

Versatile Coatings Based on Catecholamines, Polyphenols and on Prebiotic Chemistry Based Concepts: An Opportunity for Robust Industrial Coatings.

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Abstract: Almost all products and materials need some protective or functional coatings. Unfortunately coating “recipes” are essentially material specific. It is hence of the highest interest to have some versatile coating methods allowing to coat a large repertoire of materials and which in addition could be functionalizable “at demand” to afford some requested functionality to the functionalized material: protection against corrosion, antibacterial properties, sensing abilities, reduction of friction, release of flavours, etc....

Bioinspiration from the chemistry used by mussels to adhere strongly to the surface of stones and wood under water and in the presence of strong shear stresses as well as mimicry from the “prebiotic chemistry” developed by Stanley Miller in the 50th of the last century offer now such possibilities. The coating opportunities of polyphenols appear also to afford some material versatility but with less robustness. These new coating methodologies will be described herein, as well as their strength and pitfalls. The major challenges for future improvements and scalability to the industrial scale will be addressed.

I. INTRODUCTION

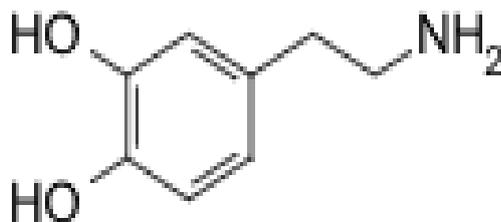
Since the beginning of civilisation, a need to protect and to improve the aesthetic appearance of the surface of materials developed by humans appeared. It is remarkable that poteries from the Neolithic age in China still conserve their external glance. This is possible through a coating, called laquer, made from polyphenols [1]. The stabilisation of these coatings, without the appearance of cracks after 5000 years of storage is due to laccase catalysed oxidation of urushiol using dissolved oxygen as the oxidant [2]. Nowadays huge interest is devoted again to such chemical processes, based on the use of naturally available molecules. This is interesting in the perspective of the need to develop sustainable chemical processes in the era of global climate change and is a transition in the evolution of surface chemistry. Indeed during the 30 last years of the 20th century, most research was undertaken, most of the time with great success, to develop well controlled coating methods at the molecular scale able to coat the surface of materials with very thin, at the monolayer scale, coatings. The used chemistry was material specific: thiol based self assembled monolayers at the surface of noble metals [3], silane chemistry to modify oxides [4], coatings based on supramolecular chemistry [5], polymer grafting technologies [6,7], the deposition of polyelectrolyte multilayers on all kinds of charged surfaces (unfortunately most polymers do not carry surface charges !) [8, 9].

But in the last ten years, inspired by the chemistry used by mussels to adhere strongly on materials as different as stones and wood pillars in a wet environment and under extremely strong shear stresses [10], some versatile coating methods based on catecholamines [11], or polyphenols [12, 13] appeared. Very recently, the resurgence of an old observation made by Stanley Miller [14], allowed also to coat the surface of all kinds of materials with a poly(amino acid) based coating obtained through the underwater polymerization of aminomalonnitrile at pH = 8.5 [15]. It is the aim of this short review to describe briefly these emerging versatile and eco-friendly coating methodologies to provide some interest to the colleagues from the industry. Before implementation of the polydopamine(PDA), polyphenol or “poly(aminomalonnitrile)” based coatings at the industrial scale, the pitfalls of these technologies need to be understood to make progress in the obtention of versatile, cheap, robust and easy to post functionalize coatings.

II. POLYDOPAMINE AND RELATED COATINGS

The giant californian mussels, *Mytilus Californianus*, up to 150 g in mass are able to withstand a traction force of up to 300N and a shear force of up to 180 N before detaching from their solid substrate [10]. Such a strong surface adhesion, required for the mussels’ survival, is due to the fact that the extremity of each byssus tread is terminated by a plaque containing a set of self-assembled proteins, the *mefp* (for *Mytilus Edulis Foot Proteins*) family. Since there are about 50 threads, each one is able to withstand a force of 6 N upon traction. Each thread extremity has a diameter of about 2 mm, meaning that the ultimate stress it can withstand is of about 2MPa. This is remarkable under water conditions. The secret for such a strong adhesion to solid substrates has been discovered after purification and sequencing of the *mefp* proteins: they are all rich in L-Lysine (amino

terminated) and in L-DOPA (hydroxylated L-tyrosine) residues. Both these amino acid residues act cooperatively to bind to either metal oxides (through coordination chemistry using the catechol moiety on L-DOPA) or to polymers and charged surfaces using the L-Lysine. In addition in basic conditions, L-DOPA undergoes oxidation in a quinone which is able to form covalent bonds with amines...opening the possibility for a rich surface chemistry and an avenue for versatile surface functionalization schemes. Unfortunately *meffpproteins* are difficult to purify or expensive to obtain in the form of recombinant proteins, impeding to implement such a concept at the industrial scale, even if it is of the highest interest from an academic point of view. Dr. H. Lee and Prof. P.B. Messersmith, that time at Northwestern university, observed that the neuromediator dopamine contains simultaneously the catechol moiety of L-Dopa and the primary amine function of L-Lysine (scheme 1) and they thought to use this compound to coat the surface of materials [11].



Scheme 1: chemical structure of dopamine.

It appeared that all known classes of materials: oxides, metals, polymers [even Teflon, poly (vinylidene difluoride) (PVDF), known to be impossible to functionalize and used for protection against adhesion !] could be coated with a film resulting from the oxidation of dopamine at pH 8.5 using Tris(Hydroxymethyl amino) methane as the buffering agent. These findings were not so surprising concerning oxides and metals: it is well known for a long time that sensing of dopamine with electrochemical sensors is a nightmare because of the deposition of an insulating film decreasing dramatically the electrode's lifetime, but was an enormous surprise concerning "inert" materials like PVDF.

The obtained films were called polydopamine (PDA) and had a maximal thickness of about 45 nm after 12h of deposition (Figure 1A) on all kinds of materials. The thickness of the PDA coating seems almost independent of the used substrate but the surface energy of the PDA coating changes slightly from substrate to substrate even if the coatings are slightly hydrophilic. It appeared rapidly that the PDA coatings are pinhole free after about 1 h of deposition [16] and can easily undergo secondary surface functionalisation with all kinds of molecules containing nucleophiles owing to the presence of quinones on PDA [17]. The chemical grafting of proteins on PDA is straightforward and a one step process owing to the presence of L-lysine residues but the reaction has to be performed at high enough pH because only the un-protonated amines are reactive towards quinone groups of PDA [17]. If the pH is low, the positively charged proteins can be adsorbed on the surface of the negatively charged PDA [18] though electrostatic interactions. This leads however to only transient adsorption with the occurrence of possible slow protein desorption when the protein solution in contact with the PDA film is replaced by buffer or water.

In addition, the catechol moieties (which are in a pH dependent equilibrium with quinones) allow for the coordination of metal cations [19] whereas the quinone moieties allow for the reduction of metal cations with a high enough standard redox potential (typically higher than 0.3 V with respect to the normal hydrogen electrode) to metallic nanoparticles, as exemplified with silver in Figure 1B [20].

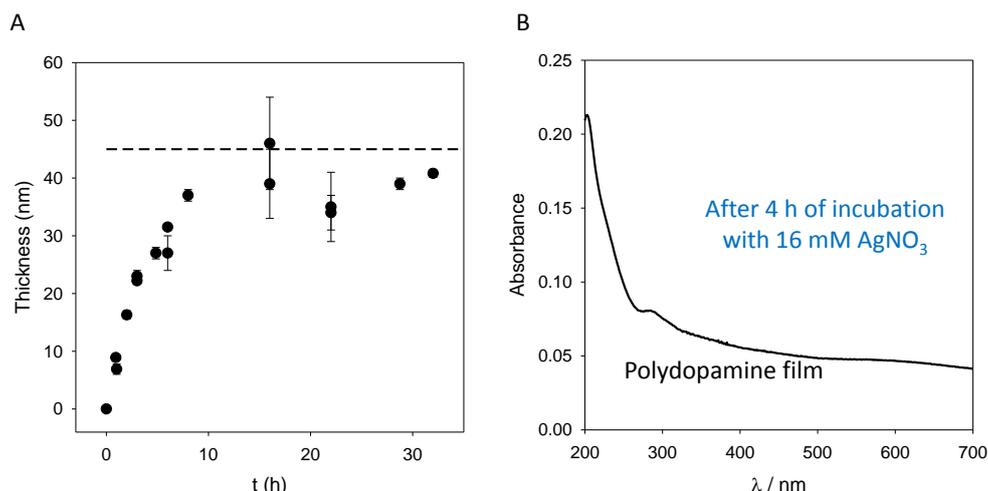


Figure 1 :

A : Deposition kinetics of PDA from a 2 mg.mL^{-1} dopamine solution in the presence of 50 mM Tris buffer at $\text{pH} = 8.5$. The substrate was silicon and the thickness was determined from ellipsometry at a wavelength of 632.8 nm using a refractive index of $1.73-0.02i$ at that wavelength. Modified from reference [21].

B: absorbance spectrum of a PDA film after 24 h of deposition on quartz from a 2 mg.mL^{-1} dopamine solution in the presence of 50 mM Tris buffer at $\text{pH} = 8.5$ (—) and of the same film put in contact with a silver nitrate solution at 16 mM during 4 h (---). Modified from reference [20].

The combined possibility to coat all kind of materials, even emulsion droplets [22] and the surface of water itself (provided the solution is not shaken) [23] and to perform secondary functionalisation of the surface of the obtained PDA raised an enormous interest for applications in materials science [24]: biomaterials, materials for water purification, materials for energy conversion, protection against fire and corrosion and reduction of the friction coefficient on solid surfaces (by functionalising PDA with long alkyl chains) [25].

Note that the repertoire of catecholamines amenable to such versatile coatings is not limited to dopamine. Changes in the film properties like their hydrophilicity and roughness [26], as well as in the maximal reached thickness [27] have been reached by using other catecholamines but with the same versatility with respect to the chosen substrate.

Finally, even with dopamine, it was found that playing with its bulk concentration it was possible to reach much thicker than the expected value of 45 nm . But at high dopamine concentrations, the obtained coatings were much rougher than those obtained at 2 mg.mL^{-1} in dopamine [28].

By changing the nature of the buffer solution (phosphate buffer instead of Tris buffer but at a constant pH of 8.5), the film deposition kinetics changes markedly. Unfortunately phosphate buffer slows the deposition down, but allows to reach much higher film thicknesses of up to 80 nm [21]. This has been explained by the strong interaction between Tris (an amine, hence a nucleophile) and quinone moieties during the formation of PDA [29].

The great versatility of PDA based coatings concerns not only the nature of the substrate to be coated but also the way the coating process can be performed. Indeed, it is not only possible to coat solid substrates by immersing them in a dopamine solution at $\text{pH} 8.5$ and in the presence of dissolved O_2 , but also by electrodeposition [30-32] and by spray coating [33] (Figure 2).

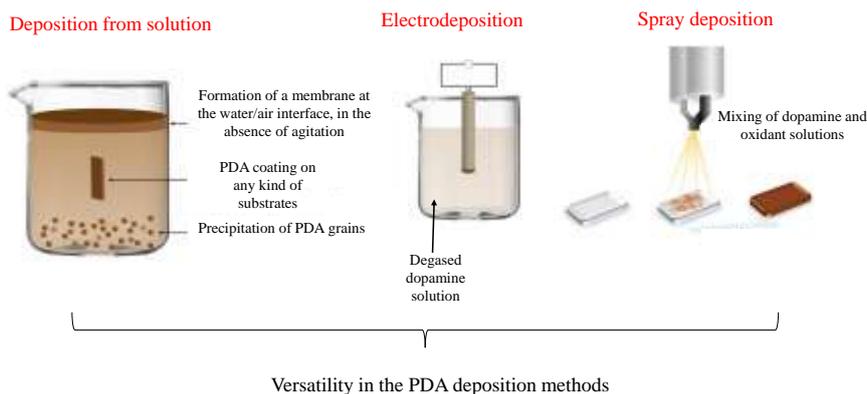


Figure 2: Versatility in the PDA deposition methods ranging from the dip coating in a dopamine solution (in the presence of an oxidant), to electrodeposition and to spray deposition.

The spray assisted deposition allows to considerably speed up the deposition process of PDA films: thicknesses of about 50 nm can be reached in a minute (provided the pH of the solutions is higher than 9) with respect to the solution deposition (Figure 1). Indeed if the maximal thickness has to be reached, 10-12 h of reaction are required in Tris buffer at pH 8.5, and even more in phosphate buffer at the same pH [21]. This is unacceptable for real world industrial applications. In addition spray coating allows minimal waste of dopamine which remains a moderately expensive compound, its cost being expected to increase if the demand in PDA coatings itself increases. In addition, during the solution oxidation process of dopamine, PDA not only deposits on the surface of the reaction vessel and the substrates to be coated, but a great majority of the compound precipitates out from the solution as a precipitate made from insoluble, heterogenous and useless aggregates. In addition to that, deposition from solution on rigid substrates will never be possible on substrates of large surface area, however spray deposition allows such a process by either moving the substrate or more easily by using commercially available movable spray nozzles. Electrodeposition of PDA from solutions also allows to avoid the uncontrolled precipitation from solution because the solutions can be deaerated and PDA deposition occurs only at the surface of the conductive substrate (in a potential window between -0.4 and +0.3 V versus Ag/AgCl) through an electrochemically triggered process. This process is self-limited because the obtained film is conformal and highly insulating which precludes further electron transfer to un-oxidized dopamine molecules in contact with the film [31]. However, electrodeposition allows to produce PDA films in the thickness range from about 3 to 45 nm in less than 1 h. [31], with a major drawback however: it is only applicable to conductive metal or conductive oxide (ITO) substrates.

For a long, time PDA deposition was only performed using dissolved O_2 as the oxidant: this requires to work in basic conditions, reminiscent from those encountered by mussels in sea water. However, the possibility to use other oxidants was overlooked for a long time [34]. Oxidants like the peroxodisulfate anion and the periodate anion allow to oxidize dopamine in slightly acidic conditions (pH= 5.0 and perhaps even below) in a nicely controlled and reproducible, oxidant concentration dependent fashion [35] (Figure 3). This coating method, if extended to spray deposition will also increase the flexibility of the coating process: dopamine and other catecholamines can be solubilized in acid pH and remain un-oxidized there for reasonable time durations (hours) and will only undergo the chemical pathway to PDA when mixed with the exogenous oxidant in the spraying nozzle.

The PDA coatings obtained using oxidants like sodium periodate (PDA- $NaIO_4$) keep the ability to undergo secondary functionalization like the reduction of Ag^+ (and other) cations (Figure 3B), but also display new properties with respect to the PDA coatings obtained using O_2 as the oxidant (PDA- O_2) at pH = 8.5: they are superhydrophilic-superoleophobic and antifouling towards proteins like BSA. On the other hand, PDA films obtained in basic conditions using O_2 as the oxidant are only moderately hydrophilic and favourable for protein adsorption or covalent immobilization as already explained. In addition, PDA coatings obtained in the presence of $NaIO_4$ are intrinsically more homogeneous than their counterparts obtained from oxygenated dopamine solutions at pH higher than 7 [35], because the oxidation process occurs homogeneously in the solution in the former case and because the deposition is faster close to the water/air interface in the latter case.

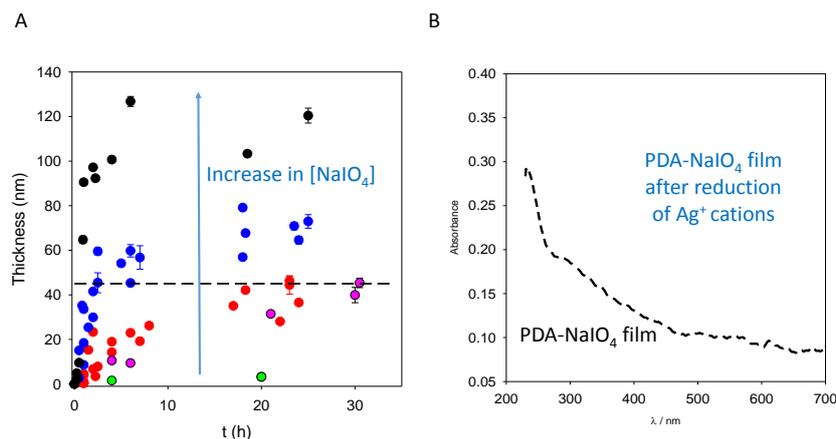


Figure 3: A: Thickness of PDA coatings, as measured by ellipsometry (same protocol as in Fig. 1) from a 2 mg.mL⁻¹ dopamine solution in the presence of 50 mM sodium acetate buffer at pH = 5.0 with added NaIO₄ as the oxidant: (●) 0 mM, (●) 0.1 mM, (●) 1mM, (●) 10 mM and (●) 20 mM. The horizontal dashed line corresponds to the maximal value of 45 nm obtained in the presence of 2 mg.mL⁻¹ dopamine in the presence of 50 mMTris buffer at pH = 8.5.

B: UV-vis spectra of a PDA-NaIO₄ 10 mM film after 1h of dopamine oxidation (---) and after its exposure to a 10 mg.mL⁻¹ AgNO₃ aqueous solution during 15 min (—).

The reason why PDA-NaIO₄ coatings are so different in their properties than the PDA-O₂ coatings has been rationalized by the dual role played by periodate as a strong oxidant: it favours a fast formation of 5,6 dihydroxyindole (DHI), the precursor of PDA without interference from Tris molecules but simultaneously it oxidizes and degrades the formed PDA explaining the appearance of carboxylic acid groups on its surface as demonstrated by X-Ray Photoelectron Spectroscopy, Infrared spectroscopy and Cross Polarization ¹³C Nuclear Magnetic Resonance spectroscopy [35]. The presence of carboxylic groups and an increased roughness explain the superhydrophilic properties of PDA-NaIO₄ films, not displayed by the PDA-O₂ films.

This last finding strongly suggest that there may be as many types of PDA coatings as experimental conditions (nature of the buffer, oxidant, nature of the used catecholamine, etc) used during their deposition. This is a fantastic avenue for new discoveries, all of them offering to target new properties and hence new possible industrial applications. However, the efficiency of this research will be significantly improved if the molecular nature of PDA would be better understood. It has to be recognized that the state of advancement in this fundamental domain lags far behind the screening of possible applications of PDA films. This is not a surprise owing to the complexity of the possible reaction pathways leading to highly heterogeneous eumelanin [36] related materials from catecholamines [37]. Even if it is not the scope of this review it has to be said that the favoured assumptions, but without real proofs, for the structure of PDA and related eumelanin materials are either that of a linear polymer or that of a supramolecular structure made from the association of small oligomers of DHI [38, 39] (Figure 4).

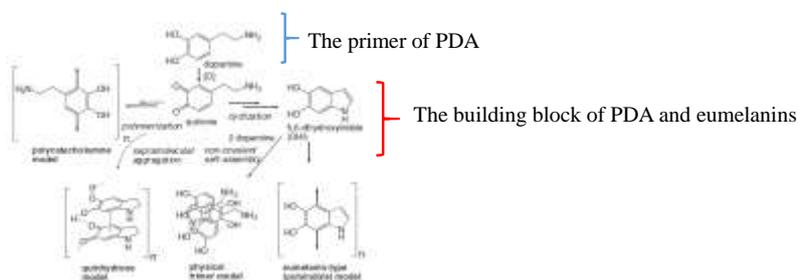


Figure 4: possible reaction pathways leading to PDA coatings and to eumelanins from dopamine and other catecholamines.

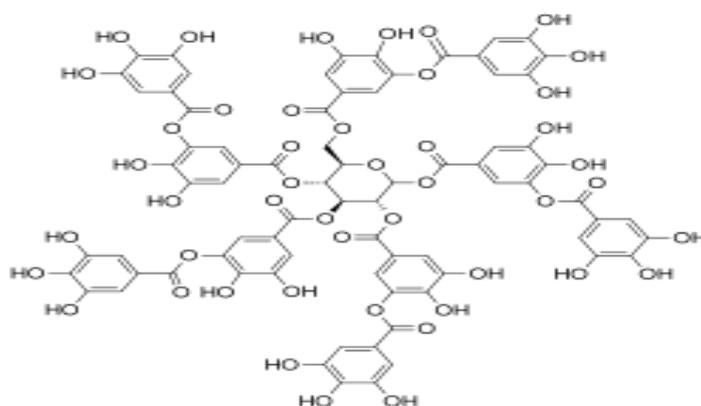
Anyway the PDA coatings are extremely stable in acidic and neutral solution, less stable when deposited on oxides in highly basic solutions (pH > 10) because of oxide leaching [40]. However, as a personal observation of the author, they tend to crack when dried for a long time. This drawback has clearly to be overcome for long term use of PDA coated materials.

The black colour of PDA decreases of course the aesthetics of the coatings but this point is not of major concern in tubings and on already opaque substrates.

In the author's opinion, even if the PDA coatings offer high versatility with respect to the chosen substrate, the application methodology (Figure 2) and the possibility of secondary functionalisation, the major hurdle for their implantation on a large industrial scale will be the prohibitive cost of dopamine and other catecholamines (of the order of a few US dollars per gram in November 2016 by most of the large scale chemical furnishers). From this point of view, versatile coatings based on polyphenols may offer an interesting perspective.

III. POLYPHENOL BASED COATINGS

We all observed the deposition of a yellowish or a reddish coating on the surface of tea cups or wine glasses during the consumption of tea or red wine respectively. It is also a common piece of experience that these deposit are hard to clean. Only very recently have these observations been qualitatively understood and exploited in a rationale manner to design versatile coatings. They are due to the deposition of polyphenols at the solid/liquid interface. A broad range of polyphenols, among them tannic acid (scheme 2) allow for such a deposition.



Scheme 2: Structure of tannic acid.

The molecular origins behind the obtention of such coatings are even less understood than the deposition of PDA coatings. In contrast to PDA, the coatings obtained from tannic acid are in the monolayer thickness range but nevertheless conformal (as inferred from cyclic voltametry) and the deposition is achieved in a few minutes over a broad concentration range of the highly water soluble tannic acid [41] (Figure 5A). Like PDA coatings, tannic acid based coatings allow secondary functionalization through the reduction of metallic cations like Ag^+ (Figure 5B), grafting of proteins after oxidizing the catechols functions into quinones. Anyway the strong interactions between proteins, like collagen and tannic acid are at the origin of many effects like the astringency of fruits. The polyphenol based coatings are perfectly biocompatible [12] and can afford protection against corrosion.

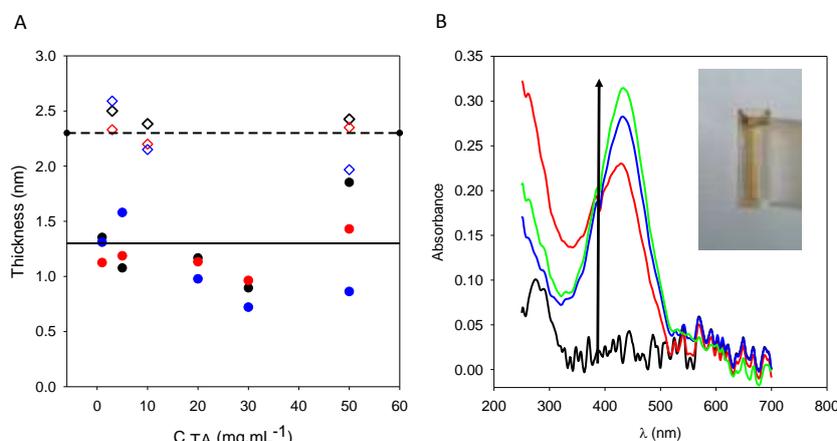


Figure 5:

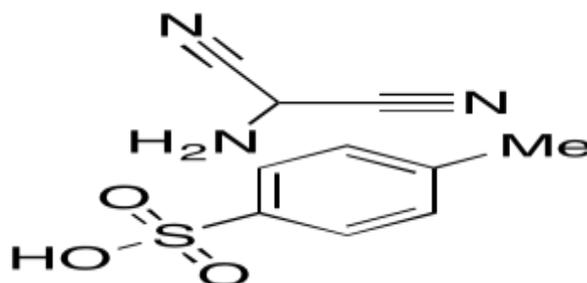
A: Steady state thickness of TA films on gold (circles) and silica (losanges) coated electrodes at the end of the buffer rinse steps as a function of the solute concentration in solution. The thickness was determined from quartz crystal microbalance measurements using the Sauerbrey equation and the film mass density to calculate the thickness from the measured frequency changes of the quartz crystal at the third (●, ◇), fifth (●, ◇) and seventh (●, ◇) overtone of the quartz crystal. The horizontal lines are aimed to guide the eye.

B: Absorption spectrum of a TA acid film deposited during 15 min from a 5 mg.mL⁻¹ solution in sodium acetate buffer (—) and after further reaction with AgNO₃ (10 mg.mL⁻¹) during 15 (—), 30 (—), 45 (—) and 60 (—) min. The black vertical arrow indicates the direction of increasing reaction time. The inset is a digital picture of the quartz cuvette after one hour of silver deposition in the presence of AgNO₃ at 10 mg.mL⁻¹. Modified from reference [41].

The major pitfall of polyphenol based coatings seems to be their lack of stability in the presence of an aqueous environment. Indeed tannic acid undergoes hydrolysis, as an ester of glucose (scheme 2). If this problem is resolved, probably by mixing polyphenols with inorganic additives to yield composite and robust coatings or after chemical crosslinking, they will become extremely interesting as a platform for versatile, substrate independent coatings, with the possibility to rapidly (in a few tens of seconds) coat materials with transparent (in the visible range of the spectrum) and cheap films (the high availability of polyphenols from plants allow to expect a cost of about one US dollar per kilogram).

IV. AMINOMALONONITRILEBASEDCOATINGS

Very recently, it was found, inspired by the possibility that amino acids can be obtained in mixture of methane, ammonia and hydrogen in the presence of an electrical discharge [14], that the paratoluene sulfonate salt of aminomalonnitrile (Scheme 3) undergoes polymerisation when the pH is adjusted to 8.5 [15]. The obtained material not only forms a polymer in solution but also a coating on all kinds of materials, like PDA and many polyphenols, an observation already quoted by Stanley Miller in his primitive soup experiment [14].



Scheme 3: Chemical structure of the paratoluene sulfonate salt of aminomalonnitrile.

The growth kinetics of those coatings is slow (an average growth rate of 3.9 nm.h⁻¹ as measured by Atomic Force Microscopy, Figure 6) but with the possibility of fixing silver cations and a partial reduction of them into metallic silver (as found by means of Auger spectroscopy) and an excellent biocompatibility. However, these coatings share a relatively weak stability with the polyphenol based coatings.

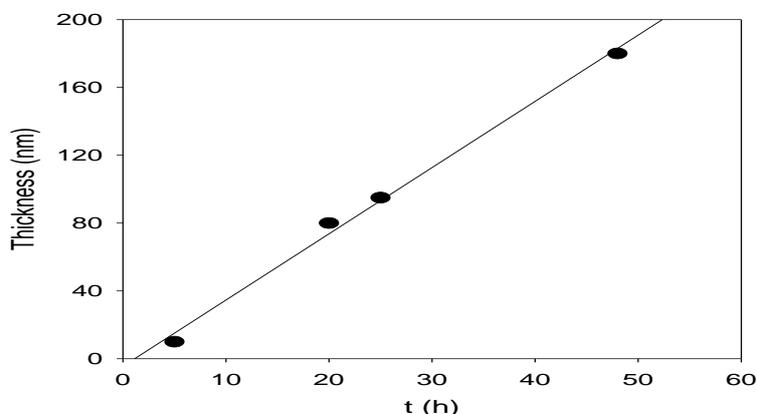


Figure 6 : Thickness of polymer coatings obtained during the polymerization of aminomalonnitrile (at 2% w/v and at pH 8.5) as measured by Atomic Force Microscopy as a function of the reaction time. Slope of the straight line obtained through linear regression: 3.91 nm.h⁻¹. Modified from reference [15].

Among the versatile coating platforms described in this article, those based on the polymerization of aminomalonnitrile are the less well known. They share many common analogies with PDA based coatings and the underlying chemistry reserves also many difficult problems to be solved and certainly many fascinating surprises not only from a technological point of view but also with respect to fundamental knowledge in prebiotic chemistry.

V. CONCLUSIONS AND FUTURE IMPROVEMENTS IN VIEW OF INDUSTRIAL APPLICATIONS.

Three possible versatile coating methodologies of all kinds of solid materials have been described in this article. The PDA and aminomalonnitrile based strategies allow to produce thick coatings up to hundred nm in thickness but with relatively slow kinetics (a few nm per hours) which may nevertheless be sufficient to obtain thin coatings. The PDA coatings are robust and strongly adhering to their substrate whereas the aminomalonnitrile based coatings, as mainly poly(amino acid) based films, will certainly undergo hydrolysis in acidic media.

The coatings based on polyphenols, mainly tannic acid, yield monomolecular thick films in a very short time but suffer still from a lack of stability. If stabilized properly, they will become extremely competitive from the point of view of their cost.

No doubt that surmounting the stability and cost problems the three classes of coating methodologies presented in this short review will provide major progress in coatings for industrial use.

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