Surface Innovations
Volume 1 Issue SI1

Smart surfaces by initiated chemical vapor deposition
Coclite

ice | science

Pages 6–14 http://dx.doi.org/10.1680/si.12.00019
Review Article
Received 29/12/2012 Accepted 17/01/2013

Keywords: coating/responsive surfaces/thin film/vapor deposition

Smart surfaces by initiated chemical vapor deposition

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The ability to modify the surface of materials with functional and responsive coatings is a powerful tool for the fabrication of smart devices for biotechnology, microfluidics, membrane technology, sensors and drug delivery systems. A recently developed method for the deposition of polymeric thin films, called initiated chemical vapor deposition (iCVD) is reviewed here. The authors will describe the high versatility of iCVD in driving application-specific properties into the material, creating a platform for the implementation of polymeric coatings into device fabrication. The significant impact of this polymerization technique lies in the possibility of obtaining polymers with chemical structure similar to the one of the polymers synthesized by conventional techniques with the advantages of a solvent-free deposition, which is totally substrate independent. Deposition has been demonstrated on paper, metal, plastics, porous substrates and very recently liquids. Tuning the process parameters allows to obtain controlled and uniform thickness over 3D substrates. Future outlook and iCVD scale-up approaches are also discussed.

1. Introduction

Polymer coatings offer innovative solutions for the development of functional materials for technological applications. Coating the top surface of materials with a thin film of polymer allows us to modify the interaction of the material with the environment without changing the bulk properties of the material itself, and thus increases the number of properties that a material can have. A significant research effort is devoted to the production of "smart" coatings, which dynamically respond to the stimuli coming from the environment.[1] Successful examples of smart polymer surfaces are pH- or temperature-responsive coatings, antistain and self cleaning coatings, biomedical coatings and heterogeneous surfaces.

Wet methods have been widely used to achieve these goals. The development of dry polymerizations in which the monomers are vaporized and then polymerize on the surface (also called chemical vapor deposition [CVD]) aims to complement and enlarge the applicability of polymer coatings to the fields where the presence of solvent is detrimental.[2] When the polymerization takes place from the vapor phase, the tridimensional features of the substrate can be uniformly coated and reproduced without the typical side effects of the presence of liquid solvents such as meniscus formation, bridging or pooling. The thermal issues associated with drying or curing are avoided and many of the vapor-phase polymerizations happen at low substrate temperature, allowing the coating of thermo-labile substrates. Adjusting the system parameters, the polymers obtained by vapor phase can have tailored chemical and physical properties, precise control over thickness and conformality.[3]

The reaction mechanism of the dry polymerizations is similar to the wet ones. In the free-radical chain-growth polymerization, the first step is the initiation step in which active species (e.g. ions, radicals,

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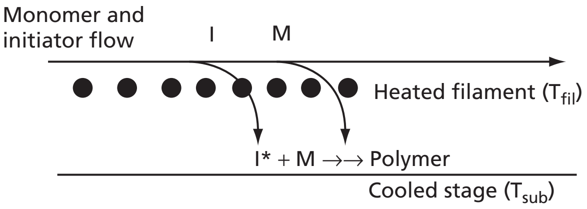
fragments) are created to react with the monomer creating active sites on the monomer molecules. The second step is the propagation: the active monomer molecules interact with other monomer molecules and the polymeric chain starts growing. Differently from liquid-phase polymerization, the growing polymeric chains are adsorbed on a cooled substrate. The third step is the termination, where the radical end of the growing polymer chain is capped by reaction with another radical. The CVD free-radical polymerization techniques differ in the initiation step. In plasma-enhanced CVD[4] and in hot-wire CVD,[5] the radicals are created by direct fragmentation of the monomer molecules by the energetic electrons of the plasma discharge or by high temperatures, respectively. Direct fragmentation of the monomer can result in the cleavage of the monomer functional groups negatively affecting polymer properties.

In the past 10 years, a new CVD method has been developed, termed initiated CVD (iCVD).[3,6–8] In the iCVD process, the radicals are not created by fragmentation of the monomer molecules but of an initiator. An initiator is a chemical compound that has a labile bond (e.g. the O-O bond in peroxides), which undergoes thermal decomposition at a relatively low temperature. The monomer and the initiator are fed to a reactor chamber in which a filament array is suspended ~2 cm above a substrate holder-heat-exchange plate. The filament is heated to the initiator decomposition temperature, which is generally below 300°C. In comparison, the decomposition temperature of the most monomers are above 400°C. The low-energy input required to fragment the initiator ensures that the monomer molecules remain intact and fully retain all the functionalities. The radicals of the initiator react with the vinyl bond of the monomer molecules adsorbed on the substrate surface to initiate the polymerization, therefore the chain-growth step takes place on the surface, as shown in Scheme 1.

In numerous articles, it has been demonstrated that iCVD is substrate-independent and takes place at low substrate temperature (between 15–60°C). Polymers have been successfully deposited on paper,[9,10] plastic,[11,12] liquids[13–16] (see Figure 1a), poly-dimethylsiloxane (PDMS),[17,18] gold nanorod.[19] The resulting polymers have full functionality retention and can be obtained at high-deposition rates. The absence of catalysts, plasticizers, solvents and dispersants improves the biocompatibility of iCVD polymers, which makes this process very attractive for biomedical applications.[20,21] The deposition parameters can be modified in order to obtain different coating profiles on tridimensional substrates, depending on the application. Figure 1b shows a planarizing polymer that can be used as pore filler,[22] and to smooth the asperities of rough substrates.[23] In this case, the coating was thicker in the pores or valleys of the substrate and thinner on the higher features. On the contrary, Figure 1c shows that it is possible to obtain also very high conformality: in this case, the polymer had a uniform thickness on the top, side and on the bottom of the trenches.[24]



Scheme 1. Schematics of the iCVD system. iCVD, initiated chemical vapor deposition. I, initiator; M, monomer; T_{fil}, filament temperature; T_{sub}, substrate temperature.

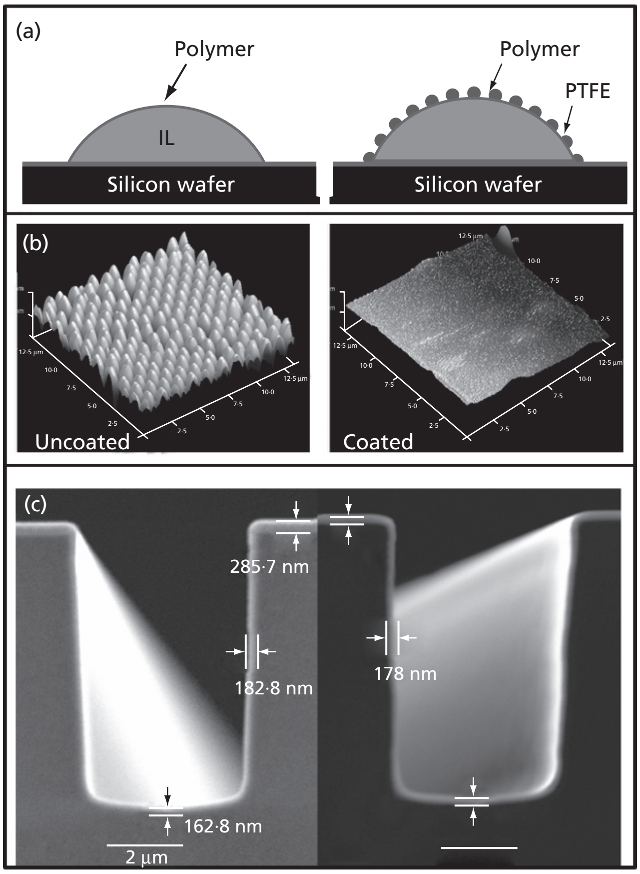


Figure 1. (a) Deposition of iCVD polymer on the surface of IL droplet without and with PTFE particles. The PFTE particles facilitate polymerization onto the entire surface area of the IL. Adapted with permission from Ref. 13. Copyright (2012) American Chemical Society. (b) Deposition of a organosilicon polymer coating on top of microspheres with diameter ~1 μm. The polymer completely filled all the gaps between the spheres giving a microscopically flat surface. Adapted with permission from Ref. 23. Copyright (2012) American Institute of Physics. (c) Deposition of a conformal polymer coating inside the trenches of a silicon wafer. The coating is uniformly distributed on top, wall and bottom of the trenches. Adapted with permission from Ref. 24. Copyright (2012) American Chemical Society. iCVD, initiated chemical vapor deposition; IL, ionic liquid; PTFE, poly(tetrafluoroethylene).

Smart surfaces have been obtained by iCVD ranging from super hydrophobic coating,[25–27] antifouling[28,29] and stimuli-responsive polymers for drug delivery[30] or protein adsorption.[31] Many polymers have been deposited by iCVD, for example, temperature-sensitive poly(*N*-isopropylacrylamide) (p(NIPAAm)),[32–34] pH-sensitive methacrylic acid (MAA) copolymers[35] or poly(hydroxyethyl methacrylate) (p(HEMA)) hydrogels.[36,37] Here, some specific applications of iCVD smart polymers will be reviewed, emphasizing the aspects that are difficult to obtain with other polymerization techniques.

2. Functional coating

The term "functional" in this context refers to that class of coating characterized by some native properties and functions that make them of high technological interest. The result of combining a functional coating and a substrate, which has some other complementary properties, is a multifunctional, or smart, material. iCVD has been demonstrated to be very successful for the development of multifunctional materials. For example, it was useful in adding super-hydrophobicity and oleophobicity to stretching fabric,[38] antifouling properties to membranes[31] or barrier properties to plastic.[39]

2.1 Superhydrophobic coatings

Superhydrophobic coatings have been obtained by iCVD, as polymers of 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA).[15, 25, 26] This monomer contains a long fluorinated chain, $\text{-(CF}_2)_7\text{CF}_3$, that is totally preserved during the iCVD process. The long fluorinated chains pending from the polymer backbone have a natural tendency to reorient toward themselves and form a crystalline bilayer structure, called smectic B phase. By tuning the iCVD parameters (filament temperature, initiator over monomer ratio and substrate temperature), it is possible to tune also the degree of crystallinity in the film.[26] Semicrystalline polymers give stable surface properties, without hydrophobic recovery and create generally rough surfaces (root mean square roughness higher than 30 nm), which can be useful for enhancing cell growth or enhancing the hydrophobicity of the surface. It has been demonstrated that grafting the polymeric p(PFDA) chains to the surface, that is, covalently bonding the chains to the substrate, produces oleophobic p(PFDA) surfaces.[25] Figure 2a shows the cosine of the contact angle (CA) when the surface was wetted with several hydrocarbon oils with different liquid-surface energies. The grafted polymer exhibits higher CAs than the ungrafted one. p(PFDA) superhydrophobic properties were used to coat a paper solar cell so that the device could produce power under light irradiation even when totally submerged in water.[9] Free-standing p(PFDA) polymer films have been obtained by depositing the iCVD polymer over droplets of ionic liquid.[15] Ionic liquids are non volatile solvents, hence compatible with vacuum systems. Other semicrystalline structures have been obtained by soft-epitaxy: depositing poly(tetrafluoroethylene) by iCVD over the surface of carbon nanotube. In this case, modifying the substrate topography, it was possible to modify the crystal structure of the polymer.[40]

2.2 Coatings for microfluidic devices

p(PFDA) coatings have also been applied on PDMS-based microfluidic devices in order to create a barrier coating and increase the chemical compatibility of the PDMS, preventing the lateral diffusion of the chemicals.[41] This type of iCVD-modified microfluidic devices have been demonstrated to be successful for synthesis, and reactor miniaturization.[16] The microchannels have the potential to provide superior control over mixing as compared with traditional batch reactions. The high conformality of iCVD coatings makes the integration of iCVD polymers on microfluidic devices a powerful tool to modify the surface of the microchannels without occluding them. A polymer of maleic anhydride was deposited on microfluidic lung-assisted device, and it allows for the selective permeation of oxygen and carbon dioxide while acting as a liquid barrier to prevent the permeation of blood of the vascular vessels (see Figure 2b).[18,42] iCVD polymers were also used to bond some microchannels together: one side of the device was coated with poly(glycidyl methacrylate) p(GMA) and the other side with poly(4-aminostyrene) p(AS).[43] The epoxy groups of p(GMA) were reacted with the amino groups of the p(AS) to assemble the device. Microchannels were also produced by using the UV-responsive properties of the poly(o-nitrobenzyl methacrylate) (PoNBMA) deposited by iCVD.[44] PoNBMA is hydrophobic but nitrobenzyl groups can be cleaved to form patterned surfaces with hydrophilic channels. Porous chromatography paper was coated with PoNBMA and irradiated with UV light to create hydrophilic channels surrounded by hydrophobic walls. The ability to deposit on porous substrates and coat the internal pores was used to sequentially deposit functional polymer coatings onto paper-based microfluidic devices, retaining the fibrous morphology necessary to generate capillary-driven flow.[10] A hydrophilic polymer coating with a high surface concentration of ionizable groups was deposited onto the surface of the paper fibers in order to passively separate analytes, into its anionic and cationic components. Sequentially, the UV-responsive PoNBMA was deposited to act as a responsive hydrophobic/hydrophilic switch to block or allow the path of fluid within the devices.

2.3 Antifouling coatings

Figure 2c shows the antifouling properties of the poly(ethylene oxide) (PEO) deposited by iCVD. The nonspecific protein adsorption was much smaller on the iCVD PEO surface than on other hydrophilic surfaces tested (i.e. silicon, amine- and hydroxyl-terminated surfaces). This was attributed to the greater wettability and hydrophilicity of the grafted iCVD PEO surfaces that were effective in minimizing the protein adsorption. Good antifouling properties were also achieved with zwitterionic coatings deposited by iCVD.[29] These coatings were used to prevent the fouling of reverse osmosis membranes for water desalination.

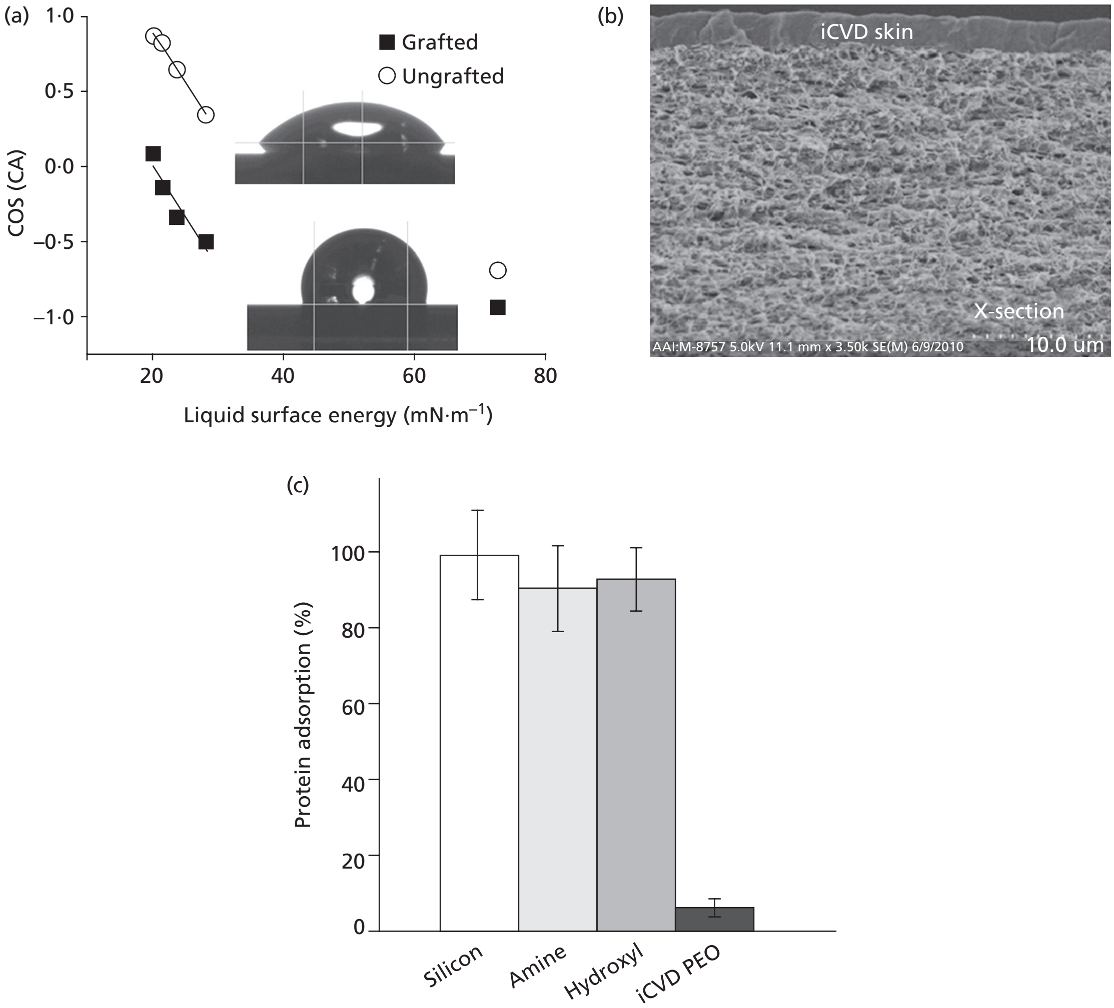


Figure 2. (a) Plot of the cosine of the CA of the grafted and ungrafted p(PFDA) as a function of the liquid surface energy of the hydrocarbon oils used to wet the surfaces. The plot shows that the grafted p(PFDA) surface has better oleophobic properties than the ungrafted one. Adapted with permission from Ref. 25. Copyright (2012) Wiley. (b) iCVD skin deposited on top of PTFE membrane to have selective permeation of gas (i.e. O_2 and CO_2) and act as liquid barrier. Adapted with permission from Ref. 42. Copyright (2012) Elsevier. (c) Histogram of the protein adsorption percentage of different hydrophilic surfaces: silicon wafer, amine and hydroxyl-terminated surfaces and iCVD-deposited PEO. The better antifouling properties of iCVD PEO is due to its enhanced wettability and hydrophilicity. Adapted with permissions from 28. Copyright (2012) Wiley. CA, contact angles; iCVD, initiated chemical vapor deposition; PTFE, poly(tetrafluoroethylene); poly(ethylene oxide) (PEO).

2.4 Permeation barrier coating

An iCVD barrier coating made of p(GMA) was deposited on NaCl particles with metallic coatings to decrease the dissolution rate of the bare NaCl.[39] The ability to coat particles is a particular strength of iCVD, since it is a non line-of-sight deposition that allows uniform coating of particles. This prevents the agglomeration that is often observed by wet methods. The combination of iCVD with the richness of organic chemistry allowed the design of an impermeable and hard but flexible coating. This was obtained as a result of copolymerization of p(MA) and p(AS), followed by annealing.

The annealing resulted in cross-linking of the polymeric chains by reaction of the anhydride and the amino groups contained in the copolymer.

iCVD was also demonstrated to be easily integrated in multilayer deposition technology. The dryness of this process is beneficial to avoid contamination and/or dissolution of the underlayers in multistack structures. iCVD polymers were coupled with inorganic layer deposition to obtain multilayer barrier structures on plastics and achieve the stringent barrier requirements of flexible electronics.[45] iCVD polymers were demonstrated to be resistant to the subsequent deposition of inorganic layers[46] so that they could be sandwiched between two inorganic layers and fill the pores of the bottom layer.[47] iCVD organosilicon polymers were also demonstrated to give global and local planarization (as shown in Figure 1b), which is useful to make the surface of the plastic substrate totally flat for subsequent deposition of the successive inorganic layers.[23,48]

2.5 Electronic applications of iCVD polymer

iCVD polymers have been successfully applied to electronic applications, as insulating dielectrics as well as conducting polymers. Poly(meta-diethynyl benzene) was deposited by iCVD with high molecular weight. This material has dielectric constant (k) between 2·3 and 3·2 in the visible wavelength range, which classifies it as a "low-k" dielectric polymer. Low dielectric constants were also obtained by creating air gaps after the decomposition of the iCVD polymer to form voids.[49]

iCVD poly(2-hydroxyethyl methacrylate) (PHEMA) was used as a polymer electrolyte to substitute the liquid electrolyte in dye-synthesized solar cells.[51] The successful integration of the iCVD PHEMA was due to its pore filling capabilities, so it could fill in the pores of the titanium dioxide used in the solar cells.[22] The cell-incorporating TiO_2 filled with the iCVD polymer showed better performance, compared with the cell filled with liquid electrolyte that is attributed to a lower rate of electron recombination.

Finally, Bakker *et al*.[51] demonstrated that by doping the iCVD-deposited oligo(phenyl acetylene) with iodine vapors, it is possible to obtain conductive polymers. These polymers exhibit electronic conductivities comparable with the values already reported in litterature for solution-processed polymers. Proton conductivity similar to the one of the commercial available Nafion membranes was obtained through a membrane made of a copolymer of MAA and PFDA deposited by iCVD.[11] The PFDA units were responsible of creating a hydrophobic backbone to ensure enough membrane stability, while the acid units with ionizable groups created the ionic channels for the proton passage.

3. Responsive coatings

Responsive coatings are characterized by dynamic switching of their properties depending on external stimuli (e.g. electrical field, temperature, pH). Nature is full of example of responsive materials, such as the skin of lizard or cuttlefish, which change their body patterns and colors depending on the surrounding environment.[53] Recently, numerous synthetic examples of responsive surfaces have emerged, which rely on conformational change in the polymer network, or pattern change. The retention of the functional groups

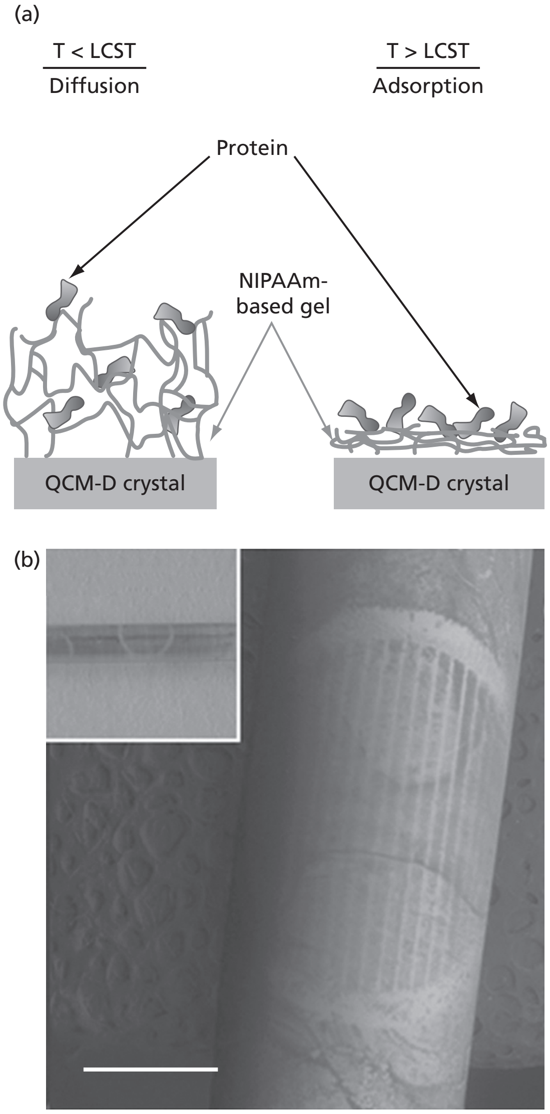


Figure 3. (a) QCM-D was used to investigate the thermo-responsive properties of p(NIPAAm). Below the LCST the polymer is in its expanded coil configuration where the proteins diffuse into the network. Above the LCST the polymer is in its collapsed state in which only surface adsorption is observed. Adapted from Ref. 32. Copyright (2012) American Chemical Society. (b) Patterning of a curved metal substrate using lithography of iCVD polymer. Adapted from Ref. 63. Copyright (2012) Wiley. LCST, lower critical solution temperature; p(NIPAAm), poly(*N*-isopropylacrylamide); QCM-D, quartz crystal microbalance with dissipation monitoring.

of polymers is critical to achieve the desired response, and this is the reason why iCVD plays an important role for the synthesis of this class of material.

A polymer known for its thermo-responsive properties is the p(NIPAAm). This polymer is characterized by a lower critical solution temperature (LCST) about 32°C, which is similar to body temperature and therefore makes the responsive properties of this polymer of high biomedical interests. Below the LCST the polymer is in a swollen state, also called extended coil configuration, in which the amide groups are exposed to the surface, resulting in high hydrophilicity. Above the LCST, the polymer is in a globular configuration in which the inter- and intra-chain amide groups are bonded, and the hydrophobic isopropyl groups are exposed to the surface. p(NIPAAm) deposited by iCVD gave 30° water CA (WCA) difference from the hydrophilic to the hydrophobic state when deposited on flat silicon surfaces and 85° WCA difference when the polymer was deposited on carbon nanotube forest.[32,34] Alf *et al*. demonstrated that when the p(NIPAAm) deposited by iCVD is in its swollen state (i.e. below the LCST) the proteins are not adsorbed on the surface but diffuse into the polymer network, as shown in Figure 3a. Above the LCST, when the polymer is in its globular configuration, the proteins show simple monolayer adsorption. This property was used to design microgrooves for tissue construct formation.[54] The p(NiPAAm) was deposited into the microgrooves of a PDMS substrate. The hydrophilic and swollen state of the polymer was used to seed the cells. Tissue formation occurred above the LCST, when the polymer was in its hydrophobic and collapsed state. The tissue constructs were then retrieved bringing the p(NIPPAm) back to its hydrophilic and swollen state, resulting in longitudinal tissue contacts.

3.1 Applications as sensors

Sensors are also based on responsive properties. A sensor for nitroaromatic explosives was developed using the dynamic swelling ability of poly(4-vinylpyridine) (P4VP).[55] The device was composed of two electrodes separated by dielectric SiO_2. A polymer line is deposited between the electrodes with a longitudinal gold contact overlaying on top. In the presence of nitroaromatic compounds, the polymer swells deforming the Au line, hence change its resistance. Another example of sensors, made by iCVD, was developed by Ozaydin-Ince *et al*.[56] In this case, the optode sensor was encapsulated in microworms of p(HEMA) for *in vivo* detection of sodium. They demonstrated that p(HEMA) encapsulation does not interfere with the activity of the optode sensor but allows the sensors to remain at the injection site.

3.2 Hydrogels for biotechnology and drug delivery

p(HEMA) belongs to a class of polymers called hydrogels. Hydrogels are known for their dynamic swelling response to aqueous environments. This results in changes in the mechanical properties, protein adsorption capabilities and hydrophilicity of the polymer. Free-standing p(HEMA) at high molecular weight was deposited by iCVD and resulted in the prevention of nonspecific protein adsorption and cells proliferation.[36,37] Free-standing p(HEMA) and p(NIPAAm) were also deposited by Frank-Finney *et al*.[14] using ionic liquids and silicone oils as substrates. The fast and reversible changes in the thickness of p(HEMA) were used in an impedance sensor to control the passage of the analyte.[57] By regulating the cross-link density of the p(HEMA) hydrogels, it is possible to systematically control the mesh size of the polymer and therefore allow the selective permeation of some analytes while preventing the passage of other species (e.g. foulant in biosensing applications).[58]

The responsive properties of p(HEMA) have been also used for controlled drug delivery systems. Coaxial nanotubes were fabricated by iCVD with a hydrogel core and a shape memory shell (SMP) for burst release of fluorescein. The nanopores of an anodic aluminum oxide (AAO) membrane were conformally coated with a SMP first and then with hydrogel. When the membrane was etched, the coaxial nanofilms were released. A fluorescent dye was encapsulated and absorbed by the hydrogel layer. At elevated temperature, the burst release of the fluorescent dye occurs due to the stress applied by the shape memory outer layer. Conformal deposition of the iCVD polymer in the pores of AAO membranes was also used to narrow down the pores of the membrane to few nm and achieve hydrophobicity-based separation of analytes. [12] Controlled release of a crop protection compound in the field was obtained by encapsulating the compound microparticles in an acrylate-based iCVD layer.[58]

Examples of pH-responsive polymers deposited by iCVD have been demonstrated by Karaman *et al*.[35] and McInnes *et al*.[30] In the first contribution, the authors demonstrated that the as-deposited poly(2-diisopropylamino)ethyl methacrylate shows reversible switching of WCA values between 87 and 28° after successive treatments of high- and low-pH water solutions, respectively. Higher WCA differences were obtained when the same polymer was deposited on electrospun fiber mat. In the second contribution, McInnes *et al*. show that the pH-dependent properties of a copolymer of MAA and ethylene dimethacrylate (p(MAA-co-EDMA)) was used to fabricate a drug delivery system: a model drug was loaded into the pores of a silicon matrix and then capped with the copolymer. At low pH, the release of the drug was four times slower, while at neutral pH the drug could be quickly delivered. The importance of such system is that it may enable site-specific targeting for drug therapy.

3.3 Patterned coatings

Patterned surfaces are frequently found in nature, for example on the feet of geckos. These are regular patterned surfaces that can create a switchable adhesive force, which allows the geckos to climb walls. Regular patterns were created by depositing the iCVD polymer on a surface with patterns of transition salt inhibitors.[60]

The underlying salt prevents polymerization, allowing to control the location of polymer. The combination of the patterning technique on tridimensional porous substrates may bring a new generation of hydrophobic, click-active and light-responsive polymers onto specific regions of the substrate. Another approach used to create regular patterns on the substrates consisted of stretching and releasing an elastic PDMS substrate coated with iCVD polymers having higher stiffness.[61] Patterns of self-assembly of pillars were obtained by depositing a hydrophilic polymer on the surface of hydrophobic PDMS pillars.[62] Submerging them in water and then letting the water evaporate induces the assembly of pillars into regular patterns. Finally, iCVD polymers were also used to create patterns on curved metal substrates, where conventional soft lithography is poorly applied (see Figure 3b).[63] A photosensitive polymeric thin film was deposited directly on nonplanar substrates by iCVD and then developed to selectively remove masked regions, creating a negative-tone patterned surface.

4. Conclusions and future outlook

Selected applications of iCVD coatings have been reviewed. iCVD offers many different advantages, which are difficult to achieve with other deposition techniques. Pure polymers (i.e. free of leachable chemicals) with chemical structures similar to those synthesized in solution can be deposited at high-deposition rates, with controlled thickness and conformality, on every kind of substrate. This results in wide applicability of this deposition technique for thin film manufacture. Functional and responsive coatings deposited by iCVD have been applied to solve technological challenges in biotechnology, electronics, microfluidics, drug delivery, sensors and membranes.

The newly demonstrated possibility of combining iCVD polymerization over liquid “substrates” opens up a wide variety of new technological applications, that is, electrolyte membranes in fuel cells, nonvolatile electrolytes in batteries and ionic liquid core-polymer shell particles for use in optical and chemical applications.

Thanks to chemical kinetics and fluid dynamics investigations of iCVD polymer reactors, the scale-up from lab to industry scale has been successful for batch processing as well as for roll-to-roll processing on flexible substrates such as plastics, papers, textiles and membranes. For commercialization, the all-dry nature of CVD has the potential to reduce environmental, health and safety impacts associated with solvents as well as the economic costs associated with solvent disposal. All these factors make iCVD a rapidly growing technique for the deposition of polymer coatings and device fabrications.

Acknowledgements

The author would like to thank Prof. Karen Gleason and Prof. Ayse Asatekin for large scientific contributions.

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