Published in: Progress in Polymer Science (2013), vol. 38, pp. 236-270.
Status : Postprint (Author's version)

Catechols as versatile platforms in polymer chemistry

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Abstract: Catechols represent an important and versatile building block for the design of mussel-inspired synthetic adhesives and coatings. Indeed, their ability to establish large panoply of interactions with both organic and inorganic substrates has promoted catechol as a universal anchor for surface modifications. In addition to its pivotal role in adhesive interfaces, the catechol unit recently emerged as a powerful building block for the preparation of a large range of polymeric materials with intriguing structures and fascinating properties. The importance of catechols as efficient anchoring groups has been highlighted in recent excellent reviews partly dedicated to the characterization of their adhesive mechanisms onto

surfaces and to their applications. The aim of this paper is to review for the first time the main synthetic approaches developed for the design of novel catechol-based polymer materials. We will also highlight the importance of these groups as versatile platforms for further functionalization of the macromolecular structures, but also surfaces. This will be illustrated by briefly discussing some advanced applications developed from these catechol-modified polymers. The review is organized according to the chemical structure of the functionalized catechol polymers. Chapter 1 discusses polymers bearing catechols embedded into the polymer main chain. Chapter 2 focuses on the attachment of catechol moieties as pendant groups and Chapter 3 describes the different approaches for incorporation of the catechol unit at the extremity of well-defined polymers.

Keywords

Catechol derivatives, functional polymers, architectures

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List of abbreviations

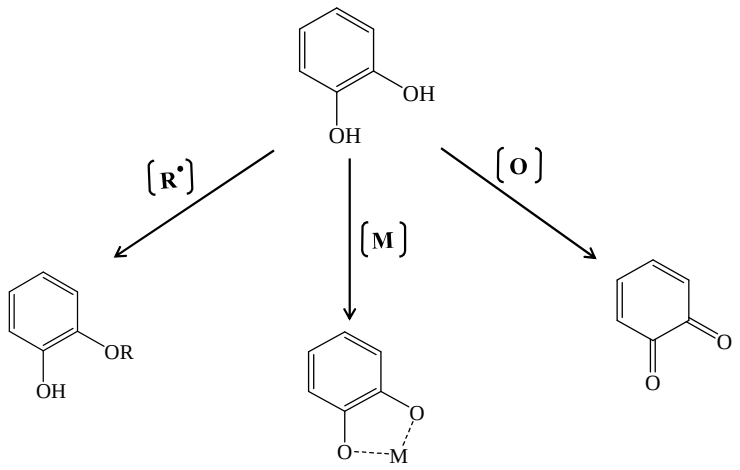
AB	TEM
AFM	antibacterial
AIBN	atomic force microscopy
ATRP	2,2'-azobisisobutyronitrile
BIBB	atom transfer radical polymerization
CNTs	2- bromoisobutyryl bromide
CRP	carbon nanotubes
CuAAC	controlled radical polymerization
DLS	copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition
$DMAEMA^+$	dynamic light scattering
DMAP	(2-(methacryloxy)ethyl) trimethylammonium chloride
DOPA	4-dimethylaminopyridine
EDC	3,4-dihydroxyphenyl-L-alanine
H_2O_2	ethyl(dimethylaminopropyl) carbodiimide
HBTU	hydrogen peroxide
	O-(benzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium
HEMA	hexafluorophosphate
HOBt	2-hydroxyethyl methacrylate
HRP	1-hydroxybenzotriazole hydrate
LbL	horseradish peroxidase
Mefp	layer-by-layer
MMT	mytilusedulis foot protein
NCA	Na^+-montmorillonite
NHS	α-amino acid *N*-carboxyanhydride
NPC	*N*-hydroxysuccinimide
PAA	*p*-nitrophenyl-chloroformate
PAH	poly(acrylic acid)
PCL	poly(allylamine hydrochloride)
PDMS	poly(ε-caprolactone)
PEG	poly(dimethylsiloxane)
PEI	poly(ethylene glycol)
PNIPAM	poly(ethylenimine)
PolyDp	poly(*N*-isopropylacrylamide)
PSS	poly(dopamine)
PTFE	poly(styrene sulfonate)
RAFT	poly(tetrafluoroethylene)
ROMP	reversible addition-fragmentation chain transfer polymerization
ROP	ring-opening metathesis polymerization
SLS	ring opening polymerization
SBP	static light scattering
SEM	soybean peroxidase
$Sn(Oct)_2$	scanning electron microscopy
TEA	tin(II) octanoate

triethylamine
transmission electron microscopy
TsT
V-501
XPS

Trichloro-*s*-triazine
4,4'-azobis(4-cyanopentanoic acid)
x-ray photoelectron spectroscopy

1. Introduction

Catechols occur naturally in fruits and vegetables but in poisons, insects and teas as well. They are small molecules widely used for synthesis in food, pharmaceuticals or agrochemical ingredients, but also as stabilizing additives. For instance, *tert*-butylcatechol is largely employed as a polymerization inhibitor.[1] In organic chemistry, catechol and its derivatives have widely attracted scientists since decades. Indeed, they can act as antioxidant agents, as chelating agents in coordination chemistry or trap radicals to cite only few (Fig. 1).



Where R• means Radical; M, Metal and O, Oxidant

Fig. 1. Main chemical properties of catechols.

In 1981, catechols have been identified by Waite and coworkers to be responsible for the versatile adhesion of mussels in the most inhospitable regions under very harsh and wet conditions.[2] This important discovery led to deeply studying the exact structure of the proteins responsible for the adhesion of mussels and their action mode.[3-6] The

posttranslationally modified amino acid, 3,4-dihydroxyphenyl-L-alanine (DOPA; **2**, Fig. 2), has been determined as the main element required for this moisture-resistant adhesion.[4] Proteins found in the mussel adhesive plaque, Mefp for *Mytilusedulis* foot protein, were largely characterized and six of them were identified to present a DOPA content ranging from 3 mole % (Mefp-2) to 30 mole % (Mefp-5).[5, 7] Evidences of its role in strong interactions with either organic or inorganic surfaces have been afforded by Atomic Force Microscopy (AFM) on both small polymer chains containing catechol end groups[8] and Mefps[9]. Specific adhesion mechanism of these small molecules to a large panel of surfaces is still not completely understood. It has been studied for many years and several proposals of interaction modes can be found in the literature. These have been reviewed elsewhere[10] and seem to be substrate dependent. However in all cases, covalent or strong non-covalent interactions (hydrogen bonds or π-π stacking interactions for instances) can be found between catechol groups and inorganic substrates such as mica[11] for example. As far as metal oxides are concerned, catechol groups are assumed to form bidentate bonding with the metal surface.[12, 13]

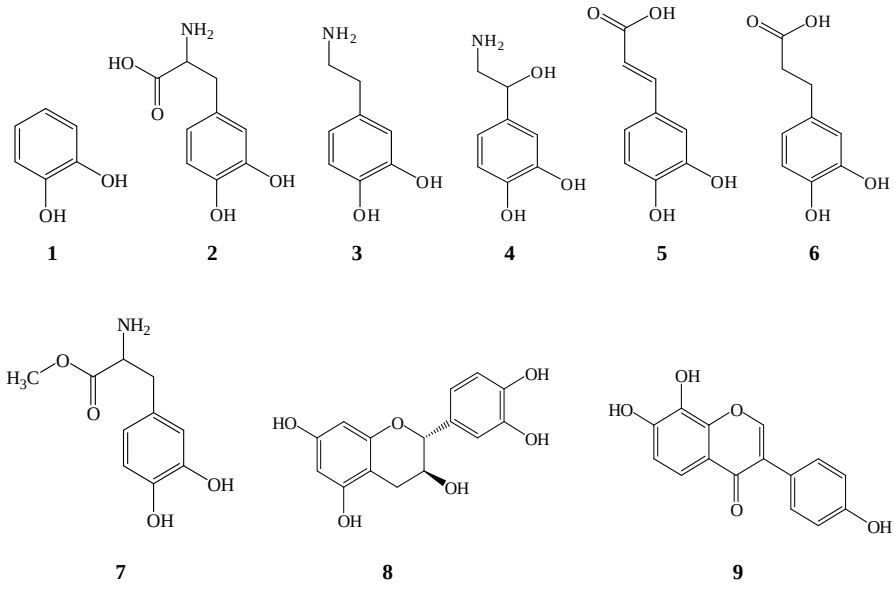


Fig. 2. Catechol and some derivatives.

This amazing adhesion under wet conditions combined with the intrinsic properties of catechols cited here above (antioxidant, ligation ability …) have opened the door to the design of new (multi)functional platforms based on catechols. This review describes the state-of-the-art research in the synthesis of (bio)macromolecules bearing catechols that are used as versatile platforms for the design of adherent materials, multifunctional materials and inorganic/polymer hybrids. Numerous scientific groups have worked worldwide on this topic since almost fifteen years. These works will be further detailed in the following sections. Briefly, catechol functions can be incorporated into macromolecules as main, side and end-chain groups by employing various synthetic pathways. The successfully employed strategies include i)either the oxidative[14] or enzymatic[15] polymerization of functional catechols; ii)the polymerization of monomers bearing catechol groups protected or not (radical polymerization[16] or peptide synthesis[17]);iii) the controlled/living polymerization of synthetic monomers in the presence of catechol basedinitiators (ATRP,[18]ROMP[19] …) or chaintransfer agents (RAFT[20]). The point that will be stressed on in this review concerns the final architecture of the different macromolecules obtained from these different synthetic approaches (Fig. 3). We will also emphasize how the reactivity of the catechol functional groups can be nicely exploited for further polymer derivatizations and for the development of advanced applications.

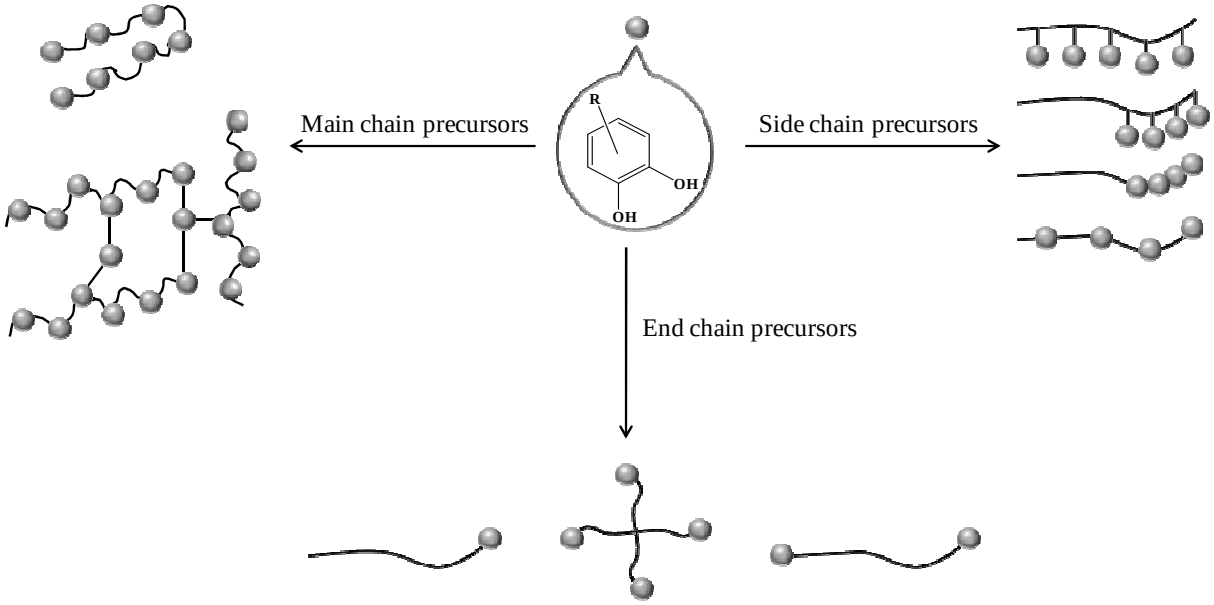


Fig. 3. Catechol based building blocks for macromolecular engineering.

2. Main chain precursors

Molecules bearing catechols are easily converted into highly reactive quinones either by a strong oxidant agent such as $NaIO_4$[21] or an enzyme (horseradish peroxidase combined with hydrogen peroxide, HRP/H_2O_2, for instance[15]), but also by an aerated aqueous solution at neutral to alkaline pH.[22] In some conditionsthat will be detailed below, self-polymerization of some of these oxidized products is observed, leading to polymers that are of prime importance in the field of surface modifications. These oxidative polymerizations result in the formation of uncontrolled cross-linked films composed of a mixture of cross-linked products bearing mostly catechol and quinone groups that can be exploited for further derivatizationsas it will be illustrated in the next sections.

2.1. Autopolymerization in aerated basic solutions.

2.1.1. General process and initial developments.

Autopolymerization of catecholamines in aerated basic conditions was first demonstrated by Messersmith *et al.* for dopamine (**3**,Fig. 2) in a Tris buffered dopamine solution at pH 8.5.[14] When this polymerization occurs in the presence of substrates, an adherent poly(dopamine) (polyDp)film is *in situ*deposited on the surface after 24 hours of immersion (Fig. 4). Film thickness increases with the immersion time as shown on Fig.5 (A) where a plateau isobtained after 24 hours.[14] Final polyDp thickness also increases with the polymerization temperature.[23] Both organic and inorganic surfaces were well covered, including poly(tetrafluoroethylene) (PTFE), known for its antiadhesion properties (Fig. 5 (B)).[14]

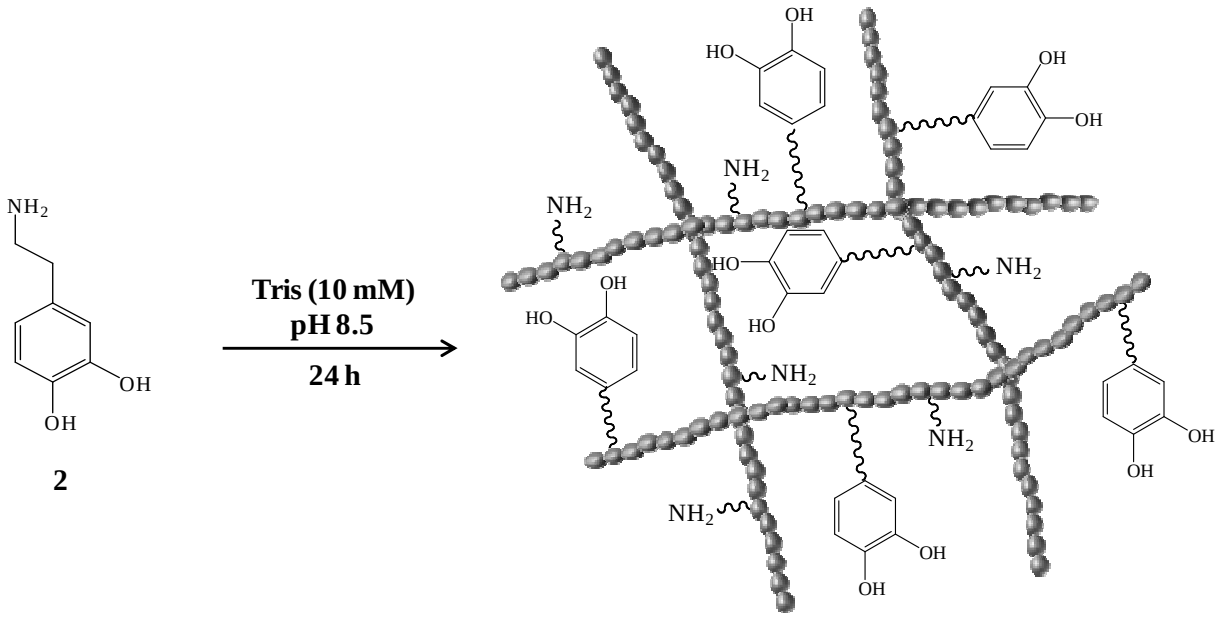


Fig. 4. Poly(dopamine) (polyDp) network adapted from Messersmith *et al.*[14]

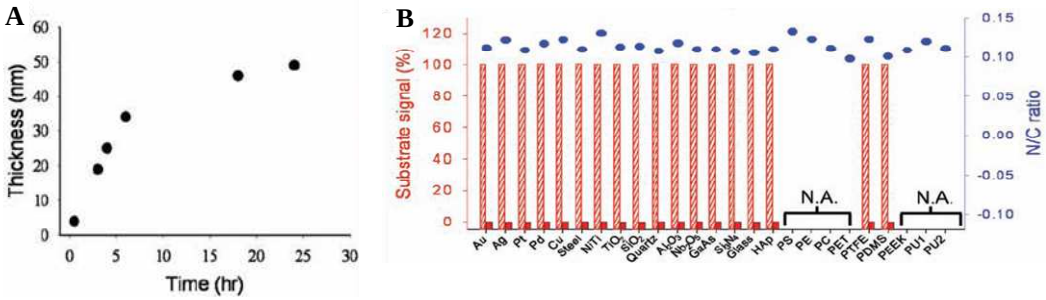


Fig. 5. Thickness evolution of poly(dopamine) (polyDp) coating on Si as measured by AFM of patterned surfaces (A), X-ray Photoelectron Spectroscopy (XPS) characterizations of several polyDp coated surfaces (B).[14] The bar graph represents the intensity of characteristic substrate signal before (hatched) and after (solid) coating with polyDp. "N.A." means that XPS signals of the substrates were indistinguishable from the polyDp signal.The blue circles represent the nitrogen/carbon ratio after polydopamine coating.

From a mechanistic point of view, the polyDp network (Fig. 4) is presumably formed by Schiff base formation and/or byMichael type addition involvingquinone groups of oxidized dopamine with its primary amino group.[8, 24, 25] Up to now, the exact structure of polyDp is still lacking in the literature but some proposals can be found in publications. As established spectrophotometrically by Linert and coworkers, dopamine oxidation leads to dopaminochrome (**10**,Fig. 6) following a multistep reaction pathway.[22] This molecule can then self-polymerize and produce polymers that are usually complex networks with free catechol groups available for further chemical reactions (**11** and **12**,Fig. 6).These catechol groups are responsible for the strong adhesion of the polymer network to any kind of surfaces,both organic (polysulfone,[26, 27]polyethersulfone,[28] polyethylene,[29]polypyrrole,[30] hydrophobic/superhydrophobic polymers, [31-33] silanes[34-37] and even yeast cells[38] or raw cherry tomato[39]) and inorganic (clays,[40] iron-based nanoparticles,[41, 42] gold,[43] SiO_2[44-47] and others[48-52]). Melanin formation follows a similar process and also produces such complex systems.[53]

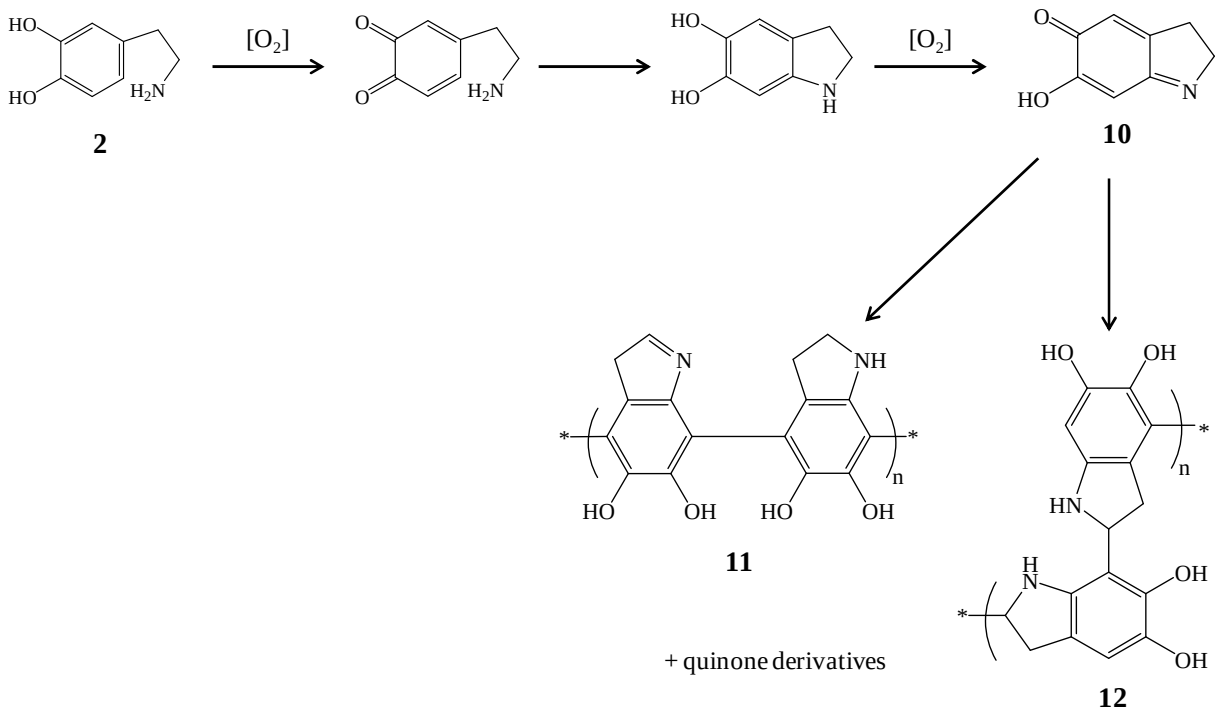


Fig. 6. Mechanistic scheme for the formation of polyDp (**11** and **12**) by self-polymerization of dopamine.[43, 51, 54]

The ability of PolyDp to adhere onto various subtrates has been largely exploited to promote cells adhesion on several surfaces such as glass, polystyrene, poly(dimethylsiloxane) (PDMS) and even PTFE.[55-58] Very recently, Jiang and coworkers managed to pattern PEG-coated surfaces with polyDp using microcontact printing (μCP) and PDMS stamps (Fig. 7) which were further exploited to spatially control the anchoring of mammalian cells.[58]

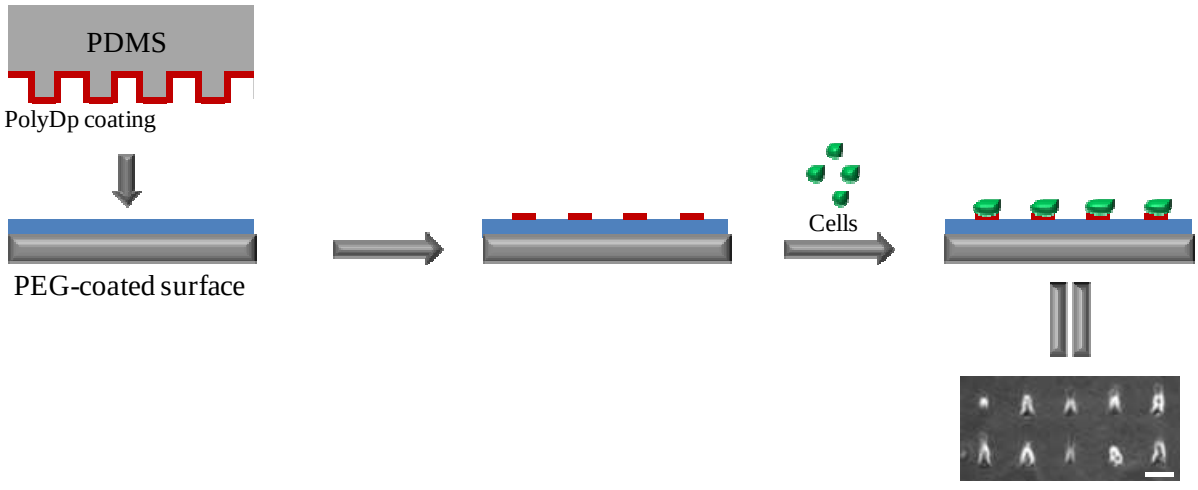


Fig. 7. Strategy for cells patterning using polyDp coating (scale bar is 100 µm).[58]

The substrates can also play the role of sacrificial templates that are removed after polyDp formation in order to form stable polyDp capsules[59-65] that can be loaded with hydrophobic drugs such as anticancer agent (thiocoraline).[66] As no drug leakage was observed after template removal, these new drug carriers have opened the door to potential applications in biotechnology and drug delivery systems for instances.More particularly, Zhou and coworkers have demonstrated pH stability for such microcapsules with outstanding unidirectional loading of rhodamine 6G (Rh6G) in some solvents.[60] Indeed, the polyDp capsules are almost impermeable to Rh6G in ethanol while the inverse is observed in aqueous solution with uptake rates that depend on pH (increased at high pH). The loading in aqueous solution is driven by the high osmotic outside pressure and gradient chemical potential. At a low pH, the amino groups of polyDp are protonated and charge repulsion between them and the positively charged dye is responsible for the low loading efficiency. At high pH, the catechols become negatively charged favoring the diffusion of the dye inside the capsules.

Beside the intrinsic properties of polyDp, the presence of residual quinone groups onto the polymer backbone allows forfurther modifications with thiol compounds (alkanethiol, thiol-terminated methoxy-poly(ethylene glycol), thiolated hyaluronic acid) [54, 67] and nitrogen derivatives (amine-terminated methoxy-poly(ethylene glycol), imidazoles)[68-70]leading to the formation of new materials with different structures and properties (Fig. 8).

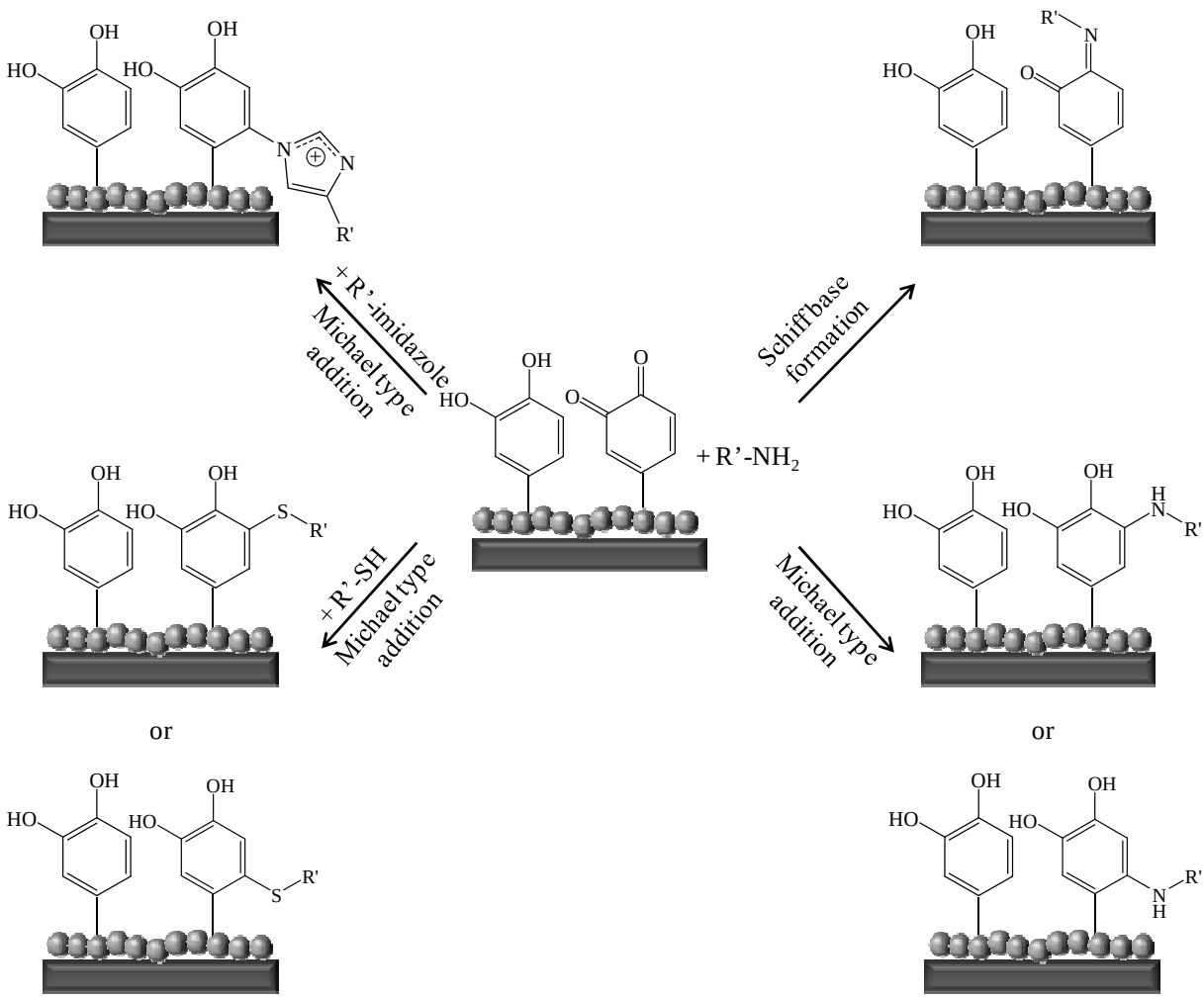


Fig. 8. Possible reaction pathways of oxidized catechols with amines, thiols or imidazoles where R' stands for a polymeric or peptidic backbone.

These pioneering works have opened up wide possibilities for the preparation of adherentpoly(catecholamines) based coatings on any kind of substrates[14, 71]. Their applications in the biomedical field has been the topic of a recent review [72]. Although the catechol groups are responsible for the strong adhesion of the coatings to the substrates, their high reactivity towards various reagentsisalso exploited for further derivatizationsto provide various surface functionalities (Fig. 9), as it will be discussed in the following sections.

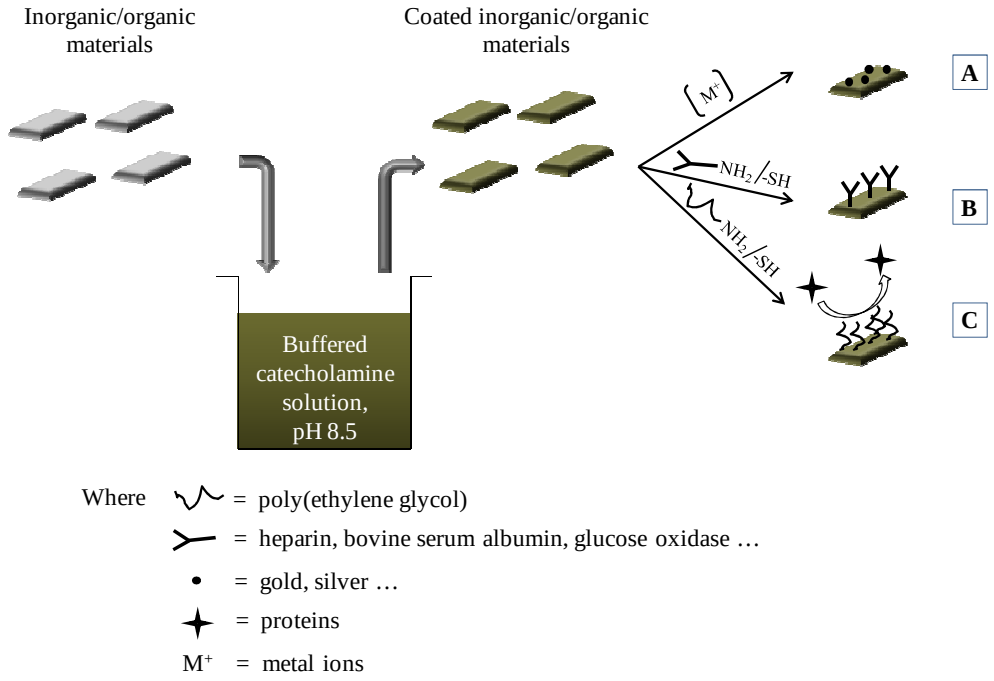


Fig. 9. Polydopamine coating and further derivatizations.

2.1.2. Poly(catecholamines) – platforms for the design of advanced (nano)hybrids.

2.1.2.1. Poly(catecholamines): reducers of metal salts and other oxides.

Catechol groups of polyDp can act as strong reducing agents for graphene oxide[54, 73, 74]and metal salts for the production of metal nanoparticles[75, 76] (Fig. 9, pathway A). For instance, Xin*et al.* have obtained carbon nanotubes (CNTs) coated with gold nanoparticles in a two steps procedure.[77] CNTs were first coated by polyDp by immersion in a buffered dopamine solution, followed by dipping into $HAuCl_4$ aqueous solution. Nanometricgold particles (20-30 nm size) were obtained by reduction of Au^{3+} by catechols of polyDp without the need of any other chemical reagent (Fig. 10).

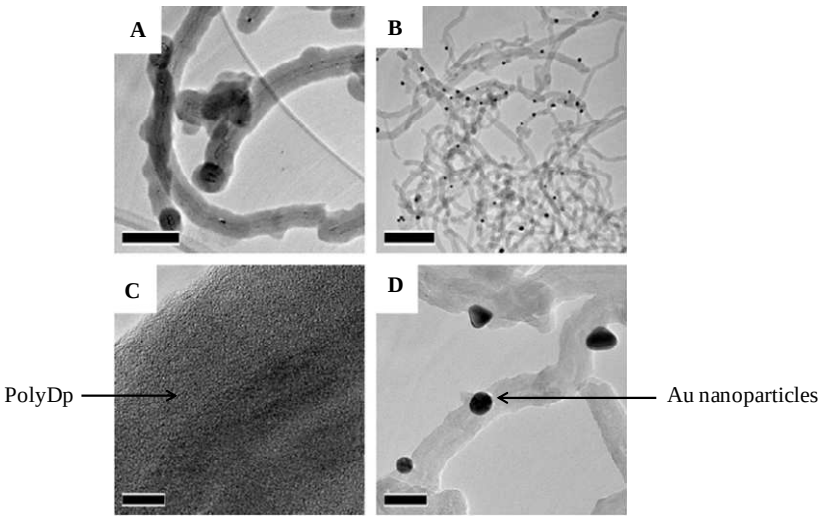


Fig. 10. Transmission Electron Microscopy (TEM) images of carbon nanotubes coated with polyDp (A,C) and carbon nanotubes coated with polyDp and Au nanoparticles (B, D).[77] Scale bars are 200 nm (A), 350 nm (B), 10 nm (C) and 50 nm (D).

Silver nanoparticles have also been immobilizedin a similar wayon various polyDp coated substrates[78-82] to obtain final antibacterial (AB) properties[83, 84]. Such silver nanoparticles can also be elaboratedin solution by mixing dopamine and $AgNO_3$ under alkaline conditionsleading to a bright yellow solution of Ag^0 nanoparticles stabilized with a polyDp coating.[85]This material was then exploited for the fast and sensitive colorimetric detection of Cu^{2+} ions. Indeed, in the presence of Cu^{2+}, the initiallybright yellow polyDp/Ag^0assemblyaggregated with the formation of a dark brown suspension (Fig. 11).

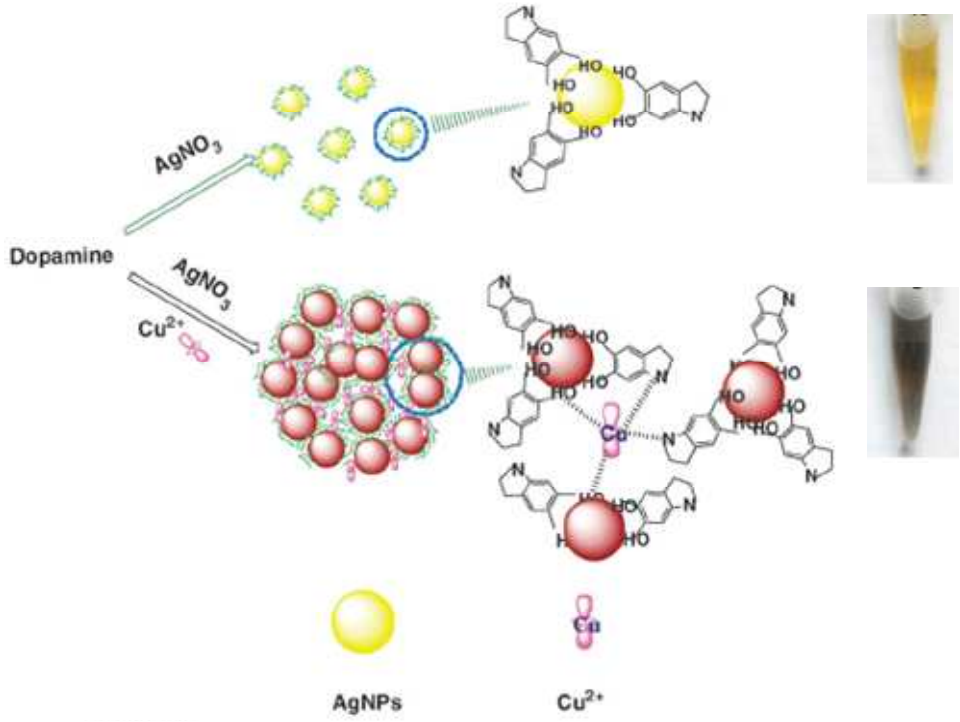


Fig. 11. Mechanism of colorimetric determination of Cu^{2+} with silver/dopamine nanoparticles.*Reproduced with permission from ref [85]. Copyright 2011 The Royal Society of Chemistry.*

2.1.2.2. Poly(catecholamines) as templates for the formation of minerals.

Based on these remarkable binding properties towards various metal ions[86, 87], different research groups havealso used polyDp coatings as templates for the formation of hydroxyapatite by co-precipitation of calcium and phosphate ions (Fig. 12).[88-90] The hydroxyapatite formation can be carried out on various kinds of surfaces such as CNTs[88, 90] or polymeric substrates (porous cellulose, polyester, polytetrafluoroethylene for instances)[89] to convert them into scaffolds for bone tissue regeneration and implantation.

Such stabilizing effect of the catechols towards ionic species has also been exploited by Park *et al.* for the mineralization of $CaCO_3$vaterite crystals which were further transformed into bone hydroxyapatite minerals in a simulated body fluid.[91-93] $CaCO_3$ microspheres

were prepared by mixing $CaCl_2$ and Na_2CO_3 with dopamine[91, 92] or by bubbling CO_2 in an aqueous mixture of $CaCl_2$, NH_4OH and dopamine[93].

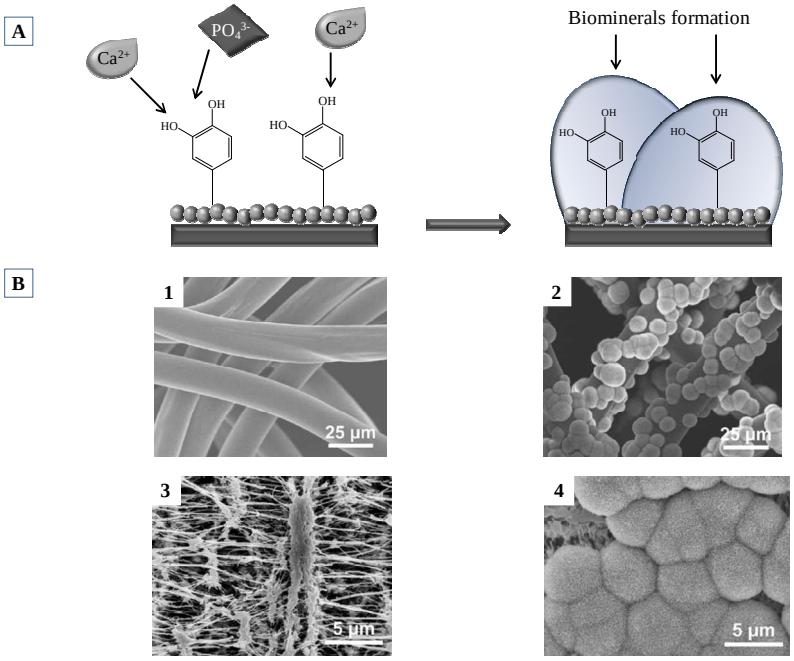


Fig. 12. A) Formation of calcium phosphate crystals on polyDp coatings, B) Scanning Electron Microscopy (SEM) images of polyester fibers (1 and 2) and PTFE membrane (3 and 4) without and with hydroxyapatites.[89]

2.1.2.3. Poly(catecholamines) as anchoring layers for polymer brushes and other (bio)macromolecules.

PolyDp coating were also exploited to graft (i) an ATRP (Atom Transfer Radical Polymerization) initiator for controlled radical polymerization[94-97] to generate well-defined polymer brushes on various surfaces via a "grafting from" approach that can be further derivatizedfor instance by the anchoring of chitosan (Fig. 13) or (ii) various (bio)macromolecules (Fig. 9, pathways B and C). These can either favor cell adhesion and improve blood compatibility by grafting heparin, concanavalin A or bovine serum albumin (BSA)[98-112] or avoid protein adhesion with poly(ethylene glycol) (PEG)[113-116], platelet activation thanks to selenocystamine[117]and even fungal colonization or bacterial fouling

when amphotericin B[118] or quaternary ammoniums salts[119] are immobilized onto the surface. Moreover, several research groupshave developedoriginal biosensors based on a polyDp coating post-functionalized with enzymes[120] such as glucose oxidase[121, 122] or antibodies[123-125].

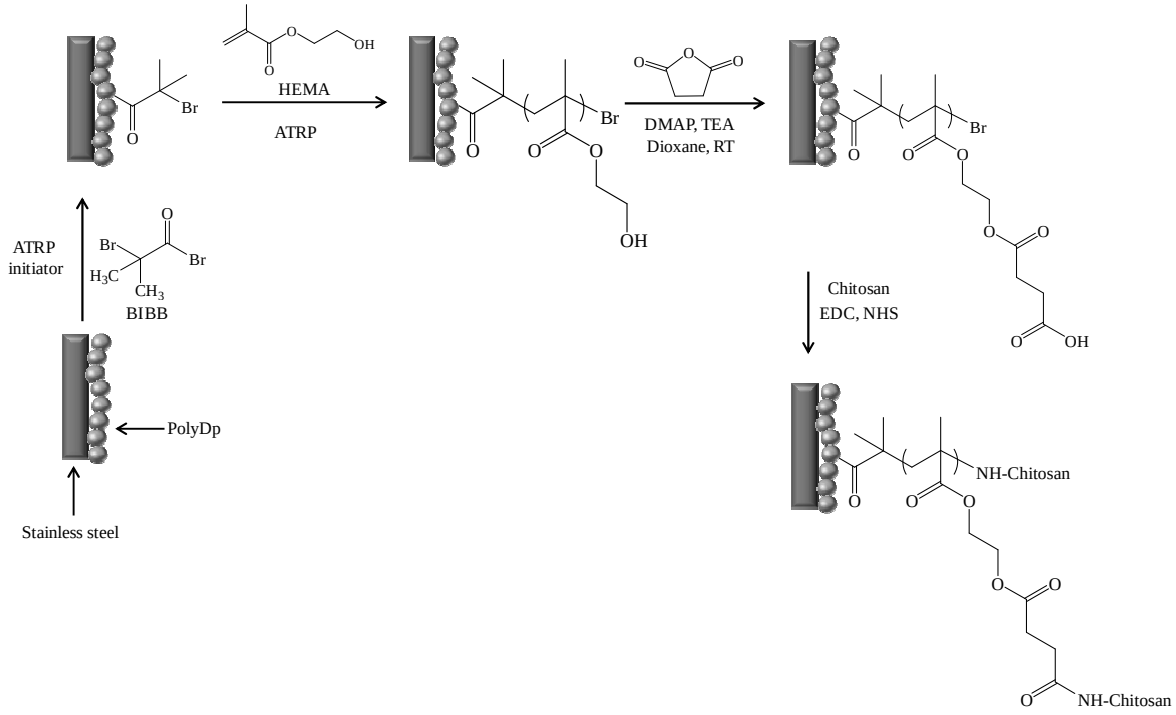


Fig. 13. ATRP immobilized initiator on polyDp coating and controlled radical polymerization of 2-hydroxyethyl methacrylate (HEMA) followed by the immobilization of chitosan.[97]

Other functional groups can also be incorporated onto biomimetic coatings from functionalized catecholamine. Messersmith *et al.* have reported on the self-polymerization of norepinephrine(**4**,Fig. 2) in the same conditions. This molecule contains an additional hydroxyl group compared to dopamine.[126] Hence, as depicted in Fig. 14, after oxidative polymerization in the presence of a gold substrate, these secondary OH groups of the resulting poly(norepinephrine) can be then exploited to initiate the ring-opening

polymerization(ROP)[127] of lactones such as ε-caprolactone, thereby providing a biodegradable poly(ε-caprolactone) (PCL) coating on the surface.

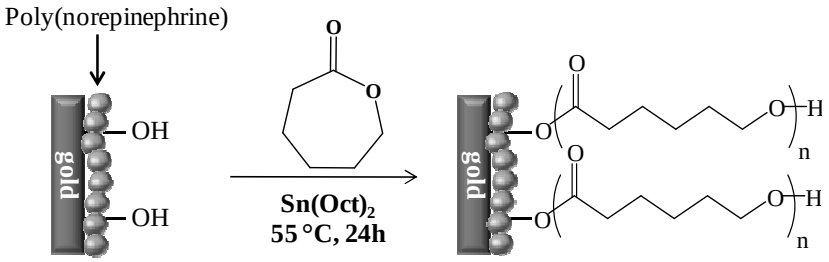


Fig. 14. Ring-Opening Polymerization[127] of ε-caprolactone on poly(norepinephrine)-modified gold substrate.[126]

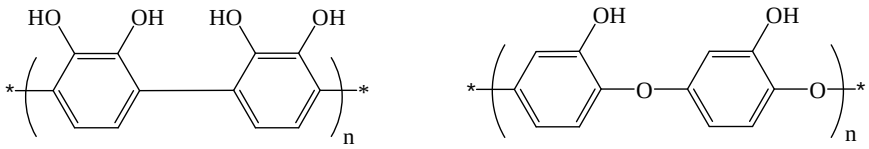
2.2. Polymerization of catechols catalyzed by enzymes.

Enzymatic polymerization is defined as "the *in vitro* polymerization of artificial substrate monomers catalyzed by an isolated enzyme *via*nonbiosynthetic (nonmetabolic) pathways".[128, 129] Polyphenols can be produced by enzymatic polymerization of catechols under very mild conditions (in water at room temperature under atmospheric pressureand at neutral pH) without using any toxic reagents. Moreover, starting substrates are most often coming from renewable resources that make the enzymatic polymerization a great alternative to other synthetic pathways that requiredpetrochemical sources. In this context, several enzymes can be involved in such polymerizations as discussed below.

Peroxidases such as soybean peroxidase (SBP) combined with hydrogen peroxide (H_2O_2) were, for example,used to polymerize catechol (**1**, Fig. 2). Indeed the peroxidase/H_2O_2 combination is well-known to form an active enzyme substrate complex able to oxidize hydrogen donors such as phenols and amines.[15]Under these conditions, a polycatechol, incorporating both (2,3-dihydroxy-1,4-phenylene) (**13**) and (2-hydroxy-1,4-oxyphenylene) (**14**) subunits (Fig. 15) was obtained. It is important to note that phenol groups of subunit **14**

are expected to have different chemical properties to catechols of **13** but this difference of reactivity is not discussed in the paper.

Dosoretz*et al.* performed enzymatic polymerization of catechols with horseradish peroxidase (HRP) in water and obtained polymers with high water solubility.[130]Nazari*et al.* compared poly(catechols) obtained by catalytic polymerization with HRP and a cationic metalloporphyrin as catalysts.[131]Tetrapyridilporphyrin seemed to be a more-efficient catalyst as final polymer has higher molecular weight and presented better thermal stability.



13 **14**

Fig. 15.(2,3-dihydroxy-1,4-phenylene) (**13**)and (2-hydroxy-1,4-oxyphenylene) (**14**) subunits found in the poly(catechol) structure.[15]

Flavonoids such as catechin (**8**,Fig. 2) were polymerized using HRP with a final average molecular weight ranging from 4000 to 12000 g/mol.[132] A polymerization mechanism proposal was based on radical polyrecombinationprocessesto produce oligomers that can further recombine into polymers (Fig. 16), although no more details were given. However this pathway has been identified to compete with the probable formation of oxidation products and so the exact structure has not been perfectly identified yet. Poly(catechin) was also synthesized using HRP and the final product showed strong radical scavenging activity and inhibition effect against xanthine oxidase, a low-density lipoprotein responsible for the formation of uric acid.[133]

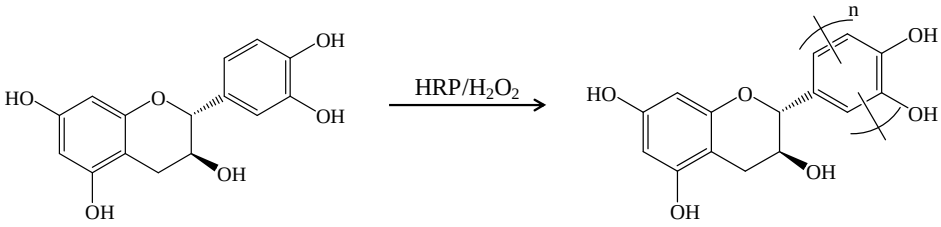


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Fig. 16. Proposed structure for flavanolbased polymers.[132]

Additionally, caffeic acid (**5**,Fig. 2) was deposited onto gold surfaces functionalized with 4-aminothiophenol by dip-pen nanolithography.[134]It was then treated with HRP directly on the surface leading to formation of polymers incorporatingquinoid subunits (**15**, Fig. 17).

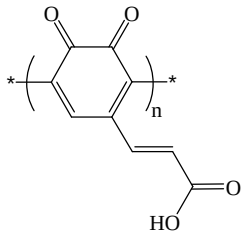

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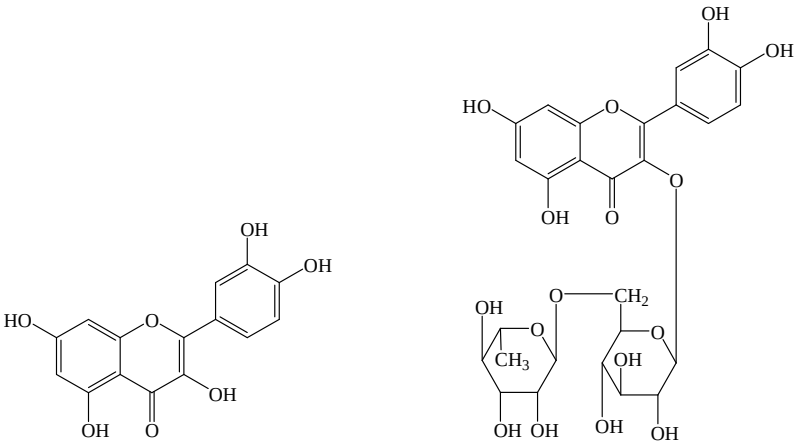
Fig. 17. Structure (**15**) of poly(caffeic acid) synthesized by enzymatic polymerization using HRP.[134]

Another peroxidase, xanthine oxidase (XO), was used to polymerize several catecholamines in Tris-HCl buffer. Rosei*et al.* observed that some of them, such as DOPA, were not polymerized presumably because of the negative influence on the enzyme activity of the α-carboxylic acid group contrary to dopamine.[135]

Poly(catechol)s, exclusively composed of (2-hydroxy-1,4-oxyphenylene) subunits (**14**, Fig. 15),were also successfully prepared by using oxidases such as laccase in combination with dissolved oxygen.[136]For example, catechin (**8**, Fig. 2), quercetin and rutin (**16** and **17**, respectively,Fig. 18) were oxidatively polymerized by laccase and, interestingly, both

polymer materials showed stronger superoxide scavenging activity compared to their monomer.[137-139]



16 **17**

Fig. 18. Chemical structures of quercetin (**16**) and rutin (**17**).

3. Side chain precursors

3.1. Polymerization of catechol basedvinyl monomers.

Catechol side chain polymers can be conveniently preparedby radical polymerization of vinyl monomers incorporating a (un)protectedcatechol unit (Fig. 19).

3.1.1. Starting from protected monomers.

When vinyl monomers bearing protected catechols are considered, borax ($Na_2B_4O_7.10H_2O$) is mainly used as the protecting reagent by forming a cyclic bidentate*o*-benzenediol subunitas depicted in Fig. 19.[140] The radical polymerization of the protected monomer occurs in water and leads to linear polymer chains. Catechol deprotection is carried out in acidic medium leading to polymers bearing pendant catechols. Other protecting groups can be employed such as 2,2-dimethoxypropane[141], benzyl bromide[142] or dichlorodiphenylmethane[143] to name only a few.

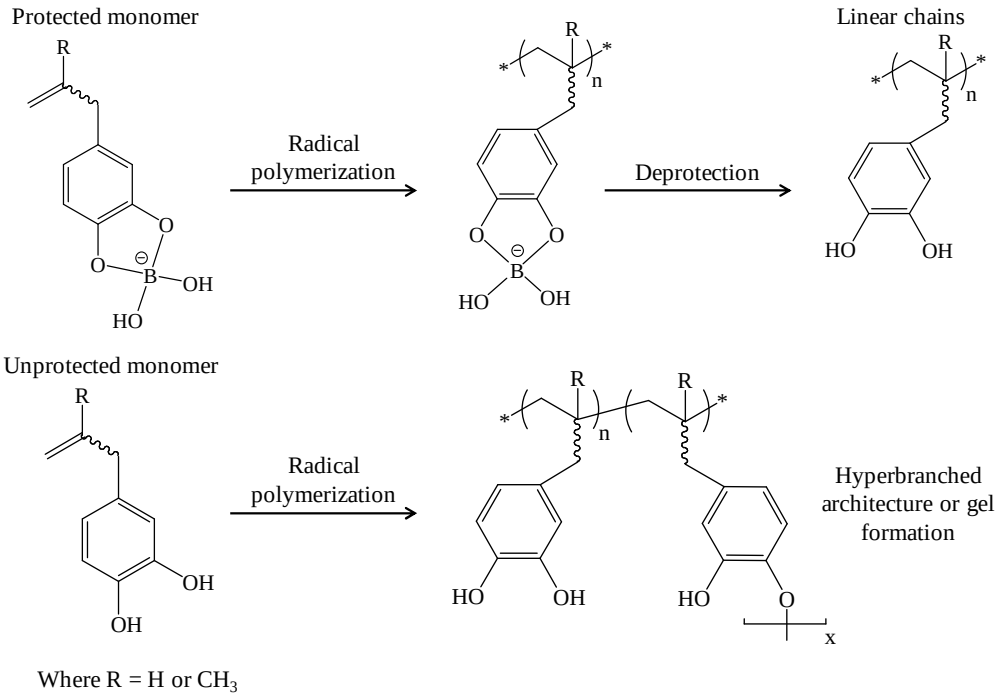
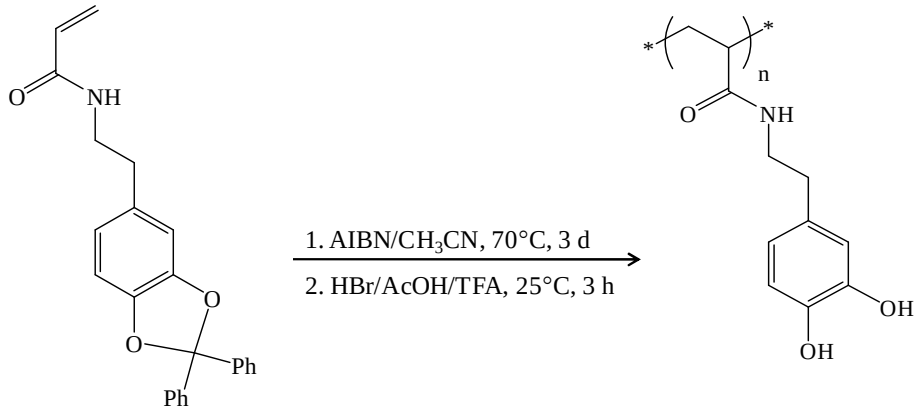


Fig. 19. Polymer architectures obtained from vinyl monomers bearing (un)protectedcatechol unit.

As an interestingexample, protected dopamine acrylamide (**18**,Fig. 20) was homopolymerized using 2,2'-azobisisobutyronitrile (AIBN) as radical initiator in acetonitrile at 70°C for 3 days (Fig. 20). Deprotection of the catechols then occurred in a mixture of acetic acid, hydrobromic acid and trifluoroacetic acid at room temperature. The so-formed polymer bearing catechol groups on each monomer unit displayed strong adhesiveproperties towards woodwhen cured at high temperature (180°C) with amine-containing polymers such as poly(ethylenimine)(PEI).[144]



18 **19**

Fig. 20. Synthesis of poly(dopamine acrylamide) (**19**).[144]

Protected DOPA monomers have also been exploited for providing sustainable and durable AB coatings on stainless steel surfaces.[25] A linear homopolymer bearing DOPArepetitive units was synthesized by free radical polymerization of protected-DOPA methacrylamide (**20**, Fig. 21) in water using 4,4'-azobis(4-cyanopentanoic acid) (V-501) as initiator, followed by deprotection with HCl. The catechol groups of the polymer were then oxidized in water under basic conditions (pH = 10), leading to the corresponding water soluble polymer bearing quinone groups (**21**, Pox(mDOPA); Fig. 21). The sequential Layer-by-Layer[145]deposition of this polymer andpoly(allylamine) (PAH) led to cross-linked films as the result of amine/quinone reactions between the two complementary partners (Fig. 22). Moreover, introducing an AB peptide (nisin) in the last layers of the multilayer filmconferredstrong AB properties to the material. Furthermore, due to the covalent anchoring of the peptide, the AB activity was maintained even after dipping the substrate in water for one night.

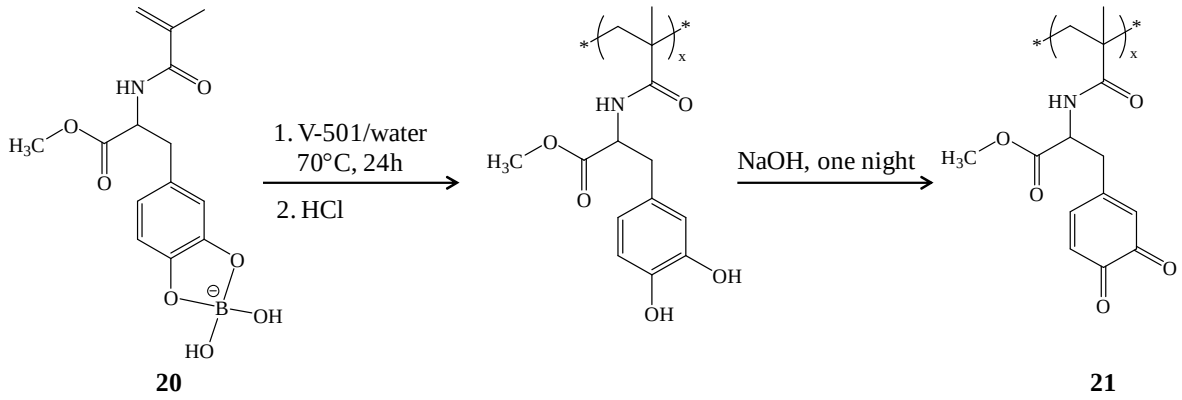


Fig. 21. Synthesis of Pox(mDOPA) (**21**).[25]

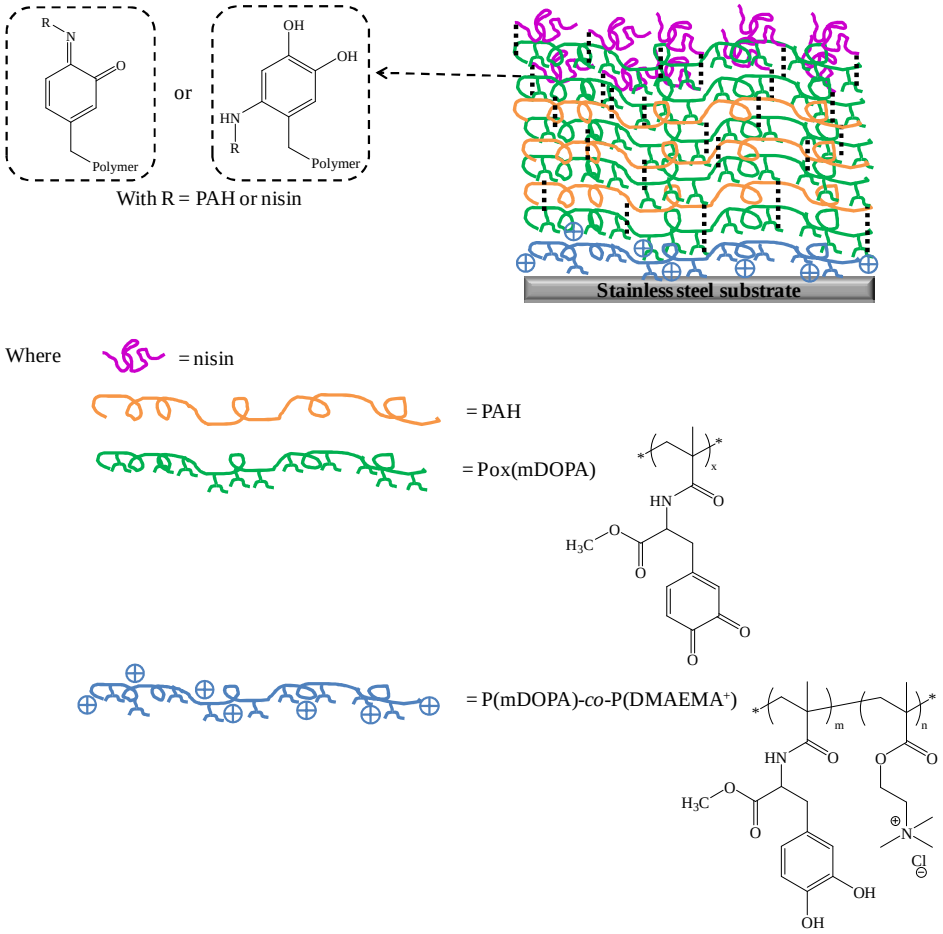
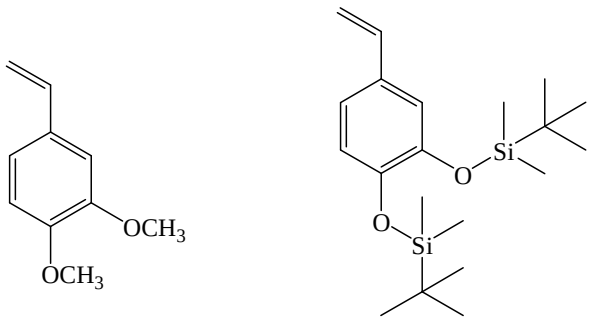


Fig. 22. Covalent LbL assembly for imparting robust AB property to stainless steel.[25]

Polymers bearing catechols can also be prepared starting from protected 3,4-dihydroxystyrene (**22** and **23**,Fig. 23)[146, 147] and were used asbio-inspired adhesives after deprotection.

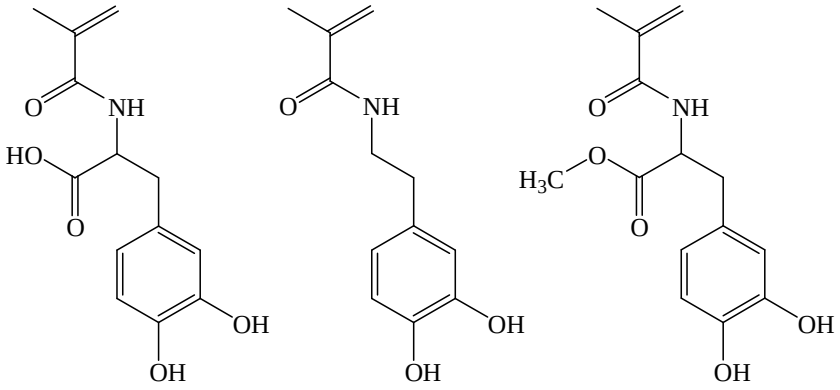


22 **23**

Fig. 23. Chemical structures of 3,4-dimethoxystyrene (**22**)[146] and 3,4-di(OTBDMS) styrene (**23**)[147].

3.1.2. Starting from unprotected monomers.

When unprotected catechols were considered, a pioneering work described the copolymerization of DOPA methacrylamide (**24**,Fig. 24) with poly(ethylene glycol) diacrylate under UV irradiation in the presence of a photoinitiator (Fig. 25). This copolymerization led to hydrogels that are of prime interest as new adhesives for biomedical applications.[16]



24 **25** **26**

Fig. 24. Monomers bearing catechol groups:DOPA methacrylamide (**24**)[16], dopamine methacrylamide (**25**)[148] and methyl ester DOPA methacrylamide (**26**)[149].

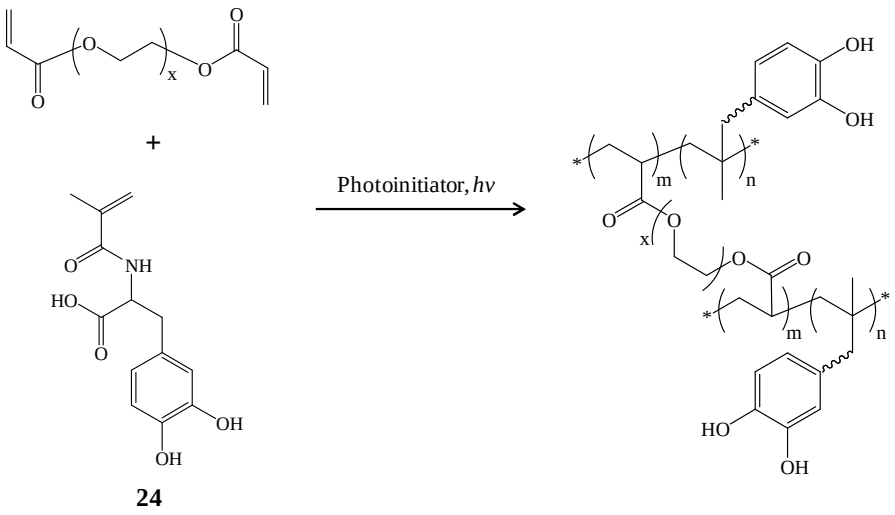


Fig. 25. Hydrogel preparation from the copolymerization of **24** withpoly(ethylene glycol) diacrylate.[16]

Importantly, since catechols are well-known polymerization inhibitors by reacting with radicals with the formation of aryloxy free radicals,[150, 151] the radical polymerization of vinyl monomers bearing unprotected catechols is at first glance surprising. Nevertheless, several recent works of free-radically polymerized catechol monomers attest to the viability of this approach.[16, 148, 152-162] Dopamine methacrylamide (**25**, Fig. 24) was copolymerized with methoxyethyl acrylate to furnish a reversible adhesive on nanostructured surfaces.[148, 152] Copolymerization of **25** with a phosphate based monomer such as 2-(methacryloyloxy)ethyl phosphate allowed preparing underwater adhesives through complex coacervates when combined with a polymer bearing positive charges (protonated amine bearing polymers) and divalent cations (Ca^{2+} or Mg^{2+}) as depicted on Fig. 26.[153-155]

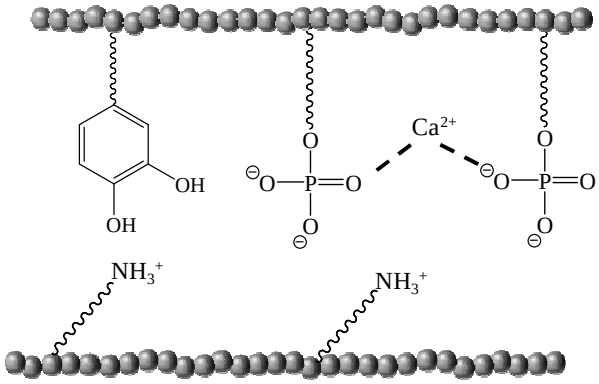


Fig. 26. Schematic representation of complex coacervates.[154]

Copolymers of **25** with 1*H*,1*H*-perfluorooctyl methacrylate were also synthesized in acetonitrile and coated onto various surfaces to impart them ultra-low surface free energy.[156] Substituting perfluorooctyl methacrylate by 2-aminoethyl methacrylamide provided copolymers useful for facile DNA immobilization onto various substrates (Fig. 27).[157] Oligomers of **25** and 2-(2-bromoisobutyryl) ethoxymethacrylate led to the design of macroinitiators for the preparation of poly(*N*-isopropylacrylamide) (PNIPAM) brushes on Ti plate by Si-ATRP.[158]Terpolymerization of **25** was also implemented, on the one hand, with methoxyethyl acrylate and ethylene glycol dimethacrylate for tuning the viscoelastic property of this pressure-sensitive adhesive[159, 160] and, on the other hand, with methoxyethyl acrylate and dodecyl quaternized 2-(dimethylamino)ethyl methacrylate for preparing antimicrobial surfaces.[161]

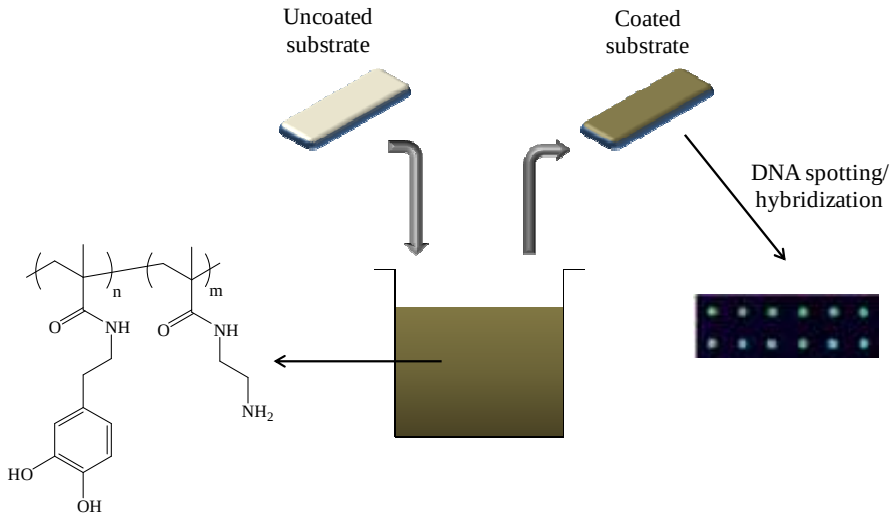


Fig. 27. Sequential method developed by Messersmith *et al.* to prepare DNA microarray on several substrates.[157]

Dual-action homopolymer of DOPA methacrylamide (**24**, Fig. 24) and copolymer of dopamine methacrylamide (**25**, Fig. 24) and *N*-[3-(dimethylamino)propyl] methacrylamide were synthesized by Alexander and coworkers.[162] Due to their positive charge and/or their catechol groups, these polymers were able to both force bacteria aggregation and suppress their quorum sensing (QS) signals. Successful bacterial capture has been confirmed with these two polymers. Furthermore, they were able to sequester bacteria without damaging cell viability, thereby rendering this new strategy very attractive for the conception of novel antimicrobial materials.

In all these works, neither the possible side reactions of propagating radicals with catechols nor their potential impact on the final polymer architecture are discussed. Polymers are always presented as linear structures. However, the radical polymerization of catechol bearing vinyl monomers is expected to provide (hyper)branched polymers or, even more, cross-linked materials, depending on the amount of catechols bearing monomers involved in the (co)polymerization process.[163] Indeed, according to the well-known reactivity of catechols with radicals, a catechol group of one polymer chain may react with a radical existing in

another chain during radical polymerization, thus forming an interchain C-O or C-C bond (Fig. 28). One or more bonds may exist between any two polymer chains leading to (hyper)branched polymers. Cross-linked materials should therefore be obtained when high amounts of catechol bearing monomers are used.

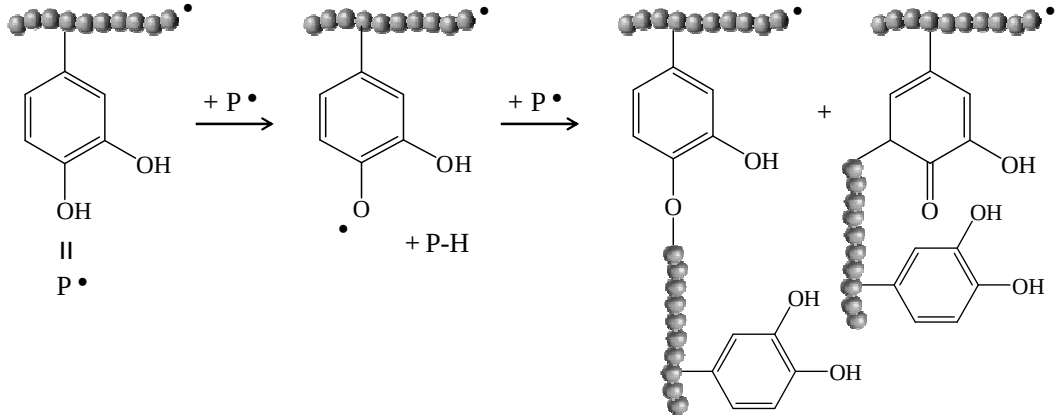


Fig. 28. Hyperbranching mechanism for the radical polymerization of vinyl monomers bearing unprotected catechols.

This expected branching reaction is however not discussed in none of the above mentioned manuscripts. Meanwhile, some authors recovered some insoluble materials when copolymerizing a conventional vinyl monomer with a catechol functionalized one, especially when large amounts of the latter were used.[148, 152, 156] Although not specifically mentioned in the above-discussed publications, these insoluble productsarepresumably the result of the cross-linking reactions promoted by the catechol based monomers.

The occurrence of this branching was demonstrated and illustrated by Detrembleur *et al.* by radically copolymerizing a DOPA derivative bearing a methacrylamide group (**26**,Fig. 24)[149, 163] with a methacrylate bearing an ammonium group ((2-(methacryloxy)ethyl) trimethylammonium chloride; $DMAEMA^+$) in water at 50°C. The combination of Dynamic (DLS) and Static Light Scattering (SLS) experiments allowed to elucidate the hyperbranched architecture of the so-formed water soluble polyelectrolyte[163] of a high molar mass

(M_w>10^6 g/mol). Thanks to its free catechol groups, this copolymer P(mDOPA)-*co*-P(DMAEMA$^+$) was used as a biomimetic glue for the strong anchoring of functional multilayers films onto stainless steel surfaces.[149, 163, 164] Antimicrobial and easy-cleaning stainless steel surfaces were obtained from multilayer films containing active biomolecules (nisin and mucin) based on that biomimetic glue.[165] The redox property of catechol was also exploited for the *in situ* formation of elemental silver nanoparticles (Ag^0) by adding a silver nitrate ($AgNO_3$) aqueous solution to this DOPA-based hyperbranched copolymer.[149, 164]Indeed, catechols reduced Ag^+ into Ag^0 while the hyperbranched copolymer stabilized the so-formed nanoparticles. The LbL deposition of this silver loaded polycation with poly(styrene sulfonate) (PSS) as the negative counterpart led to highly biocidal coatings onto stainless steel.[149] Moreover, similar surface coatings were made from galvanized steel, thereby further indicating the high versatility of such bio-inspired glue for modifying various substrates. A protecting multilayer film against corrosion was built by alternating the deposition of P(mDOPA)-*co*-P(DMAEMA$^+$) used as corrosion inhibitor with clays as negative counterparts that induced barrier properties. The whole process was conducted in water and did not release any toxic molecules in the environment while the esthetical aspect of the surface was preserved.[166]

3.2. Peptide synthesis of DOPA derivatives.

Because DOPA is largely present in the sequences of marine adhesive foot proteins, intensive research has been conducted on mimicking these structures by synthesizing peptides containing DOPA units. Some amino acids with protected side chains (lysine or glutamic acid for instances) were coupled with protected DOPA using the dicyclohexylcarbodiimidecoupling method.[167, 168]Amongst these, peptides containing up to three DOPA amino acids were synthesizedand coupled to a succinimidyl propionate-activated poly(ethylene glycol) (PEG-SPA) (Fig. 29) by reaction with their free NH_2 group at

the *N*-terminalextremity.[12]More particularly, Messersmith *et al.* studied the resistance of this conjugate to proteins adhesion when deposited on TiO_2 substrates and its ability to reduce marine algal fouling.[169]Finally, various kinds of surfaces (TiO_2 disks[170]and ureteral stents[171] for instances) coated with similar antiadhesive biomimetic peptides were found to strongly resist to both urinary film formation and bacterial attachment *in vitro*.

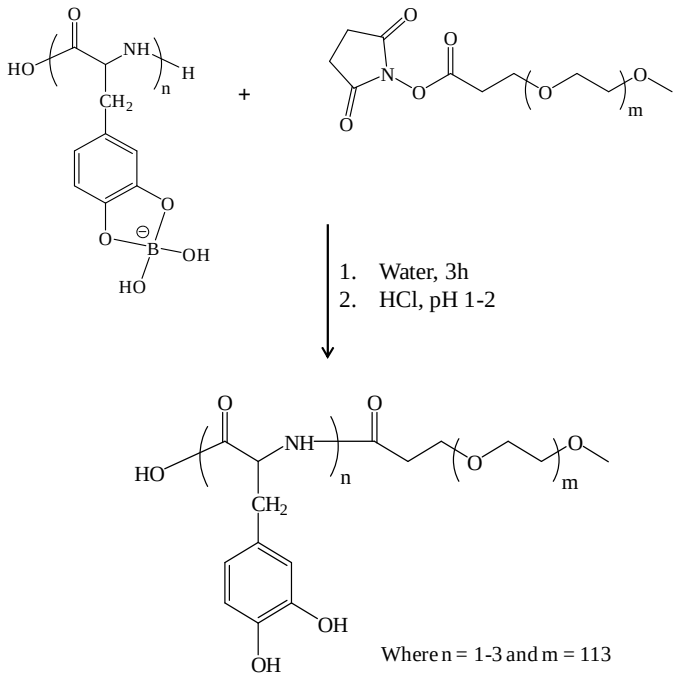


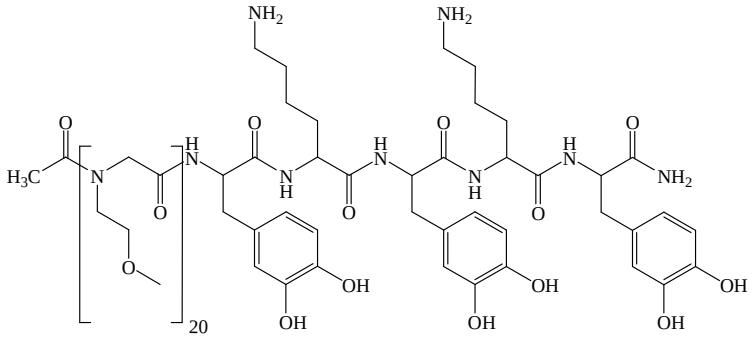
Fig. 29. Synthesis of poly(ethylene glycol) functionalized with DOPA units.[12]

Because DOPA amino acids are usually protected during peptide synthesis, final engineered macromolecules have a linear architecture with pendant DOPA moieties located at the extremity or within the peptide backbone (Fig. 3).Other peptides synthetic pathways and their final applications were reviewed elsewhere.[172]

3.2.1. Solid phase peptide synthesis.

Besides introducing this amino acid in marine adhesives mimic proteins,[173, 174] small DOPA peptides or co-peptides prepared by solid phase peptide synthesiswere intensively exploited to strongly anchor antifouling macromolecules onto surfaces. For example,

Messersmith*et al.* have designed a catechol based peptidomimetic polymer (**27**,Fig. 30) for long-lasting fouling resistance of Ti surfaces.[175] These *N*-substituted glycine chains conferred to the substrates proteins and cells resistance for several months.



27

Fig. 30. Antifouling peptidomimetic polymer.[175]

DOPA has also been incorporated into a photopolymerizable fatty acid with the aim of elaborating adhesive stable spherical vesicles after self-assembly in chloroform.[176]Methoxy-PEG-NH_2 was coupled with a tetra-DOPA peptide to prepare metal core – polymer shell nanoparticles.[177]

3.2.2. Ring-opening polymerization of α-amino acid N-carboxyanhydrides (NCAs).

The synthesis of α-amino acid *N*-carboxyanhydrides (NCAs) by phosgenation of amino acids has been developed in the late 80's by Kricheldorf.[178] Deming *et al.*then prepared high molecular weight polypeptides bearing catechols by ring-opening polymerization of NCAs containing protected catecholsfollowed by their deprotection (Fig. 31).[179] This method has the advantage to allow the preparation of large quantities of polymers and copolymers of tunable composition, opening the door to the development of new adhesives materials.[180-182]

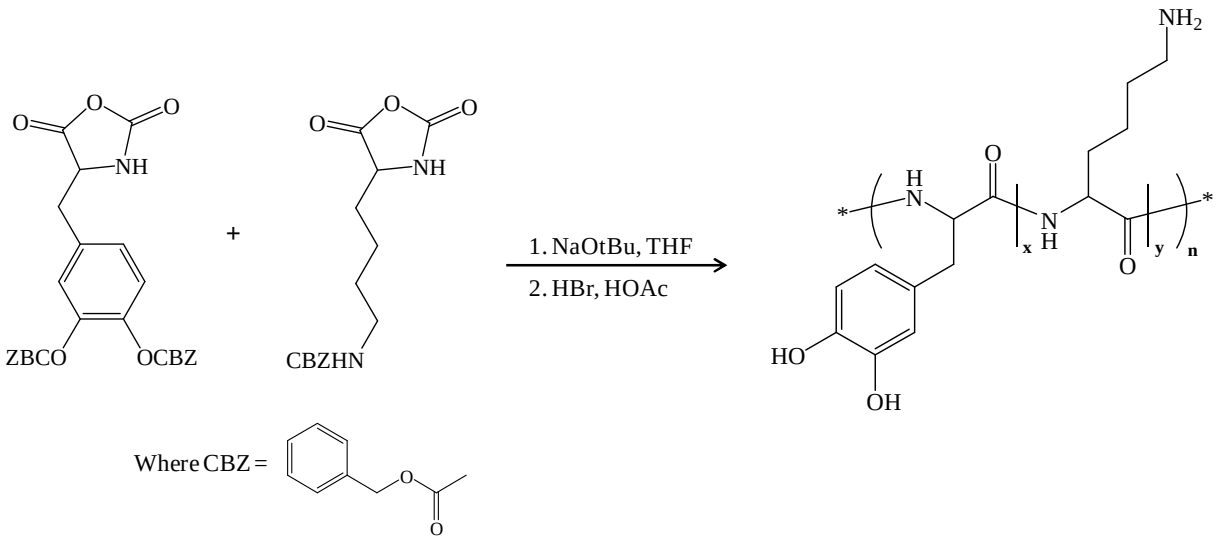


Fig. 31. Synthesis of adhesive copolypeptides by ring-opening polymerization of α-amino acid *N*-carboxyanhydride(NCAs) monomers.

For example, multiple-interaction ligand has been developed by Hyeon*et al.* for the design of ultrastable and biocompatible nanoparticles.[183] Their strategy consists in the synthesis of a macromolecule bearing three main functional parts: a central one composed of chargedPEI for electrostatic interactions with the negatively charged metal nanoparticles, a firstexternal part consisting on poly(DOPA) able to strongly anchor the macromolecule on the nanoparticles, and a second external part composed of hydrophilic PEG segment required for solubilizing the nanoparticle/macromolecule assembly in water as a micelle(Fig. 32). This versatile strategy has been also extended to various nanoparticles such as Fe_3O_4, MnO and Au thatexhibited high stability in various harsh environments and might open the door to new relevant biomedical applications.

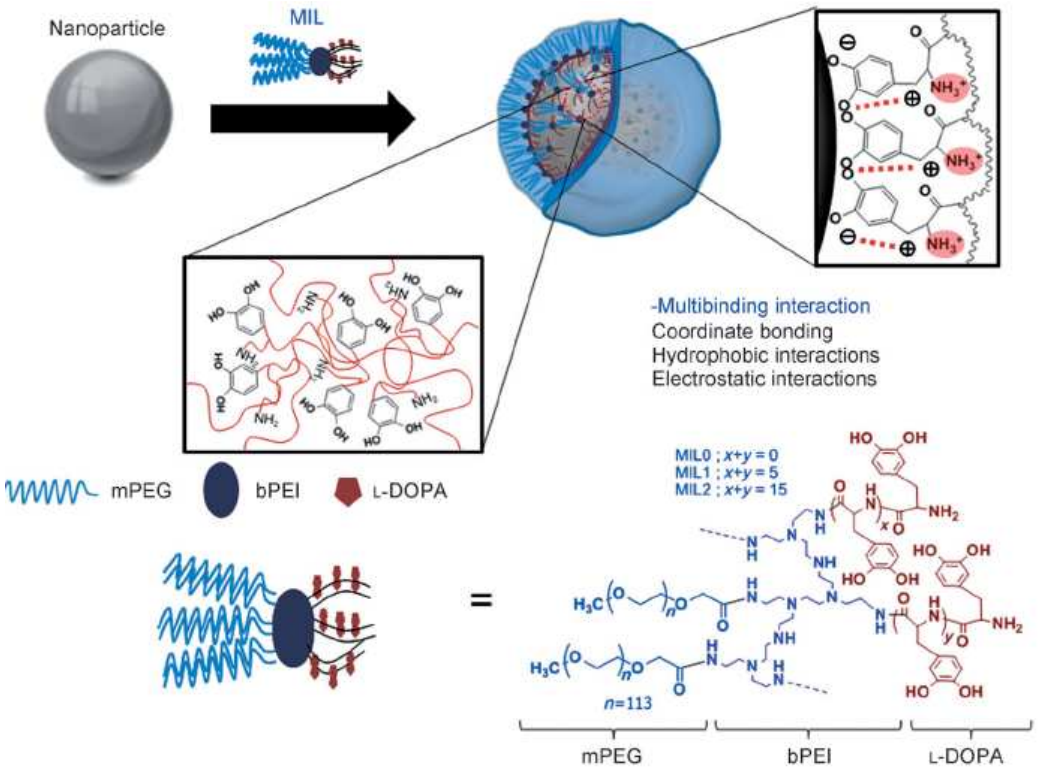
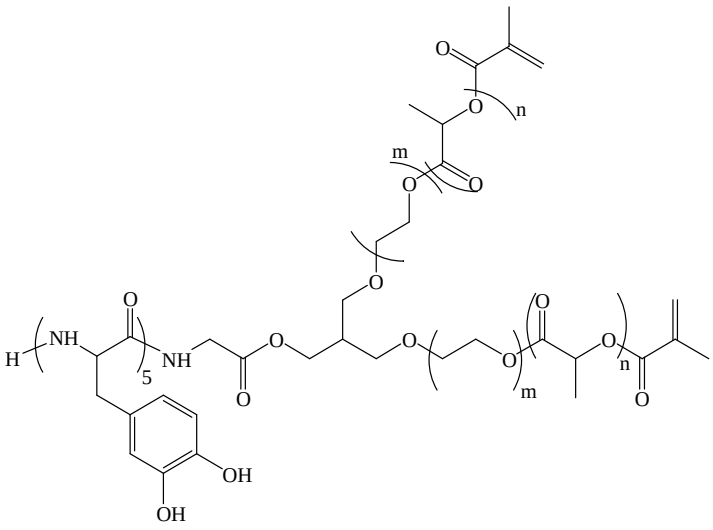


Fig. 32. Formation of water-dispersible nanoparticles through multiple-interaction ligand stabilization.[183]

Oligopeptides bearing DOPA unitswere also synthesized from amphiphilic block copolymers containing PEG blocks (hydrophilic part)and polyester blocks (hydrophobic part) in order to form adhesive hydrogels after photopolymerization of their methacrylate chain-ends (**28**, Fig. 33).[184]Biotinylated surfaces werealso prepared *via* tri-DOPA peptide synthesis from a biotin-PEG bearing an amino group as chain end.[185] Indeed, catechol groups of DOPA were used to reduce gold or silver cations into metal nanoparticles with a stabilizing PEG-shell on their surfaces.

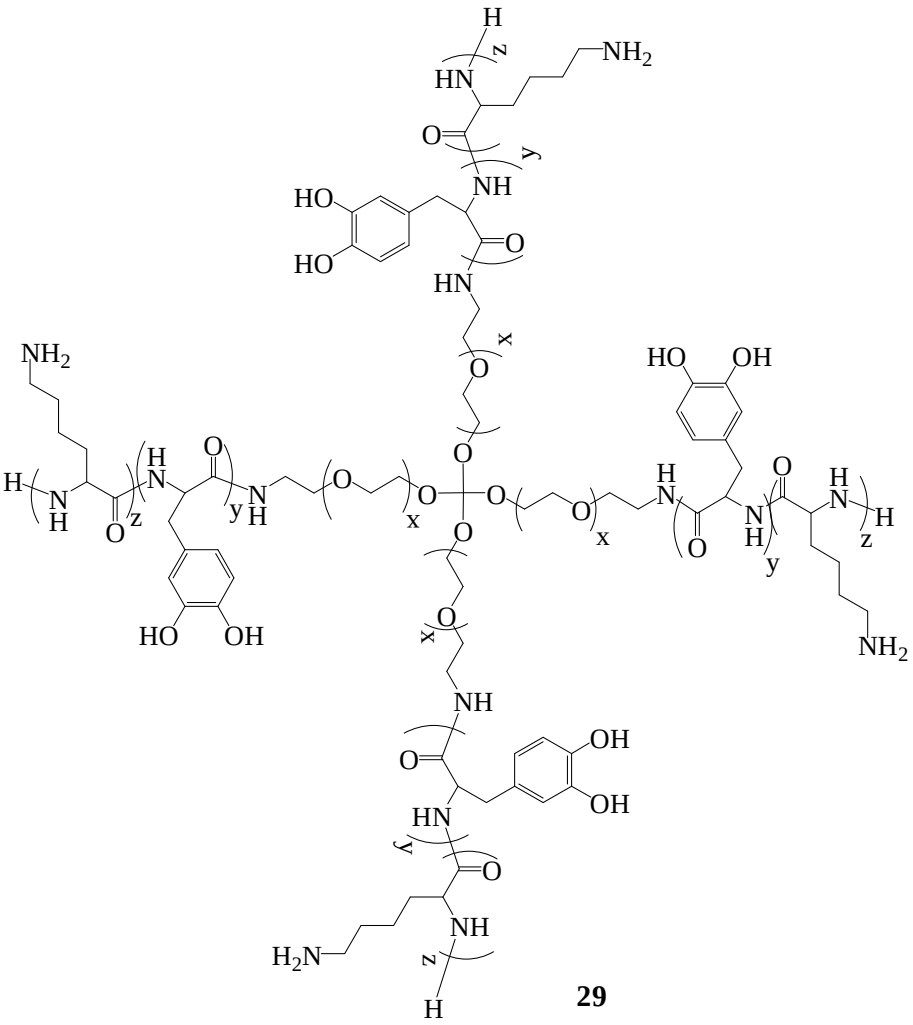


28

Fig. 33. Photocurable and biodegradable block copolymers.[184]

Interestingly,Kotov*et al.* prepared a terpolymer containing a tri-DOPA peptide, apoly(Lysine),and a PEG block (**29**, Fig. 34, A). The LbL deposition of aqueous solution of this copolymer and natural clays (Na^+-Montmorillonite, MMT) afforded nacre-like films (Fig.34, B).[186] These authors have nicely exploited the cross-linking ability of DOPA with Fe^{3+}[86, 187-190] to improve the mechanical properties of the nanohybrid films. Indeed, upon the addition of Fe^{3+} to Mefp1 (*Mytilusedulis* foot protein 1), the formation of a tris-catecholato-iron(III) complex was characterized (Fig. 35).[86] Then, iron reduction and oxidation of one DOPA bound can occur leading to the formation of a semiquinone radical which can further react with oxygen to generate other radical species that induce proteins radical-radical coupling and so the cross-linking (Fig. 35).[190]Formation of this tris-catecholato-iron(III) complex has recently been found to be strongly influenced by both iron/DOPA ratio[191] and pH[192].

A


NH2
HN
O
NH
HO
HO
HN
NH2
HO
OH
H
N
H
O
N
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O
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O
NH
H2N
H
29

B

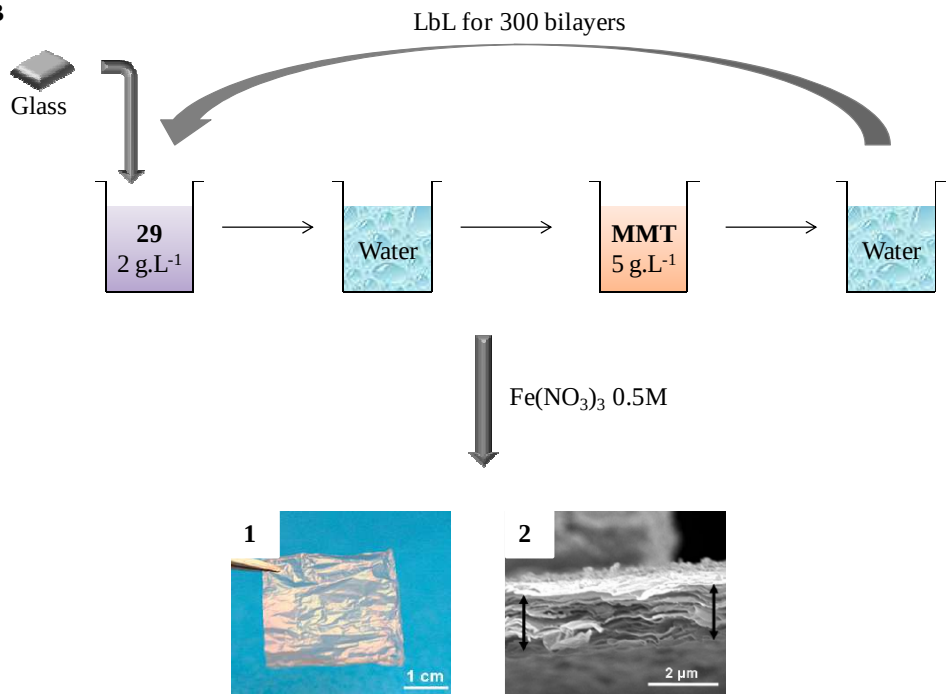

LbL for 300 bilayers
Glass
29
2 g.L-1
Water
MMT
5 g.L-1
Water
Fe(NO3)3 0.5M
1
1 cm
2
2 µm

Fig. 34. (A) Molecular structure of DOPA-Lys-PEG copolymer where x ~ 53 and y ~ z ~ 3; (B) LbL process between DOPA-Lys-PEG copolymer and MMT clay; digital photograph of a Fe^{3+} cross-linked 300 bilayer film of DOPA-Lys-PEG/clay (1); SEM cross-sectional view of Fe^{3+} cross-linked 300 bilayer film of DOPA-Lys-PEG/clay, arrows indicate the cross-section of the film (2).[186]

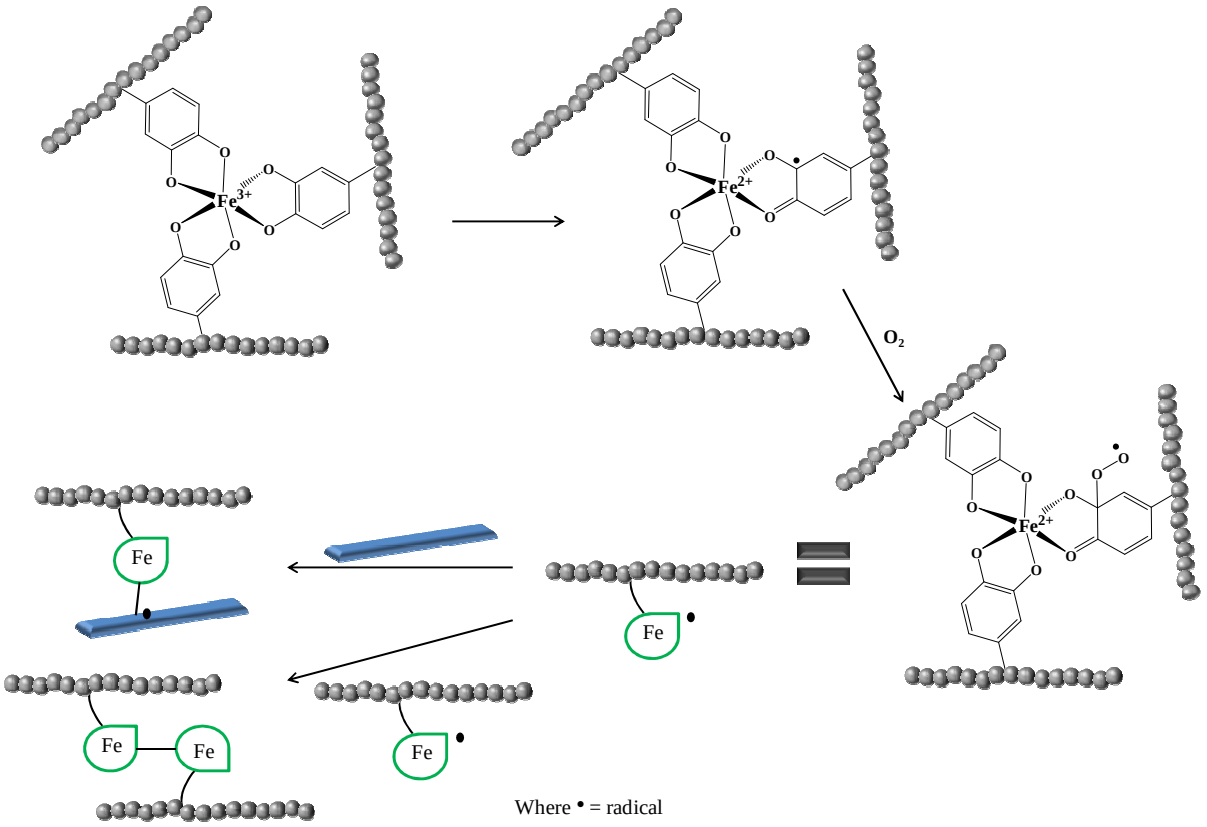


Fig. 35. Structure[86] and reactivity [190] of tris-catecholato-iron(III) complex.

3.3. Chemical ligation of catechol derivatives onto preformed (bio)polymers.

Another advantage of catechols relies on their faculty to be efficiently incorporated into polymer chains from preformed (bio)polymers. More particularly, a current trend in this domain is to use chemical ligation strategies between catecholamines(and derivatives) and appropriately selected activated polymers.The most useful ligation strategies are discussed below.

3.3.1. Grafting of catecholamines onto activated carboxylic acid functionalized polymers.

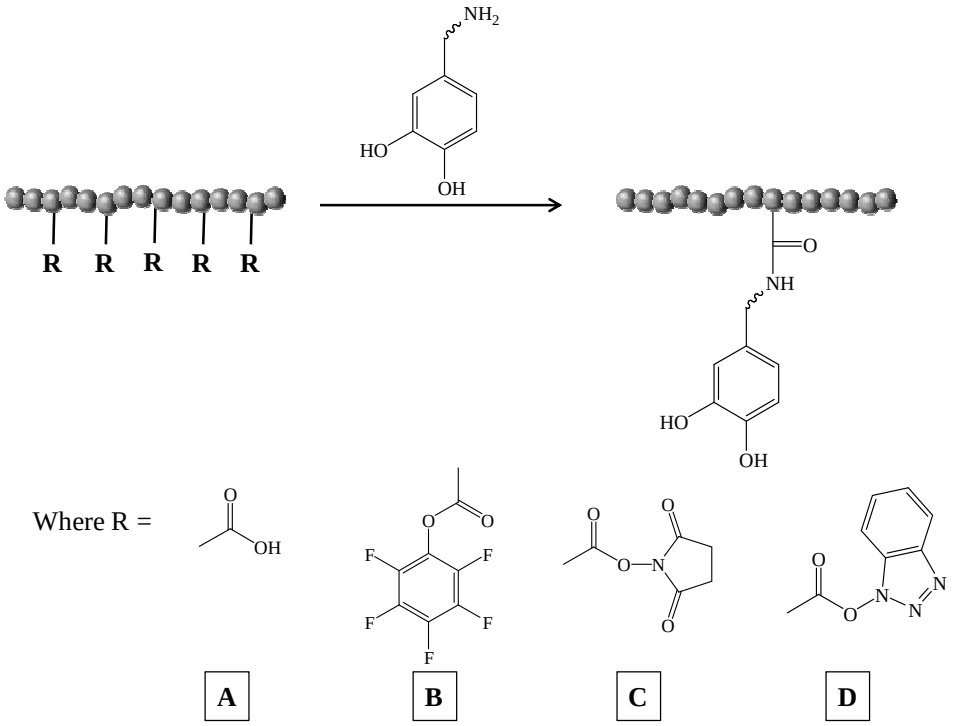


Fig. 36. Some strategies for the ligation of catecholaminesonto polymers bearing carboxylic acid (activated bycarbodiimide chemistry) (A), pentafluorophenyl (B), succinimidyl esters (C),and triazole activated esters (D).

The first developed strategy consists in reacting a polymer bearing side-chain carboxylic acid groups(Fig. 36, pathway A) with a catecholamine such as DOPA, dopamine or its derivatives in the presence of an activator like a water soluble carbodiimide compound (ethyl(dimethylaminopropyl) carbodiimide, EDC, for instance) to promote amidation. As an example, dopamine methacrylamide (**25**, Fig. 24) has been grafted onto poly(acrylic acid-*co*-butyl acrylate) in the presence of EDC to promote thecouplingreaction between the carboxylic acid side groups of the copolymer and the amino group of the dopaminederivative.[193] This chemical modification has afforded adhesive property to this copolymer and an enhancement of its mechanical properties. Such couplingwas also used i)to insert DOPA derivative (**7**, Fig.

2) into methacrylic triblock copolymers in order to improve the adhesion property of the so-formed hydrogels[194] or ii) to graft dopamine onto poly(acrylic acid) (PAA) to build robust multilayer films with PAH after oxidation by $NaIO_4$[195].In a similar way, Hammond *et al.* have grafted dopamine onto PAA with EDC in order to enhance LbL film stability with catechol-bearing PEI. This strategy allowed for the elaboration of multilayer materials displaying a better control of interlayer diffusion and so opened the door to new devices in drug delivery.[196]

Catecholamines can also be grafted to polymers bearing activated esters such as pentafluorophenyl or succinimidylesters (Fig. 36; pathways B and C respectively). This grafting strategyhas the advantage to occur at room temperature without any activator. For instance, dopamine was successfully grafted onto poly(pentafluorophenyl acrylate) and the conjugates were used for functionalizing nanoparticles such as TiO_2, MoS_2, MnO, or Fe_2O_3[197-201] and dispersing TiO_2, SnO_2, ZnO or CdTenanorods.[202-204]

Very recently, a well-defined difunctionalpoly(dopamine acrylamide-*co*-propargyl acrylamide) copolymer was also prepared from a reactive poly(pentafluorophenyl acrylate) homopolymer and exploited to sequentially modify a titanium surface (Fig. 37).[205] In a first step, the difunctional copolymer**30**,thanks to the presence of pendantcatechol units into the polymer chain, was tethered onto a titanium substrate yielding a dense alkyne-functionalized Ti platform. Then, the copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) was employed to covalently graft fluorescent probes (Fluorescein, Rhodamine), PEG chains, and sugars (mannose, β-cyclodextrin).

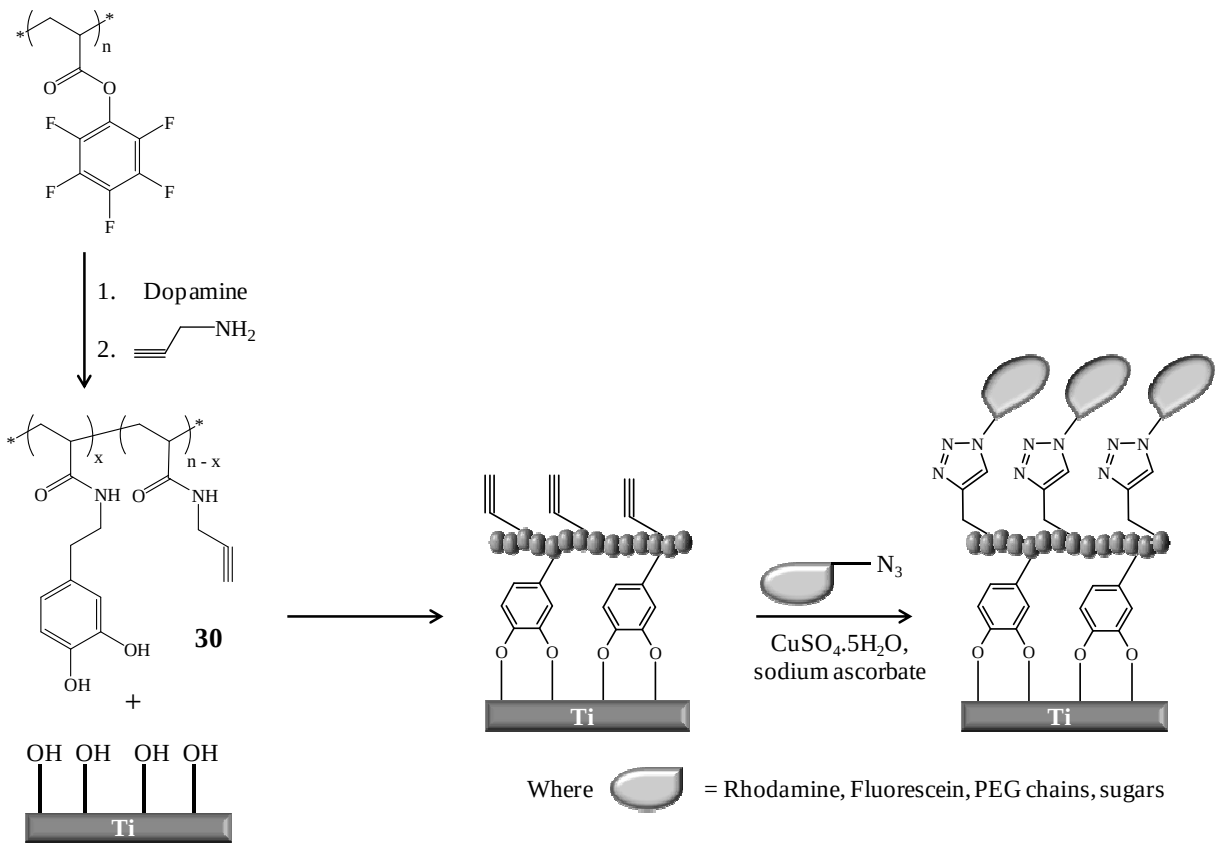


Fig. 37. Bio-inspired surface functionalization by click chemistry.[205]

Additionally, other condensing agents can be found in the literature. For instance, poly(L-glutamic acid) was modified with dopamine by using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) and further exploited in biodegradable capsules.[206]

3.3.2. Grafting of catecholamines onto hydroxyl functionalized polymers.

Hydroxyl-functional polymers can also be converted into *p*-nitrophenylcarbonate using *p*-nitrophenyl-chloroformate (NPC), and further modified by catecholamine (Fig. 38). For instance,nonfouling surfaces such as PTFE were prepared by covalent coupling of dopamine to hydroxyl-functional PEG.[207]

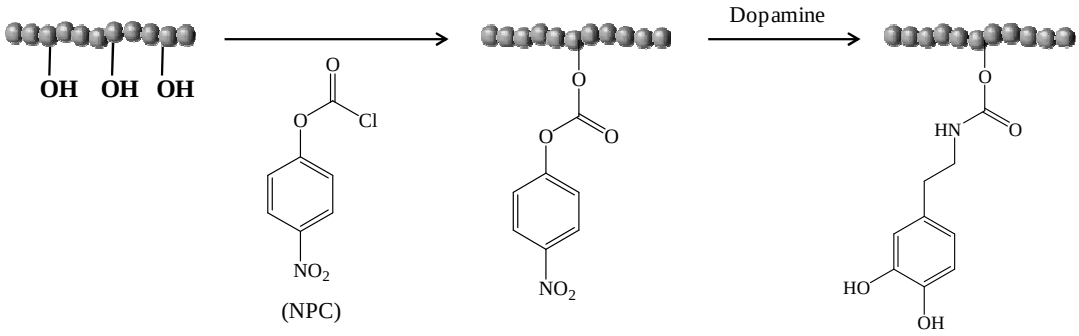


Fig. 38. Ligation of catecholamineonto hydroxyl-functionalized polymers using *p*-nitrophenyl-chloroformate (NPC) as an activator.

3.3.3. Grafting of catechol bearing a carboxylic acid group onto amino functionalized polymers.

Another approach consists in grafting a catechol derivative bearing a carboxylic acid group with amine functionalized biomolecules and biopolymers such as heparin[208, 209], hyaluronic acid[210-213], poly(L-lysine)[214] and soy protein[143] (Fig. 39). As an example, chitosan was functionalized with 3,4-dihydrocaffeic acid (**6**, Fig. 2) by coupling the primary amino groups of the polymer with the carboxylic acid of **6** using the carbodiimide activation.[215] This functionalized chitosan was then cross-linked with terminally thiolatedPluronic F-127 triblock copolymer to produce temperature-sensitive and adhesive sol-gel transition hydrogels. Modified chitosan with carboxylic acid functions was also immobilized on Ti surfaces pre-treated with polyDp in order to impart it antiadhesion property.[216]

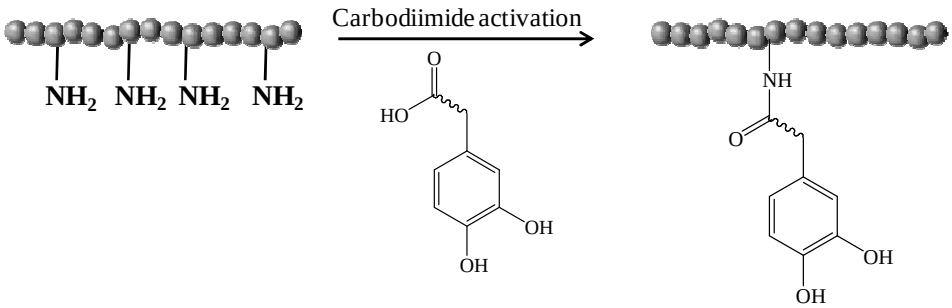


Fig. 39. Strategy for the ligation of catechol derivatives bearing a carboxylic acidfunction using carbodiimide chemistry.

Synthetic polymers containing amino groups were also grafted according to similar strategies. For instance, PEI was modified by 3,4-dihydrocaffeic acid (**6**, Fig. 2) in the presence of EDC to form an universal surface primer for multilayer assembly[217] or to reinforce the mechanical properties of CTNs fibers.[218]

Another well-known strategy consists in forming activated esters with an uronium salt such as *O*-(benzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluroniumhexafluorophosphate (HBTU) (Fig. 36; pathway D). This coupling reaction occurs at room temperature in the presence of triethylamine and 1-hydroxybenzotriazole hydrate (HOBt). Compound **6** was so coupled using these coupling reagents onto a 4-arm PEG-NH_2. The resulting catechol end-functionalized PEG precursors were *in situ* transformed into amultiblock copolymers in the presence of linear diacid-functionalized PCL. When coated onto a biologic mesh used for hernia repair, this adhesive polymer demonstrated adhesive strengths significantly higher than fibrin.[219] In addition, more recently, this intriguing adhesive material was used to greatly improve the repair of injured Achilles tendons.[220]

3.3.4. Electrochemical grafting of catechol units onto amino functionalized polymers.

Chitosan films electrodeposited onto gold surfaces were modified by electrochemical oxidation of catechols (Fig. 40).[221, 222] Gold crystals were first immersed in a chitosan solution (0.1%, pH 5.3) and potential was swept in the reducing direction. The substrates were then transferred into several aqueous catechol solutions under oxidative conditions promoting its covalent grafting onto the films. These modified surfaces behave as electrons donor and electrons acceptorin the presence of biological oxidants (O_2) and reducers (NADPH), respectively. Such phenolic matrices may play important roles in understanding biological

phenomena such as electron transfer, mode-of-action of bactericidal antibiotics, neuromelanins activity, etc.

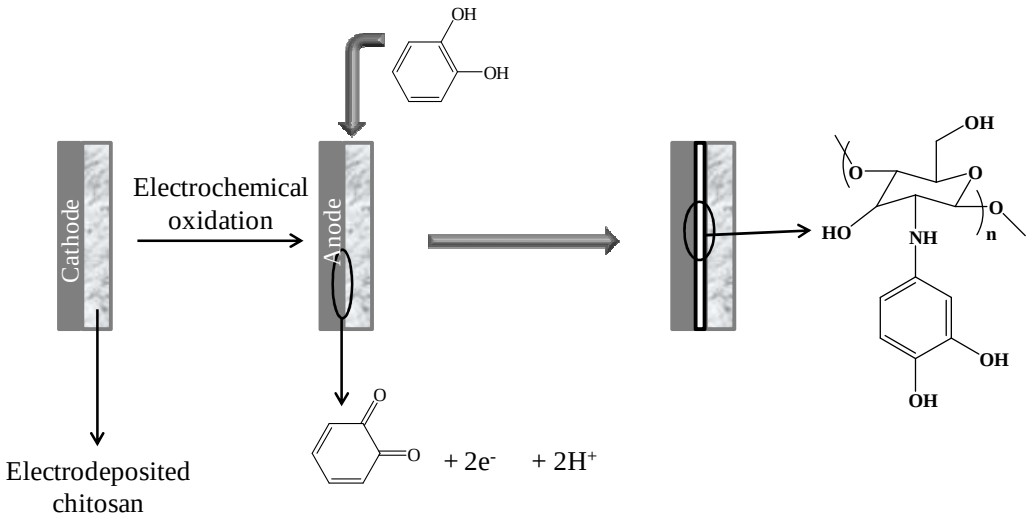


Fig. 40. Synthetic pathway for electro-modification of chitosan with catechols.[221]

3.4. Enzymatic derivatization of (bio)polymers bearing tyrosine moieties

Biopolymer-polyphenol conjugates with water resistant adhesive property can also be produced using enzymes such as tyrosinase.Tyrosinase can oxidize the tyrosine amino acids of proteinsinto catechols (Fig. 41, pathway A) but also into quinones (Fig. 41, pathway B) depending on the reaction conditions. In the presence of a reducer such as ascorbic acid, tyrosine groups are converted into the adhesive DOPA amino acids by tyrosinase in aerated conditions.[223]

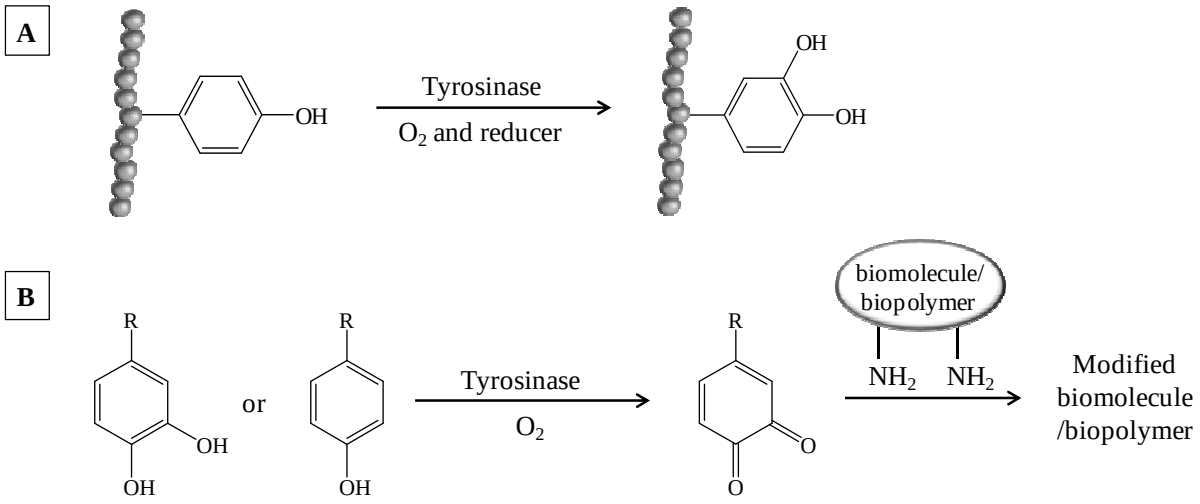


Fig. 41. (A) Conversion of tyrosine amino acids into DOPA by tyrosinase in the presence of a reducer, (B)Oxidation of phenol or catechol derivatives into reactive *o*-quinones using tyrosinase, followed by the grafting of amino-functionalized biomolecules/biopolymers

Yamamoto *et al.*exploited this strategy in various publications[224, 225]and, for example, synthesized chitosan derivatives incorporating a tetrapeptide based tyrosine residue. These phenolic amino acids were then converted into DOPA by tyrosinase, thus affording, after the cross-linking with the grafted peptide chains, a reinforced polysaccharide hydrid fiber.[226]

Tyrosinase was also used to couple different phenolic antioxidants (caffeic acid and chlorogenic acid) to wool fiber proteins[227] by oxidizing them into highly reactive *o*-quinones that rapidly reacted with the proteins *via* their amino groups (Fig. 41, (B)).Other biopolymers (poly(ε-lysine) and gelatin) and synthetic polymers (poly(allylamine) and polyhedral oligomericsilsesquioxane) have been modified withphenolic compounds following the same strategy. Such type of functionalization has been reviewed elsewhere.[228]

4. End chain precursors

4.1. Grafting of catechol unit(s) onto chain-ends by chemical ligation.

PEG polymers have also been functionalized at chain-ends with molecules bearing catechols following strategies as those depicted in Fig. 36. As far as EDC coupling agent is

concerned[229-233], final products were usually designed for metal nanoparticles stabilization such as FePt or Fe_3O_4 in the biomedical field (Fig. 36, pathway A). For example, EDC was used to catalyze the formation of amide bonds between Au-Fe_3O_4-Dopamine-PEG-COOH nanoparticles and the epidermal growth factor receptor antibody. These magnetic and optical active dumbbell Au-Fe_3O_4 nanoparticles were then exploited to image binding events between the modified nanoparticles and A431 cells.[233]

Catechol derivatives were also coupled to one *N*-hydroxysuccinimidyl activated chain-endpolymermostly to elaborate stable biomimetic surfaces with protein, bacterial-resistant adlayers or antimicrobial properties (Fig. 36, pathway C).[234-238]More recently, nitrocatecholamines were used to end-functionnalize a four-arm star PEG-$(NHS)_4$. Interestingly, these nitrocatechol functionalized polymers were employed to generate various covalently and metal-cross-linked responsive gels and coatings that can be on demand photodegraded upon light exposure (Fig. 42).[239]

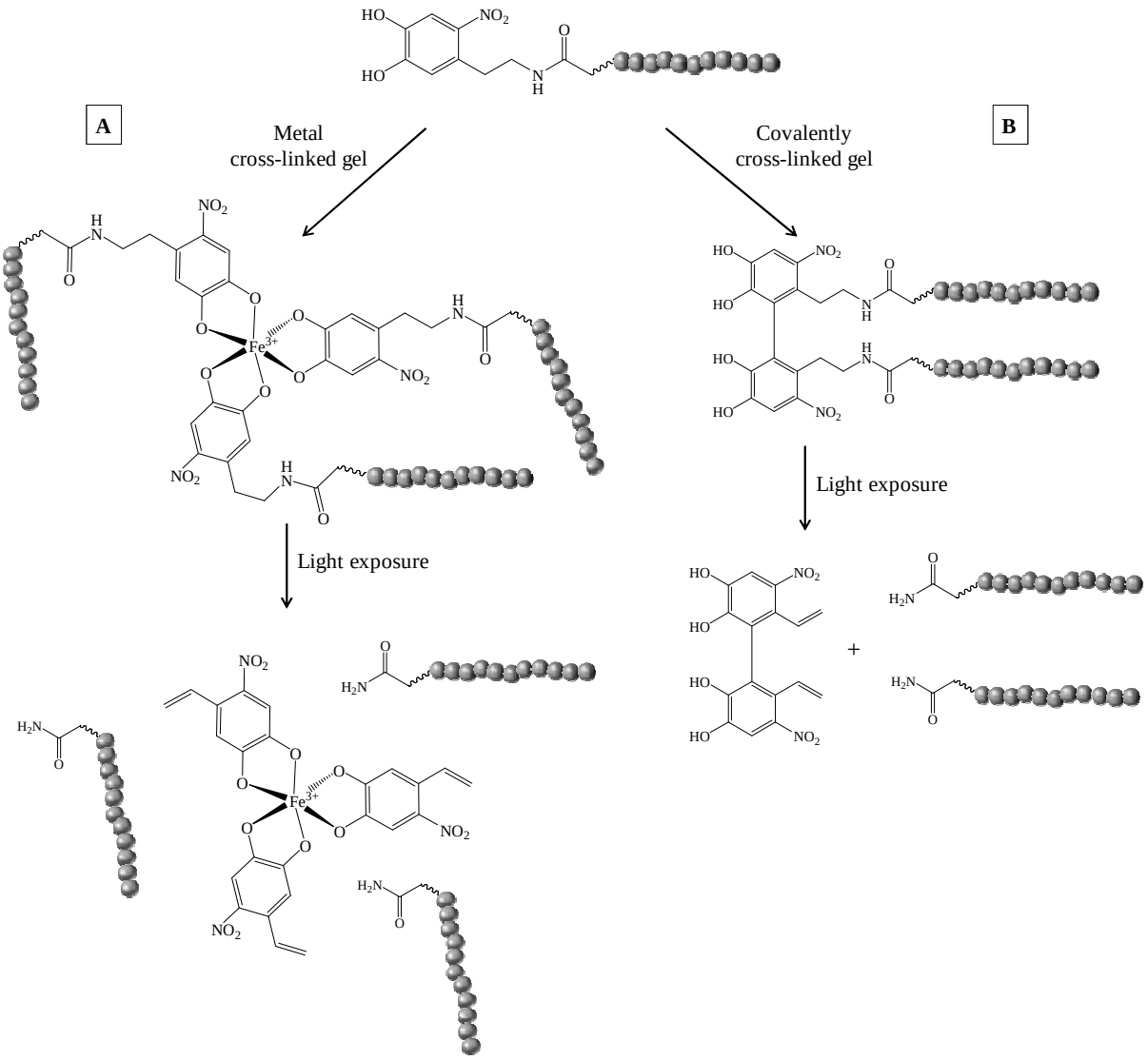
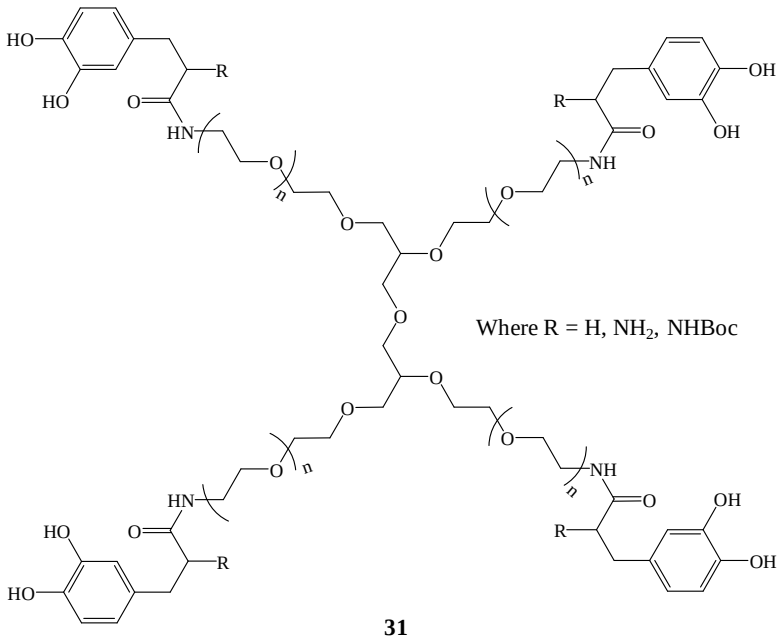


Fig. 42. Strategies to prepare photoreactive films based on nitrodopamine derivatives: through metallic complexation (A) or covalent bonds (B).

PEG modification with a catechol function using HBTU/HOBt as coupling reagents has been widely studied in the literature and is of prime interest for biological applications where a robust polymer anchoring is needed. Functionality has been integrated at one chain-end[17, 240] or at several chain-ends when multiple arms PEG-based polymers were concerned[241-244]. For instance, Messersmith *et al.* worked on the gelation conditions (natureand concentration of oxidizing agent, (un)protected*N*-terminal side chain …) of several DOPA modified PEG andobtained different hydrogels fromstar-shaped architectures such as those

depicted in Fig. 43, **31**.[245]Recently, these mussel glue hydrogels (R=H) were also employed *in vivo* as promising elastomeric tissue sealant for repairing fetal membranes[145] and for islet cell encapsulation.[244]



31

Fig. 43. Examples of multiple arm-PEG modified with DOPA moieties.

Starting from the same architecture (R = NHBoc), they developed self-healing hydrogels based on catechol-Fe^{3+} complexes and controlled their mechanical properties via pH change and the nature of the interpolymer cross-linking.[192] The tris-catechol-Fe^{3+} cross-linked gels exhibited better viscoelastic properties than the mono-catechol-Fe^{3+} complex.

Peptide dendritic ligands containing lysine or glutamic acid werealso prepared using the same coupling agents from protected dopamine and added then to magnetic nanoparticles following the ligand-exchange method.[246]These modified nanoparticles potentially represent straightforward platforms for the attachment of biological active molecules of interest for biomedical applications.

Additionally, by exploiting reversible boronic ester linkages, Messersmith *et al.* succeeded in the creation of intriguing pH-responsive, self-healing hydrogels from catechol-modified

multiple arms-PEG (Fig. 44).[247]Indeed, by mixing catechol end-chain functionalized 4-arm PEG and 1,3-benzenediboronic acid, boronate cross-linked hydrogels were conveniently obtained under basic conditions (pH above the diolpK_a, 9 in this case) within 30 minutes at 20°C. Interestingly, these boronate ester bonds were completely dissociated at pH below 3, leading back to starting materials. Self-healing property has also been demonstrated between two pieces of fractured gels that healed autonomously and rapidly without the use of cross-linking agents thanks to the presence of free boronic acid and catechol units at these frontiers.

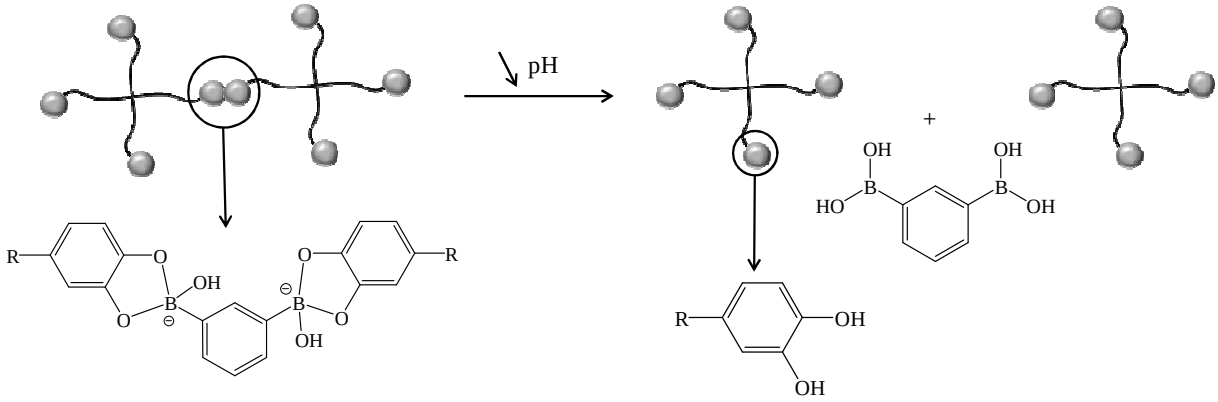


Fig. 44. Schematic representation of self-healing and pH-responsive hydrogels developed by Messersmith *et al.*.[247]

Trichloro-*s*-triazine (TsT) was used as linker between monomethoxy-poly(ethylene glycol) (mPEG) and dopamine to stabilize Fe_3O_4 nanoparticles.[248]Enzymatically degradable adhesive hydrogels were synthesized by coupling an Alanine-Alanine dipeptide-modified branched PEG and **6** with benzotriazol-1-yl-oxy-tripyrrolidinophosphonium hexafluorophosphate (PyBOP), followed by oxidative coupling of the catechol chain-ends by the addition of $NaIO_4$ (Fig. 45).[249]

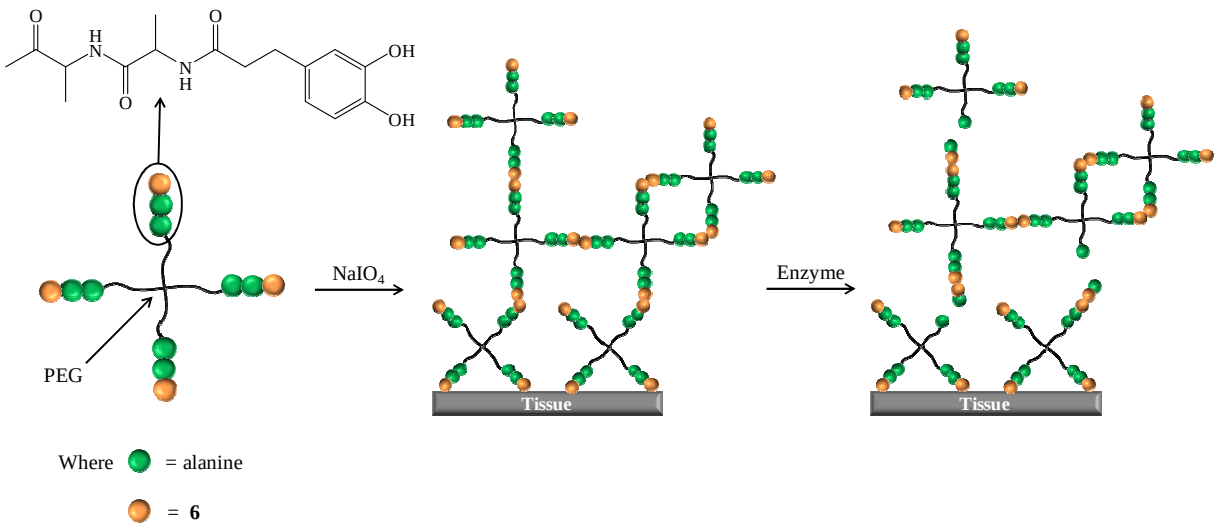


Fig. 45. Enzymatically degradable adhesive hydrogels.[249]

Dopamine was also linked to oligonucleotides bearing a carboxylic acid end group by using *N*-hydroxysuccinimide ester as the activator.[250]This activator was also involved in the modification of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers with DOPA to improve its bioadhesion.[251]

4.2. Elaboration of catechol end-functionalized polymers via controlled/living and electrochemical polymerizations techniques.

During the last decade, controlled radical polymerization (CRP) techniques such as Atom Transfer Radical Polymerization (ATRP)[252-254] and Reversible Addition-Fragmentation chain Transfer polymerization (RAFT),[255-257] to name few, have been proven to be very versatile techniques to introduce end-groups on a well-defined polymer chain. Obviously, much effort has been devoted over the last few years to prepare well-defined catechol end-functionalized synthetic polymers using CRP techniques with the ultimate goal of creating (patterned) polymer brushes or stabilizing nanoparticles via a "grafting to" approach. In this context, ATRP and RAFT were found to be highly efficient procedures for the preparation of the sus-mentioned polymers by using catechol based initiators (**32-35**, Fig. 46) or chain transfer agents (**36** and **37**, Fig. 46), respectively.

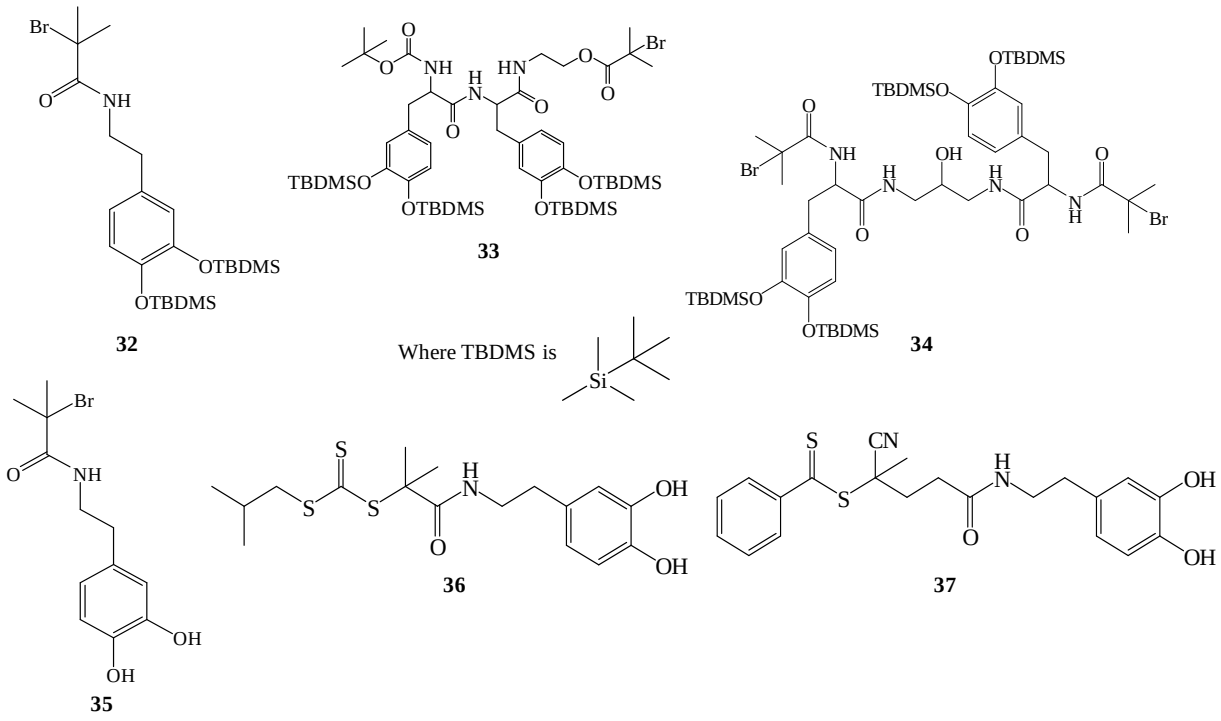


Fig. 46. Catechol derivatives as polymerization initiators in solution; ATRP initiators **32**[258], **33**[259], **34**[260] and **35**[261], RAFT agents **36**[262] and **37**[20].

When ATRP is concerned, zwitterionic polymers were prepared in solution from protected catecholic initiators (**32**, **33** and **34**, Fig. 46) and ultra low fouling property was imparted to various surfaces after their immobilization.[258-260, 263]Copolymers of di(ethylene glycol) methyl ether methacrylate (MEO_2MA) and poly((ethylene glycol) methyl ether methacrylate) (MAPEG) were synthesized from **35** (Fig. 46) and were then used for the stabilization of Fe_3O_4 nanoparticles.[261] Such modified nanoparticles were further studied for their ability to interchange their hydrophilic/hydrophobic character.[264] Indeed, they were hydrophobic enough to adsorb at the air/water interface but can simultaneously be squeezed out from the interface if the packing density exceeds a critical value. Such behavior is very promising for biomedical applications such as crossing biological membranes. The thermo-responsive character of these copolymers was also nicely exploited for inducing the controlled

nanoparticles agglomeration that enhanced the contrast ability of Fe_3O_4in magnetic resonance imaging applications.[229]

Catechols bearing a RAFT agent (**36**,Fig. 46) were also implemented for the preparation of well-defined poly(*tert*-butyl acrylate), poly(*N*-isopropylacrylamide) (PNIPAM) and poly(styrene) that were then immobilized onto Ti surfaces.[262]In this study, the immobilization of polymers on the titanium surface was monitored by using surface plasmonresonancetechnology that allowed estimating the surface coverage (Γ) of the grafted polymers onto the sensor surface.The dopamine chemistry was also successfully exploited for the preparation of thermoresponsivenanodiamond-functionalized PNIPAM particles from well-defined dopamine end-functionalized PNIPAM. These particles exhibited a reversible Lower Critical Soluble Transition (LCST) phase transition at around 32°C leading to the formation of small aggregates with a particle size of ~90 nm. Because of its simple, gentle nature and versatility, this strategy is an avenue for the preparation of other responsive (pH, redox, etc…) functional nanodiamond particles for nanobiotechnology applications.[265]

Fig. 47 points out that a large range of grafted polymer brushes can also be prepared, from the different catechol based anchors (**37**-**42**), by:

i) performingCuAAC reactions[266, 267] between either catechol-alkyne[268] or catechol-azide[269] tethered surfaces and appropriate complementary functionalized end-terminated polymers. For instance, the alkyne-modified dopamine anchor **40** was immobilized onto Fe_3O_4 nanoparticles giving rise to "clickable" nanoparticles.[268]Then, an azido-end-decorated PEG was clicked onto these nanoparticles to render these magnetic nanoparticles soluble in water. Opposite strategy was also applied to titanium surfaces where an azide-functionalized dopamine **41** was anchored to the surface prior to coupling to an alkyne-functional electroactive or fluorinated probe.[269]

ii) using "grafting from" procedures from catechol functionalized surfaces able to undergo a CRP (*e.g.* ATRP[18, 270-276] and RAFT[20]) or ROMP[19] (Ring-Opening Metathesis Polymerization[277]) polymerizations respectively.Of these polymerization techniques, the ATRP has been without doubt the most commonly used. This has notably been applied to build both antifouling and cell adhesive surfaces by grafting, for instance, PEG and zwitterionic polymers, respectively.[18, 270, 274] Poly(styrene) brushes were also grown from a catechol based RAFT transfer agent (**37**, Fig. 46) immobilized on Ti[87]$_4$-modified ITO.[20] Interestingly, these brushes were removed from the surface by dipping the surface in a phosphate buffer (pH 9.0), the Ti-diol complex being easily dissociated under weak basic conditions. ROMP was also exploited to grow polymer brushes from various surfaces modified with **39** (Fig. 47).[19] This approach allowed the elaboration of low surface energy by grafting perfluoroalkyl-substituted polymer brushes and also to immobilize polymers onto patterned surfaces by using microcontact printing (μCP).

iii) performing electropolymerization from TiO_2 nanotubes whose inner walls are coated by a catechol bearing a pyrrole group (**42**,Fig. 47).[278]These modified nanotubes presented a smaller charge transfer resistance and are potential candidates for fabricating ordered organic/inorganic p-n heterojunctions.

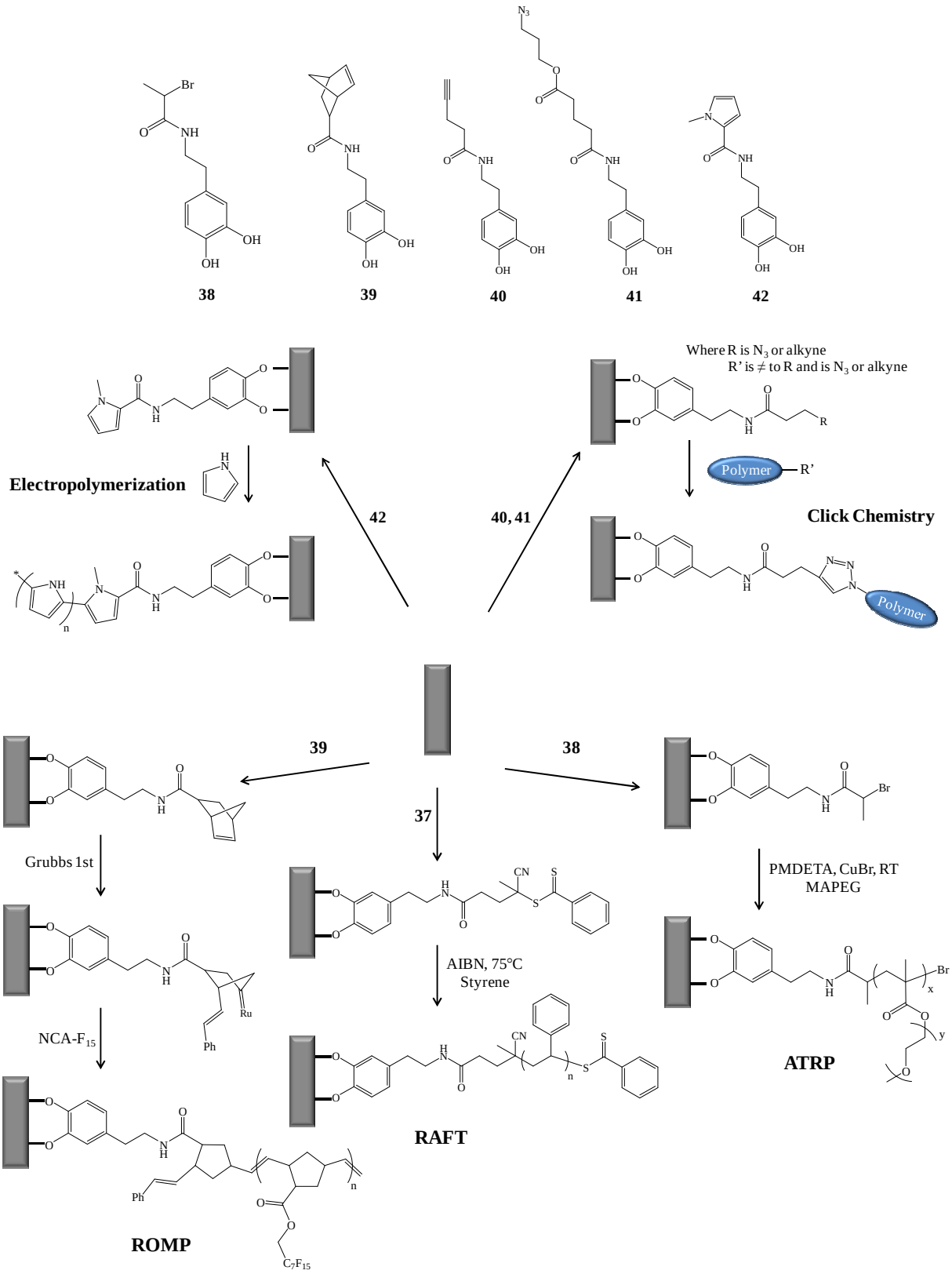


Fig. 47. Strategies to prepare polymer brushes onto surfaces: ROMP[19], RAFT[20], ATRP[18], CuAAC reaction[268, 269] and electropolymerization[278].

5. Conclusions.

The main aim of this review was to present the most important and straightforward synthetic methods allowing the incorporation of catechol units into polymer chains and to highlight the importance of these catechols for further functionalization of the macromolecules. Indeed, the field of catechol-containing polymers, owing to their fascinating intrinsic chemical properties and their practical applications, has greatly expanded over the past decade. More particularly, the combination of synthetic versatility, rich functionality and inherent binding properties towards various organic and inorganic surfaces make this class of polymers useful for many applications including synthetic adhesives and coatings, sensors, bioactive and self-healing materials, smart hydrogels and photovoltaic materials.

While most of the earlier efforts were primarily focused on the incorporation of catechol units into the main chains of polymers, by exploiting its redox properties, new methods have been explored more recently, providing for facile synthetic access to functional catechol-containing materials with advanced properties. Many biomimetic adhesive peptides incorporating side-chain catechol fragments, were, for example, readily prepared by solid-state peptide synthesis or by ring-opening polymerization of α-amino acid *N*-carboxyanhydrides. Recently, ligation techniques have also been employed i) to conveniently elaborate catechol end- and side-functionalized polymer materials, displaying self-healing and stimuli-responsive properties, from preformed activated (bio)polymers and ii) to construct, *via* « click » chemistry, bio-inspired functionalized surfaces. More recently, Living/Controlled Polymerization techniques, such as ATRP, RAFT and ROMP, have also emerged as powerful and versatile techniques allowing the immobilization, using both « grafting from » and « grafting onto » strategies, of well-defined end-decorated catechol polymers onto different substrates. Surfaces and nanoparticles with controllable interface properties and very promising biomedical applications have been created using such approaches.

Throughout this review, we have shown that the various reactivity of catechols in combination with the different polymerization methods available allow a plethora of catechol containing polymers with variable structures and interesting properties to be produced. However, we firmly believe that the development of catechol-based polymers is still a burgeoning field and that exciting new catechol-based materials with applications in interesting new fields will be reported.

Acknowledgements

The research was partly supported by BELSPO (IUAP VI/27) and the Walloon Region (PPP program BIOCOAT). We thank all the BIOCOAT team for its contribution. C. Detrembleur is Senior Research Associate by the F.R.S.-FNRS and thanks F.R.S.-FNRS for financial support.

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