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## Modification of starch by graft copolymerization

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### List of abbreviations:

APS: ammonium persulfate

ATRP: atom transfer radical polymerization

BPO: benzoyl peroxide

$\overline{M}_w$ : dispersity

GE: grafting efficiency

GP: grafting percentage

GPC: gel permeation chromatography

HRP: horse-radish peroxidase

PLGA: poly(lactic acid-co-glycolic acid)

PLGC: poly(lactic acid-co-glycolic acid-co- $\epsilon$ -caprolactam)

PPM: potassium permanganate

PPS: potassium persulfate

RAFT: reversible addition fragmentation chain transfer

ROP: ring-opening polymerization

SEM: scanning electronic microscopy

XRD: X-rays diffraction

**Keywords:** grafted starch, radical polymerization, ring-opening polymerization, coupling agents

## **Abstract**

Research toward bio-based and biodegradable polymers has received a lot of attention these last years, due to environmental concerns and the need to replace fossil resources. Starch is in this frame an interesting starting material due to its abundance and low cost. Native starch displays however poor mechanical properties and is highly hydrophilic. New starch-based thermoplastic materials can be prepared to overcome these drawbacks by chemical modification, and notably graft copolymerization. A large range of polymers can be grafted on starch by ring-opening and radical polymerizations of various monomers in order to modulate the properties of the final product. Polymers can also be directly grafted onto starch using coupling strategies. This review presents the state of the art in the field.

## 1. Introduction

Starch is a bio-based polymer which can be found in various cereal grains: corn, potatoes, cassava, wheat, rice... Native starch is mainly composed of two polymers of glucose, amylose (15-30%) and amylopectin (70-85%) while other constituents such as proteins, and lipids, can also be present.

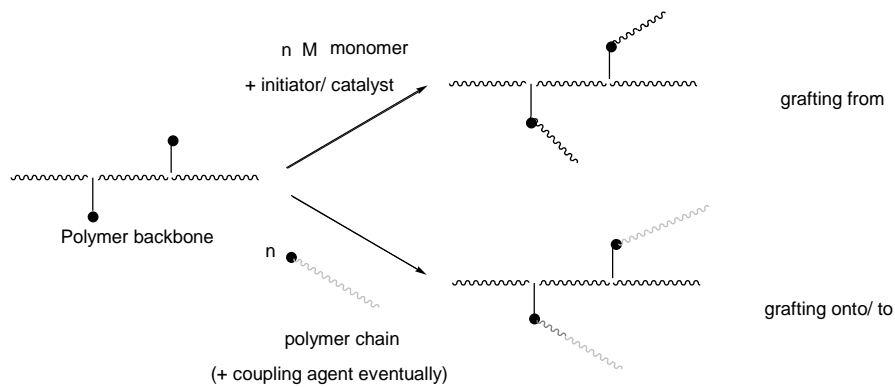
Amylose is a polysaccharide made of  $\alpha$ -D-glucose units, linked to each other through  $\alpha(1\rightarrow4)$  bonds. Even though amylose is considered as a linear molecule, some studies have shown a branched structure. Amylose is composed of 100 to 10,000 glucose units, displaying a molecular weight ranging between  $10^5$  and  $10^6$  g.mol<sup>-1</sup> (depending on its botanical source). Its chains tend to adopt a single helical conformation in the presence of a suitable complexing agent or form a double helix with themselves when no complexing agent is available.

Amylopectin is a highly branched cold water-insoluble polymer of glucose whose units are linked in a linear way with  $\alpha(1\rightarrow4)$  bonds. Branching takes place with  $\alpha(1\rightarrow6)$  bonds occurring every 19 to 30 glucose units. The molecular weight of amylopectin ranges from  $10^6$  to  $10^9$  g.mol<sup>-1</sup>, depending on the botanical source. Amylopectin has a semi-crystalline structure in which the crystalline regions contain chains with DP (degree of polymerization) about 15. These short chains form an ordered double helix structure.

Starch is found in nature under semi-crystalline granules form, characterized by growth rings (semi-crystalline shells separated by amorphous regions). Crystalline shells consist of regular alternating amorphous and crystalline lamellas. [1,2] The crystalline lamellae, are mainly composed of double helix of amylopectin (short chains) and amorphous lamellae formed of branched molecules of amylopectin and amylose. Depending on the botanical source of the starch, the degree of crystallinity may vary between 20 and 45 %. Native starch displays high water sensitivity and lack of mechanical strength. Starch can be plasticized to some degree with plasticizer such as water, polyols (glycerol, [3] glycols, [4] xylitol [5]), amides [6] or ionic liquids [7, 8, 9] notably. Plasticized starch is biodegradable and is used for packaging and agricultural purposes. However, some shortcomings such as sensitivity to water or the leaching of the plasticizer, induce brittleness and thus limit its applications.

To overcome some of these problems and to achieve desired product properties, this natural polymer can be modified by physical, chemical or enzymatic modifications including notably blending [10,11,12,13], chemical functionalization [14,15,16] (especially starch ester and ether) and graft copolymerization to obtain thermoplastic starch. In this review we present the various grafting copolymerization strategies reported in the literature.

Graft copolymerization is generally a very versatile way of functionalization allowing access to materials with a combination of the properties of the polymers involved [17]. There are two main strategies leading to starch-grafted copolymers, the "grafting from" and "the grafting onto or to" approaches (Fig. 1).



**Fig. 1** Different routes in graft copolymerization

- “Grafting from”

The first synthesis route consists in polymerizing the monomer directly from the main chain, this approach minimizing the steric hindrance. The main chain allows the initiation of the polymerization, either because it contains a potentially active function in its structure or after chemical modification of its backbone. The “grafting from” on starch is carried out mainly by radical and ring opening polymerizations.

- “Grafting onto or to”

The second synthetic way is to graft directly a chain-end functionalized polymer on the main chain of starch which must contain a functional group able to react with the starch backbone.

Three parameters are useful for the description of graft copolymerizations:

$$\text{Grafting percentage (GP) (\%)} = \frac{\text{weight of grafted polymer}}{\text{weight of starch}} \times 100$$

$$\text{Grafting efficiency (GE) (\%)} = \frac{\text{weight of grafted polymer}}{\text{weight of monomer charged}} \times 100$$

$$\text{Homopolymerization ratio (ungrafted polymer) (\%)} = \frac{\text{weight of homopolymer}}{\text{weight of monomer charged}} \times 100$$

In the following studies the grafting was confirmed by Infrared (IR) analysis after Soxhlet extraction. The absorption bands characteristic of starch and of the grafted polymer in the IR spectrum showed if the grafting actually occurred. In few cases, nuclear magnetic resonance (NMR) analysis was used, yet this technique is less current due to the lack of solubility of the graft copolymers in most common organic solvents. The percent and efficiency of grafting were determined currently via gravimetric calculations.

## 2. "Grafting from" via Radical Polymerization

A former review dealing with graft copolymerization of vinyl monomers on starch was published in 1999 [18], thus we will focus in this section on recent research in the field while reporting vicinal studies when appropriate.

### 2.1 Free radical polymerization

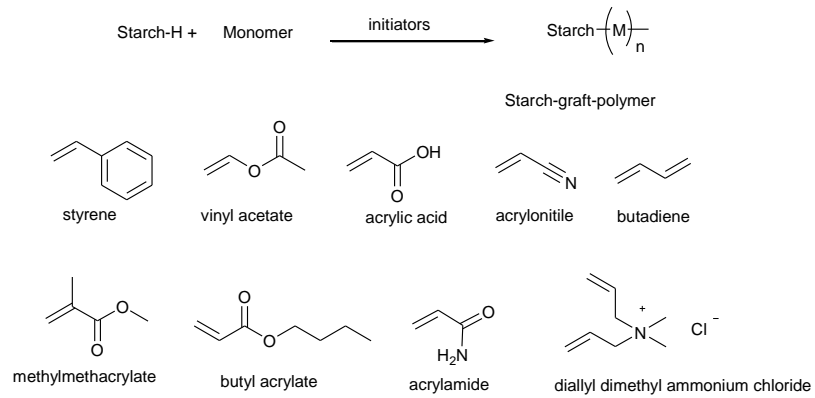
The different vinyl monomers polymerized by radical mechanism are represented in Fig. 2a. The mechanism of the graft copolymerization by free radical polymerization is divided in three steps: initiation, propagation and termination (Fig. 2b). During the initiation step, radicals are formed on starch by hydrogen transfer to initiator. These reactive starch radicals are then easily added to the double bond of the vinyl monomer, producing a starch-grafted monomer radical which can react with some additional monomer. Finally, the grafting copolymerization terminates by combination or disproportionation of two reactive chains. During this radical process, some non-grafted homopolymer is usually also formed and can be currently separated from the grafted polymer by Soxhlet extraction.

In the following studies, related to free radical copolymerization, the grafting was conducted in water. The procedure was generally divided in two steps. Starch was first pre-treated in water to obtain a slurry of starch ( $T=20-60^{\circ}\text{C}$ ) or gelatinized starch ( $T=80-95^{\circ}\text{C}$ ) and then the medium was cooled or heated to the desired graft copolymerization temperature. The monomers and initiator were then added in a second step. In the case of starch slurry, the substrate was swelled in water but the granular form was conserved, contrary to gelatinized starch where the granular structure was destroyed.

#### 2.1.1 Initiation by irradiation

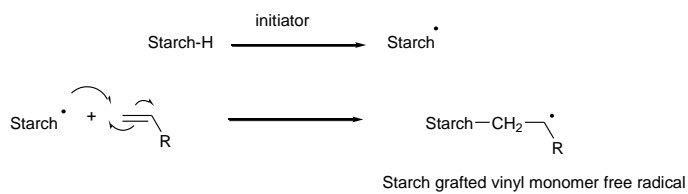
The irradiation of starch allows the formation of radicals which are able to initiate graft copolymerization. Polystyrene can be grafted on gelatinized starch in aqueous or organic media under Cobalt-60 irradiation [19], under gamma-rays [20] and their combination [21]. The results are summarized in Table 1. The best grafting efficiency was obtained via gamma rays irradiation, while Cobalt-60 gave rise to grafted polymers with a wider range of weight-average molecular weights.

The graft copolymerization of vinyl acetate on granular starch was described under cobalt irradiations (10 kGy, 10 kGy/h, GE=44-68%) [22]. A second step reported in this study consists in treating the obtained copolymers with sodium hydroxide to convert starch-*graft*-poly(vinyl acetate) into starch-*graft*-poly(vinyl alcohol) ( $M_n=30,000\text{g}\cdot\text{mol}^{-1}$ ). Poly(acrylamide-*co*-dimethyl diallyl ammonium chloride) (2-5 kGy, 2.4 kGy/h, GE=0-60%) [23] and poly(acrylamide-*co*-maleic acid) [24] can be grafted on gelatinized starch via gamma irradiation (0.5-12 kGy, 1.7 kGy/h, GE=3-70%) to obtain superabsorbent (water absorption= 67-2600 g/g).

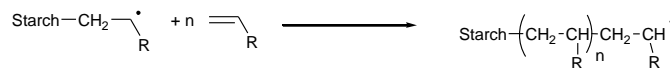


**2a. Monomers used for the "grafting from" approach via free radical polymerization**

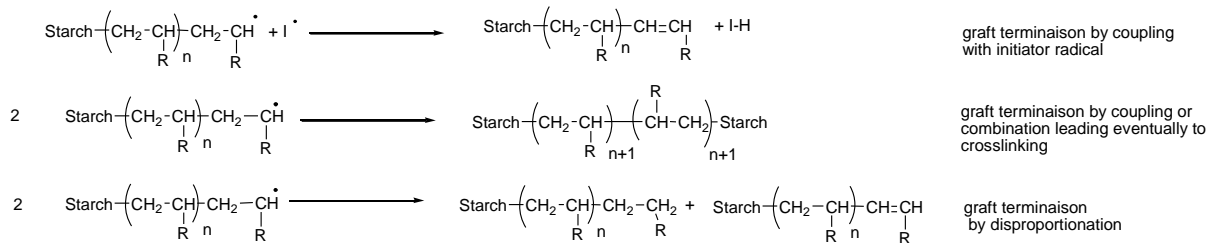
Initiation step:



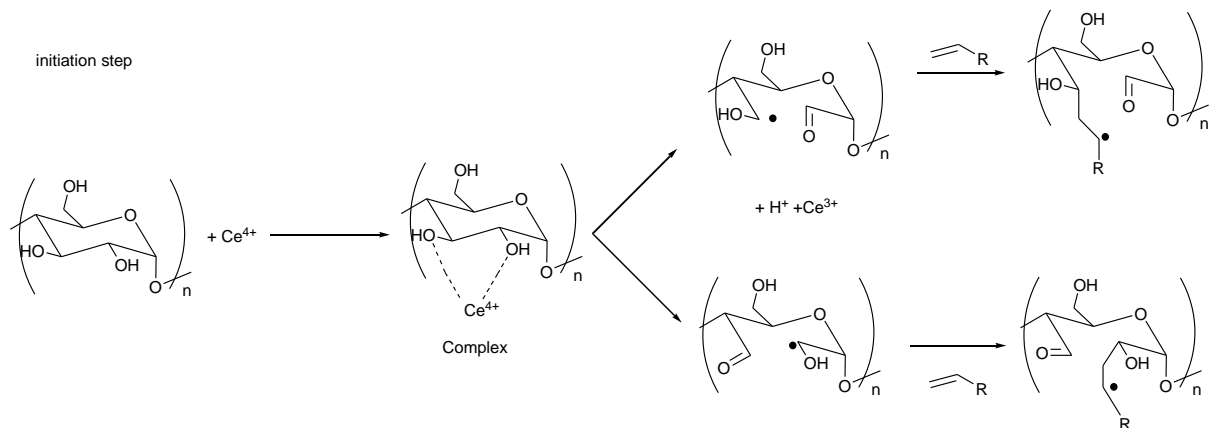
Propagation step:



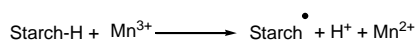
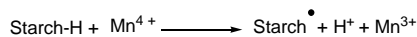
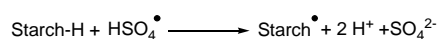
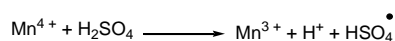
Termination step:



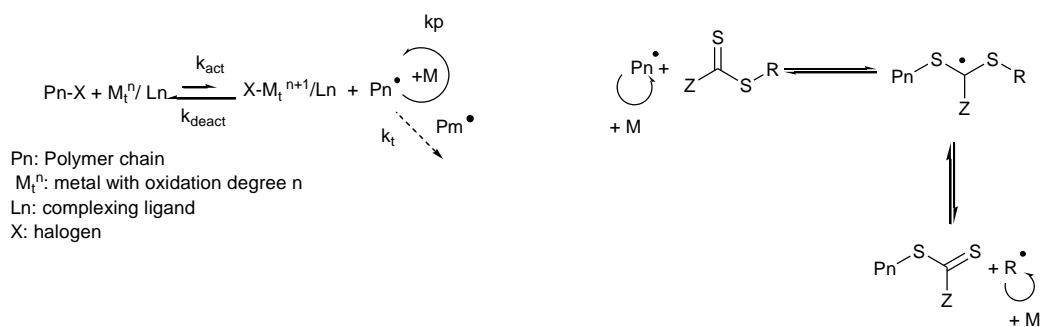
**2b. Mechanism of starch graft free radical copolymerization (reaction involving chain transfer and homopolymerization omitted and solvent/monomer transfer)**



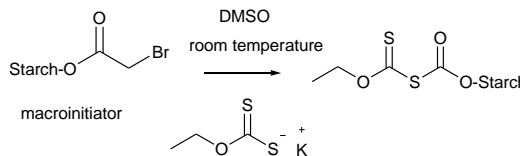
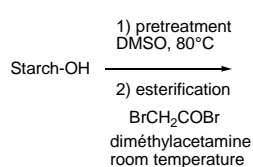
**2c. Initiation step using ceric(IV) ammonium nitrate as the initiator**



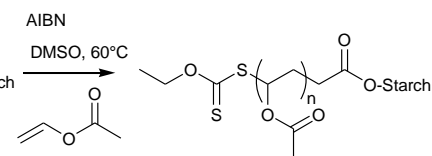
## 2d. Initiation step using potassium permanganate and sulfuric acid as the initiation system



## 2e. ATRP mechanism



## 2f. RAFT mechanism



## 2g. Synthesis of starch-graft-poly(vinyl acetate) via RAFT polymerization

Fig 2. Starch graft radical copolymerization

### 2.1.2 Cerium (IV) complexes as the initiator

Ceric (IV) ammonium nitrate is currently used to initiate the grafting of polymers on starch [25,26,27,28] due to some advantages such as the absence of free radical initiators in the reactive medium, which limits the formation of homopolymer, and the ease of application at room temperature in aqueous medium. The mechanism is based on the reduction of Ce complex from IV to III when reacting with hydroxy groups from starch, leading to the formation of radicals on the polymer backbone (Fig. 2c). The initiator is usually dissolved in nitric or sulfuric acid prior the addition to the reaction mixture.

Various kinds of polyacrylates can be grafted on starch, using cerium complexes as the initiator in water (Table 2), such as poly(methyl methacrylate) [29,30,31], poly(glycidyl methacrylate) [32], poly(butyl acrylate) [33,34] and poly(*N,N*-



diethylaminoethyl methacrylate) [35]. Table 2 summarizes the grafting efficiency and the applications of the different copolymers synthesized with ceric (IV) ammonium nitrate as the initiator. In one of these studies, the grafting of poly(methyl methacrylate) on a starch slurry was evidenced after purification by scanning electron microscopy (SEM) micrograph showing that the polymer was grafted on starch's surface [31]. For low modification (GP=30%), recrystallization behavior was observed whereas in the case of high modification (GP >60%), the formation of a deep groove in the central core region of copolymer was observed.

Glucose can be used in addition to cerium (IV) to graft poly(methyl methacrylate) on starch (GP=6-75%) [36]. Actually, cerium (IV) may interact with glucose to form a complex that dissociates to give a free radical and improve the formation of radical on starch. Starch-*graft*-poly(methyl methacrylate) can be used to form blown films [37] or to improve the properties of poly(propylene carbonate)/ starch composites blend [38].

The graft copolymerization of acrylonitrile was performed with cerium (IV) as the initiator and different parameters were studied: the conditions of starch pre-treatment in water before grafting reaction (T=65°C or 95°C, and t=15-60 min, GE=81-99%) [39], the temperature of grafting reaction (T=25-95°C, GP=20-151%) [40,41], the reaction's atmosphere (air, inert: N<sub>2</sub>, oxygen gas) [42] and the type of starch (spherocrystals vs. native starch) [43,44]. With spherocrystal starch (spherical crystal aggregates of starch formed from jet cooked), the molecular weight of polyacrylonitrile grafted was six times higher than with granular starch ( $M_w = 67,000-386,000 \text{ g}\cdot\text{mol}^{-1}$ ). The copolymer could be aerobically degraded by bacterium *Bacillus cereus* from soil [45]. The grafting of polymethacrylonitrile on a slurry of starch was performed (GP=0-105%) but no grafting occurred beyond 45°C [46]. Starch-*graft*-polyamidoxime was obtained by converting the nitrile groups of the starch-*graft*-polyacrylonitrile into amidoximes under basic conditions [47].

The grafting of polyacrylamide was reported on starch (GE=2-98%) [48] and on carboxymethyl-starch via conventional and microwave process (GP=18-50%) [49] to produce superabsorbent polymers (water absorbency=425.2 g/g).

Poly(acrylic acid) [50] and polychloroprene were grafted [51, 52] respectively on native and on cationic starch. The use of cationic starch led to latexes having strong cationic character which act as additives in wet-end addition in paper manufacturing. Polyisoprene cannot be grafted alone on starch and needs the presence of an "initiating comonomer" such as acrylonitrile to obtain copolymers [53]. Copolymers such as poly(styrene-*co*-butyl acrylate-*co*-vinyl acetate) [54] and poly(acrylamide-*co*-2-acrylamido-2-methylpropane sulfonic acid) [55] can be grafted on starch using ceric ammonium nitrate / potassium persulfate and cerium sulfate / ammonium persulfate (GE=34-90%) respectively. In these reactions, cerium (III) formed from cerium (IV) during the initiation reaction may be oxidized again by persulfate to regenerate cerium (IV). Starch-based low-density polyethylene films can be used for graft copolymerization of vinyl acetate (GP=3-12%) [56]. Vinyl acetate grafted low-density polyethylene–starch films offer better dye ability.

### 2.1.3 Benzoyl Peroxide as the initiator

Benzoyl peroxide is used in the literature to perform the grafting of polymers on starch. The radical formation occurs by thermal decomposition of the initiator. For example it can be used successfully for grafting poly(acrylic acid) on hydrolysed starch (GE=51%,  $M_w=2.07 \times 10^6 \text{ g.mol}^{-1}$ ) [57], poly(methyl methacrylate) [58] and polymethacrylamide [59] on starch respectively at 80°C (GP=5-95%) and 65-95°C (GP=0-70%). Starch-*graft*-polystyrene was also formed by steaming process using water as a blowing agent [60].

### 2.1.4 Potassium or ammonium persulfate as the initiator

Potassium or ammonium persulfate are used to initiate polymer grafting on starch via "grafting from". Various kinds of polyacrylates can be grafted on starch [61,62] and different parameters were studied such as the influence of the length of the alkyl group of four methacrylates [63] or the effect of ultrasound [64] and microwaves [65] on the grafting. The results are summarized in Table 3. Increasing the length of the alkyl chain (methyl to hexyl methacrylate) decreased the grafting efficiency due to steric hindrance induced by longer side chains, but increased the strength of the resulting films (1 MPa for butyl methacrylate compared to 0.2 MPa for methyl methacrylate). The influence of the alkyl chain length was also studied using ceric ammonium nitrate as the initiator and similar conclusions were drawn [66]. The ultrasound and microwave irradiation (30-60 seconds) improved the grafting results for reactions involving acrylate, acrylonitrile (GE=20-98%) [67] and acrylamide (GE=40-90%) [68] since this methods improved the probability of collision between the initiator, the starch and the monomer.

The grafting of polystyrene, on pre-swelled starch ( $T_{\text{pre-heating}}=70^\circ\text{C}$ , GE=29-59%, GP=27-45%) and non pre-swelled starch (GE=25% and GP=10%) was conducted in emulsion in water, using potassium persulfate as the initiator and sodium dodecylbenzenesulfonate as the surfactant [69]. The preheating of starch before grafting reaction improved the grafting results since the medium was more homogeneous. This grafting was also performed on nanocrystals starch (prepared by acid hydrolysis of native starch [70], GE=GP=0-60%) [71,72]. The crystalline structure was not modified by the grafting, indicating that polystyrene was mainly grafted on the surface. The graft copolymer became more hydrophobic, when the starch surface was covered with grafted hydrophobic polystyrene chains (contact angle=50° for GP=0% vs. 90° for GP=60%), and solubility tests showed that it can be dispersed in polar or non polar solvents, highlighting the amphiphilic character of the copolymer.

Other parameters were studied to improve the grafting on starch in emulsion conditions such as the use of ionic liquid as the solvent to get homogeneous media (complete dissolution of starch before the reaction with styrene, GP=20-110%) [73] or amine activation in the initiation step of the graft copolymerizations [74-75] involving styrene [76] and

methacrylic acid [77]. The nature of the alkyl group of the amine was shown to have a strong influence on the grafting percentage.

Starch-graft-polystyrene copolymer was also synthesized in suspension polymerization in aqueous medium with potassium persulfate as the initiator, using native (GP=31%) [78,79] or acryloylated-starch (GP=8-120%) [80]. The grafting of poly(acrylic acid) and poly(acrylamide) on acryloylated starch was also studied with ammonium persulfate as the initiator and conferring swelling properties to the obtained materials [81].

The grafting of polyacrylamide on gelatinized starch in an extruder was reported with ammonium persulfate as the initiator in two different swelling solvents: water or DMSO (GE=61-100%) [82,83]. The solvent has an influence on the weight-average molecular weight of the polyacrylamide grafts ( $M_w=925,000 \text{ g.mol}^{-1}$  in water vs.  $M_w=210,700 \text{ g.mol}^{-1}$  in DMSO). Amphoteric starch-graft-polyacrylamide (with anionic and cationic groups in the chains) was synthesized [84] and compared to cationic polyacrylamide, the copolymer having better performances for industrial waste water treatment.

Potassium or ammonium persulfate initiation were also used to graft others polymers for specific applications (Table 4) [85,86,87,88,89,90,91,92].

Two initiators can also be combined to graft polymers on starch. Potassium persulfate/benzoyl peroxide/maleic acid combinations were reported for polystyrene grafting (GPmax=60%,  $M_w=20,000$  to  $140,000 \text{ g.mol}^{-1}$  vs. GPmax=33% without maleic acid) [93] and potassium persulfate/acetone sodium bisulphite for poly(vinyl acetate) grafting on starch [94]. The latter initiation system appeared to favour the formation of starch macroradicals and to decrease the formation of non-grafted homopolymer.

### **2.1.5 Potassium permanganate as the initiator**

Poly(2-(dimethylamino)ethyl methacrylate) ( $[\text{KMnO}_4]=2 \times 10^{-3} \text{ mol/L}$ ,  $[\text{H}_2\text{SO}_4]=5 \times 10^{-2} \text{ mol/L}$ , GP=5-60%, GE=5-30%) [95] and polyacrylonitrile ( $[\text{KMnO}_4]=1 \times 10^{-3} \text{ mol/L}$ ,  $[\text{H}_2\text{SO}_4]=10 \times 10^{-2} \text{ mol/L}$ , GP=50-160%, GE=60-90%) [96,97] were grafted on gelatinized starch in water using a potassium permanganate/sulfuric acid initiation system (Fig. 2d).

A novel initiation system containing potassium permanganate, metaperiodic acid  $[\text{KMnO}_4]=2 \times 10^{-3} \text{ mol/L}$ ,  $[\text{HIO}_4]=1.5 \times 10^{-3} \text{ mol/L}$  was recently reported to graft polyacrylamide on slurry (GE=76-84%) or gelatinized starch (GE=74-94%) [98]. With this initiation system, more radicals are present in the medium, leading to an improvement of the grafting efficiency of 16% compare to the reaction involving potassium permanganate alone.

### **2.1.6 Ferrous ammonium sulfate and hydrogen peroxide as co-initiators**

The Fenton's reagent, based on Fe(II) redox system, can initiate the graft copolymerization on starch. For example, ferrous ammonium sulfate and hydrogen peroxide were used to perform the grafting on starch of polyvinyl

alcohol [99], poly(acrylic acid) [100,101] poly(styrene-co-butyl acrylate) [102], poly(styrene-co-methyl methacrylate) [103] and poly(2-acryloyloxyethyl trimethyl ammonium chloride-co-acrylic acid) [104] in water or water/methanol medium. Table 5 summarizes the grafting efficiency and the applications of different copolymers obtained with this initiation system.

### 2.1.7 Ozone initiation

Ozone was used as the initiator and stabilizer for the graft copolymerization of styrene, butyl acrylate and vinyl acetate on amylopectin to obtain surfactant-free latexes [105]. The ozone simultaneously thins the amylopectin and creates initiating grafting sites on the latter to allow the grafting copolymerization. Polystyrene was also grafted on slurry of starch nanocrystals with ozone as the initiator [106]. X-rays analysis of the resulting product gave rise to the same diffractogram, but the crystallinity ratio decreased from 43 to 33 %.

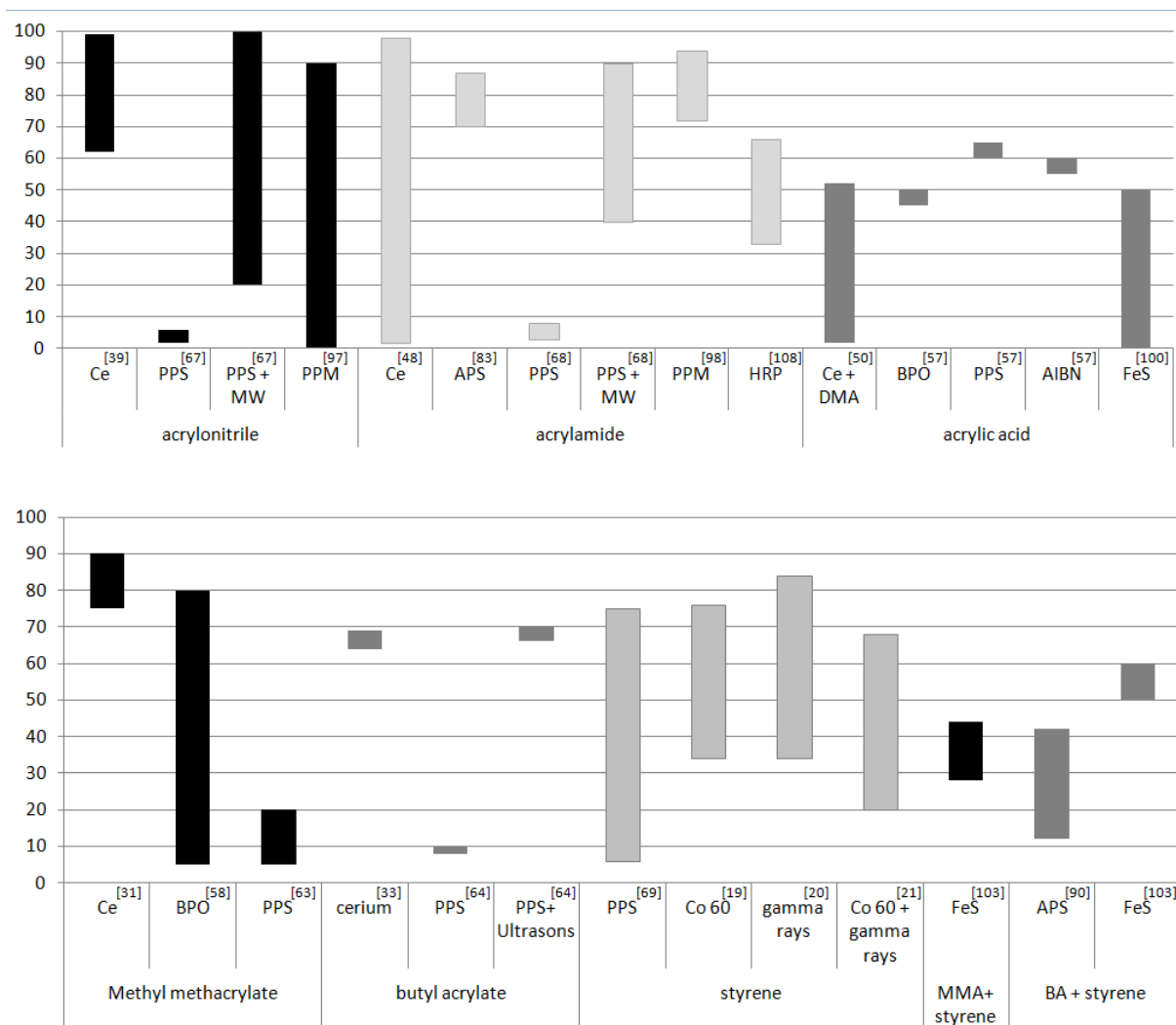
### 2.1.8 Enzymatic initiation

Enzymatic initiation of the radical polymerization of phenols was performed and allowed the production of phenolic resins without using formaldehyde. Horseradish peroxidase (roots of horseradish) is the most widely biocatalyst used for the polymerization of phenol, aniline and their derivatives. Starch-*graft*-poly(diallyl dimethyl ammonium chloride) (GE=75-99%) [107], starch-*graft*-polyacrylamide (GE=33-66%,  $M_w = 99,000-308,000 \text{ g}\cdot\text{mol}^{-1}$ ) [108], starch-*graft*-poly(p-hydroxybenzoic acid)[109], starch-*graft*-poly(methyl acrylate) (GE=20-45%) [110] or some different starch-*graft*-polyphenol (GE=60-90%) [111] were produced using horseradish peroxidase, the latter being used in tanning applications.

### 2.1.9 Comparison of the initiator systems and the monomers used

The Fig. 3 summarizes the different results of grafting regarding the nature of the monomer and the initiator. Ceric ammonium nitrate and persulfates are the most widely used initiators to graft polymers on starch via radical polymerization. Cerium (IV) leads to the best grafting efficiency among all graft copolymerizations systems involving vinyl monomers. Although the grafting of polystyrene on starch was not reported with this initiator, this was successful by using potassium persulfate or under cobalt / gamma-radiations. Concerning the influence of the nature of the monomer, the grafting efficiency increases in the following order: acrylonitrile > acrylamide > methyl methacrylate > butyl acrylate > acrylic acid. In contrast to ceric ammonium nitrate, the reaction with persulfates as the initiators leads to a low grafting efficiency (GE<20%) except for polystyrene and polyacrylic acid. The grafting results were improved by using ultrasound and microwave irradiations (GE= 20-100%). Using Fenton's reagent as the initiation system led to grafting efficiency lower than 50%.

Concerning the influence of the nature of the monomer, the grafting efficiency increases in the following order: acrylonitrile > acrylamide > methyl methacrylate > butyl acrylate > acrylic acid. In fact the grafting of polyacrylonitrile, polyacrylamide, polymethacrylate and polystyrene were well controlled in the literature with grafting efficiency around 85 to 100% after optimization, with few homopolymer and non reacted monomer in the medium. Less impressive results were obtained for poly(butyl acrylate), poly(acrylic acid) and poly (butyl acrylate-co-styrene) where the grafting efficiency was found to be lower and 70%.



APS: ammonium persulfate, BPO: benzoyl peroxide, Ce: ceric (IV) ammonium nitrate, FeS: ferrous ammonium sulfate, HRP: horse-radish peroxidase, PPM: potassium permanganate, PPS: potassium persulfate

**Fig. 3** Grafting efficiency with different monomers and initiators

Starch was removed from graft copolymers by enzyme hydrolysis ( $\alpha$ -amylase and pullulanase or amyloglucosidase) or by acid hydrolysis (HCl) prior to molecular weight determination of grafted polymer chains. The weight-average molecular weight ( $M_w$ ) of grafted polymer chains on starch was found to be in the range 1 to  $13.5 \times 10^5$

$\text{g}\cdot\text{mol}^{-1}$  (Table 6). The highest  $M_w$  was obtained for the graft copolymerization of styrene ( $13.5 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ ). For other grafted polymers  $M_w$  values were found to be in the range  $1$  to  $9.2 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ .

#### **2.1.10** Influence of synthesis parameters

For almost all initiation systems, the grafting efficiency was observed to increase along with the temperature, up to the optimized temperature value beyond which the grafting started to decrease. This may be attributed to an increase of the amount of radicals with the temperature, enhancing the number of grafting sites onto the starch backbone and improving the mobility of the monomer molecules. The decrease in grafting efficiency and percentage with high temperature can be explained by the higher rate of termination reactions of growing graft chains due to the excess of free radical formation and chain transfer reactions causing the increase of homopolymer formation. The optimized range of temperature depends on the nature of the initiator (Table 7), as for example for thermal dissociating initiators (persulfates, benzoyl peroxide), it is necessary to work above their thermal decomposition contrary to reaction with horse radish peroxidase where the enzyme is inactive above  $40^\circ\text{C}$ .

The effect of reaction time on grafting was also studied. The grafting efficiency increased until optimized time of reaction but thereafter gradually decreased. The loss in grafting could be explained by various reasons: the reduction of monomer and initiator concentration, the decreasing of the number of available active sites on starch or the loss of diffusion of reactants due to the formation of long grafted chains.

#### **2.1.11** Modification of native starch's structure and morphology after grafting polymerization

As previously mentioned, starch was pre-treated in water before radical grafting reaction. In case of a starch slurry, the substrate swelled in water but the granular form was conserved. When the grafting reaction was conducted at a temperature below the gelatinization temperature of starch, X-rays diffraction (XRD) patterns showed in the reported studies that the crystallinity structure of starch was kept after grafting reaction. In fact, the typical diffraction peaks of starch ( $2\theta = 15, 17, 18, 20$  and  $23^\circ$ ) were observed on modified starch [72]. The crystallinity can however be slightly altered in some cases [46] highlighted by slight modification of the diffraction pattern. The degree of crystallinity was in the same range for native starch (37%) and grafted starch (39%) when the grafting is low (GP=23%) [78]. It decreased slightly with the increasing of grafting percentage. In another configuration, when starch was gelatinized before grafting reaction, the granular structure was destroyed and the grafted copolymer obtained was amorphous due to this pre-treatment. On X-rays diffraction patterns, only a broad dispersive peak around  $2\theta = 19.5^\circ$  was observed [73].

SEM analysis can be used to compare the structure and morphological changes in the polymer before and after grafting. When the graft copolymerization was carried out on starch slurry at temperature lower than gelatinized

temperature, no significant change was observed in granular shape of starch. The birefringent property of the granule was observed on grafted starch [43]. The microscopy showed the grafting occurred on starch surface and the granules were covered with a layer of polymer grafts [31, 46]. On gelatinized starch substrate, the granular structure of starch was lost and the grafted polymer formed flocculent network structures [98] or aggregates [61].

## 2.2 Controlled radical polymerization

A former review dealing with graft copolymerization of vinyl monomers on polysaccharides through living radical polymerization was published in 2010 [112]. Thus we will focus in this section on recent research in the field while reporting vicinal studies when appropriate.

### 2.2.1 Atom Transfer Radical Polymerization (ATRP)

ATRP is a living radical polymerization technique [113] (Fig. 2e), which involves a reversible homolytic halogen transfer between a dormant specie, an added initiator or dormant propagating chain end and a metal complex in the lower oxidation state ( $Mt^n/Ln$ ), resulting in the formation of propagating radicals ( $Pn^\bullet$ ) and the metal complex in the higher oxidation state with a coordinated halide ligand ( $X-Mt^{n+1}/Ln$ ). The active radical can react either with the monomer and propagate or either with the metal halide complex to form a dormant alkyl halide species, this process being reversible. Butyl acrylate (GP=10-21%) [114], styrene, acrylamide [115] and methyl methacrylate [116] were polymerized on granular starch surface using starch bromo-acetic ester as the macroinitiator and Cu(I)Br associated to 1,10-phenantroline or *N,N,N',N'',N'''*-pentamethyldiethylenetriamine in DMA/LiCl. The main advantage of this approach is the absence of homopolymer formation, due to the living character of ATRP. The drawback is however the difficulty to remove the residual copper after the reaction. The fact that surface-initiated graft copolymerization is performed in heterogeneous media due to the poor solubility of native starch greatly limits the grafting efficiency. Instead of DMA/LiCl used in the previous study, ionic liquid can be used as the swelling solvent to get gelatinized starch and homogeneous media during the formation of the starch macroinitiator for ATRP of polystyrene (GP=94-1,795%,  $M_w$  grafted chains = 2,430-28,116 g.mol<sup>-1</sup>,  $D_M$  =1.3-2.2) and poly(methyl methacrylate) (GP=118-3,147%,  $M_w$  grafted chains = 19,875-38,070 g.mol<sup>-1</sup>,  $D_M$  =1.2-1.5) [117].

### 2.2.2 Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization

RAFT is another living radical polymerization method consisting in the use of thiocarbonyl thio compounds to trap the active radical in a reversible manner (Fig. 2f). Starch-*graft*-poly(vinyl acetate) was synthesized by RAFT polymerization in several step (Fig. 2g, conversion=20-70%,  $M_w$  grafted chains = 22,320 – 124,756 g.mol<sup>-1</sup>,  $D_M$  =1.2-1.5) [118].

### 3. "Grafting from" via Ring Opening Polymerization (ROP)

ROP is a route to polymerize cyclic esters such as lactones and lactides. The hydroxy function of starch can initiate the ROP of these monomers in the presence of a catalyst according to several mechanisms represented Fig.4. Starch-*graft*-poly( $\epsilon$ -caprolactone) and starch-*graft*-polylactide copolymers can be completely biodegraded by bacteria or under natural conditions. In almost all studies presented below, some homopolymer was also formed during the graft reaction and was separated from the grafted copolymer by Soxhlet extraction.

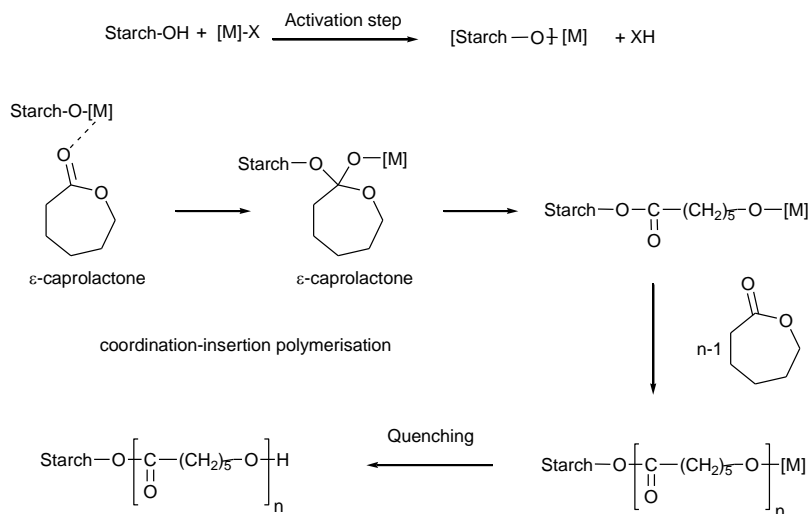
#### 3.1 Metal catalyzed via coordination-insertion mechanism

In the first step of coordination-insertion mechanism, the metal-based catalyst reacts with starch hydroxy groups to form alkoxides, which initiate the ROP of cyclic esters (Fig. 4a). Several reports describe graft copolymerization of  $\epsilon$ -caprolactone or  $\gamma$ -valerolactone via ROP, in bulk or in toluene suspension, involving metal-based catalysts such as stannous octoate, titanium tetrabutoxide [119] and triethyl or isopropoxide aluminium ( $M_w=571,000\text{g}\cdot\text{mol}^{-1}$ ,  $D_M=2.54$ ) [120,121,122]. With stannous octoate as the catalyst, the grafting of poly( $\epsilon$ -caprolactone) in water was reported on gelatinized starch [123]. The water plasticized starch, promoted the reactions between the starch and  $\epsilon$ -caprolactone monomer (yield of grafting =60-91% determined by NMR).

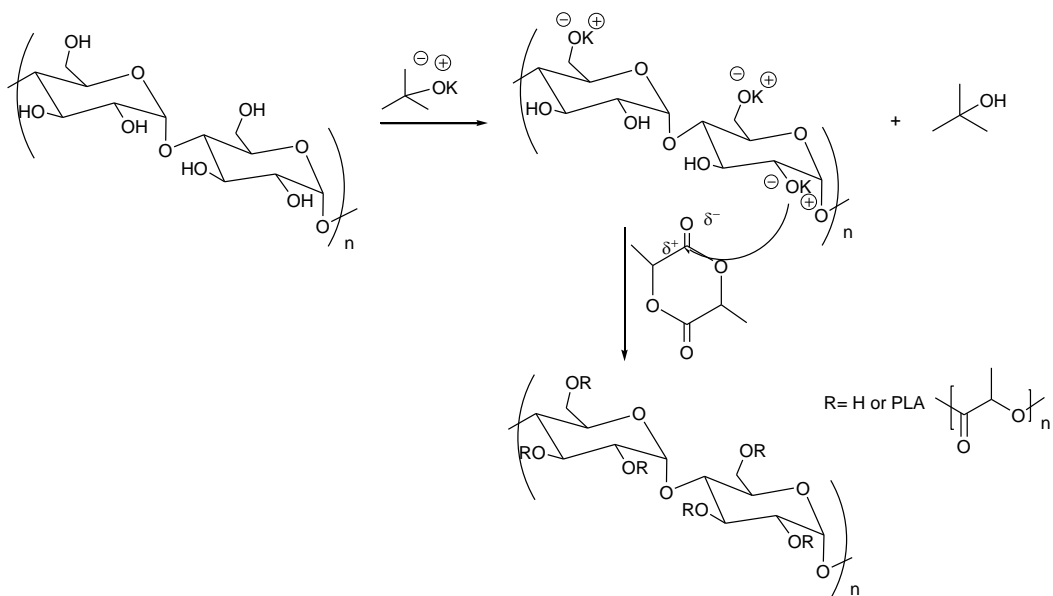
Table 8 summarizes the grafting efficiency obtained with various catalysts and reaction media. Low grafting efficiencies ( $GE<40\%$ ) are observed with stannous octoate as the catalyst in toluene suspension, due to the heterogeneous nature of the reaction [124]. The grafting occurred only on the starch surface and modified the morphology of the granule. On SEM micrograph, the surface of the copolymer was rough and polygonal and some connections between granules and poly( $\epsilon$ -caprolactone) could be seen. The semicrystallinity of starch granules was still observed after grafting. In order to get a homogeneous solution and gelatinized starch as the substrate, the ionic liquid 1-allyl-3-methylimidazolium chloride can be added in the reaction media as swelling agent ( $GE=24\%$ ) [125]. Compare to previous studied the surface of copolymer is smooth (SEM) and the copolymer is amorphous (X-rays diffraction). An alternative method to graft poly( $\epsilon$ -caprolactone) on gelatinized starch was described starting from silylated-starch precursors [126] which are less hydrophilic and thus more soluble in organic solvents providing homogenous media. In the first step, the starch was silylated using hexamethyl disilazane ( $DS=0.45-0.7$ ) in THF then,  $\epsilon$ -caprolactone is grafted to silylated starch by ROP with aluminium isopropoxide as the catalyst ( $GE=28-58\%$ ). According to the table, when stannous octoate was used as the catalyst, the reaction times were longer ( $t>20$  hours) and more heating was needed ( $T> 110^\circ\text{C}$ ) than for experiments with other metal-based catalysts ( $T<90^\circ\text{C}$ ,  $t<4$  hours) to graft polymer on starch.

The grafting of poly( $\epsilon$ -caprolactone), on granular starch [127] or starch nanocrystals [128, 129] can also be conducted in bulk conditions under micro-waves. This copolymer can be used as thermoformable biocomposite

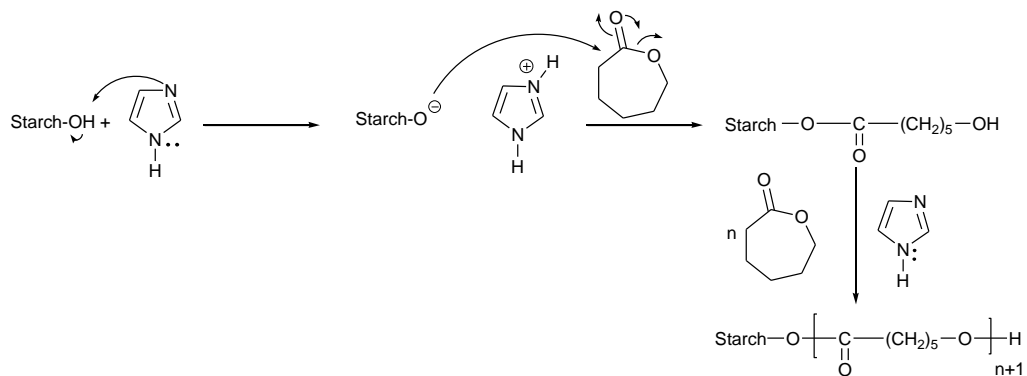




**4a. ROP with metal-based catalyst**



**4b. ROP via anionic catalyst[138]**



**4c. ROP with basic organo-catalyst [142]**

**Fig 4.** Mechanisms of ROP with different ways of catalyse

(strength=10-20Mpa, elongation at break=4-11%) or incorporated into polylactide to improve the adhesion between the matrix and the filler. The grafting of poly(*p*-dioxanone) on acetylated starch was performed via ROP with stannous octoate as the catalyst in bulk conditions (GE=67-85%,  $M_w=20,000-100,000 \text{ g mol}^{-1}$ ). This copolymer can be used for drugs release [130].

Stannous octoate can also be used to graft poly(L-lactide) on gelatinized starch (water was removed before grafting reaction) with lactide or lactic acid (formation of L-lactide *in situ* in the reaction medium) [131] as the substrate. This grafting reaction was performed under various conditions on gelatinized starch: microwave heating (GP=62%) [132], supercritical carbon dioxide medium (GP=21-52%) [133], ionic liquid as the solvent (GE=30%) [134]. In the previous studies, XRD analysis showed that the grafting reaction modified the crystallinity of native starch and polylactide. The grafted copolymer was found to be amorphous (broad peak at  $2\theta=19.1^\circ$ ) in opposition to native starch and polylactide (crystallinity peaks:  $2\theta=16.6^\circ$  and  $19.18^\circ$ ).

In order to improve the efficiency of this grafting, a process in two steps was developed [135,136]. First, the surface of starch granules was modified with L-lactic acid in THF suspension. Then the grafting polymerization of L-lactide from the hydroxy groups of the starch-*graft*-(L-lactide) was then carried out with stannous octoate as the catalyst under anhydrous condition (GE=36-64% vs. 14%).

Amylose-*graft*-poly(D,L-lactide) was synthesized with stannous octoate as the catalyst using a three-step synthetic pathway: a partial silylation of hydroxy functions followed by the polymerization of lactide, and finally the deprotection of the silylether groups [137].

### 3.2 Anionic Ring-Opening Polymerization

Poly(L-lactide) can be grafted on gelatinized starch in DMSO via anionic polymerization activated by potassium *tert*-butoxide (Fig. 4b) [138] or by sodium hydroxide [139,140]. First, the hydroxy groups from starch were activated by the initiator. Then the L-lactide was added or was formed *in situ* from lactic acid and its carbonyl groups were attacked by the generated anions in the starch, leading to ring-opening of L-lactide. Sodium hydroxide is less efficient than potassium *tert*-butoxide as the initiator for this grafting reaction (GE=6% vs GE=42%).

### 3.3 Organocatalysis

#### 3.3.1 Basic catalysis

Poly( $\epsilon$ -caprolactone) was grafted on starch in bulk conditions using *N*-methylimidazole [141] and imidazole [142] as the catalysts (Fig. 4c). The advantage of using these catalysts, despite of a high catalyst ratio, is the absence of homopolymer formation (GE up to 55% with 25wt catalyst). Actually, imidazole alone does not initiate the polymerization of  $\epsilon$ -caprolactone in the experimental conditions of the study, and a co-initiator such as a hydroxy group is required. XRD

analysis showed that the grafted copolymer was amorphous displaying only a large band at  $2\theta = 20^\circ$  whereas intense peaks were observed in the diffractograms of native starch (intense peaks at  $2\theta = 6$  and  $17^\circ$ ) and polycaprolactone (intense peaks at  $2\theta = 21$  and  $23^\circ$ ), indicating that the polymer chains grafted on starch were too short to crystallize.

Poly(trimethylene carbonate) was grafted on starch surface in bulk conditions at  $150^\circ\text{C}$  with base catalysts such as guanidine base and phosphazene superbases ( $DP=2-12$ ) [143]. Organic base catalysts considerably improved the polymerization rate of trimethylene carbonate (conversion=98% after 2 min with 0.1% of catalyst) compared to stannous octoate (conversion=25% after 2 min with 1 mol % of catalyst).

### 3.3.2 Ionic liquid as the catalyst

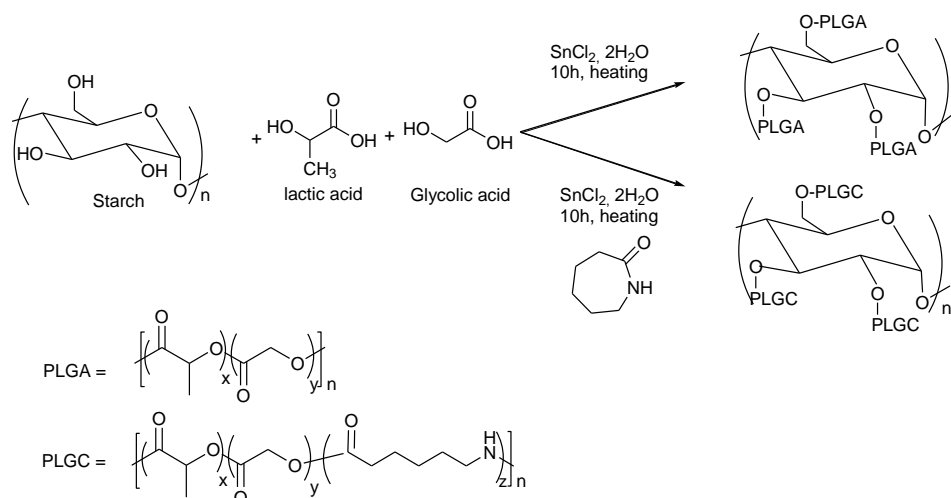
Starch-*graft*-poly( $\epsilon$ -caprolactone) was synthesized using pyrrolidinium chloride as the catalyst ( $GE=11\%$ ,  $M_w=0.78-1.36 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ) [144].

### 3.4 Comparison of catalysts

The Table 9 summarizes the grafting efficiency of polyesters on starch performed with various ROP catalysts (metal, anionic and organic catalysts). The metal-based catalysts are in general found to be more efficient, stannous octoate being the most commonly used to graft polyester on starch with correct efficiency ( $GE=6-85\%$ ).

## 4. "Grafting from" by polycondensation

Starch-*graft*-poly(lactic acid) ( $GP=13\%$ ), [145] starch-*graft*-poly(lactic acid-*co*-glycolic acid) (PLGA) and starch-*graft*-poly(lactic acid-*co*-glycolic acid-*co*- $\epsilon$ -caprolactam) (PLGC) copolymers were prepared by direct polycondensation from starch, lactic acid, glycolic acid and  $\epsilon$ -caprolactam in aqueous media in the presence of stannous chloride at  $120-170^\circ\text{C}$  (Fig. 5) [146].



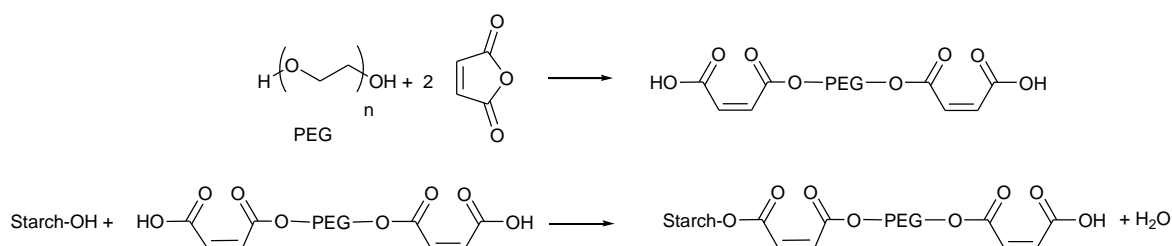
**Fig. 5** Graft copolymerization of starch with lactic acid, glycolic acid and  $\epsilon$ -caprolactam [146]

The synthesis of starch-*graft*-poly(lactic acid) was performed with ammonia and water as the catalyst (GP=30-60%) and urea as the solvent (to improve the dissolution of starch in order to reach homogeneous conditions) [147]. An alternative method to graft poly(L-lactic acid) on starch with carboxymethyl starch as the precursor was reported via polycondensation with stannous octoate as the catalyst [148,149].

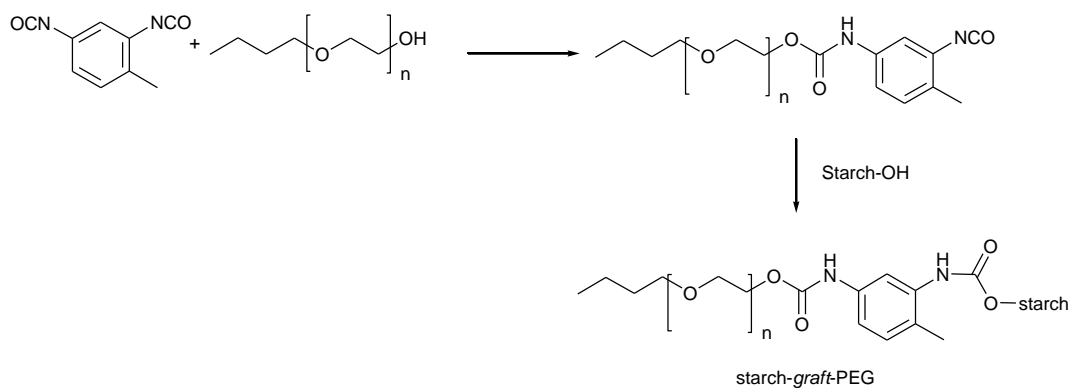
## 5. "Grafting onto/ to"

### 5.1 Via coupling agents

Maleic anhydride can be used as coupling agent to graft polyethylene glycol ( $M_w=2,000-6,000\text{g}\cdot\text{mol}^{-1}$ ) on starch by esterification (Fig. 6a) [150]. Maleic anhydride was reacted with the polyether hydroxy end groups in a first step. The resulting carboxylic acids can further react with the hydroxy groups of starch. The copolymer was shown to be soluble at 92% in cold water in opposition to native starch which is usually insoluble in these conditions (0.4%). SEM analysis showed a loose and porous outer layer, meaning the grafting occurred at the outer layer of starch granules. The granule size, shape and degree of crystallinity of native starch remained unchanged after grafting reaction. The blend of polylactide with starch-*graft*-poly(ethylene glycol) was achieved in an extruder [151]. The surface grafted with polyethylene glycol induced a novel interphase transition layer between polylactide and starch, leading to the improvement of the compatibility. The elongation at break increased from 6 to 254.5%.



#### 6a. Synthesis of starch-*graft*-poly(ethylene glycol) using maleic anhydride as the coupling agent[150]



#### 6b. Synthesis of starch-*graft*-poly(ethylene glycol) using 2,4-toluene diisocyanate as the coupling agent[154]

Fig 6. "Grafting from" via coupling agent

Maleated starch-*graft*-poly(vinyl alcohol) was prepared by esterification reaction between poly(vinyl alcohol) ( $M_w=89,000-98,000\text{ g}\cdot\text{mol}^{-1}$ ) and maleic acid substituted gelatinized starch in order to obtain hydrogels (swelling ratio =1.8-12 g/g) for various biomedical applications such as drug delivery system, tissue engineering and artificial implants [152, 153]. The reaction between maleic starch and poly(vinyl alcohol) modified the morphology of grafted starch. For example, after 2 hours of reaction the structure was composed of individual spherical particles whereas after 4 hours SEM analysis showed a smooth surface with gel network structure attributed to crosslinking between the polymers.

Different grafting on nanocrystals of starch were conducted with some polyethers such as poly(ethylene glycol) methyl ether ( $M_n=550\text{g}\cdot\text{mol}^{-1}$ ), poly(tetrahydrofuran) ( $M_n=1,400\text{g}\cdot\text{mol}^{-1}$ ) and poly(propylene glycol) monobutyl ether ( $M_n=4,000\text{g}\cdot\text{mol}^{-1}$ ) using 2,4-toluene diisocyanate as the coupling agent (Fig. 6b) in a two-step process [154-155]. In the first step, the polyether reacted with one isocyanate of 2,4-toluene diisocyanate. In the second step, the unreacted isocyanate was reacted with the hydroxy groups of the granular starch in toluene. The crystalline structure of the nanoparticles was preserved after grafting reaction. The hydrophobic properties of starch were improved since contact angle water value increase from  $32.6^\circ$  to  $97^\circ$ . Starch-*graft*-poly(1,4-dioxan-2-one) was synthesized in the same way (GE=21-63%) [156].

Poly( $\epsilon$ -caprolactone), polylactide and poly(butylene succinate) were grafted on granular starch with different diisocyanates as the coupling agents including 2,4-toluene diisocyanate, hexamethylene diisocyanate or lysine diisocyanate in bulk condition [157, 158]. These copolymers were shown to be an efficient compatibilizer for starch/poly( $\epsilon$ -caprolactone) [159] or starch/ poly(lactic acid) blends [160].

Poly(vinyl alcohol) ( $M_w=30,000$  and  $68,000\text{g}\cdot\text{mol}^{-1}$ ) was grafted onto hydrolysed starch with *N*-methylolacrylamide as the coupling agent (GE=30-70%) [161].

## 5.2 Via radical coupling

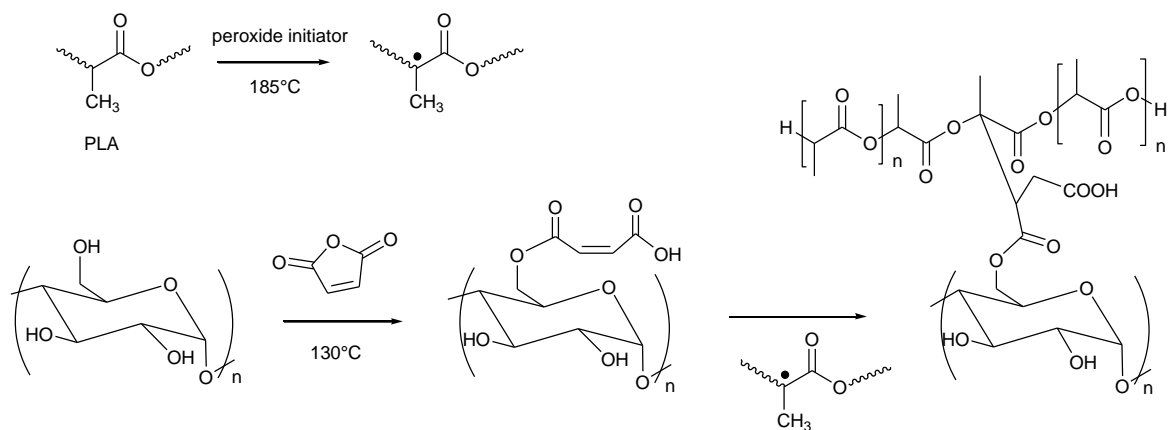
Maleic anhydride was used as the coupling agent for the radical grafting of polylactide on granular starch with a lab-scale co-extruder ( $T=125-180^\circ\text{C}$ ) in the presence of 2,5-bis(*tert*-butylperoxy)-2,5 dimethylhexane as the initiator [162,163,164]. Maleic anhydride reacted with hydroxys from starch and peroxide initiator reacted with polylactide, allowing the formation of radicals on the polyester. The latter radicals can then react with the anhydride group from starch to form ester linkages (Fig. 7a).

The graft copolymerization of low-density polyethylene onto starch was performed using glucose-cerium(IV) (GE=1-86%) [165] or benzoyl peroxide/potassium persulfate [166] initiation systems. Pre-irradiated polyethylene (GE=90%) [167], and polypropylene [168] were grafted in water using benzoyl peroxide as the radical initiator. The activation of polydienes was performed through gamma radiations which generated macro oxy-radicals. These peroxidic linkages

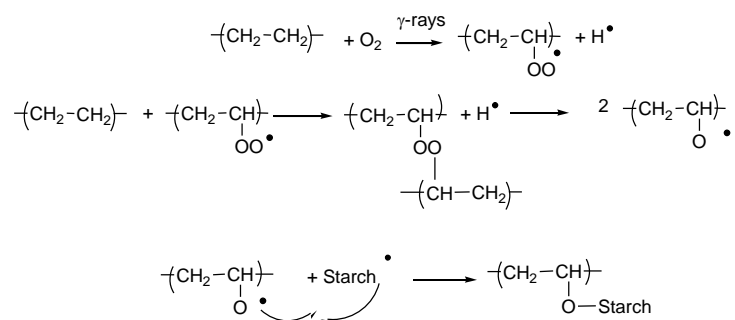
generate macroperoxy radicals under heating. Benzoyl peroxide generates active sites on starch via the capture of hydrogen by the phenyl radical and the graft copolymer is formed via radical coupling (Fig. 7b).

Natural rubber was grafted on a slurry of starch with potassium persulfate as the initiator in aqueous suspension conditions [169]. The rubber increased the flexural modulus of the foams and the impact strength under certain conditions (impact strength 137-900 J/m<sup>2</sup>, elongation at break 3%).

Starch-*graft*-(sodium lignosulfonate) was synthesised using oxidoreductase (laccase) biocatalyst in aqueous solution via free radical polymerization [170]. During the initiation step, laccase was oxidized by oxygen which then catalysed the oxidation of phenol groups in sodium lignosulfonate to afford phenoxy radicals. Phenoxy radicals can then abstract hydrogen from gelatinized starch and allowed the grafting. The grafted polymer was water soluble (solubility= 84-100%)



**7a.** Synthesis of starch-graft-poly(lactide) via radical coupling using maleic anhydride as the coupling agent [162]



**7b.** Synthesis of starch-graft-poly(ethylene) via radical coupling using gamma rays activation [166]

**Fig 7.** "Grafting from" via radical coupling

### 5.3 Via activated ester or acid

“Grafting onto” was also performed in three steps with carbonyldiimidazole [171] as the coupling agent between poly( $\epsilon$ -caprolactone) ( $M_w=1,000-2,000 \text{ g.mol}^{-1}$ ) and starch (Fig. 8a). First, the monohydroxy-terminated poly( $\epsilon$ -caprolactone) was synthesized via the ROP of  $\epsilon$ -caprolactone with benzyl alcohol as the initiator and stannous octoate as the catalyst (step 1). Then carboimidazole-terminated poly( $\epsilon$ -caprolactone) was prepared by reaction between carbonyldiimidazole and end-functionalized poly( $\epsilon$ -caprolactone) (step 2). Finally poly( $\epsilon$ -caprolactone) was grafted onto starch in DMSO (GP=86-140%, GE=13-70%) by reacting carboimidazole function with the hydroxy group of starch, imidazole being a good leaving group (step 3). The SEM analysis showed the grafting occurred on the surface of the starch granules.

The grafting of poly(butylene succinate) ( $M_w= 47,000 \text{ g.mol}^{-1}$ ) onto starch was also reported by a coupling reaction between hydroxy groups of starch and carboxylic acid terminal groups of poly(butylenes succinate) using *N-N*-dicyclohexylcarbodiimide as the coupling agent and chloroform as the solvent (GP=20–30%) [172].

### 5.4 Via acyl halide

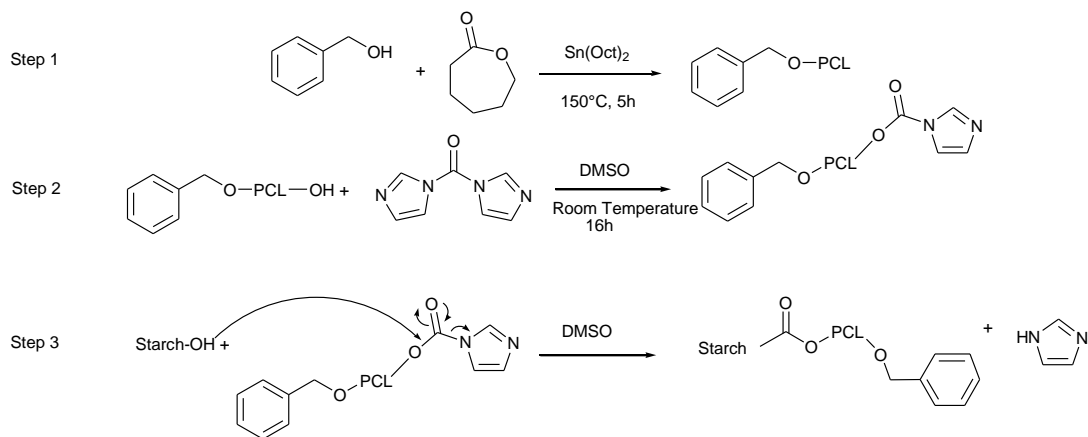
Copolymers of starch grafted with methoxypoly(ethylene glycol) were synthesized through bromoacetylation of starch followed by reaction with methoxypoly(ethylene glycol) of various molecular weights ( $M_w= 500, 2,000$  and  $5,000 \text{ g.mol}^{-1}$ ) at  $50^\circ\text{C}$  (Fig. 8b) [173]. According to XRD pattern, the crystallinity of the grafted copolymer depended on the molecular weight of polymer grafted. The crystalline structure of starch slightly changed when the starch was modified with methoxypoly(ethylene glycol) ( $M_w= 500 \text{ g/mol}$ ). When methoxypoly(ethylene glycol) with  $M_w= 2,000 \text{ g/mol}$  was grafted, a wide peak appeared at  $2\theta = 20^\circ$  so the amorphous nature of these copolymers increased with the length of grafted chains. These copolymers can find industrial applications as various drug delivery vectors.

Starch stearate can be achieved by reaction between starch nanocrystals and stearic acid chloride in methyl ethyl ketone [154]. Triethylamine was added as the catalyst and also to trap HCl. Stearate was grafted onto the starch nanoparticle surface, forming a crystalline hydrophobic shell displaying good hydrophobic properties (contact angle from  $33^\circ$  to  $102^\circ$ ). Polylactide ( $M_n= 49,860 \text{ g.mol}^{-1}$ ) was grafted onto the starch nanoparticles via acyl halide mechanism [174].

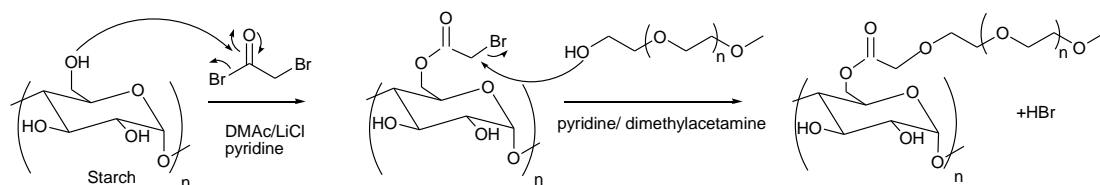
### 5.5 Via click chemistry

Starch-*graft*-poly(vinyl acetate) was synthesized via RAFT polymerization combined to click chemistry via azide-alkyne cycloaddition (Fig. 8c) [175]. Alkyne-terminated poly(vinyl acetate) was first polymerised by RAFT and in a second step, azide-functionalized starch was synthesized by the nucleophilic substitution of starch tosylate and sodium azide, followed at last by the click reaction.

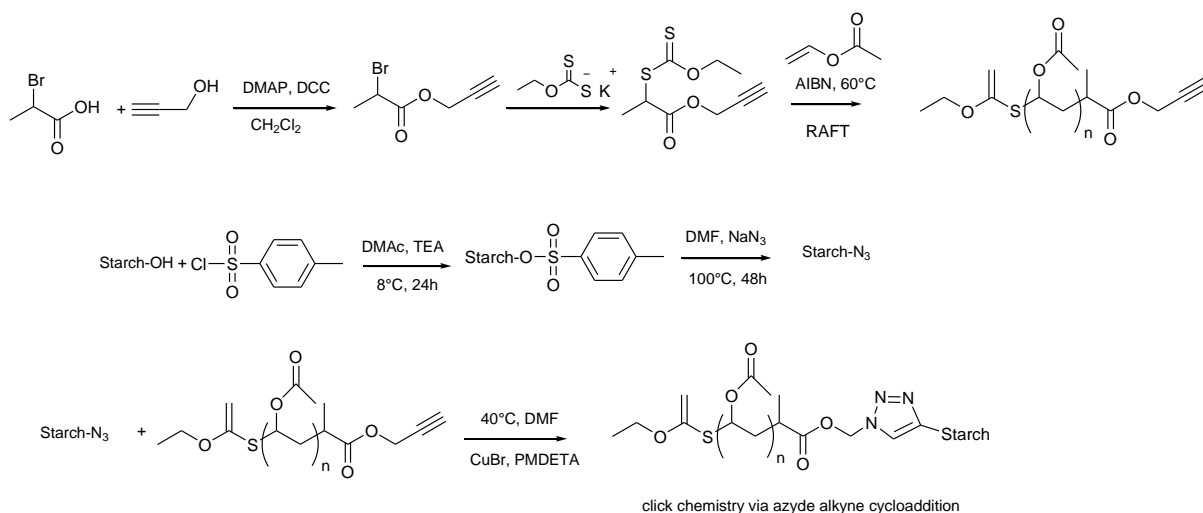
In a similar way, poly(*n*-butyl methacrylate) [176] and polymethacrylate [177] were grafted on starch by coupling azide-end functionalized polyacrylate and alkyne-functionalized amylose under click conditions.



**8a. Synthesis of starch-graft-poly( $\epsilon$ -caprolactone) via activated ester way[171]**



**8b. Synthesis of starch-graft-methoxypoly(ethylene glycol) via acyl halide way [173]**



**8c. Synthesis of starch-graft-polyvinyl acetate via RAFT polymerization and click chemistry[175]:** AIBN: *N,N'*-Azobisisobutyronitrile, DCC: *N,N'*- dicyclohexylcarbodiimide, DMA: dimethylacetamine, DMAC: *N,N'*- dimethylacetamide, DMAP: 4- dimethylaminopyridine, PMDETA: *N,N,N',N',N''*-pentamethyldiethylenetriamine, TEA: triethylamine

**Fig 8.** "Grafting from" via others couplings strategies



## 5.6 Comparison of chemistry ways to perform “grafting onto”

The tables 10 and 11 showed the different results of grafting for different coupling strategies. Only few studies reported the grafting efficiency via “grafting onto” copolymerization (Table 9). Grafting efficiencies of up to 60-75% were obtained using coupling agent based strategies, while radical initiators gave rise to starch-*graft*-polyethylene with 80-90% of grafting efficiency.

The weight-average molecular weight of grafted polymer chains onto starch was found in the range 500 to 7,500 g.mol<sup>-1</sup> whatever the strategies, except for poly(vinyl alcohol) and poly(butylene succinate) where it was higher (Table 10).

## CONCLUSION

Various methods of grafting polymers on starch were reported to date in the literature. Vinyl monomers can be grafted via radical copolymerization involving different initiator systems in aqueous and organic media such as ceric ammonium nitrate, potassium persulfate, hydrogen peroxide-ferrous ammonium sulfate and benzoyl peroxide. Non-grafted homopolymer is usually formed via this way of grafting, in contrast to controlled radical polymerizations such as ATRP and RAFT where, in addition, the molecular weight of the graft can also be controlled. These types of reactions require in turn an additional step, which is the formation of the macroinitiator on starch before the grafting step. Aliphatic polyesters such as poly( $\epsilon$ -caprolactone) and polylactide can also be grafted on starch via ROP initiated by the hydroxy group of starch in the presence of a pre-catalyst. The reaction can be conducted with organocatalysts or with metal-based catalysts (stannous octoate, alkyl aluminium) in bulk conditions or in solvents such as water, toluene, and in unusual medium such as ionic liquids. In all studies, except with imidazole as the catalyst, free homopolymer was also formed during the graft copolymerization reaction and had to be extracted after the reaction. High amount of imidazole were however necessary to catalyse the polymerization. Finally, in addition to polyesters, polyethers, and polyolefins can also be grafted onto starch by the “grafting onto” strategy using coupling agents such as isocyanates or maleic anhydride, in order to improve the hydrophobicity of starch. Polyolefins or polylactide were also grafted onto starch by “grafting onto” in the presence of radicals initiators such as peroxide, cerium (IV) or maleic anhydride. The recent advent of controlled radical polymerization of ethylene [178] may open the way for interesting future trends in the field.

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## Figure Legends

**Fig. 1** Different routes in graft copolymerization

**Fig 2.** Starch graft radical copolymerization

**Fig. 3** Grafting efficiency with different monomers and initiators

**Fig 4.** Mechanisms of ROP with different ways of catalyse

**Fig. 5** Graft copolymerization of starch with lactic acid, glycolic acid and  $\epsilon$ -caprolactam

**Fig 6.** "Grafting from" via coupling agent

**Fig 7.** "Grafting from" via radical coupling

**Fig 8.** "Grafting from" via others couplings strategies

**Table 1.** Effect of irradiation type on grafting efficiency and weight-average molecular weight of the grafted polymer chains

Initiator	Applied dose of irradiation (kGy)	Dose rate (kGy/h)	GE(%)	$M_w$ (g.mol <sup>-1</sup> ) <sup>a</sup>	Reference
Cobalt-60 (water media)	10	10	28-44	590,000-795,000	[19]
Cobalt-60 (organic media)	10	10	34-76	500,000-955,000	[19]
Gamma rays	5-40	1.6	34-84	/	[20]
Cobalt-60 + gamma rays	2-16	9	20-68	440,000-450,000	[21]

<sup>a</sup> The starch backbone was hydrolyzed before GPC or intrinsic viscosity analysis

**Table 2.** Starch-*graft*-polyacrylates: grafting results using ceric ammonium nitrate as the initiator and applications of the resulting material

Copolymer	GE(%)	GP(%)	$M_w$ (g.mol <sup>-1</sup> ) of grafted polymer chains	Applications	Reference
Starch- <i>graft</i> -poly(methyl methacrylate) <sup>a</sup>	75-90	30-110	$3-7 \times 10^5$	Films	[31]
Starch- <i>graft</i> -poly(glycidyl methacrylate) <sup>a</sup>	83-99	0-50	/	Cured film in coating formulation	[32]
Starch- <i>graft</i> -poly(butyl acrylate) <sup>a</sup>	64-69	3-10	$1-2 \times 10^5$	Encapsulating carboxylic acid	[33]
Carboxymethylated starch- <i>graft</i> -poly(butyl acrylate) (DS=0.35) <sup>a</sup>	70-85	117-235	/	/	[34]
Starch- <i>graft</i> -poly( <i>N,N</i> -diethylaminoethyl methacrylate) <sup>b</sup>	/	5-50	/	Hydrogel (swelling ratio=100%)	[35]

Starch structure in the reactive medium: a: slurry of starch, b: gelatinized starch



**Table 3.** Grafting efficiency of starch-*graft*-poly(acrylate) depending on the nature of the acrylate and the different synthesis parameters

Kinds of polyacrylate	Starch structure in the reactive medium	Optimal parameters of grafting reaction		GE(%)	Reference
		T(°C)	t(min)		
		Phenyl methacrylate	gelatinized		
Methyl methacrylate	slurry	60	60	35-70	[63]
Butyl methacrylate	slurry	60	60	35-60	[63]
Hexyl methacrylate	slurry	60	60	30-65	[63]
Butyl acrylate	gelatinized	80	75	22-28	[64]
Butyl acrylate (ultrasound)	gelatinized	70	75	68-71	[64]

**Table 4.** Applications of starch-*graft*-polymer synthesized using persulfates as the initiator

Polymer grafted	Applications	Reference
poly(acryloyloxyethyltrimethyl ammonium chloride)	Flocculent properties	[85]
poly-( <i>N,N</i> -dimethyl acrylamide- <i>co</i> -acrylic acid)	Metal removal in water	[86][87]
poly(methyl acrylate) and poly(diacetone acrylamide)	Humidity control for interior wall coatings	[88]
poly(styrene- <i>co</i> -butyl acrylate)	Latex for paper coating application	[89][90]
natural rubber	Controlling release of urea fertilizer in agriculture	[91][92]

**Table 5.** Starch-*graft*-polymers: grafting results using Fenton's reagent as the initiator and polymers applications

Copolymer	GE(%)	Applications	Reference
Starch- <i>graft</i> -poly(vinyl alcohol) <sup>a</sup>	46-50 <sup>1</sup>	Encapsulating 2,4,5-trichlorophenoxyacetic acid for slow herbicide release	[99]
Starch- <i>graft</i> -poly(acrylic acid) <sup>a</sup>	58 <sup>2</sup>	Films (breaking strength: 28.6 N/mm <sup>2</sup> )	[101]
Acryloylated starch- <i>graft</i> -poly(acrylic acid) (DS=0.01-0.036) <sup>a</sup>	67-81 <sup>2</sup>	Films (breaking strength:29-35 N/mm <sup>2</sup> )	[101]
Cationic acetylated starch- <i>graft</i> -poly(styrene- <i>co</i> - butyl acrylate) <sup>b</sup>	14-31 <sup>3</sup>	Films (bursting strength: 107.5 to 248.4 kPa)	[102]
Starch- <i>graft</i> - poly(styrene- <i>co</i> -butyl acrylate) <sup>b</sup>	50-60 <sup>4</sup>	Cotton fabric sizing applications	[103]
Starch- <i>graft</i> - poly(styrene- <i>co</i> -methyl methacrylate) <sup>b</sup>	28-44 <sup>4</sup>	(elongation at break 6-8%)	

Starch structure in the reactive medium: a: slurry of starch, b: gelatinized starch

1: [Fe(SO<sub>4</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>] =6.2 x 10<sup>-3</sup> mol/L / [H<sub>2</sub>O<sub>2</sub>] = 0.134 mol/L, 2: [Fe(SO<sub>4</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>] =2 x 10<sup>-3</sup> mol/L / [H<sub>2</sub>O<sub>2</sub>] = 0.04 mol/L,

3: [Fe(SO<sub>4</sub>)<sub>2</sub>] =1x 10<sup>-3</sup> mol/L / [H<sub>2</sub>O<sub>2</sub>] = 0.18 mol/L, 4: [Fe(SO<sub>4</sub>)<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>] non specified / [H<sub>2</sub>O<sub>2</sub>] = 0.1 mol/L

**Table 6.** Weight-average molecular weight of grafted polymer chains with different monomers and initiators determined by intrinsic viscosity (left) or by GPC with polystyrene or polyacrylamide standards (right)

Polymer grafted	Initiator	$M_w$ (g.mol <sup>-1</sup> )		Reference
		Intrinsic viscosity	GPC with polystyrene or polyacrylamide standards	
Poly(acrylonitrile)	Ce	300,000-700,000	/	[43]
Poly(butyl acrylate)	Ce	100,000-200,000	/	[33]
	APS	140,000	/	[65]
Poly(methyl methacrylate)	PPS	70,000-450,000	/	[62]
	Ce	/	300,000-700,000	[31]
	Co 60	500,000-955,000	/	[19]
Poly(styrene)	PPS	/	190,400-1,346,000	[69]
	Co 60 + gamma rays	/	440,000-450,000	[21]
Poly(acrylamide)	APS	/	317,000-769,000	[83]
	HRP	/	99,000-308,000	[108]

Ce: ceric ammonium nitrate, APS: ammonium persulfate, PPS: potassium persulfate, HRP: horse-radish peroxidase

**Table 7.** Optimal parameters according to initiator system

Initiation system	Temperature (°C)	Time (hours)	Reference
Ceric ammonium nitrate	35-50	1-3	[29] [36]
Persulfates	70-80	2	[61] [64]
Potassium permanganate	40-50	6	[95]
Ferrous ammonium sulfate	30-60	2-4	[99] [103]
Horse radish peroxidase	30-40	5-7	[110][111]

**Table 8.** Grafting efficiency for the synthesis of starch-*graft*-poly( $\epsilon$ -caprolactone) with metal based catalysis

	Triethyl aluminium		Stannous octoate			Silylated starch	
	Bulk	Toluene suspension	Bulk	Toluene suspension	Suspension/ bulk	Ionic liquid solvent	Aluminium isopropoxide
T (°C)	90	65	130	130	130	120	50
time (h)	0.15	4	48	70	24	22	2
GE (%)	7-22	18-100	14-18	6-8	26-40	8-26	28-58
Reference	[122]	[122]	[124][125]	[124][125]	[124][125]	[125]	[126]

**Table 9.** Grafting efficiency (GE) for the synthesis of starch-*graft*-polyester

Grafted polymer	Catalyst	GE(%)	Reference
Polycaprolactone	Triethyl aluminium	7-100	[122]
	Stannous octoate	6-40	[124]
	N-methylimidazole	12-55	[141]
	Ionic liquid	11	[143]
Polydioxanone	Stannous octoate	67-85	[130]
Polylactide	Stannous octoate	14-64	[135]
	Potassium t-butoxide	7-42	[138]
	Sodium hydroxide	6	[139]
	Ammonia/water	8-12	[144]

**Table 10.** Grafting efficiency regarding different coupling strategies

Grafted polymer	Coupling strategie	GE(%)	Reference
Polycaprolactone	2,4-toluene diisocyanate	21-63	[157]
	Carbonyldiimidazole	64-76	[171]
Polydioxanone	2,4-toluene diisocyanate	15-70	[156]
Poly(vinyl alcohol)	<i>N</i> -methylolacrylamide	30-70	[161]
Polyethylene	Ce(IV)	1-86	[165]
	Benzoyl peroxide	85-92	[166]



**Table 11.** Weight-average molecular weight of grafted polymer chains onto starch regarding different coupling strategies

Grafted polymer	Coupling strategie	<i>Mw</i> (g.mol <sup>-1</sup> )	Reference
polyether	maleic anhydride	2,000-6,000	[150]
	2,4-toluene diisocyanate	3,000-4,500	[154]
	Acyl halide	500-5,000	[173]
polytetrahydrofuran	2,4-toluene diisocyanate	1,200-1,600	[155]
polyvinyl(alcohol)	N-methylolacrylamide	30,000-68,000	[161]
polycaprolactone	2,4-toluene diisocyanate	1,250-2,000	[157]
	carbonyldiimidazole	1,000-2,000	[171]
poly(butylene succinate)	N,N-dicyclohexylcarbodiimide	46,000-2,000	[172]
poly(butyl methacrylate)	click chemistry	7,000-7,500	[177]