

Gel Surface Polymerization

Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Patent Application No. 63/556,195, titled
5 "Gel Surface Polymerization" and filed February 21, 2024, the disclosure of which is
incorporated by reference in its entirety herein.

Field of the invention

The present disclosure relates to the formation of surface polymers on substrates. Specifically,
10 the formation of surface polymers on a substrate may be accomplished by applying a reaction
composition forming a gel on the substrate, wherein the formed gel comprises components
for propagating surface polymers, wherein the gel forms on the substrate due to specific
components present in the reaction composition.

15 Background

Forming polymeric structures on surfaces have become increasingly important in many
technologies and applications. "Surface polymers", "surface bound polymers" or "polymers on
a surface" may all describe a polymeric structure having polymer chains that are chemically
bonded to a surface at one end through covalent bond, although the terminology may also
20 be used to describe polymers that a spin coated on a surface. Two methods, known by persons
skilled in the art, can be used to achieve such polymeric structure, namely the "grafting to"-
approach and the "grafting from"-approach (See Fig. 1 and Fig. 2). In the "grafting to"-
approach (Fig. 1), polymers are usually pre-prepared and then deposited onto the surface in
question, since the pre-prepared polymers are designed in such a way that one of the chain-
25 ends has some affinity for the surface of interest. Upon contact with the surface of interest,
the polymers will self-assemble on said surface forming surface bound polymers. In the
"grafting from"-approach (Fig. 2), small molecules capable of acting as polymerization
initiators are covalently bound to the surface of interest in a pre-polymerization step.
Subsequently polymerization is initiated via the polymerization initiators bonded on the
30 surface. Accordingly, surface polymers are formed from the surface monomer-by-monomer.

The "grafting to" approach allows for simple preparation procedures and detailed
characterization, since the polymers may be prepared using conventional methods, and such
polymers may maintain the bonding-to-surface property of the one end of the pre-formed
35 polymer. Then, the self-assembly procedure may be initiated using the preservation and
ability of the viable ends to attach to the surface. However, the "grafting to"-approach lacks
the ability to form high density surface bound polymeric structures. Main equilibrium
conformation of long polymeric structures in solution is a contracted, or a coiled polymer

chain, unless the polymer solution is extremely diluted with highly solvating solvent or other means employed to stabilize extended conformation (e.g., pH for ionic polymers). Such extra means to stabilize extended polymer chain conformation may complicate and interfere with the "grafting to" process conditions and make the approach less practical. Therefore, the self-assembly process is being halted by the steric repulsion between the coils of pre-made polymer chains as they self-assemble on the surface leading to loosely packed polymer coils on the surface (see Fig. 1). The "grafting from"-approach allows for the formation of highly dense surface bound polymer structures, as the small initiating molecules can form a much more densely packed layer on the surface (compared to large polymer molecules, see Fig. 2). Such a densely packed layer of initiating molecules is guiding monomer molecule-by-monomer molecule formation of polymer chains, where the extended conformation of growing polymer chains is sterically stabilized by their close proximity to each other. As such, the surface bound polymer structure formed by a "grafting from" approach results in a much higher density of polymer chains. Additionally, as the "grafting from"-approach allows for highly dense surface bound polymer structures, a brush-like structure can be achieved, thus, the name "polymer brush". In these structures, the polymers are stretched and forced to stand upright due to the steric repulsion between neighbouring polymers creating a unique structure known by people skilled in the art as a "polymer brush" structure. On surfaces, these structures are tethered/attached, usually covalently, at one end to the surface, typically to a solid or semisolid surface, thereby differing from polymers formed in solution and subsequently deposited onto a surface.

As mentioned above, surface polymers are prepared by one of the following two main strategies: "grafting to" or "grafting from". In the "grafting to"-approach, polymer chains are deposited onto the surface in question. The "grafting to"-approach suffers from several drawbacks and limitations making it difficult to produce thick and dense surface polymers. In the "grafting from"-approach, the surface polymer growth (surface polymer chain propagation, extension of the chain by monomer units) is initiated from initiator-functionalized surfaces, using, for example, a controlled/"living" polymerization technique, such as anionic polymerization, cationic polymerization, ring-opening polymerization, and controlled radical polymerization.

Surface polymers within the present context are, thus, polymeric structures having polymer chains that are chemically bonded to a surface at one end. Such polymers can be tailored to provide specific chemical and/or physical properties and can produce precisely tailored chemical structures on a molecular scale. They may be used, for example, for storing certain chemical species, controlling transport properties, improving surface stability and properties, creating an interface in which dissimilar materials can bind or interact, and other functions.

Surface polymers can subsequently join otherwise incompatible materials such as metals and plastics and improve adhesion between such otherwise incompatible materials (see, e.g., WO 2014/075695 A1).

5 Different polymerization techniques have facilitated the specific design and synthesis of surface polymers with strict molecular control and desired properties. In particular, the surface polymers can be viewed as nanoscale "building blocks" with a wide range of uses, varying from redox activity to biocompatibility and surface alteration, and due to the flexibility of the surface polymers, highly tailored thin films of surface polymers can be created with
10 respect to chemical composition, thickness, density and architecture.

To further exploit the potential of surface-polymer technology, there is a need for alternative ways of forming surface polymers, both on a small, R&D, scale, and on a large, high-volume manufacturing, scale. Though surface polymer-forming techniques are often performed as
15 dip coating procedures (i.e., in solution polymerization), the technique may for some applications have reduced versatility and may further be waste heavy as regards reagents. To accommodate this, a paint-on technique has been applied illustrated in ACS Appl. Mater. Interfaces 2014, 6, 11864–11868. Herein, an ATRP paint-on method is used to form polymer brushes on a surface (piece of aluminum). However, the surface dried out, resulting in poor
20 polymer brush formation, and, thus, to ensure high wettability of the surface a piece of filter paper was employed to accommodate this issue. The study concluded that polymer brushes are formed using this paint-on ATRP method, but the method may suffer from the drawback of diffusion of ambient oxygen, terminating the catalyst activity. While the use of filter paper in polymer brush forming technique may provide some benefits due to the use of a
25 "container" (the filter) for the reagents, the technique may be less suited for industrial potential and applicability as the use of filter paper does not generally fit into an industrial setting.

Thus, there is still a need for alternative polymerization methods.

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Summary of the invention

In an aspect of the present disclosure, a reaction composition for surface polymer formation is provided 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
35 solvent; and at least one gelating substance. The reaction composition may be such, wherein the at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel. The at least one polymeric compound may have at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of

repeating unit. Examples of gelating substances are sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid. The at least one ligand may be selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me₆TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam), and/or 2,2'-bipyridyl (BiPy). The at least one catalyst may be selected from copper (Cu) and iron (Fe). Examples of the complex formed between the at least one ligand and the at least one catalyst are Cu/Me₆TREN, Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam. Furthermore, the reaction composition may include at least one additive. The at least one additive may be selected from at least one surfactants, and/or at least one polyquaternium compounds. The at least one surfactant may be selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and the least one polyquaternium compound may be selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79. The reaction composition may further comprise a buffer. The buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. In particular, the Good's buffer may be selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The reaction composition may further comprise at least one cross-linking agent. The at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with a counter ion. In an embodiment, the at least one cross-linking agent may be a di-valent metal ion selected from Mg²⁺, Ca²⁺, Fe²⁺, Cu²⁺, Sr²⁺, and/or Zn²⁺; the at least one cross-linking agent may be a tri-valent metal ion selected from Fe³⁺, Al³⁺, Ga³⁺, and/or In³⁺; and the at least one cross-linking agent may be tetra-valent metal ion selected from Ce⁴⁺, Zr⁴⁺, and/or Ti⁴⁺. In an embodiment, the at least one di-valent metal ion in combination with a counter ion may be selected from MgCl₂, CaCl₂, FeCl₂, CuCl₂, Cu(NO₃)₂, SrCl₂, Sr(NO₃)₂, Zn(NO₃)₂, ZnCl₂, Zn(CH₃CO₂)₂, and/or hydrates thereof; the at least one cross-linking agent may be a tri-valent metal ion in combination with a counter ion is selected from FeCl₃, AlCl₃, Fe(NO₃)₃, Al₂(SO₄)₃, Fe₂(SO₄)₃, Ga(NO₃)₃, InCl₃, and/or hydrates thereof; and the at least one cross-linking agent may be a tetra-valent metal ion in combination with a counter ion is selected from Ce(SO₄)₂, (NH₄)₄Ce(SO₄)₄, Zr(NO₃)₄, Zr(SO₄)₂, ZrCl₄, TiCl₄, and/or hydrates thereof. In particular, the at least one cross-linking agent may be selected from CaCl₂, CuCl₂, Zn(NO₃)₂, AlCl₃, FeCl₃, and/or (NH₄)₄Ce(SO₄)₄. The reaction composition may further comprise at least one catalyst activator. The at least one catalyst activator may

be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x , and/or pyrogalllic acid. The at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation. In an
5 embodiment, the at least one catalyst activator may be added to the reaction composition prior to formation of surface polymers.

In an aspect of the present disclosure, a reaction composition for surface polymer formation is provided comprising a first separate liquid and a second separate liquid, wherein: the first
10 separate liquid comprises: at least one gelating substance; and at least one solvent; and the second separate liquid comprises: at least one cross-linking agent; and at least one solvent; wherein the first separate liquid and the second separate liquid may be provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of
at least one polymerization initiator-modified substrate. In an embodiment, the first separate
15 liquid and/or the second separate liquid may further comprise: at least one monomer; and/or at least one catalyst and at least one ligand, wherein the at least one catalyst and the at least one ligand form a complex. In an embodiment, the first separate liquid and/or the second separate liquid may comprise one or more additives. In an embodiment, the first and/or the second separate liquid may comprise one or more buffers. In an embodiment, the
20 reaction composition may be such, wherein the first separate liquid may comprise: 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 solvent; at least one gelating substance; optionally at least one additive; and optionally at least one buffer; and wherein the second separate liquid may comprise: at least one cross-linking agent; at least one
25 solvent; optionally at least one additive; and optionally at least one buffer; wherein the first separate liquid and the second separate liquid may be provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of at least one polymerization initiator-modified substrate. The at least one gelating substance may be at least one polymeric compound chelating with at least one metal ion and forming a gel. The
30 at least one polymeric compound may have at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit. Examples of the at least one gelating substance include sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid. The at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with at least one counter ion. In an
35 embodiment, the at least one cross-linking agent may be a di-valent metal ion selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ; the at least one cross-linking agent may be a tri-valent metal ion selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and the at least one cross-linking agent may be a tetra-valent metal ion selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} . In particular,

the at least one di-valent metal ion in combination with a counter ion may be selected from MgCl_2 , CaCl_2 , FeCl_2 , CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, SrCl_2 , $\text{Sr}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, ZnCl_2 , $\text{Zn}(\text{CH}_3\text{CO}_2)_2$, and/or hydrates thereof; the at least one tri-valent metal ion in combination with a counter ion may be selected from FeCl_3 , AlCl_3 , $\text{Fe}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ga}(\text{NO}_3)_3$, InCl_3 , and/or hydrates thereof; and the at least one tetra-valent metal ion in combination with a counter ion may be selected from $\text{Ce}(\text{SO}_4)_2$, $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, $\text{Zr}(\text{NO}_3)_4$, $\text{Zr}(\text{SO}_4)_2$, ZrCl_4 , TiCl_4 , and/or hydrates thereof. In an embodiment, the at least one cross-linking agent is selected from CaCl_2 , CuCl_2 , $\text{Zn}(\text{NO}_3)_2$, AlCl_3 , FeCl_3 , and/or $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, and/or hydrates thereof. The at least one ligand may be selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), and/or 2,2'-bipyridyl (BiPy). The at least one catalyst may be selected from copper (Cu), iron (Fe), and ruthenium (Ru). In an embodiment, the complex formed between the at least one ligand at the at least one catalyst may be selected from $\text{Cu}/\text{Me}_6\text{TREN}$, Cu/PMDETA , Cu/TPMA , Cu/TREN , Cu/HMTETA , Cu/TMEDA , and/or $\text{Cu}/\text{Me}_4\text{Cyclam}$. The at least one additive may be selected from at least one surfactants, and/or at least one polyquaternium compounds. In an embodiment, the at least one surfactant may be selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and the least one polyquaternium compound may be selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79. The buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. The Good's buffer may be selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The first separate liquid and/or the second separate liquid may further comprise at least one catalyst activator. The at least one catalyst activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x , and/or pyrogalllic acid. The at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation. In an embodiment, the at least one catalyst activator may be added to the first separate liquid and/or the second separate liquid prior to surface polymer formation.

In an aspect of the present disclosure, there is provided a method for forming surface polymers on a substrate comprising: providing at least a portion of at least one polymerization initiator-modified substrate; bringing the at least a portion of the at least one polymerization initiator-modified substrate into contact with a reaction composition comprising: a first separate liquid; a second separate liquid; and a number of other separate liquids; wherein the first separate liquid may comprise: at least one gelating substance; wherein the second separate liquid may comprise: at least one cross-linking agent; and wherein the number of other separate liquids may comprise one or more of: 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; optionally at least one additive; and optionally at least one buffer; wherein one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids further may comprise at least one solvent; wherein one or more of the first separate liquid; the second separate liquid; and the number of other separate liquids may be mixed prior to bringing the reaction composition in contact with the at least a portion of the at least one polymerization initiator-modified substrate; and forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate. The at least one gelating substance may be at least one polymeric compound chelating with at least one metal ion and forming a gel. The at least one polymeric compound may have at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit. In an embodiment, the at least one gelating substance may be selected from sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid. The at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with a counter ion. The at least one di-valent metal ion may be selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ; the at least one tri-valent metal ion may be selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and the at least one tetra-valent metal ion may be selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} . In an embodiment, the at least one di-valent metal ion in combination with a counter ion may be selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or hydrates thereof; the at least one tri-valent metal ion in combination with a counter ion may be selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and the at least one tetra-valent metal ion in combination with a counter ion may be selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof. In an embodiment, the at least one cross-linking agent may be selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or $(NH_4)_4Ce(SO_4)_4$. The at least one ligand may be selected from *N,N,N',N''*-penta-methyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyl-

triethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam), and/or 2,2'-bipyridyl (BiPy). The at least one catalyst is selected from copper (Cu), iron (Fe), and ruthenium (Ru). In an embodiment, the complex formed between the at least one ligand at the at least one catalyst

5 may be selected from Cu/Me₆TREN, Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam. The at least one additive may be selected from at least one surfactants, and/or at least one polyquaternium compounds. The at least one surfactant may be selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or

10 dimethyldioctadecylammonium chloride; and the least one polyquaternium compound may be selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79. The buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate

15 buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. In an embodiment, the Good's buffer may be selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The at least one catalyst activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate,

20 sodium sulfite, sodium dithionite, glucose with GO_x, and/or pyrogalllic acid. The at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation. In an embodiment, the at least one catalyst activator may be mixed with the at least one catalyst and the at least one ligand prior to applying the reaction composition to the at least a portion of the at least one

25 polymerization initiator-modified substrate. In an embodiment, one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying. In an embodiment, the first separate liquid, the second separate liquid, and one or more of the other separate liquids may be applied by a first spray unit, a second

30 spray unit and a third spray unit, respectively. In an embodiment, one or more of the first separate liquid; the second separate liquid and/or the number of other separate liquids may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by dip coating.

35 In an aspect of the present disclosure, there is provided a method for forming surface polymers on a substrate comprising: providing at least a portion of at least one polymerization initiator-modified substrate; bringing the at least a portion of the at least one polymerization initiator-modified substrate into contact with a reaction composition

comprising: a first separate liquid; and a second separate liquid; wherein the first separate liquid may comprise: at least one gelating substance; and at least one solvent; wherein the second separate liquid may comprise: at least one cross-linking agent; and at least one solvent; wherein the first separate liquid and/or the second separate liquid may further

5 comprise: 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; optionally at least one additive; and optionally at least one buffer; wherein each of the first separate liquid and the second component may be applied to the at least a portion of the at least one polymerization initiator-modified substrate to form surface polymers on

10 the at least a portion of the at least one polymerization initiator-modified substrate; and forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate. The at least one gelating substance may be at least one polymeric compound chelating with at least one metal ion and forming a gel. The at least one polymeric compound may have at least one functional group chelating di-, tri-, or tetra-valent metal

15 ions in at least one type of repeating unit. In an embodiment, the at least one gelating substance may be selected from sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid. The at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with a counter ion. The at least one di-valent metal ion may be selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ;

20 the at least one tri-valent metal ion may be selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and the at least one tetra-valent metal ion may be selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} . In an embodiment, the at least one di-valent metal ion in combination with a counter ion may be selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or hydrates thereof; the at least one tri-valent metal ion in combination

25 with a counter ion may be selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and the at least one tetra-valent metal ion in combination with a counter ion may be selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof. In an embodiment, the at least one cross-linking agent may be selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or

30 $(NH_4)_4Ce(SO_4)_4$. The at least one ligand may be selected from *N,N,N',N'',N'''*-penta-methyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetra-methyl-1,4,8,11-tetraazacyclotetradecane ($Me_4Cyclam$), and/or 2,2'-bipyridyl (BiPy). The at

35 least one catalyst is selected from copper (Cu), iron (Fe), and ruthenium (Ru). In an embodiment, the complex formed between the at least one ligand at the at least one catalyst may be selected from Cu/ Me_6TREN , Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/ $Me_4Cyclam$. The at least one additive may be selected from at least

one surfactants, and/or at least one polyquaternium compounds. The at least one surfactant may be selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and the least one polyquaternium compound may be selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79. The buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. In an embodiment, the Good's buffer may be selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The at least one catalyst activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x, and/or pyrogalllic acid. The at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation. In an embodiment, the at least one catalyst activator may be mixed with the at least one catalyst and the at least one ligand prior to applying the reaction composition to the at least a portion of the at least one polymerization initiator-modified substrate. In an embodiment, one or more of the first separate liquid; and the second separate liquid may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying. In an embodiment, the first separate liquid, and the second separate liquid may be applied by a first spray unit, and a second spray unit, respectively. In an embodiment, one or more of the first separate liquid; and the second separate liquid may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by dip coating.

In an aspect of the present disclosure, there is provided an apparatus for forming surface polymers on polymerization initiator-modified substrates, the apparatus comprising: a first system for spray depositing, from separate spray nozzles, a first separate liquid including a gelating substance and a second separate liquid including a cross-linking agent, on the substrates, wherein one or more of the first separate liquid and the second separate liquid include a monomer and an activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form a gel on the substrates; and a second system for rinsing the gel off the substrates leaving behind surface polymers which have grown from polymerization initiator-modified sites on the substrates. The apparatus may further comprise a third system for spray depositing, from separate spray nozzles, the first separate liquid including the gelating substance, and the second separate liquid including the cross-linking agent, on the substrates, wherein one or more of the first separate liquid and

the second separate liquid include the monomer and the activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form an increased thickness of the gel on the substrates. The apparatus may further comprise a conveyor belt for moving the substrates through one or more of the first, second and third systems. The apparatus may further comprise a reel-to-reel system for moving a continuous foil/substrate through one or more of the first, second and third systems, wherein the continuous foil comprises a multiplicity of the substrates. The apparatus may be configured to process the substrates in a horizontal or a vertical plane, or in any plane between the horizontal and the vertical.

Description of the drawings

Certain embodiments of the matter disclosed herein are illustrated in the accompanying drawings. The drawings are, however, in no way intended to limit the scope of the disclosure. In the drawings:

- Fig. 1 illustrates the "grafting to" concept schematically.
- Fig. 2 illustrates the "grafting from" concept schematically.
- Fig. 3 illustrates metal ions cross-linking with functional group(s) of the gelating substance in an intermolecular manner.
- Fig. 4 illustrates metal ions cross-linking with functional groups of the gelating substance in an intramolecular manner.
- Fig. 5 is a schematic representation of a spray apparatus for forming gel on substrates for forming surface polymers from grafting sites on the substrates, according to embodiments.
- Fig. 6 is a schematic representation of a spray apparatus for forming thicker gel on substrates for forming surface polymers from grafting sites on the substrate, according to embodiments.
- Fig. 7 is a schematic representation of a spray apparatus for forming gel on a continuous foil or other continuous surface for forming surface polymers from grafting sites on the continuous surface, according to embodiments.
- Fig. 8 shows the flip vial test of Example 3, where gelating substances are transferred to vials (Fig. 8 a.-f.) and inverted (Fig. 8 g.-l.). The gelating substance is fluid and does not stay in place.
- Fig. 9 shows the flip vial test of Example 3 following addition of a cross-linking agent to vials holding gelating substances (Fig. 9 a.-f.). The vials were flipped and in case of gelation between the gelating substance and the cross-linking agent, the gel formed stayed in place (Fig. 9 g.-l.).

- Fig. 10 illustrates the spray-on method on horizontally oriented substrates (see general description in General Method Example).
- Fig. 11 illustrates the spray-on method on vertically oriented substrates (see general description in General Method Example).
- 5 Fig. 12 shows the results of Example 4, where Fig. 12 a. is the substrate covered with gel formed between gelating substance and cross-linking agent, and Fig. 12 b. is the substrate with surface polymers after rinsing the gel off.
- Fig. 13 shows the gelated reaction composition of Example 8 with polyquaternium-D16 (Fig. 13 a.) or polyquaternium-10 (Fig. 13 b.) as additive when sprayed onto a substrate.
- 10 Fig. 14 shows the gelated reaction composition of Example 9 with a combination of Triton-X100 and polyquaternium-D16 (Fig. 14 a.) or a combination of Triton-X100 and polyquaternium-10 (Fig. 14 b.) as additive.
- Fig. 15 shows the gelated reaction composition of Example 9 with SDS (Fig. 15 a.), polyquaternium-10 (Fig. 15 b.), polyquaternium-D16 (Fig. 15 c.), a combination of Triton-X100 and either of polyquaternium-10 (Fig. 15 d.) and polyquaternium-D16 (Fig. 15 e.).
- 15

Detailed description of the invention

- 20 The present disclosure relates to the formation of surface polymers on substrates. Specifically, the formation of surface polymers on a substrate may be accomplished by applying a reaction composition forming a gel on the substrate, the formed gel comprising components for propagating surface polymers. The gel forms on the substrate due to specific components present in the reaction composition. In accordance herewith, a gelating
- 25 substance and a cross-linking agent are brought into contact during the applying of the reaction composition to at least a portion of at least one substrate for surface polymer formation.

- In one aspect of the present disclosure, a reaction composition for surface polymer formation is provided, the 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 solvent; and at least one gelating substance.
- 30

- Polymer gels are generally well-known substances. Polymer gels find their use in many applications from diapers to contact lenses and implants as well as in tissue engineering. Polymer gels are three-dimensional, polymeric networks capable of absorbing large amounts of water (hydrogel) or organic solvents (organo-gel), up to 500 times their own weight. Polymer gels are obtained by cross-linking polymers into a cross-linked polymer matrix.
- 35

Polymer gels possess a number of features, such as the viscoelastic response to mechanical deformation. In particular, polymer gels have been hypothesized for various applications such as artificial muscle, purification or separation systems, regenerative medicine, biosensors, shape memory materials, transporting systems, sustained release system, and molecular
5 recognition systems.

Although polymer gels *per se* are known, it is not straightforward to use polymer gels for transporting reagents onto a site, where a reaction is to take place subsequently. E.g., reagents may be absorbed by the polymer gel thereby preventing migration of the reactants,
10 cross-linking sites on the polymer gel may react with reagents in an adverse manner, and some cross-linking sites may act as a metal coordinator, meaning that the metal catalyst applied in surface polymer formation reactions may be absorbed, resulting in distorting the surface polymer formation reaction.

15 Despite the above challenges, the present inventors have surprisingly found that certain gelating substances may beneficially form gels with certain cross-linking agents, allowing surface polymer formation to take place on the surface of the substrate following formation of the gel on the surface of the substrate. It is believed that the gel formed may in fact act as a reaction vessel or container for the reaction composition components for surface polymer
20 formation. The formation of surface polymers in a gel has several benefits, including reduction of chemicals used and less waste.

Established methods for forming surface polymers utilize dip-coating processes, which may become problematic when there is a need to form surface polymers on large and, in some
25 cases, complex surfaces. In order to form surface polymers on a large substrate using the dip-coating process, large reaction vessels are needed, implying the use of excess of chemical reagents which may not be consumed in a productive fashion for the surface polymer formation, in particular in view of the usually limited lifetime of conventionally used reagents. Furthermore, forming surface polymers on only certain areas of a substrate may be
30 challenging using the dip-coating approach. Accordingly, the gel approach as disclosed herein offers an advantageous alternative to the dip-coating processes, reducing also the challenges in forming surface polymers only on specific portions of a substrate.

The at least one gelating substance to be applied in accordance with the disclosure herein
35 may be at least one polymeric compound chelating with at least one metal ion and forming a gel. The at least one gelating substance may be a polymeric compound having at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit. The metal ions may cross-link with functional group(s) of the gelating substance

resulting in the gel formation. The concept is illustrated in Fig. 3. The formed gel may suitably be solid or semi-solid. Non-limiting examples of gelating substances within the meaning of the present context include sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid. In particular, gelating substances having at least one functional group chelating di-valent metal ions include sodium alginate, and/or poly(vinyl imidazole), and/or poly(acrylic acid), pectin, and carrageenan. In particular, gelating substances having at least one functional group chelating tri-valent metal ions include sodium alginate, xanthan gum, hyaluronic acid, pectin, and carrageenan. In particular, gelating substances having at least one functional group chelating tetra-valent metal ions include sodium alginate, xanthan gum, hyaluronic acid, and pectin. Thus, the at least one gelating substance may chelate more than one type of metal ions.

The functional groups of the at least one gelating substance chelating with metal ions may be groups such as carboxylic acids, sodium carboxylates, hydroxyls, alkoxides, phosphates, sulphates, amines, imidazoles, ethers, pyrocatechol (1,2-dihydroxybenzene), and/or pyrogallol (1,2,3-trihydroxybenzene), and/or sulphonates.

The gelating substance should be chosen so as to primarily form intermolecular crosslinks upon contact with the metal ion(s) instead of intramolecular crosslinks with the metal ion(s) as intramolecular crosslinks may result in a decreased viscosity, reducing gel formation. The concept of inter- and intramolecular crosslinking is shown in Fig. 3 and Fig. 4, respectively.

Ligands to be used in the reaction composition disclosed herein may comprise nitrogen-containing ligands. Non-limiting examples of such nitrogen-containing compounds are bi-, tri-, or tetradentate amine ligands (containing two, three or four amine substituents) which are aliphatic and/or aromatic in nature. In particular, such ligands include *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me₆TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine), TMEDA (tetramethylethylenediamine), Me₄Cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), and/or 2,2'-bipyridyl (BiPy). The amount of ligand in the reaction composition is defined as a ratio to the concentration of catalyst in the reaction composition. The ratio of ligand to catalyst in the reaction composition is in the range 0.001:1 – 1000:1. The ratio of ligand to catalyst in the reaction composition is preferable in the range 0.005:1 – 100:1, for example 0.13:1, 0.5:1, 1.0:1, 2.0:1, 3.5:1, 7.5:1 or 12:1. In general, excess amount ligand as compared to amount catalyst may be used.

The catalyst of the reaction composition as defined herein may be based on a transition metal (as defined in the Periodic Table of Elements). Non-limiting examples of catalysts are compounds derived from transition metals like copper (Cu), iron (Fe), and ruthenium (Ru). Specific examples of such catalyst compounds include Cu₂O, CuO, CuCl, CuCl₂, CuBr, CuBr₂, FeCl₂, FeCl₃, RuCl₂, and RuCl₃, as well as combinations thereof. The catalyst concentration in the reaction composition may typically be in the range 0.0001–1 mM. The concentration of catalyst in the reaction composition may be in the range 0.0001–0.32 mM, for example 0.001 mM, 0.01 mM, 0.02 mM, 0.04 mM, 0.08 mM, 0.16 mM, or 0.32 mM. The activator for the catalyst (e.g., oxygen scavenger) may be used in excess compared to the catalyst. Excess catalyst activator may, e.g., be 10-250 times. In accordance with the methods disclosed herein, catalyst activator may be added several times during surface polymer formation to control surface polymer formation with progressing time. In a certain embodiment the catalyst may be based on Cu, and is prepared from Cu oxides, or Cu chlorides as specified above.

Herein, the terms "complex formed between a ligand and a catalyst", "complex formed between a catalyst and a ligand", and "catalyst/ligand complex" may be used interchangeably.

Herein, the term "catalyst" is used to denote the transition metal when the transition metal is coordinated with a ligand. One, two, or three ligands may form complexes with one transition metal catalyst. The term "catalyst compound" is used to denote the transition metal in combination with another ion, by way of example, Cu oxides, and Cu chlorides, on which the catalyst may be based.

The reaction composition may further comprise at least one additive. The at least one additive include, but are not limited to, surfactants, polyquaternium compounds, polysaccharides, polypeptides, proteins, and/or rubber emulsions such as styrene-butadiene rubber (SBR) in water. The additive should be soluble in the solvent used for spraying. The additive may increase the adhesion to the at least a portion of the surface of the at least one substrate or increase the film-forming before or during the spray on application. Some additives may increase wetting of the surface of the substrate. The additive may further support gel formation and facilitate distribution of the other components of the reaction composition within the formed gel. In one embodiment, the at least one additive may be at least one surfactant selected from sodium dodecyl sulfate (SDS), dioctyl sulfosuccinate (DOSS), polyethylene glycol tert-octylphenyl ether (Triton X-100), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and dimethyldioctadecylammonium chloride (DDAC). In one embodiment, the at least one additive may be a polyquaternium compound selected from

polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

- 5 It is well-known to persons skilled in the art that additives may manipulate the polarity of a product to which it is added and even interact with the item to which it is applied, blocking the item to some extent, to ensure the desired properties of the additive. The inventors have surprisingly found that such additives as defined herein do not have an adverse effect on the surface polymer formation, even if the additive may change the reaction composition polarity and interact with the surface for surface polymer formation. Furthermore, the inventors surprisingly found that additives may even aid the application and/or the distribution of the reaction composition, and, in some embodiments, the reaction composition may appear highly viscous and, thus, may be more easily distributed with the addition of an additive.
- 10
- 15 The reaction composition may further comprise a buffer. The term "buffer" is defined herein as an agent which, when added to the reaction composition, can within a certain pH range withstand changes in pH during the course of the surface polymer formation. Buffer systems include combinations of a weak acid and its conjugate base, or a weak base and its conjugate acid. The buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. Examples of Good's buffers include MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS. The buffer may be a combination of various buffers. The buffer may further be useful during the surface polymer formation in order to facilitate surface polymer formation.
- 20
- 25 Different buffers have different buffering ranges, and in an embodiment the buffer is chosen such that the pH of the reaction composition is above a pK_aH value of the catalyst/ligand complex, such as above the pK_{aH_2} value or above the pK_{aH_1} value of the catalyst/ligand complex. By way of example, an *N*-cyclohexyl-2-aminoethanesulfonic acid (CHES) buffer system may be used to maintain a pH value in the interval 8.6–10.0, or a glycine buffer system may be used to maintain pH in the interval 8.6–10.6. By keeping the $pH > pK_{aH_1}$, the surface polymerization rate may be kept high and uniform, and the rate of bulk polymer formation may be kept low. At $pK_{aH_1} > pH > pK_{aH_2}$ the kinetics of the surface polymer formation may be kept stable. A certain buffer or combination of buffers may be selected taking into account the pK_a values of the applied catalyst/ligand complex. pK_a values of representative catalyst/ligand complexes formed between copper (Cu) and a ligand are summarized in Table 1.
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- 35

Table 1. Catalyst/ligand complex pK_aH_1 and pK_aH_2 values.

Ligand	Catalyst/ligand complex	pK_aH_1	pK_aH_2
Me ₆ TREN	Cu/Me ₆ TREN	8.4	4.1
PMDETA	Cu/PMDETA	8.6	3.4
TPMA	Cu/TPMA	7.4	-0.4
TREN	Cu/TREN	9.4	3.5

The pH of the reaction may be modulated using an acidic substance or an alkaline substance. Examples of acidic substances include methanesulfonic acid (MSA), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), 2,2,2-trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (pTSA), and/or nitric acid (HNO₃). Examples of alkaline substances include potassium hydroxide (KOH), lithium hydroxide (LiOH) tripotassium phosphate (K₃PO₄), sodium carbonate (Na₂CO₃), and/or sodium ethoxide (CH₃CH₂ONa).

- 10 The reaction composition disclosed herein may comprise further comprising at least one cross-linking agent. The at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with at least one counter ion. Non-limiting examples of cross-linking agents include di-valent metal ions selected from Mg²⁺, Ca²⁺, Fe²⁺, Cu²⁺, Sr²⁺, and/or Zn²⁺; tri-valent metal ions selected from Fe³⁺, Al³⁺, Ga³⁺, and/or In³⁺; and tetra-valent metal ions selected from Ce⁴⁺, Zr⁴⁺, and/or Ti⁴⁺. In one embodiment, the at least one di-valent metal ion in combination with at least one counter ion may be selected from MgCl₂, CaCl₂, FeCl₂, CuCl₂, Cu(NO₃)₂, SrCl₂, Sr(NO₃)₂, Zn(NO₃)₂, ZnCl₂, Zn(CH₃CO₂)₂, and/or hydrates thereof; the at least one cross-linking agent may be a tri-valent metal ion in combination with at least one counter ion selected from FeCl₃, AlCl₃, Fe(NO₃)₃, Al₂(SO₄)₃, Fe₂(SO₄)₃, Ga(NO₃)₃, InCl₃, and/or hydrates thereof; and the at least one cross-linking agent may be a tetra-valent metal ion in combination with at least one counter ion selected from Ce(SO₄)₂, (NH₄)₄Ce(SO₄)₄, Zr(NO₃)₄, Zr(SO₄)₂, ZrCl₄, TiCl₄, and/or hydrates thereof. In a specific embodiment, the at least one cross-linking agent may be selected from CaCl₂, CuCl₂, Zn(NO₃)₂, AlCl₃, FeCl₃, and/or (NH₄)₄Ce(SO₄)₄. In particular CaCl₂, CuCl₂, Zn(NO₃)₂, AlCl₃, FeCl₃, and (NH₄)₄Ce(SO₄)₄ may be useful. It is to be understood that cross-linking agents may include one type of counter ions, like CaCl₂, or more types of counter ions, like (NH₄)₄Ce(SO₄)₄. It is expected that only a low amount of cross-linking agent may be sufficient to cross-link the gelating substance, however, the cross-linking agent may be used in excess compared to cross-linking sites (functional groups) on the gelating substance.

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The reaction composition may further comprise at least one catalyst activator. The at least one catalyst activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc),

hydrazine, hydrazine hydrate, sodium thiosulfate, sodium hypophosphite, tin ethylhexanoate, sodium phenoxide, sodium sulfite, sodium dithionite, glucose with GO_x , and/or pyrogallol acid. The catalyst activator may be used in excess compared to the catalyst. Excess catalyst activator may, e.g., be 10-250 times. It is believed that the catalyst activator reduces the transition metal of the catalyst/ligand complex, thus, transforming the inactive catalyst/ligand complex to its activated form, and accordingly activates the complex formed between the at least one ligand and the at least one catalyst. Prior to activation, the complex formed between the at least one ligand and the at least one catalyst may be inactive for surface polymerization.

The reaction composition according to embodiments of the present disclosure may further comprise a halide compound for increasing the "livingness" of the surface polymer formation. A "living" polymerization refers to a surface polymer formation where the rate of termination is minor in comparison to the rate of propagation of surface polymer chains (extension of a surface polymer by monomeric units). As a result, living polymer formations show a linear relationship between polymer chain length and time. A living polymer formation also allows for propagating block copolymers. The halide compound to be used herein is a compound capable of providing a halide anion. Non-limiting examples of such compounds are NaCl, NaBr, KCl, KBr, MgCl_2 , MgBr_2 , CaCl_2 , HCl, HBr, LiCl, LiBr, CaBr_2 , CuBr_2 and CuCl_2 as well as combinations thereof. Halide compounds may disassociate in the reaction composition, generating halide anions which may form complexes with and/or bind to catalysts in solution, resulting in an increased concentration of catalyst/ligand-X complexes which are responsible for end-capping, and thus deactivating, propagating surface polymer chain-end radicals to deliver alkyl halides. Consequently, the number of propagating surface polymer chain-end radicals at any given time may be lowered, which may result in at least effects; (1) a lowering of the rate with which surface polymers grow initially due to a lower number of propagating chains, and (2) a lowering of the rate with which chain termination between two propagating surface polymer chain-end radicals occur (through recombination or disproportionation), leading to an increased living character of the surface polymer formation. In an embodiment, the catalyst is Cu, the ligand may be Me_6TREN , PMDETA, TREN, HMTETA, TMEDA, or Me_4Cyclam , and the halide compound may be NaCl.

The reaction composition as disclosed herein comprises at least one monomer. Monomers include several types of monomers. Suitable examples are indicated below. The monomers for surface polymer formation may be any such desired for the final product.

Non-limiting examples of appropriate monomer types include anionic, cationic, zwitterionic, protic and aprotic monomers, and include acrylates, methacrylates, halogen-substituted

alkenes, acrylamides, methacrylamides, and styrenes, as well as mixtures thereof. The generic monomer structure comprises a polymerizable part (an alkenyl group), which in certain embodiments is connected to a functional group responsible for the specific functionality (e.g., adhesion, permeability, electric and ionic conductivities) of the certain monomer through a certain linker chemistry.

For acrylate monomers, non-limiting examples of functional moieties include but are not limited to: alkyl groups, hydroxyl groups, sulfonates, fluorosulfonates, carboxyls, metal carboxylates, ethers, poly(ether) groups, bis(sulfonyl)amides, fluorinated sulfonates, perfluoroalkyl carboxylate, borate, fluorinated borate, borate ester derivatives, tetraphenylborate, bis(trifluoromethane)sulfonimide, triflimides and derivatives thereof, halogenated alkyl chains, and mono-, di-, and tri-alkoxy silanes.

The polymerizable part and the functional part of monomer can, in certain embodiments, be connected by linker moiety. Non-limiting examples of appropriate linker chemistries include but are not limited to: alkyl chains, esters, ethers, poly(ethers), amines, amides, aryls, and any combination(s) thereof. Non-limiting examples of appropriate acrylate monomers containing alkyl linkers include but are not limited to: methyl acrylate, ethyl acrylate, and lauryl acrylate. Non-limiting examples of monomers using ether and poly(ether) linker chemistry include but are not limited to: poly(ethylene glycol) methyl ether acrylate, and poly(ethylene glycol) acrylate. Non-limiting examples of monomers without linker chemistry include but are not limited to: acrylic acid, lithium acrylate, and sodium acrylate.

For methacrylate monomers, non-limiting examples of appropriate functional moieties include but are not limited to: carboxylic acids, metal carboxylates, esters, alkyl alcohols, oxiranes (epoxides), linear and branched alkyl groups, sulfonates, fluorosulfonates, bis(sulfonyl)-amides, fluorinated sulfonates, perfluoroalkyl carboxylate, borate, fluorinated borate, borate ester derivatives, tetraphenylborate, bis(trifluoromethane)sulfonimide, triflimides, and derivatives thereof, halogenated alkyl chains, and mono, di, and tri-alkoxy silanes.

Non-limiting examples of linker chemistries include but are not limited to: alkyl chains, esters, ethers, poly(ethers), amines, amides, aryls, and any combination(s) thereof.

Non-limiting examples of methacrylate monomers include but are not limited to: methacrylic acid, lithium methacrylate, sodium methacrylate, methyl methacrylate (MMA), potassium 3-sulfpropyl methacrylate, 2-hydroxyethylmethacrylate (HEMA), glycidyl methacrylate (GMA), ethyl methacrylate, *n*-butyl methacrylate, *tert*-butyl methacrylate (*t*BMA), lauryl methacryl-

ate, (((perfluorobutyl)sulfonyl)oxy)methyl methacrylate ; 3-(*N*-((trifluoromethyl)sulfonyl)-sulfamoyl)propyl methacrylate, 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl methacrylate (HFDMA), 2-((triethoxysilyl)oxy)ethyl methacrylate, and 2-(3-(triethoxysilyl)propoxy)ethyl methacrylate.

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Non-limiting examples of acrylate monomers include but are not limited to: methyl acrylate (MA), *tert*-butyl acrylate (*t*BA), lauryl acrylate, and 2-hydroxyethylacrylate (HEA).

Non-limiting examples of appropriate halogen-substituted alkene monomers include but are not limited to: vinyl chloride, vinylidene difluoride, tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropylene.

Non-limiting examples of appropriate acrylamide monomers include but are not limited to: acrylamide, *N*-*iso*-propylacrylamide, *N*-*tert*-butylacrylamide, and *N*-hydroxyethyl acrylamide (HEAm).

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Non-limiting examples of appropriate methacrylamide monomers include but are not limited to: *N*-*iso*-propylmethacrylamide, methacrylamide, *N*-*tert*-butylmethacrylamide, and *N*-hydroxyethyl methacrylamide (HEMAm).

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Non-limiting examples of appropriate styrene monomers include but are not limited to styrene, 4-methylstyrene, 2,3,4,5,6-pentafluorostyrene, *p*-divinylbenzene, 4-chlorostyrene, sodium 4-vinylbenzenesulfonate, lithium 4-vinylbenzenesulfonate, and 4-vinylphenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate.

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Monomer(s) may be chosen to provide compatibility/adhesion/elasticity, as appropriate for a specific application. Monomer(s) can also be selected to enhance or diminish electrical and/or ionic conductivity, and/or permeability. Monomers may be chosen to improve interface stability of a surface in question. Furthermore, introduction of functional groups or combination of functional groups may provide improvement over various desired properties, like density, dielectric constants, diffusion barrier, wettability, etc. Monomers may suitably be used in an amount corresponding to a percentage of the total volume of the reaction medium. For example, a liquid monomer may constitute e.g. 0.5 vol%, 2 vol%, or 10 vol% of a reaction medium. In each application, an amount of monomer may be chosen to obtain desired polymerization kinetics, solubility of the monomer, and cost of the monomer. In most cases, the amount of monomer may be in the range of 0.5 vol% to 50 vol%.

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Following formation of the surface polymer, the surface polymer is indicated with a "P" as prefix to the monomer. By way of example, methyl methacrylate monomer is denoted MMA, and after polymerization, the polymer molecule is denoted PMMA. Likewise, 2-hydroxyethyl methacrylate is denoted HEMA, and after polymerization, the polymer molecule is denoted PHEMA.

In a particular embodiment of the present disclosure, the surface polymer is a polymer brush. Throughout the disclosure herein, the term "surface polymer" may also include polymer brush.

The reaction composition to be used herein may comprise at least one solvent. Each of the components of the reaction composition disclosed herein may be dissolved/dispersed in at least one solvent. The solvent may be any solvent that provides sufficient solubility of the components of the reaction composition. Suitable solvents include but are not limited to: alcohols; dipolar aprotic solvents (for examples, tetrahydrofuran, methyl acetate, ethyl acetate, butyl acetate, dimethyl sulfoxide, dimethyl formamide); methylene carbonate; ethylene carbonate; propylene carbonate; ethyl lactate alcohol; toluene ionic liquids; supercritical CO₂; and water, as well as mixtures thereof. In an embodiment, the solvent may be mixture of one or more miscible solvents.

In an aspect of the present disclosure, a reaction composition is provided comprising: a first separate liquid and a second separate liquid, wherein: the first separate liquid may comprise: at least one gelating substance; and at least one solvent; and the second separate liquid may comprise: at least one cross-linking agent; and at least one solvent; wherein the first separate liquid and the second separate liquid may be provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of at least one polymerization initiator-modified substrate. By "separate liquids" is meant that each of the separate liquids are provided in separate containers or other type of storage entity and brought together when applied to the at least one polymerization initiator-modified substrate in a sequential or simultaneous manner. By "liquid" is meant a fluid with a viscosity suited for the intended application and is intended to include dispersions, emulsions and solutions.

The first separate liquid and/or the second separate liquid may further comprise: at least one monomer; and/or at least one catalyst and at least one ligand, wherein the at least one catalyst and the at least one ligand form a complex.

The first separate liquid and/or the second separate liquid may comprise one or more additives. In an embodiment, the first and/or the second separate liquid may comprise one or more buffers.

- 5 The reaction composition may comprise a first separate liquid and a second separate liquid, wherein the first separate liquid may comprise: 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 solvent; at least one gelating substance; optionally at least one additive; and optionally at least one buffer; and wherein the second separate liquid may
10 comprise: at least one cross-linking agent; at least one solvent; optionally at least one additive; and optionally at least one buffer; wherein the first separate liquid and the second separate liquid may be provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of at least one polymerization initiator-modified substrate.

- 15 The at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel as specified above. The at least one polymeric compound has at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit. Examples of gelating substances include sodium alginate,
20 poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid.

- The at least one cross-linking agent is a di-, tri-, or tetra-valent metal ion in combination with at least one counter ion as specified above, and may be at least one di-valent metal ion
25 selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ; at least one tri-valent metal ion selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; or at least one tetra-valent metal ion selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} . Examples of cross-linking agents include di-valent metal ion in combination with a counter ion selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or hydrates thereof; tri-valent metal ion in
30 combination with a counter ion selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and tetra-valent metal ion in combination with a counter ion is selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof. In an embodiment, the at least one cross-linking agent may selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or $(NH_4)_4Ce(SO_4)_4$, and/or hydrates thereof.

- 35 The at least one ligand may selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine

(HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (Me₄Cyclam), and/or 2,2'-bipyridyl (BiPy). The at least one catalyst may be selected from copper (Cu) and iron (Fe). In an embodiment, the complex formed between the at least one ligand at the at least one catalyst may be selected from Cu/Me₆TREN, 5 Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam.

The reaction composition may further comprise at least one additive selected from at least one surfactants, and/or at least one polyquaternium compounds as specified above, including surfactants such as sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate 10 (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and polyquaternium compound such as polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

15 At least one buffer may be included and may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. Good's buffer include MES, PIPES, MOPS, HEPES, 20 CHES, CAPSO and/or CAPS.

The first separate liquid and/or the second separate liquid may further comprise at least one catalyst activator as specified above, including sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, 25 glucose with GO_x, and/or pyrogalllic acid. The at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation as specified above. In an embodiment, the at least one catalyst activator may be added to the first separate liquid and/or the second separate liquid prior to surface polymer formation. In an embodiment, the at least one catalyst activator may be added to 30 the first separate liquid.

The first separate liquid and/or the second separate liquid may further comprise a metal halide for increasing livingness of the surface polymer formation. Metal halides may be as specified above.

35 The first separate liquid may comprise at least one monomer. Suitable monomers may be those specified above.

In an aspect of the present disclosure, a method for forming surface polymers on a substrate is provided comprising: providing at least a portion of at least one polymerization initiator-modified substrate; bringing the at least a portion of the at least one polymerization initiator-modified substrate into contact with a reaction composition comprising: a first separate liquid; a second separate liquid; and a number of other separate liquids; wherein the first separate liquid comprises: at least one gelating substance; wherein the second separate liquid comprises: at least one cross-linking agent; and wherein the number of other separate liquids comprise one or more of: 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; optionally at least one additive; and optionally at least one buffer; wherein one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids further comprises at least one solvent; wherein one or more of the first separate liquid; the second separate liquid; and the number of other separate liquids are mixed prior to bringing the reaction composition in contact with the at least a portion of the at least one polymerization initiator-modified substrate; and forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate.

In an aspect of the present disclosure, a method for forming surface polymers on a substrate is provided comprising: providing at least a portion of at least one polymerization initiator-modified substrate; bringing the at least a portion of the at least one polymerization initiator-modified substrate into contact with a reaction composition comprising: a first separate liquid; and a second separate liquid; wherein the first separate liquid comprises: at least one gelating substance; and at least one solvent; wherein the second separate liquid comprises: at least one cross-linking agent; and at least one solvent; wherein the first separate liquid and/or the second separate liquid further comprises: 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; optionally at least one additive; and optionally at least one buffer; wherein each of the first separate liquid and the second component is applied to the at least a portion of the at least one polymerization initiator-modified substrate to form surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate; and forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate.

In the methods above, the at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel. The polymeric compound is as specified above, and may be such wherein the at least one polymeric compound has at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of

repeating unit. Suitable gelating substances include sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid.

In the methods disclosed above, the at least one cross-linking agent may be a di-, tri-, or tetra-valent metal ion in combination with a counter ion, and include at least one di-valent metal ion selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ; at least one tri-valent metal ion selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and at least one tetra-valent metal ion is selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} . Suitable examples include di-valent metal ion in combination with a counter ion selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or hydrates thereof; tri-valent metal ion in combination with a counter ion selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and tetra-valent metal ion in combination with a counter ion selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof. In an embodiment, the at least one cross-linking agent may be selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or $(NH_4)_4Ce(SO_4)_4$.

In the methods disclosed above, the at least one ligand may be selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me₆TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam), and/or 2,2'-bipyridyl (BiPy).

In the methods above, the at least one catalyst is selected from copper (Cu) and iron (Fe). In an embodiment the at least one ligand at the at least one catalyst may be selected from Cu/Me₆TREN, Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam.

In the method above, the at least one additive may be selected from at least one surfactants, and/or at least one polyquaternium compounds. The at least one surfactant may be selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and the least one polyquaternium compound may be selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

In the methods above, the buffer may be selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers. The Good's buffer may be selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS.

In the methods above, one or more of the first separate liquid, the second separate liquid and/or the number of other separate liquids may comprise at least one metal halide to increase livingness. Metal halides are as specified above.

In the methods above, the at least one catalyst activator may be selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x, and/or pyrogallol acid. As specified above, the at least one catalyst activator may activate the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation. In an embodiment, the at least one catalyst activator may be mixed with the complex formed between the at least one catalyst and the at least one ligand prior to applying the reaction composition to the at least a portion of the at least one polymerization initiator-modified substrate.

In the method described above, one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying. Spraying may be accomplished by a first spray unit, a second spray unit and a third spray unit, respectively.

In the method described above, one or more of the first separate liquid, the second separate liquid and/or the number of other separate liquids may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by dip coating. In the method described above, a combination of dip coating and spraying may be applied. Thus, one or more of the first separate liquid, the second separate liquid, and/or the number of other separate liquids may be applied by spraying, and one or more of the first separate liquid, the second separate liquid, and/or the number of other separate liquids may be applied by dip coating.

In the method described above, one or more of the first separate liquid, and the second separate liquid may be applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying. Spraying may be accomplished by a first spray unit, and a second spray unit, respectively. In the method described above, one or more of the first separate liquid; and the second separate liquid may be applied to the at least a portion

of the at least one polymerization initiator-modified substrate by dip coating. In the method described above, a combination of dip coating and spraying may be applied. In an embodiment, the first separate liquid may be applied by spraying, and the second separate liquid may be applied by dip coating. In an embodiment, the first separate liquid may be applied by dip coating, and the second separate liquid may be applied by spraying.

The inventors have surprisingly found that applying the reaction composition by spraying does not hamper the formation of surface polymers. It is widely recognized that the presence of oxygen inhibits and even terminates controlled radical polymerization reactions as both the active radical species and active propagating chain radical may be highly oxygen sensitive. Thus, there exists a technical prejudice for spraying reagents for surface polymer formation onto a substrate as moving such reagents through ambient air will definitely cause uptake of ambient oxygen by the reagents. The inventors believe that providing a gelating substance and forming a gel with a cross-linking agent, the formed gel may in fact increase the oxygen stability of the gelated reaction composition following spraying.

Some methods for preparing a substrate for surface polymer formation have been described in the art. A brief description of the usually used processes is given herein. However, it is to be understood that alternative processes may also be suited and workable within the context of the present disclosure.

To propagate surface polymer chains from the surface of the substrate, polymerization initiators may firstly be attached to a portion of the surface of interest for surface polymer formation. The attachment process is further described below. The procedures may in general apply to all types of substrates. It is to be understood that modifying a substrate with initiators will generally result in a multiplicity of initiators being attached to the surface of the substrate. The initiators may be attached to available surface modification sites on the substrate. Prior to attachment of polymerization initiators, the surface of the substrate may be cleaned using various techniques, including sonication in ammonia, ABC-clean A200, a solution of DI-water: NH_3 : H_2O_2 (5:1:1), acetone, and/or water. Following attachment of polymerization initiators, the substrate may be annealed at ambient conditions or at elevated temperatures.

If only specific areas of a material surface are to be exposed to polymerization initiators, the particular area(s) on the surface may be blocked, e.g., chemically or by using a foil, seal or cover, or etched, or masked, protected, or defined by lithographic patterning. Also, a non-polymerization initiator ("dummy" initiator, i.e. a substance that cannot initiate surface polymer propagation) may be used together with the polymerization initiator to "dilute" the attachment of polymerization initiators. "Dummy" initiators may be a substance which is

suited for further modification, e.g., attachment of a functional group or moiety. "Dummy" initiators may also be a substance adding certain chemical properties to the resulting substrate with surface polymers.

5 1-step silane grafting:

Surface modification substances (polymerization initiators and/or "dummy" initiators) may be attached to at least a surface or a portion of a surface in one step by silane grafting of trialkoxysilane with substituted benzyl/benzyl halide or substituted tertiary/tertiary halide groups. Silane grafting is normally performed by vapor deposition, in solution, by spray
10 coating, or paint-on coating.

1-step diazonium grafting:

Surface modification substances (polymerization initiators and/or "dummy" initiators) may be attached to at least a surface or a portion of a surface in one step by grafting aryl diazonium
15 salts with substituted benzyl groups/benzyl halide groups. The diazonium grafting is normally performed either by activating the aryl diazonium salt electrochemically or chemically or by spontaneous reaction. Diazonium salts can be pre-synthesized before being used for grafting reaction or formed in-situ during grafting reaction from a set of precursors added to the grafting reaction solution.

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2-step diazonium grafting:

Another route of initiator attachment is by a two-step process. The first step being grafting of an aryl diazonium salt that contains a nucleophilic group (alcohol or amine). In a second step, the polymerization initiator is attached by performing a nucleophilic acyl substitution
25 reaction with an acid or acid-chloride or -bromide containing a -C-X moiety (polymerization initiator moiety) with X being a halogen such as Cl or Br. A "dummy" initiator is attached by performing a nucleophilic acyl substitution reaction with an acid or acid-chloride or -bromide containing a -C-X moiety (non-polymerization initiator) with X being H or -CH₃. The nucleophilic group may be subjected to nucleophilic acyl substitution reaction with an acid or
30 acid-chloride or -bromide containing a -C-X moiety with X being Cl, Br, H or CH₃ to add polymerization initiator and/or "dummy" initiator", respectively. The polymerization initiator moiety of the surface modification may be, e.g., benzyl halide, secondary alkyl-halide and tertiary alkyl-halide, whereas the non-polymerization initiator may be the same with the halide being substituted by H or CH₃.

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2-step silane grafting:

The first step in the 2-step silane grafting procedure is grafting of a silane that contains a nucleophilic group (alcohol or amine). In the second step, the polymerization initiator is

attached by performing a nucleophilic acyl substitution reaction with an acid or acid-chloride or -bromide containing a -C-X moiety with X being a halogen such as Cl or Br. A dummy initiator is attached by performing a nucleophilic acyl substitution reaction with an acid or acid-chloride or -bromide containing a -C-X moiety with X being H or -CH₃.

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Other processes for attaching surface modification substances (polymerization initiators and/or non-polymerization initiators) may be applied. An example is the polymerization initiator *p*-(chloromethyl)phenyltrimethoxysilane (CPTMS) which may be attached using a vapor deposition method or a dipping method. Another example is the polymerization initiator *p*-(chloromethyl)phenyltrimethoxysilane (CPTMS) in combination with the "dummy" initiator (3-glycidyloxypropyl)trimethoxysilane (GPTMS), the latter which display an epoxy (epoxide) group suited for further modification by ring-opening of the epoxy (epoxide) group.

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The presence of polymerization initiators on the surface of the substrate may be "diluted" by the simultaneous presence of "dummy" initiators. The "dummy" initiator may be added in a certain percentage together with the polymerization initiator, thus, competing with the polymerization initiator about available attachment sites on the substrate surface. Suitable "dummy" initiators include such specified above where X is H or CH₃ and functional "dummy" initiators as GPTMS mentioned above. Dilution of the polymerization initiator with a "dummy" initiator may be used to adjust the density of the polymerization initiators on the surface of the substrate, thus, aiding in controlling density ("grafting density", i.e. the number of surface polymer chains per unit area of the substrate) of subsequently formed surface polymers. The density of the initiators (both polymerization initiators and non-polymerization/"dummy" initiators) influences the density of the subsequently formed surface polymer propagated from the polymerization initiators. As mentioned above, the density of polymerization initiators is intended to mean the number of polymerization initiators per unit area of the substrate. The density of polymerization initiators to non-polymerization ("dummy") initiators may be controlled by, e.g., co-grafting of the polymerization initiator and the non-polymerization initiator in varying percentages. Non-limiting examples of suitable percentage ratios (molecular-% (mol%) of polymerization initiator to non-polymerization initiator) may be in the range 100:0 (no non-polymerization initiator), 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90. The initiator density affects the morphology of surface polymers formed on the surface by "diluting" the availability of surface polymer propagating sites.

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35 Formation of surface polymers:

Surface polymer is then grown or formed from the surface-attached initiators upon contact with a reaction composition as defined herein.

Surface polymer thickness may be of any thickness. By way of example, e.g., from 1–1,000 nm. The thickness of surface polymer may depend on the specific intended application and may be from 1–500, 1–250 nm, 5–100 nm, 120–250 nm, 10–80 nm, or 10–30 nm thick, measured as the dry film thickness of collapsed surface polymer. The thickness refers to the dry film thickness of surface polymer formed. The dry film thickness is dependent on the density (anchoring points per area) of end bonded polymer chains and the length of the individual chains.

In certain embodiments, surface polymer layer can possess specific properties obtained through block co-polymers, random polymers, or binary mixed polymer, where two or more disparate monomers are used to grow the surface polymer in different surface polymer architectures. In such embodiments the individual components (different monomers) of block co-polymers, random polymers or binary mixed polymers can contribute different properties resulting in a surface polymer with a combination of desired properties.

Surface polymer layer can be applied or formed by repeating certain of the above steps to build up block co-polymers from chain end alkyl halide units of the formed surface polymer. The same or different monomers can be applied relative to the monomers used to form previous layers. Forming additional layers of surface polymer can be repeated multiple times to obtain a more complex or thicker surface polymer. Surface polymers can also be formed using two or more different monomers propagates from one type or different types of initiators thereby forming random or mixed surface polymers, respectively. Hence, two or more functional groups (e.g., halogen atoms, hydroxyl groups, or amine groups) can be incorporated, resulting in surface polymers with a unique set of combined properties, each of which is inherent from individual monomers.

For forming surface polymers, the substrate and the reaction composition are typically kept in contact with each other for a suitable period (residence time), sufficiently to form surface polymers essentially having an average dry film thickness within a desired range. The residence time may be as long as needed. Suited residence times include, but is not limited to, up to 24 hours, e.g., 2 seconds, 5 seconds, 10 seconds, 20 seconds, 30 seconds, 40 seconds, 50 seconds, 1 minute, 5 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. The surface polymer formation may take place at ambient temperature (room temperature), or with cooling or heating. Suitable temperatures include, but are not limited to, such from 5 °C up to 120 °C, such as from room temperature (approximately 20°C) to 120°C. Specific temperatures include, but are not limited to, 5°C 10°C, 15°C, 20°C, room/ambient temperature (approximately 20°C), 30°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, and 120°C. The residence time and temperature during the residence time

may suitably be computer controlled. Following formation of surface polymers, the substrate may be subjected to a rinsing and cleaning process, typically flushing with a suitable solvent, sonicating, and/or drying.

- 5 The properties of surface polymers formed on the surface of a substrate depend on the length of surface polymers (number of monomeric units in the chain(s)) formed on the substrate. This is also referred to as "thickness" of surface polymer layer. The achievable thickness depends on several factors, e.g., availability and density of polymerization initiators on the substrate, the monomer for surface polymer formation and reaction conditions such as the
10 rate of surface polymer formation.

Surface polymers as formed by the methods described herein are formed by the "grafting from" approach from the surface-attached initiators upon contact with a reaction composition as defined.

15

As used herein, the terms "a substrate" and "the substrate" are intended to include both a single substrate and a plurality of substrates in any form and shape.

- Surface polymers may suitably be formed on a portion of a substrate or on all surfaces
20 available on a substrate. Surface polymers may be formed on available surfaces at the same time (e.g., in the case of single-piece substrates) or on available surfaces in a sequential manner (e.g., in the case of reel-to-reel processing of fibers, threads, wires etc.).

- Apparatus for performing methods of the present disclosure, which may be suitable for
25 manufacturing and high throughput applications, are shown schematically in Figs. 5-7. Fig. 5 is a schematic representation of a spray apparatus 100 for forming gel 141 on substrates 140 for forming surface polymers 142 from grafting sites on the substrates, according to embodiments. Fig. 7 is a schematic representation of a spray apparatus 200 for forming gel 241 on a continuous foil or other continuous surface 240 for forming surface polymers 242
30 from grafting sites on the continuous surface, according to embodiments. Figs. 5 and 7 show polymerization initiator-modified substrates 140, 240 moving through systems 101, 201 for spray depositing first and second separate liquids from separate nozzles on to substrates 140, 240 forming a gel 141, 241 on the surfaces of the substrates. One or more of the first separate liquid and the second separate liquid include a monomer and an activated
35 catalyst/ligand complex for growing surface polymers 142, 242 on the polymerization initiator sites on the surfaces of the substrates. The substrates 140, 240 continue moving through the apparatus, coming next to systems 103, 203 for rinsing gel off the substrates, leaving behind surface polymers 142, 242 which have grown from polymerization initiator sites on

the substrates. Systems 101, 201 comprise holding tanks 110, 210 for the first separate liquid including the gelating substance, the holding tanks including mixing devices 114, 214 which may be mechanical stirrers, pumps for circulating the liquid, combinations of the same, etc. The first separate liquid is delivered to the substrates as a spray/mist 113, 213 via the plumbing 111, 211 with optional in-line filters 115, 215, and spray nozzles 112, 212. Systems 101, 201 further comprise holding tanks 120, 220 for the second separate liquid including cross-linking agent, the holding tanks including mixing devices 124, 224 which may be mechanical stirrers, pumps for circulating the liquid, combinations of the same, etc. The second separate liquid is delivered to the substrates as a spray/mist 123, 223 via the plumbing 121, 221 with optional in-line filters 125, 225, and spray nozzles 122, 222. The spray/mists for the first and second separate solutions may overlap at or above the substrate and/or may be applied to the substrate one after the other, in either order. Systems 103, 203 comprise holding tanks 130, 230 for the rinsing solution. The rinsing solution is delivered to the substrates as a spray 133, 233 via the plumbing 131, 231 and spray nozzles 132, 232. The spray systems 101, 201 and rinsing systems 103, 203 may be pressurized, can include control systems, etc. Fig. 6 is a schematic representation of a spray apparatus for forming thicker gel on substrates for forming surface polymers from grafting sites on the substrate, according to embodiments. Thicker gel layers 141 on the substrates 140 can be provided by the addition of a system 102 for further spray depositing first and second separate liquids from separate nozzles on to substrates. The process illustrated in Fig. 6, is as for Fig. 5 with the addition of a second spray deposition system – Fig. 6 having two identical spray deposition systems 101 and 102. If needed, further spray deposition systems may be added. Even though Fig. 6 shows a conveyor specifically for substrates, the conveyor may be replaced by a reel-to-reel system for moving a continuous substrate/foil such as shown in Fig. 7.

Figs. 5 & 7 show apparatus 100, 200 for forming surface polymers 142, 242 on polymerization initiator-modified substrates 140, 240, wherein the apparatus may comprise: a first system 101 for spray depositing, from separate spray nozzles 112, 132 and 212, 222, a first separate liquid 113, 213 including a gelating substance and a second separate liquid 123, 223 including a cross-linking agent on the substrates, wherein one or more of the first separate liquid and the second separate liquid include a monomer and an activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form a gel 141, 241 on the substrates; and a second system 103, 203 for rinsing the gel off the substrates leaving behind surface polymers which have grown from polymerization initiator sites on the substrates. The apparatus may further comprising, as shown in Fig. 6, a third system 102 for spray depositing, from separate spray nozzles, the first separate liquid 163 including the gelating substance and the second separate liquid 162 including the cross-linking agent on

the substrates, wherein one or more of the first separate liquid and the second separate liquid include the monomer and the activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form an increased thickness of the gel 141 on the substrates 140. The apparatus may further comprise a conveyor belt for moving the substrates through one or more of the first, second and third systems or a reel-to-reel system for moving a continuous substrate through one or more of the first, second and third systems, wherein the continuous foil comprises a multiplicity of the substrates.

Figs. 5-7 show processing of substrates in the horizontal plane, however the substrates may instead be processed in a vertical plane – examples of processing in the vertical plane are provided in the Examples.

In some embodiments, it may be desirable to configure an apparatus to combine bath coating of one of the first or second separate liquids with spray coating of the other. Furthermore, in some embodiments it may be desirable to configure an apparatus to provide spray coating of the reaction composition in not just two separate liquids, but in three or more separate liquids.

Aspects and embodiments of the disclosure are further illustrated by the following, non-limiting examples.

Examples

List of materials used in the Examples:

Throughout the examples, DI-water refers to tap water deionized using the deionizing equipment Silhorko with M22-F softening plant, RO B1-2 Reverse Osmosis plant and Silex 2BS mixed bed plant. The DI-water has a conductivity of $<0.5 \mu\text{S}/\text{cm}$, indicating an ultrapure quality with very low presence of ions. The quality of the DI-water is confirmed at least weekly. DI-water holds a conductivity of less than $0.5 \mu\text{S}/\text{cm}$, indicating very low presence of ions, below $0.1 \text{ mg}/\text{L}$.

Silicon wafer substrates, Test CZ-Si wafer, 4 inch, thickness = $525 \pm 25 \mu\text{m}$, (100), p-type (Boron), were purchased from MicroChemicals GmbH ($r = 5.08 \text{ cm}$) and cut into 1/4th of a wafer.

Ammonia was purchased from Chemsolute, in a grade 25% p. a.

Acetone was purchased from Chemsolute as a >99% grade.

Dimethylsulfoxide (DMSO) ($\geq 99 \%$) was purchased from Tokyo Chemical Industry (lot no. YVQCL-KF).

Dichloromethane (DCM) (99.9 %) was purchased from ChemSolute (batch no. P3F019273F).

ABC clean A200 was purchased from ABC-Clean ApS.

p-(chloromethyl)phenyltrimethoxysilane (CPTMS) (95%) was purchased from Gelest.

tris[2-(dimethylamino)ethyl]amine (Me₆TREN) ($\geq 98\%$) was purchased from Alfa Aesar.

5 Sodium alginate (NaAlg) (lot no. SHBL1627) was purchased from Sigma Aldrich.

CaCl₂ ($\geq 93\%$) was purchased from Sigma Aldrich.

Methyl methacrylate (MMA) (99 %, 30 ppm MEHQ inhibitor) was purchased from Sigma Aldrich (lot no. STBK8834).

10 Sodium dodecyl sulfate (SDS) (99 %) was purchased from Sigma Aldrich (lot no. MKCQ6608).

Sodium ascorbate (NaAsc) ($\geq 98\%$) was purchased from Sigma Aldrich (lot no. SLCP3829).

Glycidyl methacrylate (GMA) ($\geq 97\%$) was purchased from Sigma Aldrich (lot no. STBL1520).

15 Styrene (ST) ($\geq 99\%$) was purchased from Sigma Aldrich (lot no. STBJ0264).

Pentafluorostyrene (PFS) ($\geq 98\%$) was purchased from Tokyo Chemical Industry (lot no. 2N73A-GO).

Xanthan gum (XG) (food grade) was purchased from Doves Farm.

FeCl₃ ($\geq 99\%$) was purchased from ChemSolute (Batch no. 27.2131106).

20 Triton X-100 (99 %, max 1% water) was purchased from ChemSolute (batch no. 5CB86A58).

Diocetyl sodium sulfosuccinate (DOSS) ($\geq 97\%$) was purchased from Aldrich Chemistry (Lot no. BCCB4676).

Polyquaternium-D16 (PQ-D16) was purchased from Sigma Aldrich (Lot no. BCCD9913).

25 Polyquaternium-10 (PQ-10) was purchased from Sigma Aldrich (Lot no. MKBH7404V).

List of equipment used in the Examples:

"Big sonicator" refers to an ULTRASONIC CLEANER PROCLEAN 28.0 from Ulsonix (40 kHz, 480 W).

30 "Sonicator" refers to a Bandelin Sonorex Super RK100 sonicator (35 kHz ultrasound frequency, 80 W nominal ultrasonic power).

"Vacuum oven" refers to a Faithful Vacuum Drying Oven-DZ-BCII.

"Oven" refers to a Binder model FD 56.

35 Ellipsometry is measured on a J.A. Woollam M-2000 Ellipsometer. This instrument was set to measure 10 points on each substrate. Each point was analyzed using a Cauchy model providing a thickness and a Mean Square Error (MSE), the latter referring to the goodness of the fit. Thicknesses are thus given as the average of all measured points on the substrate. Standard deviation are the standard deviation based on the entirety of the measured

thicknesses. As such the standard deviation is an estimate of the homogeneity of a surface polymers formed.

5 Infrared Reflection Absorption Spectroscopy (IRRAS) was measured on a Nicolet 6700 FTIR Spectrometer (Thermo Fisher Scientific, Denmark), equipped with a liquid nitrogen-cooled narrow-band mercury cadmium telluride (MCT/A) detector. The spectral resolution was 4 cm^{-1} , and 100 spectra were recorded and averaged for each measurement. The spectra were recorded in dry air, at room temperature. The substrates were irradiated with p-polarized light, at an angle of approximately 65° . The spectra were baseline corrected using the OMNIC 8.2 software.

10 Water contact angles (WCA) are measured on a Krüss Mobile Surface Analyzer. In 5 separate points, the contact angle of a DI-water and a CH_2I_2 drop is measured. Using the software ADVANCED v. 1.14, the surface free energy (SFE) can be calculated. The SFE indicates the maximum surface tension of a liquid that wets a solid surface, under ideal conditions. Accordingly, a material with a high SFE is easier to wet than a material with a lower SFE, and low SFE materials will generally exhibit higher water contact angles than those materials with a higher SFE.

Example 1

Pre-cleaning of silicon wafers

20 Below a procedure for pre-cleaning of substrates for surface polymer formation is described. The total number of substrates subjected to pre-cleaning may vary in the subsequent examples.

Silicon wafer substrates were cleaned prior to further processing using the following method:

25 Racks holding the substrates were placed in a 15% aqueous solution of ammonia and sonicated for 10 minutes. Then, the substrates were flushed with DI-water and sonicated in DI-water for 10 minutes using a big sonicator. Thereafter, the racks holding the substrates were transferred to a 5% solution of ABC clean A200 and sonicated for 10 minutes with previously described equipment. This step was followed by flushing the substrates in DI-water and sonicating the substrates in DI-water for 5 minutes with previously described equipment. Finally, the substrates were flushed with acetone and left to dry at room temperature.

Example 2

35 Chemical vapor deposition of (*p*-chloromethyl)phenyltrimethoxysilane (polymerization initiator)

Silicon wafer (Si) substrates, pre-cleaned as described in Example 1, were used for surface modification with CPTMS polymerization initiators using the below-described chemical vapor

deposition method.

The substrates were placed in a rack and placed in a vacuum oven with 16 vials of 100 μ L CPTMS (polymerization initiator liquid) at approximately 45°C for 150 minutes. The gauge pressure was lowered to -1.0 bar, whereby the CPTMS evaporated, and the substrates were left in the vapor for 150 minutes. Thereafter, the substrates were removed and placed in an oven at approximately 80°C for 5 minutes to anneal the formed silane layer. The surface modification was verified using WCA. The surface free energy (SFE) for both blank Si substrates and CPTMS-modified Si substrates are provided in Table 2. Compared to the blank Si substrate the CPTMS-modified substrate displays lowered SFE, indicative of an increased hydrophobicity caused by the successful attachment of the organic CPTMS layer.

Table 2. Surface free energy of untreated (blank) and CPTMS-modified surface substrates.

	Blank	CPTMS
SFE (mN/m)	51 $\pm$ 3	45 $\pm$ 2

Example 3

Inverted vial tests for evaluating gel-forming properties of combined gelating substance and cross-linking agent.

This example provides a qualitative method for evaluating the gelation of a gelating substance in combination with a cross-linking agent. In this method, a solution comprising a cross-linking agent and a solvent or mixture of solvents was added to a vial holding a solution of a gelating substance and the vial was subsequently sealed with a cap. After mixing, the vial was inverted, placing the lid downwards, and the mixture of gelating substance(s) and cross-linking agent(s) were evaluated visually at different time intervals. In some cases, the time between sealing the vial and inverting the vial was varied to estimate time of gelation, defined as the time from mixing to the time at which a gel was fully formed.

Observations regarding reaction (formation of gel) of the mixture of the gelating substance and the cross-linking were made and included: no apparent movement of the formed gel, and resistance towards deformation of the gel in the vial as a function of time and inversion. Fulfilment of such criteria was taken as an indicator of a successfully formed gel. Observations such as phase separation (separation of gelating substance and cross-linking agent), low retention of solvent, or the combined mixture flowing without resistance, optionally appearing to shear easily, were taken as indicators of poor or little gelation.

The desired gel properties may, however, vary from application to application. As an example, if a reaction composition is to be applied to a vertical substrate, the gel should provide sufficient surface adhesion, and the gel should form quickly, e.g., within seconds, during the spraying of the first separate liquid comprising the gelating substance and the second separate liquid comprising the cross-linking agent. On the other hand, if the reaction composition is to be applied to a substrate lying flat, the gelated reaction composition may not need to possess as good film forming and adhesive properties as when applied to a vertical substrate, and other gel properties may be favored, e.g., increased mechanical stability enabling handling and transfer of the substrate while the surface polymer formation is taking place within the gelated reaction composition.

The following gelating substances were tested: sodium alginate (NaAlg) (18.4 g/L), xanthan gum (XG) (10 g/L), and a combination of NaAlg and XG in a 1:1 (V/V) ratio. The following cross-linking agents were tested: FeCl₃ or CaCl₂. The inverted vial test as described above was employed, and the results outlined in Table 3.

1 mL of the gelating substance to be tested was placed in an 8 mL screwcap vial (Table 3 and Fig. 8 a.-f.). The vials were then inverted (Table 3 and Fig. 8 g.-l.) to demonstrate the low viscosity of the gelating substance, which flows to the lower end of the inverted vials prior to forming a gel with the cross-linking agent. Before addition of cross-linking agent, the vials were un-inverted and 1 mL of the cross-linking agent (0.1 M in DI-water) was added, the vials were gently shaken to mix (Table 3 and Fig. 9 a.-f.), and after standing for 3 minutes, the vials were inverted again. The inverted vials were visually inspected (Table 3 and Fig. 9 g.-l.).

Table 3. Tested combinations of gel-forming substances and cross-linking agents.

Vial number:	a/g	b/h	c/i	d/j	e/k	f/k
Gelating substance	XG	XG	NaAlg	NaAlg	XG/NaAlg (1:1 by volume)	XG/NaAlg (1:1 by volume)
Metal ion of cross-linking agent	Fe ³⁺	Ca ²⁺	Fe ³⁺	Ca ²⁺	Fe ³⁺	Ca ²⁺

As expected, before addition of cross-linking agent all the gelating substances fell down upon vial inversion, see Fig. 8 g.-l.. After addition of cross-linking agent, all combinations listed in

Table 3 except for the combination of XG and CaCl_2 (vial b/h, Fig. 9 h.) results in the gels staying in place upon inverting the vials. XG is believed primarily to form intramolecular cross-links upon cross-linking with Ca^{2+} ion, instead of forming intermolecular cross-links, thus, leading to a poorer gel formation. Surprisingly, combining the XG with NaAlg results in a gel that remains in place upon vial inversion (Fig. 9 l.). The inventors hypothesize that the addition of NaAlg allows for intermolecular cross-linking between both gelating substances (XG and NaAlg) or a purely NaAlg cross-linked gel with XG acting as an additive rather than a gelating substance. Either case allows for a more versatile gel structure.

10 **General Method Example**

General description of the method for forming surface polymers on horizontally oriented substrates and vertically oriented substrates.

Fig. 10 and Fig. 11 schematically and generally show the spray-on application described in this example. The spray-on method may be applied on horizontally oriented substrates (Fig. 10) or vertically oriented substrates (Fig. 11). As can be seen from Fig. 10, the substrate 340 is subjected to a spraying process, where spraying device 1 360 (holding a first separate liquid comprising monomer, catalyst/ligand complex, solvent, optionally additive, and gelating substance) is used to generate a mist 362 of the first separate liquid and spraying device 361 (holding a second separate liquid comprising cross-linking agent and solvent) is used to generate a mist 363 of the second separate liquid. The two mists combine on and above the surface of the substrate 340 – the combination of the gelating substance and cross-linking agent forming a gel 341 on the substrate 340. Surface polymers form from the initiation sites on the substrate where the substrate is covered by gel 341. Growth of the surface polymers continues for a timed period, after which the growth is stopped by removing the gel 341 from the substrate 340 by rinsing with a rinsing solution 365 (e.g. DI-water) from a rinsing bottle 364, leaving surface polymers 342 attached to the substrate 340. The formation of surface polymers on vertical substrates is demonstrated in Examples 8 and 9. The spray-on method on vertically orientated substrates is shown schematically and generally in Fig. 11. The substrate 440 is adhered to a vertical substrate mount 470 using a double-sided adhesive tape 471. Spraying device 460 (holding a first separate liquid comprising monomer, catalyst/ligand complex, solvent, optionally additive and gelating substance) is used to generate a mist 462 of the first separate liquid and spraying device 461 (holding a second separate liquid comprising cross-linking agent and solvent) is used to generate a mist 363 of the second separate liquid. The two mists combine on and above the surface of substrate 440 – the combination of the gelating substance and cross-linking agent forming a gel 441 on the substrate 440. Surface polymers form from the initiation sites on the substrate where the substrate is covered by gel 441. Growth of the surface polymers continues for a

timed period, after which the growth is stopped by removing the gel 441 from the substrate 440 by rinsing with a rinsing solution 465 (e.g. DI-water) from a rinsing bottle 464, leaving surface polymers 442 attached to the substrate 440. The formation of surface polymers on vertical substrates is demonstrated in Example 4.

5

Example 4

Poly(methyl methacrylate) surface polymerization rate experiment using the spray-on method for surface polymer (polymer brush) formation on horizontally placed surfaces.

10 NaAlg solution (198.2 mL, 18.4 g/L, aq.), MMA (1.4 M), SDS (207 mg), and catalyst solution (0.14 mM) comprising Me₆TREN (15 µL), DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) were added to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl₂ (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

15

To activate the catalyst/ligand complex for surface polymer formation, NaAsc dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM), the contents of which were again mixed by shaking Spraying Vessel 1 and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.

20

The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto horizontally placed polymerization initiator-modified substrates (pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the 10 substrates when the mist from Spraying Vessel 1 and Spraying Vessel 2 combined. The spraying was done as quickly and
25 evenly as possible on the 10 substrates, until the 10 substrates were covered with gelated reaction composition. By spraying 2 substrates with DI-water at times 5, 10, 20, and 40 minutes, the gel was removed from 2 substrates at a time to stop the surface polymer formation. The rinsed substrates were placed in a water bath and sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5 minutes, and finally left to air dry at
30 ambient conditions.

After cleaning and drying the surface polymerized substrates, the dry film thicknesses of the formed (collapsed) polymer brushes were analyzed using ellipsometry. For each substrate, the average dry film thicknesses (in nm) of the surface polymers were reported against time
35 (in minutes) at which the formed gel was removed. In this way, the rate of surface polymer formation was evaluated as a function of time. From here, the "rate" of a given reaction composition is referred to as the thickness (in nm) of surface polymers formed as a function of time. The obtained surface polymer thicknesses (average of 2 substrates for each

polymerization time, although it was noted that only 1 substrate was recovered from the 40 minutes polymerization time) were determined using spectroscopic ellipsometry and are reported as a function of time in Table 4.

5 Table 4. Polymerization time and corresponding thickness for poly(methyl methacrylate) surface polymer formed on Si wafer substrates using the spray-on surface polymerization method.

Polymerization time (min)	5	10	20	40
Surface polymer thickness (nm)	12 ± 0.6	25 ± 1	41 ± 6	57 ± 13

10 Impressively, the surface polymer forming reaction proceeds in a linear fashion in the initial 20 minutes. This is compatible with the surface polymer formation being a living radical polymerization with a rate of 2 nm surface polymer per minute. Considering that the gelated components of the reaction composition could be expected to reduce reactant diffusion and mobility and given the fact that the reaction composition of Spraying Vessel 1 was first activated for surface polymer formation and subsequently misted through ambient air just 5

15 minutes prior to terminating surface polymer formation (first measurement after 5 minutes), the actual formation of a surface polymers in a linear fashion at 2 nm pr minute is both promising and surprising. Due to the spray-on technique (mist of small droplets), the components of the reaction composition are mixed with much more ambient oxygen than would have been the case if the surface polymerization was performed in solution instead.

20 Surprisingly, the presence of more ambient oxygen within the atomized droplets of solution does not appear to hamper the surface polymer formation significantly. Thus, the formation of a gel on the substrate appears to be both a robust and versatile method for forming surface polymers on a substrate. Fig. 12 a. shows exemplary photographs of wafer substrates covered with the gel formed by spraying with gelating substance and cross-linking agent. Fig.

25 12 b. shows exemplary photographs of wafer substrates after rinsing the gel off with DI-water. Notice how the rinsing with DI-water reveals the shiny Si substrate, with the formed surface polymers (note: the white reflection seen in Fig. 12b. is the scientist taking the photograph). This simple rinsing method illustrates the versatility and scalability of the spray-on method for surface polymer formation.

30

Example 5

Monomer screening for surface polymer (polymer brush) formation using spray-on method, on horizontally placed substrates.

The monomers investigated were MMA, GMA, ST, and PFS. It is well-known that the monomers all have different reactivities in polymerizations. They may, thus, be useful in different applications, depending on the desired reactivity, surface properties imparted, and thickness of surface polymers obtained. Thus, variation in yielded surface polymer thicknesses from different monomers is to be expected.

NaAlg (96.8 mL, 18.4 g/L, aq.), monomer (MMA, GMA, ST and PFS, respectively), SDS (3.5 mM), and catalyst solution (0.14mM) comprising Me₆TREN (15 µL), DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) was added to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl₂ (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

To activate the catalyst/ligand complex for surface polymer formation, NaAsc dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM), the contents of which were again mixed by shaking the device and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.

The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto horizontally placed polymerization initiator-modified substrates (2 Si wafers for each monomer, pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the on the substrates when the mist from Spraying Vessel 1 and Spraying Vessel 2 combined. The spraying was done as quickly and evenly as possible on the 2 substrates, until the 2 substrates were covered with gelated reaction composition. By spraying the 2 substrates with DI-water after 60 minutes, the gel was removed, and the polymerization stopped. The rinsed substrates were placed in a water bath and sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5 minutes.

After cleaning and drying the surface polymerized substrates, the dry film thicknesses of the formed (collapsed) surface polymers were analyzed using ellipsometry. It is noted that substrates from the GMA polymerization were additionally cleaned in DMSO then DCM. For the obtained surface polymer thicknesses (average on 2 substrates per monomer for each polymerization time), measurements with MSE values > 100 were considered as outliers and not included in the reported average thickness. It was noted that for the MMA monomer screening, only 1 substrate was recovered. The surface polymer thicknesses were determined using spectroscopic ellipsometry and are reported in Table 5.

Table 5. Experimental conditions as well as Surface Free Energy and the thickness of the surface polymers (nm) obtained for each experiment. PMMA = poly(methyl methacrylate), PGMA = poly(glycidyl methacrylate), PST = poly(styrene), and PPFS = poly(pentafluorostyrene).

5

	Vessel 1 total volume (mL)	Catalyst solution (mM)	Monomer concentration (M)	Surface free energy (mN/M)	Thickness of surface polymers (nm)
PMMA	241	0.14	1.4	49 ± 1	56 ± 10
PGMA	118	0.14	1.4	56 ± 2	71 ± 40
PST	110	0.28	0.32	45 ± 1	20 ± 2
PPFS	110	0.28	0.17	25 ± 0.2	7 ± 1

Surprisingly, all monomers tested resulted in a surface modification (formation of surface polymers) as seen from the surface free energy compared to that of the polymerization initiator-modified substrates, as well as the reported (collapsed) surface polymer thickness.

10 The trend of the surface free energy matches the expectations, since the more polar surface polymers, poly(glycidyl methacrylate) (PGMA) and poly(methyl methacrylate) (PMMA), present relatively higher surface free energies than that of poly(styrene) (PST), and especially poly(pentafluorostyrene) (PPFS), which has the lowest surface free energy, in line with expectations for its fluorinated structure. Impressively, the styrenic monomers (ST and

15 PFS) produce surface films with high uniformity (cf. low standard deviations). The homogeneity of the surface polymers formed from the styrenic monomers (ST, PFS) is surprising, since the monomers are not fully soluble in the aqueous mixture in Spraying Vessel 1. This finding underlines the applicability of reaction compositions and the methods described herein to form smooth and homogeneous surface polymers, even with monomers

20 that are not fully soluble in the used solvents. It furthermore underlines the positive impact of using surfactants and/or emulsifiers to improve mixing of the monomer(s) in the separate liquids.

Example 6

25 Surface polymer (polymer brush) formation using a combination of gelating substances on horizontally placed substrates.

A 1:1 mix of gelating substance (NaAlg (18.4 g/L) and XG (10 g/L), total volume 96.8 mL), MMA (1.4 M), SDS (3.5 mM), and catalyst solution (0.14mM) comprising Me₆TREN (15 µL),

30 DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) was added

to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl_2 (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

- 5 To activate the catalyst/ligand complex for surface polymer formation, NaAsc dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM), the contents of which were again mixed by shaking the device and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.
- 10 The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto horizontally placed polymerization initiator-modified substrates (pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the on the 2 substrates when the mist from Spraying Vessel 1 and Spraying Vessel 2 combined. The spraying was done as quickly and evenly as possible on the 2 substrates for each reaction composition, until the substrates
- 15 were covered with gelated reaction composition. By spraying the substrates with DI-water at a polymerization time of 20 minutes, the gel was removed from the substrates to stop the surface polymer (polymer brush) formation. The rinsed substrates were placed in a water bath and sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5 minutes, and finally dried under ambient conditions.
- 20 After cleaning and drying the surface polymerized substrates, the dry film thicknesses of the formed (collapsed) surface polymers were analyzed using ellipsometry. The obtained surface polymer thicknesses (average of 2 substrates) were determined using spectroscopic ellipsometry and are found to be 41 ± 5 nm.
- 25 As shown in Example 3, the XG/ Ca^{2+} combination does not produce a significant gel structure, whereas a combination of NaAlg and XG cross-linked with Ca^{2+} was shown to result in a viable gel. The option to add a chelating, but non-gelating (when using Ca^{2+} as cross-linking agent) gelating substance (polymer) points to the possibility of modulating mechanical properties
- 30 such as stiffness of the gel by combining a gelating substance with a certain amount of not gel-forming gelating substance (polymer), with the cross-linking agent used. Hereby, the chelating, but not gelating, gelating substance (polymer) serves the role of making some of the cross-linking agent unavailable for the formation of intermolecular cross-links, resulting in different gel properties, and thus the option of fine-tuning mechanical gel properties to
- 35 specific application needs. Surprisingly, the XG/NaAlg gelating substance cross-linked via Ca^{2+} still adhered sufficiently to the substrate and formed a gel with sufficient mechanical stability to produce surface polymers. The thickness of the surface polymers formed using NaAlg/XG cross-linked with Ca^{2+} is comparable to the thickness obtained with NaAlg cross-

linked with Ca^{2+} (see Example 5) despite the supposedly different degree of intermolecular cross-links between NaAlg polymer chains, and intra- and intermolecular cross-links of XG and NaAlg polymer chains.

5 **Example 7**

Poly(methyl methacrylate) surface polymer (polymer brush) formation using the spray-on method with additives on horizontal surfaces.

NaAlg (96.8 mL, 18.4 g/L, aq.), MMA (1.4 M), additive (one of: SDS, Triton X-100, or DOSS),
10 and catalyst solution (0.14mM) comprising Me₆TREN (15 μL), DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) were added to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl_2 (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

15

To activate the catalyst/ligand complex for surface polymer formation, NaAsc dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM), the contents of which were again mixed by shaking the device and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.

20

The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto horizontally placed polymerization initiator-modified substrates (2 Si wafer substrate, pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the on the 2 substrates when the mist from Spraying Vessel 1 and Spraying Vessel 2 combined. The
25 spraying was done as quickly and evenly as possible on the 2 substrates, until the substrates were covered with gelated reaction composition. By spraying the substrates with deionized water at a polymerization time of 20 minutes, the gel was removed from 2 substrates at a time to stop the surface polymer formation. The rinsed substrates were placed in a water bath and sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5
30 minutes.

After cleaning and drying the surface polymerized substrates, the dry film thicknesses of the formed (collapsed) surface polymers were analyzed using ellipsometry. The obtained surface polymer thicknesses (average on 2 substrates) were determined using spectroscopic ellip-
35 sometry and reported in Table 6.

Table 6. Tested surfactants and the measured polymer brush thickness (collapsed) as determined by ellipsometry.

	Surfactant	Thickness of surface polymers (nm)
No surfactant	-	35 ± 3
SDS*	207 mg (200 mL scale)	41 ± 6
Triton X-100	0.1 mL	43 ± 4
DOSS	97 mg	37 ± 11

*Results reproduced from Example 4.

5 The use of additives such as surfactants (SDS, Triton X-100, or DOSS), aid the mixing of the solution in Spraying Vessel 1, the spraying of the composition in Spraying vessel 1, and the wetting of the surface upon spraying. As an effect of that, the inventors hypothesized better dispersion/mixing of the monomers in the aqueous phase in Spraying Vessel 1, as well as improved misting of the solution in Spraying Vessel 1. Surprisingly, the use of any of the
10 tested surfactants aided the misting of the solution in Spraying Vessel 1 and wetting of the surface upon spraying. Impressively, adding surfactants to the reaction composition does not prevent formation of surface polymers, as could be expected from a blocking layer of surfactants on the substrate surface. Of the three surfactants tested, Triton X-100 performed the best, with better misting and wetting (as observed by the lower average standard
15 deviation), but this could be due to less optimization of the amounts for SDS and DOSS.

Example 8

Poly(methyl methacrylate) surface polymer (polymer brush) formation using the spray-on method with additives on vertical surfaces.

20 NaAlg (96.8 mL, 18.4 g/L, aq.), MMA (1.4 M), additive (SDS, or PQ-D16, or PQ-10), and catalyst solution (0.14mM) comprising Me₆TREN (15 µL), DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source were added to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl₂
25 (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

To activate the catalyst/ligand complex for surface polymer formation, sodium ascorbate dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM),
30 the contents of which were again mixed by shaking the device and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.

The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto vertically placed polymerization initiator-modified substrates (polymerization initiator-modified Si wafer substrates, pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the on the 2 substrates when the mist from Spraying Vessel 1 and
5 Spraying Vessel 2 combined. The spraying was done as quickly and evenly as possible on the 2 substrates, until the substrates were covered with gelated reaction composition. By spraying the substrates with deionized water at a polymerization time of 20 minutes (for SDS as additive, a 40 minutes polymerization time), the gel was removed from 2 substrates at a time to stop the surface polymer. The rinsed substrates were placed in a water bath and
10 sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5 minutes.

After cleaning and drying the surface polymerized substrates, the dry film thicknesses of the formed (collapsed) surface polymers were analyzed using ellipsometry. The obtained surface polymer thicknesses (average of 2 substrates for PQ-D16 and PQ-10 additives and 3
15 substrates for the SDS additive) were determined using spectroscopic ellipsometry and reported in Table 7.

Table 7. Tested additives or surfactants and the measured polymer brush thickness (collapsed) as determined by ellipsometry.

Additive Name	Additive (mg)	Thickness (nm)
SDS	97 mg	19 ± 20
PQ 16D	0.1 mL	27 ± 9
PQ 10	98 mg	59 ± 25

20 While surfactant (SDS in this example) provides improved mixing and misting of the liquid in Spraying Vessel 1, and improved substrate wetting during the spraying process (as described in previous examples), the film-forming capability of the sprayed compositions with surfactant (SDS) may be less optimal for reliable gel formation on vertical substrates, at least
25 when used in this concentration. Due to the vertically placed surfaces the formed gels slid off at certain places. This resulted in varying contact exposure of the polymerization initiator-modified substrate to the surface polymer-forming components of the reaction composition within the applied gel and led to large in the measured thicknesses of the surface polymers, with large standard deviation of the thickness of the formed surface polymers (19 ± 20 nm).
30 The inventors hypothesized that by using polyquaterniums in the reaction compositions and methods presented herein, the film-forming ability of the gels could be improved, enabling better adhesion of the gel to the vertical substrates, ultimately leading to enhanced surface polymer uniformity on vertical surfaces. Accordingly, it was found that employing poly-quaterniums led to improved film-forming ability of the reaction compositions, and thereby

the gel stayed on the substrate for the duration of surface polymerization as seen in Fig. 13a. (with polyquaternium-D16 as additive) and in Fig. 13b. (with polyquaternium-10 as additive), resulting in thicker surface polymers formed, and a lower relative average standard deviation of surface polymer thickness. The wetting and misting of the compositions with polyquaternium could be improved using a surfactant with the polyquaternium compounds as shown in Fig. 14a. (Triton-X100 and polyquaternium-D16) and Fig. 14b. (Triton-X100 and polyquaternium-10) (see Example 9).

Example 9

Poly(methyl methacrylate) surface polymer (polymer brush) formation using the spray-on method with multiple additives on vertical surfaces.

NaAlg (96.8 mL, 18.4 g/L, aq.), MMA (1.4 M), combined additives (PQ-D16/Triton X-100 or PQ-10/Triton X-100, 0.1 mL Triton X-100 used), and catalyst solution (0.14mM) comprising Me₆TREN (15 µL), DI-water (3.2 mL), and Cu(II) (324 mg/L, obtained from a solid copper source) was added to Spraying Vessel 1 (manually pumped spraying device) and mixed by shaking the vessel for 30 seconds. A solution of CaCl₂ (150 mL, 0.1 M, in EtOH) was added to Spraying Vessel 2 (manually pumped spraying device).

To activate the catalyst/ligand complex for surface polymer formation, NaAsc dissolved in DI-water was added to Spraying Vessel 1 (yielding a final solution of 40 mM), the contents of which were again mixed by shaking the device and left to stand for 5 minutes to fully activate the catalyst/ligand complex and, thus, obtain the reaction composition.

The contents of Spraying Vessel 1 and Spraying Vessel 2 were misted onto vertically placed polymerization initiator-modified substrates (2 Si wafers, pre-cleaned and CPTMS-modified according to Example 1 and 2). A gel was observed to form on the on the 2 substrates when the mist from Spraying Vessel 1 and Spraying Vessel 2 combined. The spraying was done as quickly and evenly as possible on the 2 substrates, until the substrates were covered with gelated reaction composition. By spraying the substrates with DI-water at a polymerization time of 20 minutes, the gel was removed from 2 substrates at a time to stop the surface polymer formation. The rinsed substrates were placed in a water bath and sonicated for 5 minutes, then transferred to an acetone bath and sonicated for 5 minutes, and finally the substrates were air dried under ambient conditions.

After cleaning and drying the surface polymerized substrates, the average dry film thicknesses of the formed (collapsed) surface polymers were analyzed using ellipsometry. The obtained surface polymer thicknesses (average on 2 substrates, the reported

thickness for the substrates produced using PQ-10 was only based on 1 substrate) were determined using spectroscopic ellipsometry and are reported as a function of time in Table 8.

5 Table 8. Tested additives and the measured surface polymer (polymer brush) thickness (collapsed) as determined by ellipsometry.

	Triton-X100	Additive PQ	Thickness (nm)
PQ-16D	0.1 mL	0.1 mL	35 ± 11
PQ-10	0.1 mL	103 mg	26 ± 9

Surprisingly, the inventors found that by combining additives such as surfactants (Triton X-100 in this Example) and polyquaterniums (PQ-D16 or PQ-10 in this Example), improved mixing, improved misting of the liquid in Spraying Vessel 1, improved wetting of the surface upon spraying, and improved film-forming ability could be achieved. Improved film forming ability led to formation of stable gels on vertical substrates, leading to the ability to form satisfactory polymer brushes on vertical surfaces, showing the strong versatility of the spraying method for polymer brush formation, and unlocking any substrate orientation, even vertical surfaces. The use of surfactant, in this example Triton X-100, led to improved mixing of components in Spraying vessel 1, improved misting and spraying, and ultimately, to much more even and smooth gels being applied to the substrates, see Fig. 14a. (with Triton-X100 and polyquaternium-D16) and Fig. 14b. (with Triton-X100 and polyquaternium-10). Furthermore, the polymerization forming ability does not seem to be adversely affected by adding Triton X-100 in combination with either of the polyquaterniums, compared to the results in Example 8. In Fig. 15a.-15e., the gel quality for compositions with either SDS (Fig. 15a.), polyquaternium-10 (Fig. 15b.) or polyquaternium-D16 (Fig. 15c.), or a combination of Triton-X100 and either of polyquaternium-10 (Fig. 15d.) or polyquaternium-D16 (Fig. 15e.) is shown. Evidently using just SDS leads to less film-forming ability on vertically oriented substrates, with the gel sliding off, but SDS can be used on horizontally oriented surfaces. Adding either PQ-D16 or PQ-10 (Fig. 15b. and 15c.) instead of SDS leads to strong film formation and well-adhered gels on vertically oriented substrates that remain on the substrate, although the gels appear a bit lumpy and unevenly distributed, due to less mixing ability in Spraying Vessels 1 and 2, however, this may be improved with better spraying equipment. Combining surfactant (Triton-X100) and either of PQ-D16 and PQ-10 leads to smooth and even gels (Fig. 15d. and Fig. 15e.), which show very good film-forming ability and substrate adhesion on vertically oriented substrates.

List of reference numerals

	100	Apparatus for forming gel on substrates for forming surface polymers from grafting sites on the substrates
5	101	System for spray depositing first and second separate liquids from separate nozzles on to substrates
	102	System for further spray depositing first and second separate liquids from separate nozzles on to substrates
	103	System for rinsing gel off substrates
	110	Holding tank for first separate liquid including gelating substance
10	111	First separate liquid spray system plumbing
	112	First separate liquid spray nozzle
	113	First separate liquid spray mist
	114	First separate liquid mixing device
	115	First separate liquid in-line filter
15	120	Holding tank for second separate liquid including cross-linking agent
	121	Second separate liquid spray system plumbing
	122	Second separate liquid spray nozzle
	123	Second separate liquid spray mist
	124	Second separate liquid mixing device
20	125	Second separate liquid in-line filter
	130	Holding tank for rinsing solution
	131	Rinsing system plumbing
	132	Rinsing system spray nozzle
	133	Rinsing solution spray
25	140	Polymerization initiator-modified substrate
	141	Gel
	142	Surface polymers
	150	Conveyor device for substrates
	162	Second separate liquid mist
30	163	First separate liquid mist
	165	Rinsing solution spray
	200	Apparatus for forming gel on a continuous foil or other continuous surface for forming surface polymers from grafting sites on the continuous surface
35	201	System for spray depositing first and second separate liquids from separate nozzles on to substrates
	203	System for rinsing gel off substrates
	210	Holding tank for first separate liquid including gelating substance
	211	First separate liquid spray system plumbing

- 212 First separate liquid spray nozzle
- 213 First separate liquid spray mist
- 214 First separate liquid mixing device
- 215 First separate liquid in-line filter
- 5 220 Holding tank for second separate liquid including cross-linking agent
- 221 Second separate liquid spray system plumbing
- 222 Second separate liquid spray nozzle
- 223 Second separate liquid spray mist
- 224 Second separate liquid mixing device
- 10 225 Second separate liquid in-line filter
- 230 Holding tank for rinsing solution
- 231 Rinsing system plumbing
- 232 Rinsing system spray nozzle
- 233 Rinsing solution spray
- 15 240 Polymerization initiator-modified continuous substrate/foil
- 241 Gel
- 242 Surface polymers
- 250 Reel-to-reel system for moving a continuous substrate/foil
- 340 Polymerization initiator-modified substrate
- 20 341 Gel
- 342 Surface polymers
- 360 Spraying device with first separate liquid including gelating substance
- 361 Spraying device with second separate liquid including cross-linking agent
- 362 Mist of first separate liquid
- 25 363 Mist of second separate liquid
- 364 Rinsing bottle with rinsing solution
- 365 Spray of rinsing solution
- 440 Polymerization initiator-modified substrate
- 441 Gel
- 30 442 Surface polymers
- 460 Spraying device with first separate liquid including gelating substance
- 461 Spraying device with second separate liquid including cross-linking agent
- 462 Mist of first separate liquid
- 463 Mist of second separate liquid
- 35 464 Rinsing bottle with rinsing solution
- 465 Spray of rinsing solution
- 470 Substrate mount
- 471 Double sided adhesive tape

Claims

1. A reaction composition for surface polymer formation comprising:
 - at least one monomer;
 - 5 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 solvent; and
 - at least one gelating substance.
- 10 2. A reaction composition according to claim 1, wherein the at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel.
3. A reaction composition according to claim 2, wherein the at least one polymeric compound has at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one
- 15 type of repeating unit.
4. A reaction composition according to any one of claims 1-3, wherein the at least one gelating substance is selected from sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid.
- 20 5. A reaction composition according to any one of claims 1-4, wherein the at least one ligand is selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethyl-amino)ethyl]amine (Me₆TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylene-
- 25 diamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam), and/or 2,2'-bipyridyl (BiPy).
6. A reaction composition according to any one of claims 1-5, wherein the at least one catalyst is selected from copper (Cu), iron (Fe) or ruthenium (Ru).
- 30 7. A reaction composition according to any one of claims 1-6, wherein the complex formed between the at least one ligand and the at least one catalyst is selected from Cu/Me₆TREN, Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam.
- 35 8. A reaction composition according to any one of claims 1-7, further comprising at least one additive.

9. A reaction composition according to claim 8, wherein the at least one additive is selected from at least one surfactants, and/or at least one polyquaternium compounds.

10. A reaction composition according to claim 8 or 9, wherein

5 the at least one surfactant is selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and

10 the least one polyquaternium compound is selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

11. A reaction composition according to any one of claims 1-10 further comprising a buffer.

15 12. A reaction composition according to claim 11, wherein the buffer is selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers.

20 13. A reaction composition according to claim 11 or 12, wherein the Good's buffer is selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS.

14. A reaction composition according to any one of claims 1-13, further comprising at least one cross-linking agent.

25

15. A reaction composition according to claim 14, wherein the at least one cross-linking agent is a di-, tri-, or tetra-valent metal ion in combination with a counter ion.

16. A reaction composition according to claim 14 or 15, wherein

30 the at least one cross-linking agent is a di-valent metal ion selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ;

 the at least one cross-linking agent is a tri-valent metal ion selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and

35 the at least one cross-linking agent is a tetra-valent metal ion selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} .

17. A reaction composition according to claim 16, wherein

the at least one di-valent metal ion in combination with a counter ion is selected from MgCl_2 , CaCl_2 , FeCl_2 , CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, SrCl_2 , $\text{Sr}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, ZnCl_2 , $\text{Zn}(\text{CH}_3\text{CO}_2)_2$, and/or hydrates thereof;

the at least one cross-linking agent is a tri-valent metal ion in combination with a counter ion is selected from FeCl_3 , AlCl_3 , $\text{Fe}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ga}(\text{NO}_3)_3$, InCl_3 , and/or hydrates thereof; and

the at least one cross-linking agent is a tetra-valent metal ion in combination with a counter ion is selected from $\text{Ce}(\text{SO}_4)_2$, $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, $\text{Zr}(\text{NO}_3)_4$, $\text{Zr}(\text{SO}_4)_2$, ZrCl_4 , TiCl_4 , and/or hydrates thereof.

10

18. A reaction composition according to claim 17, wherein the at least one cross-linking agent is selected from CaCl_2 , CuCl_2 , $\text{Zn}(\text{NO}_3)_2$, AlCl_3 , FeCl_3 , and/or $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$.

19. A reaction composition according to any one of claims 1-18, further comprising at least one catalyst activator.

15

20. A reaction composition according to claim 19, wherein the at least one catalyst activator is selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x , and/or pyrogalllic acid.

20

21. A reaction composition according to claims 19 or 20, wherein the at least one catalyst activator activates the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation.

25

22. A reaction composition according to any one of claims 19-21, wherein the at least one catalyst activator is added to the reaction composition prior to formation of surface polymers.

23. A reaction composition for surface polymer formation comprising a first separate liquid and a second separate liquid, wherein:

30

the first separate liquid comprises:

at least one gelating substance; and

at least one solvent; and

the second separate liquid comprises:

35

at least one cross-linking agent; and

at least one solvent;

wherein the first separate liquid and the second separate liquid are provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of at least one polymerization initiator-modified substrate.

- 5 24. A reaction composition according to claim 23, wherein the first separate liquid and/or the second separate liquid further comprises:
 at least one monomer; and/or
 at least one catalyst and at least one ligand, wherein the at least one catalyst and the at least one ligand form a complex.
- 10 25. A reaction composition according to claim 23 or 24, wherein the first separate liquid and/or the second separate liquid comprises one or more additives.
- 15 26. A reaction composition according to any one of claims 23-25, wherein the first and/or the second separate liquid comprises one or more buffers.
- 20 27. A reaction composition according to any one of claims 23-26, wherein
 the first separate liquid comprises:
 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 solvent;
 at least one gelating substance;
 optionally at least one additive; and
25 optionally at least one buffer; and
 the second separate liquid comprises:
 at least one cross-linking agent;
 at least one solvent;
 optionally at least one additive; and
30 optionally at least one buffer;
 wherein the first separate liquid and the second separate liquid are provided as discrete components uncombined until surface polymers are to be formed on an at least a portion of at least one polymerization initiator-modified substrate.
- 35 28. A reaction composition according to any one of claims 23-27, wherein the at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel.

29. A reaction composition according to claim 28, wherein the at least one polymeric compound has at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit.

5 30. A reaction composition according to claim 28 or 29, wherein the at least one gelating substance is selected from sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid.

31. A reaction composition according to any one of claims 23-30, wherein the at least one
10 cross-linking agent is a di-, tri-, or tetra-valent metal ion in combination with at least one counter ion.

32. A reaction composition according to claim 31, wherein
the at least one di-valent metal ion is selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or
15 Zn^{2+} ;
the at least one tri-valent metal ion is selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and
the at least one tetra-valent metal ion is selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} .

33. A reaction composition according to claim 32, wherein
20 the at least one di-valent metal ion in combination with a counter ion is selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or hydrates thereof;
the at least one tri-valent metal ion in combination with a counter ion is selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and
25 the at least one tetra-valent metal ion in combination with a counter ion is selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof.

34. A reaction composition according to claim 33, wherein the at least one cross-linking agent
30 is selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or $(NH_4)_4Ce(SO_4)_4$, and/or hydrates thereof.

35. A reaction composition according to any one of claims 23-34, wherein the at least one
ligand is selected from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-
(dimethylamino)ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridyl-
35 methyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetra-
methylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
($Me_4Cyclam$), and/or 2,2'-bipyridyl (BiPy).

36. A reaction composition according to any one of claims 23-35, wherein the at least one catalyst is selected from copper (Cu), iron (Fe), and ruthenium (Ru).

37. A reaction composition according to any one of claims 23-36, wherein the complex formed
5 between the at least one ligand at the at least one catalyst is selected from Cu/Me₆TREN, Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/Me₄Cyclam.

38. A reaction composition according to any one of claims 25-37, wherein the at least one additive is selected from at least one surfactants, and/or at least one polyquaternium
10 compounds.

39. A reaction composition according to claim 38, wherein
the at least one surfactant is selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride
15 (CTAC), and/or dimethyldioctadecylammonium chloride; and

the least one polyquaternium compound is selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.
20

40. A reaction composition according to any one of claims 26-39, wherein the buffer is selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers.
25

41. A reaction composition according to claim 40, wherein the Good's buffer is selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS.

42. A reaction composition according to claim 23-41, wherein the first separate liquid and/or
30 the second separate liquid further comprises at least one catalyst activator.

43. A reaction composition according to claim 42, wherein the at least one catalyst activator is selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x, and/or
35 pyrogalllic acid.

44. A reaction composition according to claim 42 or 43, wherein the at least one catalyst activator activates the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation.

5 45. A reaction composition according to any one of claims 42-44, wherein the at least one catalyst activator is added to the first separate liquid and/or the second separate liquid prior to surface polymer formation.

46. A method for forming surface polymers on a substrate comprising:
10 providing at least a portion of at least one polymerization initiator-modified substrate;
bringing the at least a portion of the at least one polymerization initiator-modified substrate into contact with a reaction composition comprising:
a first separate liquid;
a second separate liquid; and
15 a number of other separate liquids;
wherein the first separate liquid comprises:
at least one gelating substance;
wherein the second separate liquid comprises:
at least one cross-linking agent; and
20 wherein the number of other separate liquids comprise one or more of:
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;
25 optionally at least one additive; and
optionally at least one buffer;
wherein one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids further comprises at least one solvent;
wherein one or more of the first separate liquid; the second separate liquid; and
30 the number of other separate liquids are mixed prior to bringing the reaction composition in contact with the at least a portion of the at least one polymerization initiator-modified substrate; and
forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate.

35

47. A method for forming surface polymers on a substrate comprising:
providing at least a portion of at least one polymerization initiator-modified substrate;

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

a first separate liquid; and

a second separate liquid;

5 wherein the first separate liquid comprises:

at least one gelating substance; and

at least one solvent;

wherein the second separate liquid comprises:

at least one cross-linking agent; and

10 at least one solvent;

wherein the first separate liquid and/or the second separate liquid further comprises:

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;

15 at least one catalyst activator;

optionally at least one additive; and

optionally at least one buffer;

wherein each of the first separate liquid and the second component is applied to the at least a portion of the at least one polymerization initiator-modified substrate to form surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate; and

20 forming surface polymers on the at least a portion of the at least one polymerization initiator-modified substrate.

25 48. A method according to claim 46 or 47, wherein the at least one gelating substance is at least one polymeric compound chelating with at least one metal ion and forming a gel.

49. A method according claim 48, wherein the at least one polymeric compound has at least one functional group chelating di-, tri-, or tetra-valent metal ions in at least one type of repeating unit.

50. A method according to claim 48 or 49, wherein the at least one gelating substance is selected from sodium alginate, poly(vinyl imidazole), poly(acrylic acid), pectin, carrageenan, xanthan gum, and/or hyaluronic acid.

35

51. A method according to claim 46 or 47, wherein the at least one cross-linking agent is a di-, tri-, or tetra-valent metal ion in combination with a counter ion.

52. A method according to claim 51, wherein
the at least one di-valent metal ion is selected from Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Sr^{2+} , and/or Zn^{2+} ;
the at least one tri-valent metal ion is selected from Fe^{3+} , Al^{3+} , Ga^{3+} , and/or In^{3+} ; and
5 the at least one tetra-valent metal ion is selected from Ce^{4+} , Zr^{4+} , and/or Ti^{4+} .
53. A method according to claim 51 or 52, wherein
the at least one di-valent metal ion in combination with a counter ion is selected from $MgCl_2$, $CaCl_2$, $FeCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3CO_2)_2$, and/or
10 hydrates thereof;
the at least one tri-valent metal ion in combination with a counter ion is selected from $FeCl_3$, $AlCl_3$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ga(NO_3)_3$, $InCl_3$, and/or hydrates thereof; and
the at least one tetra-valent metal ion in combination with a counter ion is selected from $Ce(SO_4)_2$, $(NH_4)_4Ce(SO_4)_4$, $Zr(NO_3)_4$, $Zr(SO_4)_2$, $ZrCl_4$, $TiCl_4$, and/or hydrates thereof.
15
54. A method according to claim 53, wherein the at least one cross-linking agent is selected from $CaCl_2$, $CuCl_2$, $Zn(NO_3)_2$, $AlCl_3$, $FeCl_3$, and/or $(NH_4)_4Ce(SO_4)_4$.
55. A method according to any one of claims 46-54, wherein the at least one ligand is selected
20 from *N,N,N',N'',N'''*-pentamethyldiethylene-triamine (PMDETA), tris[2-(dimethylamino)-ethyl]amine (Me_6TREN), tris(2-aminoethyl)amine (TREN), tris(2-pyridylmethyl)amine (TPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), tetramethylethylenediamine (TMEDA), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ($Me_4Cyclam$), and/or 2,2'-bipyridyl (BiPy).
25
56. A method according to any one of claims 46-54, wherein the at least one catalyst is selected from copper (Cu), iron (Fe), and ruthenium (Ru).
57. A method according to any one of claims 46-56, wherein the complex formed between
30 the at least one ligand at the at least one catalyst is selected from Cu/ Me_6TREN , Cu/PMDETA, Cu/TPMA, Cu/TREN, Cu/HMTETA, Cu/TMEDA, and/or Cu/ $Me_4Cyclam$.
58. A method according to claim 46 or 47, wherein the at least one additive is selected from at least one surfactants, and/or at least one polyquaternium compounds.
35
59. A method according to claim 58, wherein

the at least one surfactant is selected from sodium dodecyl sulfate (SDS), Triton-X100, dioctyl sodium sulfosuccinate (DOSS), cetrimonium bromide (CTAB), cetrimonium chloride (CTAC), and/or dimethyldioctadecylammonium chloride; and

the least one polyquaternium compound is selected from polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-14, polyquaternium-D16, polyquaternium-31, polyquaternium-36, polyquaternium-46, polyquaternium-65, polyquaternium-68, polyquaternium-79.

60. A method according to claim 46 or 47, wherein the buffer is selected from carbonate buffer, glycine buffer, citrate buffer, phosphate buffer, acetate buffer, ammonium buffer (ammonium chloride/ammonia), formate buffer, sodium ascorbate/ascorbic acid buffer, and/or zwitterionic buffers such as Good's buffers.

61. A method according to claim 60, wherein the Good's buffer is selected from MES, PIPES, MOPS, HEPES, CHES, CAPSO and/or CAPS.

62. A method according to any one of claims 46-61, wherein the at least one catalyst activator is selected from sodium ascorbate (NaAsc), ascorbic acid (Asc), hydrazine, hydrazine hydrate, sodium thiosulfate, sodium sulfite, sodium dithionite, glucose with GO_x, and/or pyrogalllic acid.

63. A method according to claim 62, wherein the at least one catalyst activator activates the complex formed between the at least one ligand and the at least one catalyst for surface polymer formation.

64. A method according to claim 46 or 47, wherein the at least one catalyst activator is mixed with the at least one catalyst and the at least one ligand prior to applying the reaction composition to the at least a portion of the at least one polymerization initiator-modified substrate.

65. A method according to any one of claims 46, 48-64, wherein one or more of the first separate liquid; the second separate liquid; and/or the number of other separate liquids are applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying.

66. A method according to claim 65, the first separate liquid, the second separate liquid, and one or more of the other separate liquids are applied by a first spray unit, a second spray unit and a third spray unit, respectively.

67. A method according to any one of claims 47-64, wherein one or more of the first separate liquid; and the second separate liquid are applied to the at least a portion of the at least one polymerization initiator-modified substrate by spraying.

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68. A method according to claim 67, the first separate liquid, and the second separate liquid are applied by a first spray unit, and a second spray unit, respectively.

69. A method according to any one of claims 46, 48-64, wherein one or more of the first separate liquid; the second separate liquid and/or the number of other separate liquids are applied to the at least a portion of the at least one polymerization initiator-modified substrate by dip coating.

70. A method according to any one of claims 47-64, wherein one or more of the first separate component; and the second separate component are applied to the at least a portion of the at least one polymerization initiator-modified substrate by dip coating.

71. An apparatus for forming surface polymers on polymerization initiator-modified substrates, the apparatus comprising:

20 a first system for spray depositing, from separate spray nozzles, a first separate liquid including a gelating substance and a second separate liquid including a cross-linking agent on the substrates, wherein one or more of the first separate liquid and the second separate liquid include a monomer and an activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form a gel on the substrates; and

25 a second system for rinsing the gel off the substrates leaving behind surface polymers which have grown from polymerization initiator sites on the substrates.

72. An apparatus according to claim 71, further comprising a third system for spray depositing, from separate spray nozzles, the first separate liquid including the gelating substance and the second separate liquid including the cross-linking agent on the substrates, wherein one or more of the first separate liquid and the second separate liquid include the monomer and the activated catalyst/ligand complex, and wherein the first separate liquid and the second separate liquid together form an increased thickness of the gel on the substrates.

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73. An apparatus according to any one of claims 71-72, further comprising a conveyor belt for moving the substrates through one or more of the first, second and third systems.

74. An apparatus according to any one of claims 71-72, further comprising a reel-to-reel system for moving a continuous substrate through one or more of the first, second and third systems, wherein the continuous foil comprises a multiplicity of the substrates.
- 5 75. An apparatus according to any one of claims 71-74, wherein the substrates are processed in a horizontal or a vertical plane.