. A reaction composition according any one of claims 1-2, further comprising an oxygen control agent for controlling the molecular oxygen concentration in the reaction composition, wherein the at least one oxygen control agent is an oxygen scavenger that maintains the molecular oxygen concentration in the reaction composition below a partial pressure of 25 hPa as measured by an O_2-selective sensor and converted to dissolved molecular oxygen concentration using Henry's law.

4. A method for forming surface polymers comprising:

bringing at least a portion of a polymerization initiator-modified substrate into contact with a reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent;

controlling the surface polymerization by means of pH of the reaction composition by adding at least one polymerization control agent, at least once during, or prior to, the surface polymer formation, to adjust the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand,

wherein the at least one polymerization control agent is:

(i) at least one pH control agent, or

(ii) at least one pH control agent and at least one oxygen control agent.

5. A method for forming surface polymers comprising:

providing a reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent;

wherein the reaction composition is held in a reaction composition container;

bringing at least a portion of a first polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container thereby forming surface polymers on said first substrate;

withdrawing said first substrate from the reaction composition in the reaction composition container;

subsequent to the withdrawing said first substrate, bringing at least a portion of a second polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container, thereby forming surface polymers on said second substrate; and

withdrawing said second substrate from the reaction composition in the reaction composition container;

wherein the pH and/or the molecular oxygen concentration in the reaction composition is controlled by adding at least one polymerization control agent, at least once during, or prior to, the surface polymer formation, wherein the polymerization control agent is at least one pH control agent that maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand, and/or at least one oxygen control agent that maintains the molecular oxygen concentration in the reaction composition below a partial pressure of 25 hPa as measured by an O_2-selective sensor and converted to dissolved molecular oxygen concentration using Henry’s law.

6. A method according to claim 5, wherein the reaction composition is modified during the surface polymer formation by addition of further components of the reaction composition, and/or removal of bulk polymer byproducts, preferably wherein the removal of bulk polymer byproducts is via limiting the rate and extent of bulk polymer formation.

7. A method according to claim 5 or 6, wherein pH of the reaction composition and/or molecular oxygen concentration of the reaction composition is controlled by measuring pH and/or molecular oxygen concentration during the surface polymer formation in combination with supplying at least one polymerization control agent.

8. A method according to any one of claims 5-7, wherein one or more components of the reaction composition is dispensed in response to a measured characteristic of the reaction composition, or in response to an observed time variance of the characteristic, for instance dispensed independent of any specific sensor measurement and based on known rates of consumption of components of the reaction composition or on known variation over time of the pH or molecular oxygen concentration.

9. A method according to any one of claims 5-8, wherein a plurality of substrates is subjected to surface polymer formation in the reaction composition container in a consecutive manner.

10. A system for forming surface polymers on a substrate, the system comprising:

a reaction composition container containing a reaction composition, said reaction composition comprising:

at least one monomer;

at least one ligand and at least one catalyst, wherein the at least one ligand and the at least one catalyst form a complex;

at least one catalyst activator; and

at least one solvent; and

at least one polymerization control agent, wherein the at least one polymerization control agent is at least one pH control agent that maintains the pH of the reaction composition above a pK_aH of the complex formed between the at least one catalyst and the at least one ligand, and/or at least one oxygen control agent that maintains the molecular oxygen concentration in the reaction composition below a partial pressure of 25 hPa as measured by an O_2-selective sensor and converted to dissolved molecular oxygen concentration using Henry's law; and

a substrate displacement device for bringing at least a portion of a polymerization initiator-modified substrate into contact with the reaction composition in the reaction composition container for a controlled time;

wherein the controlled time is sufficient for surface polymers to be formed on the portion of the polymerization initiator-modified substrate.

11. A system of claim 10, wherein the substrate displacement device comprises any one of:

a conveyor system;

a programmable mechanical arm; or

a roll-to-roll mechanism.

12. A system of claim 10 or 11, further comprising:

one or more sensors, each sensor configured to measure a different value of a characteristic of the reaction composition;

one or more dispensers configured to dispense one or more polymerization control agents and/or one or more components of the reaction composition into the reaction composition, preferably wherein the component of the reaction composition comprises any one or more of: at least one monomer, at least one ligand, at least one catalyst, at least one catalyst activator, and at least one solvent; and

a control unit operatively connected to the one or more sensors;

wherein the control unit is configured to output a control signal to the dispenser for dispensing the one or more polymerization control agents and/or the one or more components of the reaction composition into the reaction composition, and

preferably wherein the control unit is configured to output the control signal periodically to the dispenser, causing the dispenser to periodically dispense the polymerization control agent and/or a component of the reaction composition into the reaction composition.

13. A system of claim 10, wherein the control unit is configured to output the control signal in dependence on receipt of a sensor signal indicative of a change in a value of a characteristic of the reaction composition or in dependence on receipt of a sensor signal indicative of the measured value of the characteristic or the reaction composition not complying with a predetermined threshold value of the characteristic of the reaction composition, preferably

wherein the predetermined threshold value is a pH value and/or molecular oxygen concentration and preferably

wherein a pH control agent and/or an oxygen control agent is dispensed into the reaction composition.

14. A system according to any one of claims 10-13, further comprising a polymerization initiator container containing a polymerization initiator agent, wherein the substrate displacement device is configured to bring the portion of the substrate for attachment of polymerization initiators into contact with the polymerization initiator agent to form

polymerization initiators at the substrate surface, prior to bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition; and/or

a cleaning container, the cleaning container containing a cleaning agent, wherein the substrate displacement device is configured to bring the portion of the polymerization initiator-modified substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the polymerization initiator-modified substrate into contact with the reaction composition; or

the substrate displacement device is configured to bring the portion of substrate into contact with the cleaning agent prior to, or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator, and/or

an annealing container, the annealing container containing an annealing agent, wherein the substrate displacement device is configured to bring the portion of the substrate into contact with the annealing agent prior to, or subsequent to, bringing the portion of the substrate into contact with the polymerization initiator; or prior to, or subsequent to bringing the portion of the substrate into contact with the reaction composition.

15. A composition according to any one of claims 1-3, a method according to any one of claims 4-9, or a system according to any one of claims 10-14, wherein

wherein the at least one polymerization control agent is at least one pH control agent that maintains the pH of the reaction composition above pK_aH_1 of the complex formed between the at least one catalyst and the at least one ligand; or

wherein the at least one pH control agent maintains the pH of the reaction composition above the pK_aH_2 of the complex formed between the at least one catalyst and the at least one ligand; or

wherein the at least one pH control agent maintains the pH of the reaction composition between pK_aH_1 and pK_aH_2 of the complex formed between the at least one catalyst and the at least one ligand.

16. A composition according to any of claims 1-3, or a method according to any one of claims 4-9, or a system according to any one of claims 10-14, wherein

Cu is used as catalyst and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition above $pK_aH_1 = 8.4$; or

Cu is used as catalyst and Me_6TREN is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition between pK_aH_1 and pK_aH_2 from 8.4 to 4.1; or

Cu is used as catalyst and N,N,N',N",N'"-pentamethyldiethylene-triamine (PMDETA) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition above pK_aH_1 = 8.6; or

Cu is used as catalyst and N,N,N',N",N'"-pentamethyldiethylene-triamine (PMDETA) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition between pK_aH_1 and pK_aH_2 from 8.6 to 3.4; or

Cu is used as catalyst and tris(2-pyridylmethyl)amine (TPMA) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition above pK_aH_1 = 7.4; or

Cu is used as catalyst and tris(2-pyridylmethyl)amine (TPMA) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition between pK_aH_1 and pK_aH_2 from 7.4 to -0.4; or

Cu is used as catalyst and tris(2-aminoethyl)amine (TREN) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition above pK_aH_1 = 9.4; or

Cu is used as catalyst and tris(2-aminoethyl)amine (TREN) is used as ligand, and the at least one pH control agent maintains the pH of the reaction composition between pK_aH_1 and pK_aH_2 from 9.4 to 3.5.

17. A composition according to any one of claims 1-3, a method according to any one of claims 4-9, or a system according to any one of claims 10-14, wherein a Cu concentration in the reaction composition is in a range between 0.001 mM and 1 mM.