Elaboration of poly(vinylidene chloride)-based nanostructured latexes by emulsion polymerization
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Elaboration of poly(vinylidene chloride)-based nanostructured latexes by emulsion polymerization

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op dinsdag 30 oktober 2012 om 16.00 uur

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Introduction

Considering the current development of the food and pharmaceutical industries and the societal needs for better product quality and longer shelf life, the packaging of products should nowadays fit a wide range of criteria\(^1\). Furthermore, due to our growing environmental concerns, packages should not only preserve products, but must also be safer, more energy-efficient and disposable. As a result, the packaging industry has progressively replaced glass and metals by light-weight materials like paper, carton, plastic and metal foil.

Barrier polymers, such as - among others - polyethylene, polypropylene, ethylene vinyl alcohol (EVOH), poly(vinyl alcohol) (PVOH) or poly(vinylidene chloride) (PVDC), have played a key role in this evolution towards alternative packaging materials while preserving the long term stability and quality of the wrapped product. However, polyethylene and polypropylene only display a high impermeability to water, and EVOH and PVOH only to oxygen, while PVDC offers a more complete protection, owing to its excellent barrier properties towards water, oxygen and aroma\(^2,3\), as well as a chemical resistance to a large variety of solvents\(^3\). Moreover, the production of poly(vinylidene chloride) is performed industrially in aqueous media, by suspension and emulsion polymerization\(^3,4\), which reduces the use of volatile organic compounds that raise concerns about health and environmental impacts. Emulsion polymerization presents the advantage that it gives a polymer latex that is
directly applicable as a waterborne coating on plastic substrates, resulting in a transparent and glossy film.

Vinylidene chloride copolymers were among the first synthetic polymers to be studied and commercialized in the late 1930’s[3]. Nevertheless, despite the fact that the synthesis and the coating of poly(vinylidene chloride) latexes are well-established technologies, some limitations are still encountered as far as thermal processing and light stability of PVDC films are concerned. Indeed poly(vinylidene chloride) suffers from a limited thermal stability at thermoforming temperatures[5] and tends to degrade when exposed to UV radiation[6], both degradation processes leading to yellowing of the film and a decrease of the polymer barrier properties. This effect is particularly pronounced in the case of PVDC latexes, due to the presence of larger amounts of additives that are believed to promote the polymer degradation[3]. Therefore, waterborne PVDC films with improved stability to processing temperatures and/or UV radiation are of great interest in order to extend the range of applications of poly(vinylidene chloride) latexes.

At the same time, REACH (Registration, Evaluation, Authorisation and restriction of CHemical substances), the European Community regulation on chemicals, entered into force in June 2007. In order to provide a better protection of human health and of the environment, this new legislation imposes chemical companies to gather data on the properties of their chemical products and to register this information at the European CHemicals Agency (ECHA). As a result, the chemical industry should now – as much as possible – explore innovative strategies that do not require the use of unregistered chemical substances. In that sense, the synthesis of composite systems appears as an attractive and elegant
technique to develop new products combining the properties of different materials, while employing already REACH registered reactants.

This research project, initiated in October 2008 and funded by Solvay and by the French Agence Nationale de la Recherche et de la Technologie (ANRT) as a CIFRE grant, was conducted in collaboration between the group “Ingénierie et Architectures Macromoléculaires” (IAM) of the Institut Charles Gerhardt of Montpellier (at the National School of Chemistry of Montpellier, ENSCM, France), the Polymer Chemistry group (SPC) of Eindhoven University of Technology (TU/e, The Netherlands) and the Solvay Company (NOH, Bruxelles, Belgium and Tavaux, France). An agreement for joint doctoral degree between ENSCM and TU/e was signed. The project aimed at improving specific properties of poly(vinylidene chloride) waterborne films via the synthesis of nanostructured latexes. From January 2011, it also entered in the framework of the ANR-ASAP project funded by the French Agence Nationale de la Recherche, involving Solvay as scientific coordinator and the Université Pierre et Marie Curie (Paris), the Laboratoire de Chimie des Polymères of the Université Claude Bernard (Lyon), the Laboratoire Chimie, Catalyse, Polymère et Procédé of the Université de Chimie Provence (Marseille), the Institut Charles Gerhardt (Montpellier) (in collaboration with Eindhoven University of Technology) as scientific partners. This project aims at the development of a novel, more innocuous poly(vinylidene chloride) displaying enhanced properties.

Considering the mechanisms of degradation and stabilization of vinylidene chloride copolymers under the action of heat and UV radiation, the work presented in this thesis aims at improving the thermal and UV stability of PVDC latexes via the incorporation of nanometric stabilizers. As a strategy to enhance the polymer thermal stability, epoxy-functional seed
latexes were synthesized by emulsion polymerization, followed by the second-stage copolymerization of vinlylidene chloride and methyl acrylate to obtain composite PVDC particles containing heat-stabilizing groups. In order to enhance the UV stability of poly(vinylidene chloride), the incorporation of cerium oxide nanoparticles into PVDC latexes was then attempted via two different surface modification routes: the first one employing alkoxysilanes and the second one using amphiphatic macro-RAFT (Reversible Addition-Fragmentation chain Transfer) agents.

Chapter 1 provides a literature overview on the synthesis and properties of poly(vinylidene chloride) and on emulsion polymerization processes for the synthesis of conventional, composite and inorganic/organic hybrid latexes.

Chapter 2 presents the synthesis of PVDC-based composite latexes from epoxy-functional seeds for use as waterborne barrier films with improved thermal stability.

Chapter 3 tackles the synthesis of cerium oxide-based hybrid latexes employing an alkoxysilane as grafting agent.

Chapter 4 deals with the synthesis of amphiphatic random macro-RAFT agents for use as precursors of inorganic/organic hybrid latexes.

Finally Chapter 5 discusses the results obtained on the synthesis of cerium oxide-based hybrid latexes via the macro-RAFT agent route.

In a last section Conclusions and perspectives to this thesis work will be proposed.
References


Chapter 1. Literature overview – Poly(vinylidene chloride) and emulsion polymerization processes for the synthesis of nanostructured latexes

1.1. Introduction

The first part of this chapter will provide an overview of vinylidene chloride (co)polymers: their synthesis, properties, degradation mechanisms and possible stabilization routes will be treated. The second part will deal with the emulsion polymerization technique for the synthesis of conventional polymer latexes, as well as more complex polymer composite and inorganic/organic hybrid latexes. Finally, conclusions will be drawn from this literature study and the various strategies considered for this thesis work will be detailed.

1.2. Poly(vinylidene chloride)

1.2.1. History of poly(vinylidene chloride)

In 1838, Regnault\cite{1,2} first reported the synthesis of 1,1-dichloroethylene from trichloroethane by reaction with alcoholic potassium hydroxide. The volatile liquid, when placed in a closed tube under a lamp, became hazy and a white material was observed at the bottom of the tube. Although Regnault believed that this substance corresponded to a simple isomeric modification of the chlorinated compound, he actually witnessed
the spontaneous polymerization of vinylidene chloride under the action of light. Krämer[3] and Baumann[4] further studied the synthesis and properties of vinylidene chloride, and the latter also noticed the formation of a white substance when exposed to sunlight. Ostromislensky[5] discovered that vinylidene chloride polymerized in light to form a white product insoluble in many solvents. It was only in 1930 that Staudinger and Feisst[6] studied more extensively the polymerization of vinylidene chloride and the polymer structure. The material was initially commercialized in 1939 under the name Saran ® by the Dow chemical company[7-9] as a dark green film for military applications: sprayed on fighter planes, it served as a protective layer against corrosion caused by salty sea water. Poly(vinylidene chloride) also found applications in the automotive industry as a protective layer for car seats. The formulation of Saran ® was then modified in order to get rid of its green color and strong odor. After the Second World War, PVDC found its main application in the high barrier packaging industry. It is still widely commercialized under various trademarks, including Daran ® (Owensboro Specialty Polymers) and Serfene ® (Rohm & Haas) in the United States, Diofan ®, Ixan ® (SolVin) and Polidene ® (Scott-Bader) in Europe and Kurehalon ® (Kureha) and Asahi Kasei ® (Asahi) in Japan.

1.2.2. Vinylidene chloride monomer

1,1-dichloroethylene or vinylidene chloride (VDC) is a colorless liquid (at 25°C under air atmosphere) with a characteristic sweet odor. Its commercial synthesis from vinyl chloride (or 1,1-dichloroethane) is carried out in two stages (Scheme 1.1). The first step involves the chlorination of vinyl chloride catalyzed by FeCl₃. The dehydrochlorination of 1,1,2-trichloroethane is then performed in presence of sodium hydroxide (or
calcium hydroxide) in slight excess, via a continuous liquid phase reaction at 98-99°C yielding about 90% VDC\textsuperscript{[10]}. In order to avoid the spontaneous polymerization of vinylidene chloride during storage, low amounts of inhibitor are added at that stage. Hence, commercial vinylidene chloride typically contains 200 ppm monomethyl ether hydroquinone (MEHQ). MEHQ may be removed prior to polymerization by distillation or by washing with 25 wt% aqueous caustic soda. After purification, the monomer should be stored in the dark at -10°C under inert atmosphere.

\[\text{Scheme 1.1: Two-step synthesis of vinylidene chloride from vinyl chloride.}\]

1.2.3. Polymerization of vinylidene chloride

Homopolymerization of vinylidene chloride:

Vinylidene chloride polymerizes via both free-radical and ionic reactions. Anionic polymerization of VDC may be carried out\textsuperscript{[11]}, however the use of anionic catalysts is often undesirable as it leads to extensive degradation of the polymer\textsuperscript{[12]}. For instance the polymerization of vinylidene chloride catalyzed by butyl lithium has been reported, but resulting
polymers exhibited low molecular weights and low chlorine contents, due to side reactions involving the elimination of chlorine atoms as lithium chloride from the polymer chains. Due to the strong electron withdrawing effect of chlorine atoms, vinylidene chloride is not susceptible to be polymerized via cationic catalysis\textsuperscript{[11]}. 

Radical processes are thus by far the most employed. Free-radical polymerization of VDC has been studied in solution, in a solvent that dissolves both the monomer and the polymer\textsuperscript{[13]}. Polymerizations of VDC in bulk or in solvents, such as hexane or benzene, have also been reported at the laboratory scale and enabled to gain a better understanding of polymerization kinetics\textsuperscript{[14]}. However these processes are heterogeneous, given that poly(vinylidene chloride) is insoluble in these media and tends to phase separate from the liquid in form of a crystalline powder. As a result, abnormal reaction kinetics was observed. Mass and heat transfer limitations originating from the heterogeneity of the reaction also tend to make slurry polymerizations difficult to implement at a large scale.

Therefore, aqueous suspension and emulsion processes are preferred for the polymerization of VDC at the industrial scale. These reactions are doubly heterogeneous, since the polymer is insoluble in both the monomer and water, while the monomer displays a very low solubility in water\textsuperscript{[15]}. Suspension polymerization of VDC, also known as bead polymerization, is very similar to slurry reactions. Oil-soluble initiators being employed, monomer/polymer droplets may be approximated as small distinct reactors. The presence of fewer additives in VDC suspension polymerization is a considerable asset compared to emulsion processes, as it imparts the polymer a better stability. Nonetheless, longer reaction times are required and high molecular weights are more difficult to obtain.
Emulsion polymerization of vinylidene chloride is more complex compared to that of other vinyl monomers, due to the monomer insolubility in polymer particles. Indeed, the Smith-Ewart theory\cite{16} that describes typical emulsion polymerization reactions cannot be applied in this case. Studies of the reaction mechanism and kinetics strongly suggest that the polymerization occurs at the particle/water interface\cite{17}. Emulsion polymerization of VDC is usually carried out in the presence of redox initiators in order to achieve high polymerization rates while keeping a reaction temperature below 80°C in order to avoid the thermal degradation of PVDC. Furthermore, the polymerization is performed at an acidic pH to prevent the dehydrochlorination of the polymer that occurs in alkaline conditions\cite{15}. The possibility of reaching high molecular weights within shorter reaction times is the main advantage of the emulsion process compared to VDC suspension polymerization. However, it requires the presence of higher amounts of additives in the recipe, resulting in a poorer UV and thermal stabilities: water-soluble initiators as well as surfactants are indeed assumed to accelerate the polymer degradation.

Although conflicting literature stated that chain transfer to vinylidene chloride was unlikely\cite{18} due to the 1,1-disubstitution by chlorine atoms that may cause steric interactions\cite{19}, Matsuo et al. evidenced that the free radical polymerization of vinylidene chloride could be dominated by chain transfer to monomer.\cite{13} They reported the following chain transfer constants at two different temperatures: \( C_{\text{tr},\text{VDC}} = \frac{k_{\text{tr}}}{k_p} = 2.2 \times 10^{-3} \) at 50°C and \( 3.8 \times 10^{-3} \) at 60°C. This transfer reaction was later shown to have a detrimental impact on the molecular weight control in the RAFT (Reversible Addition-Fragmentation chain Transfer) copolymerization of vinylidene chloride and methyl acrylate at high targeted molecular weights (> 20,000 g/mol) and high monomer conversions (> 50%)\cite{20}. 
Copolymerization of vinylidene chloride:

“Poly(vinylidene chloride)” is most of the time employed abusively as a generic term to actually refer to copolymers of vinylidene chloride. Indeed, poly(vinylidene chloride) cannot be commercialized as a homopolymer due to processing limitations originating from its high melting point (203°C\[^{[21]}\]) and poor thermal stability. Vinylidene chloride is thus generally copolymerized with certain amounts of comonomers\[^{[15,21-23]}\] – typically alkyl acrylates or vinyl chloride – which not only limits the polymer degradation but also decreases the melting temperature of the polymer, allowing thermal processing under milder conditions: both effects contribute to improve the polymer processability. Combinations of several comonomers may be employed to improve specific properties of the final polymer: for instance alkyl acrylates are mainly used to enhance the polymer processability, acrylonitrile is applied to reinforce the polymer impermeability towards oxygen and to increase its polarity. Vinyl chloride is typically employed to strengthen PVDC mechanical properties. Additionally, vinylidene chloride copolymers display a better solubility in organic solvents compared to the homopolymer. Nonetheless copolymers with high VDC contents (> 85 mol%) remain insoluble in the monomer\[^{[15]}\].

Vinylidene chloride copolymerizes randomly with methyl acrylate, while dramatic composition drifts occur in batch copolymerizations with vinyl chloride or methacrylates (Table 1.1). Semi-batch processes are then required in order to obtain copolymers with uniform intermolecular chemical composition distribution, i.e. homogeneous copolymerization. In VDC-VC suspension copolymerization, a good control of the comonomer distribution can be achieved by continuously removing vinyl chloride, the less reactive and more volatile monomer, to maintain a constant composition in the unreacted monomer mixture\[^{[24]}\]. The emulsion polymerization process
allows an easier control of the copolymer composition, due to the possibility to feed the monomers continuously during the reaction.

**Table 1.1.** Reactivity ratios of vinylidene chloride ($r_1$) with typical comonomers ($r_2$)[25].

<table>
<thead>
<tr>
<th>Monomers</th>
<th>$r_1$</th>
<th>$r_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>0.14</td>
<td>2.0</td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>3.2</td>
<td>0.3</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>0.37</td>
<td>0.91</td>
</tr>
<tr>
<td>methyl acrylate</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>0.24</td>
<td>2.53</td>
</tr>
<tr>
<td>vinyl acetate</td>
<td>6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

1.2.4. Barrier properties of poly(vinylidene chloride) copolymers

Poly(vinylidene chloride) displays an extremely low permeability to a wide variety of gases, originating from the combination of two characteristics: a high degree of crystallinity (up to 80%[26]) and a high packing density of polymer chains. These specific properties are assumed to result from the symmetric nature of vinylidene chloride units that would enable a good packing of polymer chains with very low free volumes in the amorphous phase. This argument is strongly supported by the fact that poly(vinylidene chloride) and polyisobutylene, both displaying symmetrical monomer units, exhibit a very low permeability to water compared to their dissymmetrical counterparts, poly(vinyl chloride) and polypropylene[27].

Copolymerizing VDC with a comonomer often results in an increase of the gas permeability, depending on the type and amount of comonomer
employed. For instance, when other factors are kept constant, a more polar comonomer such as acrylonitrile (AN) leads to a stronger increase of the water vapor permeability compared to vinyl chloride (VC). Comonomers that lower the glass transition temperature ($T_g$) and increase the free volume in the amorphous phase, such as acrylates with long pendant chains, are also detrimental in terms of barrier properties to gases. Nevertheless, vinylidene chloride copolymers still display a much lower permeability when compared to other classes of polymers (Table 1.2).

Table 1.2. Comparison of barrier properties of polymers (from reference[15]).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gas permeability at 23°C*</th>
<th>WVTRb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_2$</td>
<td>$N_2$</td>
</tr>
<tr>
<td>Vinylidene chloride copolymers</td>
<td>0.04-0.03</td>
<td>0.01-0.1</td>
</tr>
<tr>
<td>Nitrile barrier resin</td>
<td>1.6</td>
<td>6</td>
</tr>
<tr>
<td>Nylon-6,6; nylon-6</td>
<td>2-5</td>
<td>3-9</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>300</td>
<td>60</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>10-18</td>
<td>2-4</td>
</tr>
<tr>
<td>(PET)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rigid poly(vinyl chloride)</td>
<td>10-40</td>
<td>40-100</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>300</td>
<td>1200</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>500-700</td>
<td>200-400</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>600-800</td>
<td>40-50</td>
</tr>
<tr>
<td>Ethylene vinyl alcohol (32 mol%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethylene) at 0% rh</td>
<td>0.02</td>
<td>0.002</td>
</tr>
<tr>
<td>at 100% rh</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

*Expressed in nmol.m$^{-1}$.s$^{-1}$.GPa$^{-1}$.

bWater vapor transmission rate at 90% relative humidity (rh) and 38°C, expressed in nmol.m$^{-1}$.s$^{-1}$.

cDetermined at 40°C.
1.2.5. Thermal degradation and stabilization of poly(vinylidene chloride)

As already mentioned in this chapter, thermal stability is a major limitation when processing poly(vinylidene chloride), since its melting point (203°C\textsuperscript{[21]}) is situated in a range of temperatures where fast degradation of the polymer occurs. When heated, the polymer color gradually changes from transparent to yellow and further to brown and black and loses its barrier properties, which is undesirable as far as final applications are concerned\textsuperscript{[28]}. For this reason, vinylidene chloride is usually copolymerized with a small percentage of other monomers, typically acrylates, in order to improve the polymer stability\textsuperscript{[22]}. Nonetheless this strategy is limited, since the addition of greater amounts of comonomers tends to decrease the polymer barrier properties, due to a reduction of the crystallinity of PVDC\textsuperscript{[15,22]}. Poly(vinylidene chloride) homopolymer starts to degrade at about 120°C, hydrochloric acid being the only gas product released below 190°C. PVDC decomposition can thus be described by the reaction given in Scheme 1.2.

![Scheme 1.2: Reaction of PVDC thermal degradation.](image)

Degradation processes occurring at moderate temperatures are more relevant as far as polymer processing is concerned: below 190°C, dehydrochlorination is a typical chain process that involves distinct initiation, propagation and termination steps. Initiation is assumed to consist
in the cleavage of a C-Cl bond creating a tight carbon-chlorine radical pair. This bond scission is presumed to be activated by the presence of structural defects, such as unsaturations\[^{29,30}\], supported by the fact that the theoretical bond energy is lower for a C-Cl bond situated in allylic position. Random double bonds may be introduced into the polymer structure by several detrimental factors, such as, among others, ultraviolet irradiation\[^{31}\], electron beam irradiation\[^{32}\], basic solvents or reagents\[^{33,34}\], an oxygen atmosphere, or by the presence of emulsifying agent residues\[^{35}\], peroxide initiator residues\[^{31}\] or metal ions\[^{35,36}\]. The labile chlorine atom then abstracts an adjacent hydrogen atom, which extends the unsaturation by one unit and creates a new allylic dichloromethylene group that will further propagate the degradation reaction (Fig.1.1).

\[\text{conjugated polychloroacetylene sequences}\]

**Fig.1.1:** Mechanism of PVDC thermal dehydrochlorination (from reference\[^{37}\]).
The fact that certain radical scavengers tended to inhibit PVDC dehydrochlorination strongly supported the radical nature of the polymer degradation. This was further confirmed by studying the reaction by Electron Spin Resonance (ESR)\textsuperscript{[38]} and in a bibenzyl solution\textsuperscript{[29,30]}: by interacting with a radical, bibenzyl can be converted into stilbene. In the case of PVDC dehydrochlorination, the ratio of HCl evolved to stilbene produced equals 35:1, suggesting that the propagating species is a tight radical pair that only dissociates to a small extent. However, this high ratio could also indicate that other types of non-radical processes may be involved in PVDC degradation.

The apparent acceleration of PVDC dehydrochlorination in the presence of HCl was first believed to occur through a process of direct acid catalysis. It was later shown that HCl had no effect on the degradation of “pure” PVDC. This effect was then attributed to metal oxides, present in the polymer as impurities and converted to catalytically active metal chlorides when reacting with hydrochloric acid\textsuperscript{[36,39]}. Consequently, special attention has to be paid when processing PVDC, as HCl evolved at early stages of the polymer degradation may interact with the metal surface of the process equipment to form metal chlorides that will increase the rate of initiation of degradation by introducing new defect sites into the polymer chains. The efficiency of metal chlorides to promote PVDC degradation is related to the Lewis acidity of the corresponding metal cations. In particular, iron, cobalt, copper and zinc chlorides have the most dramatic impact on PVDC thermal degradation\textsuperscript{[36]}.

Considering the degradation mechanism and the different factors promoting the polymer dehydrochlorination, potential PVDC thermal stabilizers should thus be able to:
- Scavenge evolved hydrogen chloride, without stripping it from the polymer chain. Inorganic compounds, such as pyrophosphates\(^{[40]}\), magnesium oxide and hydrotalcites, belong to this category. However, these mineral additives, above certain levels, tend to form agglomerates and decrease the polymer transparency. Organic acid acceptors, such as aromatic ethers\(^{[41,42]}\) (phenoxypropylene oxide or dimethyl dibenzyl ether) or epoxy-containing compounds\(^{[9]}\) (epoxidized soybean oil, glycidyl esters or ethers) are also widely employed to enhance the polymer thermal stability, although these additives present problems of migration. Furthermore, epoxidized soybean oil, which also behaves as a plasticizer, is detrimental to the polymer in terms of barrier properties\(^{[15]}\). Therefore, to avoid problems related to additive migration and loss of barrier properties, polymers such as poly(glycidyl methacrylate), yet containing a lower epoxy content than epoxidized soybean oil, seem to be a better alternative to other types of HCl-scavenging stabilizers\(^{[43]}\).

- React with conjugated polymer sequences to block the unzipping process of dehydrochlorination and limit the polymer coloration. The use of esters of maleic acid or tributyl aconitate have been reported in the literature: these compounds contain dienophilic moieties capable of reacting with conjugated sequences via Diels-Alder-type condensations\(^{[44-46]}\).

- Remove allylic chlorine by nucleophilic substitution: metal carboxylates have been considered as nucleophilic agents
capable of converting allylic dichloromethylene units into non-reactive groups to block the polymer dehydrochlorination\textsuperscript{[37,47,48]}, according to the mechanism depicted in Scheme 1.3. However, tin, lead or cadmium carboxylates, which are typically employed as PVC heat stabilizers, appeared to accelerate the polymer degradation due to their high Lewis acidity. To behave as an efficient stabilizer, carboxylates should contain a metal acidic enough to promote the substitution of allylic chlorides by carboxylates, but not too acidic to avoid stripping chlorine from the polymer chain.

\textbf{Scheme 1.3.} Mechanism of nucleophilic substitution of allylic chlorides by metal carboxylates (adapted from reference\textsuperscript{[48]}).

- Scavenge free radicals: phenolic antioxidants, such as 2,6-di-tert-butyl-4-methylphenol and substituted bisphenols react with radicals to stop the dehydrochlorination process.
Nonetheless this type of antioxidants displays a very limited efficiency, given that the propagating species are tight chlorine-carbon radical pairs that only dissociate to a limited extent according to the degradation mechanism \cite{49}.

- Chelate metals to avoid the formation of metal chlorides \cite{50}: phosphites, ethylenediaminetetraacetic acid (EDTA), citric acid and citrates were reported to impart PVDC a better thermal stability by complexation of metal ions.

1.2.6. **UV degradation and stabilization of poly(vinylidene chloride)**

When exposed to ultraviolet light, poly(vinylidene chloride) copolymers undergo a similar release of hydrogen chloride resulting in the formation of polyene sequences in the polymer backbone. Crosslinking between polymer chains may also occur when these double bonds undergo Diels-Alder condensations. PVDC properties are therefore strongly affected by UV-treatment: it will indeed lead to coloration and an increase of the permeability and the polymer gel content. Moreover, as already mentioned previously, double bonds created by pre-treatment of PVDC by UV-radiation play the role of activating sites for the polymer thermal degradation.

Given that processes of thermal and UV degradations of PVDC follow a similar mechanism of dehydrochlorination, it is not surprising that most compounds used for the thermal stabilization of PVDC may also be employed to protect the polymer from degradation due to UV-radiations \cite{51}. UV absorbing compounds are, however, more specific to the UV-
stabilization of poly(vinylidene chloride): these include organic UV-absorbers, such as derivatives of salicylic acid, resorcylic acid, benzophenone\textsuperscript{[52]} (2,2\textsuperscript{'-dihydroxybenzophenone for instance) or benzotriazole, or certain types of mineral nanoparticles. Nonetheless the latter type is preferred given that some organic absorbers were reported to display an anisotropy in their UV-filtering properties\textsuperscript{[53]} and often suffer from a low long-term stability. It is also worth mentioning that the combination of a UV-absorber and a UV/thermal versatile stabilizer is often recommended, considering that in the presence of a UV-absorber only the outer surface of the sample will be unprotected and subjected to a more pronounced dehydrochlorination compared to deeper layers of the material\textsuperscript{[51]}. 

UV-screening inorganic nanoparticles are widely employed to enhance the stability of polymeric materials to UV radiation. These additives should display two main characteristics: a high transparency in the visible range and a high absorption in the UV range (below 400 nm). Hence, semiconductors such as titanium dioxide (TiO\textsubscript{2}), zinc oxide (ZnO) and cerium oxide (CeO\textsubscript{2}) are so far the most interesting candidates for this application, owing to their bulk bandgap energies of about 3 eV and their absorption threshold close to 400 nm\textsuperscript{[54]}. For nanoparticles of small size (about 10 nm), a blue shift of the absorption edge compared to the bulk material may be observed due to a quantum confinement effect\textsuperscript{[55]}. 

Hybrid materials containing UV-absorbing nanoparticles have been extensively studied according to the scientific literature and various synthethic routes were proposed: ZnO and TiO\textsubscript{2}-containing polyolefin-based nanocomposites could be obtained by melt compounding\textsuperscript{[56-58]}, ZnO/PMMA hybrid films were formed by film casting of a mixture of a solution of PMMA in toluene with ZnO nanoparticles synthesized in inverse
emulsion in the presence of modified amphiphilic copolymers of lauryl methacrylate and dimethylaminoethyl methacrylate\textsuperscript{[59]}, CeO$_2$/epoxy and transparent ZnO/epoxy composites were synthesized by dispersion of oxide nanoparticles in a mixture of epoxy and curing agent before carrying out the curing process\textsuperscript{[60,61]}. 

Very different trends could be observed in terms of UV-stability of metal oxide-based nanocomposites depending on the type of nanoparticles employed. In comparison to the pure polymer, ZnO/polypropylene and ZnO/polyethylene nanocomposites displayed a much reduced photo-oxidation\textsuperscript{[57,58]}, while TiO$_2$-based hybrids showed contrasting results, depending on the type of titanium dioxide phase employed\textsuperscript{[56]}: for the anatase crystal structure, a too high photocatalytic activity resulted in a faster degradation of the polymer under UV radiation, whereas for rutile an enhanced UV-stability was observed due to a sufficiently low oxidation activity. Issues related to photocatalysis exerted by metal oxides may be circumvented by coating nanoparticles with a layer of inorganic material, such as SiO$_2$, Al$_2$O$_3$ or ZrO$_2$\textsuperscript{[56,62]}. Cerium oxide is a more attractive material in that respect, as it displays a lower photocatalytic activity compared to zinc oxide and titanium dioxide. Moreover this property may be further reduced by doping cerium oxide with calcium oxide or zinc oxide\textsuperscript{[63]}.

Only few references deal, however, with the UV-stabilization of poly(vinylidene chloride) by metal oxide-based nanoparticles. The main reason why ZnO has not been employed for these applications could be the catalytic activity played by zinc oxide on the polymer degradation via the formation of zinc chloride species that would be detrimental during PVDC thermal processing\textsuperscript{[39]}. Cerium oxide and titanium dioxide-based PVDC hybrid films obtained by direct mixing of PVDC latexes with waterborne
oxide dispersions or dry oxide particles showed promising results in terms of UV-stability\cite{64}. Moreover coating the particles with a layer of silica appeared to improve the transparency and the UV stability of the hybrid PVDC films.

1.3. Emulsion polymerization processes for the synthesis of nanostructured latexes

1.3.1. Introduction

The emulsion polymerization technique has triggered much interest for the production of synthetic latexes since its first use on an industrial scale in 1930. Since the pioneering work by Harkins\cite{65} and Smith and Ewart\cite{16} that enabled to gain a better understanding of mechanisms of micellar nucleation, the process has been studied in greater details and enables now to prepare more and more complex latexes, with controlled compositions (homopolymers, copolymers, terpolymers) and structures (composite, hybrid) with various morphologies. Nowadays, it remains the most industrially employed polymerization process in dispersed media\cite{66} for the synthesis of polymer colloids with various applications (paints, coatings, adhesives, synthetic rubber…).

The first part of this section describes the mechanism of formation and growth of latex particles by emulsion polymerization. In a second part, the synthesis of two-phased polymer latexes will be presented, with a focus on the mechanisms of formation and driving forces towards the development of composite particle morphology. The last part of this section
deals with the various possible strategies employed for the synthesis of inorganic/organic hybrid latexes from mineral particles.

1.3.2. Synthesis of conventional polymer latexes by emulsion polymerization

Similarly to other techniques of polymerization in dispersed media (dispersion, suspension, miniemulsion, etc), the emulsion polymerization technique presents several advantages compared to processes carried out in bulk or in organic solvents:

- Due to compartmentalization, emulsion polymerization enables to reach high molecular weights and high monomer conversions while maintaining high polymerization rates.
- The heat generated by exothermic reactions is easily dissipated by the aqueous medium owing to the high heat capacity of water.
- The reaction medium displays a much lower viscosity.
- The final product, a latex, is easier to handle than products obtained from bulk or solution polymerization.
- The elimination of organic solvents decreases risks related to safety and pollution.

The control of copolymer compositions through the continuous addition of monomers during the reaction is another remarkable asset of this process.

**Mechanism:**

At the initial stage of a typical batch emulsion polymerization reaction (Fig.1.2), the reaction medium contains water, a hydrophobic monomer, a surfactant and a water-soluble initiator.
Fig. 1.2. Initial stage of a batch emulsion polymerization reaction ($I_2$: initiator; $M$: monomer).

The monomer is distributed between 3 distinct phases:

- Monomer droplets (diameter $> 1 \mu m$), stabilized by surfactant molecules adsorbed at the droplet/water interface.
- The aqueous phase, containing low amounts of monomer, as well as the initiator and free surfactant molecules.
- Micelles (diameter $\approx 1 – 10$ nm), swollen by a certain amount of monomer, formed by self-assembly of emulsifier molecules if the surfactant concentration is higher than its CMC (critical micelle concentration).

**Step 1 – Particle nucleation:**

The initiation occurs in the aqueous phase by dissociation of the water-soluble initiator. It results in the formation of radicals that propagate in the aqueous phase by adding monomer units to form oligomer radicals.
The formation of particle precursors may then occur via various processes, depending on the fate undergone by the growing radicals:

- Micellar nucleation\cite{65,66}: by entry of an oligomer radical into a surfactant micelle. It is admitted that this process occurs when the surfactant concentration is much higher than the CMC.

- Homogeneous nucleation\cite{67,70}: once a radical reaches a certain critical size, it may precipitate to form a particle nucleus. Two critical chain lengths may, however, be distinguished. When a radical is a \( j \)-mer (consisting of \( j \) monomer units), it becomes insoluble in water and precipitates to form a particle. Depending on the types of initiator and monomer employed in the process, oligomer radicals may also acquire surfactant properties once they reach a \( z \) critical size (consisting of \( z \) monomer units, with \( z < j \)).

- Coagulative nucleation\cite{71,72}: mature particles are formed by coagulation of unstable primary particles formed by homogeneous nucleation.

Therefore, the first step of an emulsion polymerization reaction, the particles nucleation phase, is featured by an increase of the number of particles and an increase of the rate of polymerization and ends once the number of particles reaches a plateau. This is illustrated by equation (1)\cite{73} that gives the rate of polymerization \( R_P \) as a function of the propagation rate constant \( k_P \), the monomer concentration in polymer particles \([M]_P\), the average number of free radicals per particle \( \bar{n} \), the number of particles per unit volume of the aqueous phase \( N_P \) and Avogadro’s number \( N_A \):

\[
R_P = k_P [M]_P (\bar{n}N_P/N_A) \tag{1}
\]
Step 2 – Particle growth:

The second step, consisting in the particles growth (Fig.1.3), occurs through the capture of oligomer radicals formed in the aqueous phase by polymer particles.

Fig.1.3. Particle growth stage of an emulsion polymerization reaction.

Monomer droplets behave as reservoirs, constantly replacing the monomer consumed by propagation processes via the transport of monomer molecules across the aqueous phase towards polymer particles. Morton et al. established the following equation to calculate the equilibrium concentration of monomer in the particles\(^7\) during that stage:

\[
2V_m\gamma / (RT\phi_p) = - \left[ \ln(1 - \phi_p) + (1 - 1/X_n) \phi_p + \mu \phi_p^2 \right]
\]  \hspace{1cm} (2)

where \(V_m\) is the partial molar volume of the monomer, \(\phi_p\) the volume fraction of polymer in the particle, \(\gamma\) the polymer/water interfacial tension at
swelling equilibrium, \( R \) the ideal gas constant, \( T \) the absolute temperature, \( r_p \) the particle radius, \( X_n \) the number average degree of polymerization and \( \mu \) the Flory-Huggins interaction parameter.

Given that the number of particles and the monomer concentration in polymer particles remain constant (assuming complete colloidal stability), the rate of polymerization does not vary all along the particles growth phase, as evidenced by equation (1), until the complete consumption of monomer droplets that marks the end of this stage.

**Step 3 – End of polymerization:**

At the beginning of the third stage of the process (corresponding for instance to about 50-60% monomer conversion in the case of styrene) monomer droplets have disappeared (Fig.1.4). This step is thus characterized by a diminishing rate of polymerization due to a progressive decrease of the monomer concentration inside polymer particles, as illustrated by equation 1. At the end of the polymerization reaction, a latex is obtained, consisting of polymer particles with diameters varying between 50 and 500 nm dispersed in water.

However, some unreacted monomer usually remains inside the polymer particles and should generally be eliminated to limit risks of toxicity and environmental impact. Two methods are mainly employed for removing the residual monomer\(^{[75,76]}\): post-polymerization\(^{[77,78]}\), performed by addition of an initiator, or monomer devolatilization\(^{[79,80]}\), by stripping the latexes under vacuum with the aid of steam or of an inert gas. The latex can then be used directly for coating applications, or it may be destabilized and flocculated (typically by addition of a salt) to recover the dry polymeric material.
For more details on the theory of emulsion polymerization, the reader may refer to reviews\textsuperscript{81,82} and books\textsuperscript{66,73,83,84} dealing extensively with the subject.

\textbf{1.3.3. Synthesis of composite polymer latexes via two-stage emulsion polymerization processes}

Since the late 1980’s, a route aiming at improving latex properties has been extensively explored: it consists in the encapsulation of a seed polymer latex by at least one second-stage polymer in order to obtain a composite product combining the characteristics of both materials. The control of the composite particles morphology is probably the main point to consider as it has a major influence on the final latex properties. Although the core-shell structure first comes to one’s mind, it is only a particular case among a great variety of morphologies adopted by composite latexes when the seed material is of organic nature. This part deals with the different
processes influencing the composite particle morphology, by detailing their mechanism of formation and the parameters affecting the final particle structure.

Composite latexes may adopt various structures (Fig.1.5) that can be classified into two main categories:
- Thermodynamically governed morphologies (core-shell, inverse core-shell, hemisphere, onion)
- Kinetically governed morphologies (snowman, sandwich, micro-domains, etc.)

![Diagram showing possible morphologies](image)

**Fig.1.5.** Possible morphologies displayed by polymer composite latexes (reprinted from reference[85] with permission from John Wiley & Sons, Inc.).
Thermodynamic control

When the latex structure corresponds to the minimum particle interfacial energy, thermodynamic control prevails and the equilibrium morphology is obtained. The minimum value of the total interfacial energy depends on the following parameters:\(^{(86)}\):

- The seed and second stage polymer nature.
- The ratio polymer 1 / polymer 2.
- The nature and amount of surfactant\(^{(87)}\).
- The nature and amount of initiator\(^{(88)}\).
- The presence of block copolymers\(^{(89,90)}\).

The thermodynamically favored morphology can be predicted by calculating the values of the total interfacial Gibbs energy (G) corresponding to all possible configurations and then determining the structure related to the minimum value of G:

\[
G = \sum_{ij} \gamma_{ij} A_{ij} = \gamma_{1w} A_{1w} + \gamma_{2w} A_{2w} + \gamma_{12} A_{12} \quad (3),
\]

where \(\gamma_{ij}\) is the interfacial tension at the interface \(ij\) and \(A_{ij}\) is the area of the interface \(ij\). The indices 1, 2 and \(w\) refer respectively to polymer 1, polymer 2 and water.

Gonzalez-Ortiz et al.\(^{(91)}\) developed a convenient method to predict the equilibrium morphology of a given composite particle, using the graphical representation presented in Fig.1.6.
Fig. 1.6. Prediction of the equilibrium morphology of composite latex particles consisting of a seed polymer (1) and a second-stage polymer (2) dispersed in the aqueous phase (3)[91].

This plot is based on the theory developed by Torza and Mason[92,93] to predict the morphology obtained when bringing into contact two immiscible liquid drops (1 and 2) in a third immiscible liquid (3). By calculating the spreading coefficient $S_i$ for each phase $I$ of the system:

$$S_i = \frac{\gamma_{jk} - (\gamma_{ij} + \gamma_{ik})}{\gamma_{13}}$$

they showed that only 4 possible sets of values existed:

$$S_1 < 0 \quad S_2 > 0 \quad S_3 < 0 \quad (5a)$$
$$S_1 > 0 \quad S_2 < 0 \quad S_3 < 0 \quad (5a')$$
$$S_1 < 0 \quad S_2 < 0 \quad S_3 < 0 \quad (5b)$$
$$S_1 < 0 \quad S_2 > 0 \quad S_3 > 0 \quad (5c)$$
Case (5a) and (5a’) corresponding to a complete engulfing of phase 1 by phase 2 (core-shell morphology), case (5b) corresponding to a partial engulfment of phase 1 by phase 2 (hemispherical morphology), while in case (5c) no engulfing occurs and droplets 1 and 2 remain fully separated.

**Kinetic control**

Thermodynamic equilibrium may, however, not always be reached due to kinetic considerations. Indeed if the latex final morphology originates from limitations of entry and/or phase rearrangement inside the particles, kinetic control prevails and the final morphology will depend on the following parameters:

- The degree of cross-linking of the seed and second-stage polymers\[^{94}\].
- The concentration of second stage monomer in the seed particles (which depends on the monomer feed policy, the reaction rate and the monomer conversion)\[^{95}\].
- The glass transition and crystallization temperatures\[^{96,97}\].
- The reaction temperature (one must actually look at the relative position of T\(_g\) and T\(_m\) compared to T\(_\text{reaction}\)).

The kinetic factors influencing the final particle morphology can be explained by detailing the mechanism of formation of composite particles, which can be divided in 3 main steps:

**Step 1 – Penetration of second-stage oligoradicals into seed particles:**

Similarly to classical emulsion polymerization, the seeded second-stage emulsion polymerization is initiated in the water phase, where radicals are formed. Once the radical chains contain a certain number of
units, they start to diffuse towards seed particles swollen by monomer molecules: macro-radicals react with the monomer while diffusing until the occurrence of a chain stop event, i.e. bimolecular termination or chain transfer. A theory developed by Stubbs et al.[94] enables to determine the extent of penetration of polymer chains by calculating a fractional penetration ratio ($FP$) that takes into account the termination rate, the center of mass diffusion and reaction diffusion of radicals:

$$FP = \frac{\text{distance of penetration}}{\text{particle radius}}$$  \hspace{1cm} (6)

$FP$ depends on:

- The seed polymer $T_g$ compared to the reaction temperature: for a high $T_g$, the seed polymer is in a glassy state, which tends to limit the penetration of the macro-radicals. On the contrary, for a low $T_g$ seed polymer, the penetration depth is expected to be high.

- The second stage monomer feed rate: for example, at low monomer feed rates corresponding to monomer-starved conditions, the seed is swollen with less monomer, which limits the penetration of radicals. For any feed rate, at the end of the reaction, the extent of penetration will be lower due to a decrease of the monomer concentration.

**Step 2 – Phase separation of first-stage and second-stage polymers:**

As the penetration of the second-stage polymer chains continues, the amount of polymer 2 increases in the particle and phase separation starts to occur: this phenomenon is well illustrated by the use of a ternary
phase diagram. Depending on the characteristics of the seed polymer and the second stage monomer feed rate, two different separation processes may occur\cite{98}:

- Nucleation and growth: in this case phase separation happens at nucleation sites and requires overcoming an energy barrier. It is favored for monomer feed rates higher than monomer-starved conditions, low $T_g$ seed polymers (compared to the temperature of reaction) and small particles.

- Spinodal decomposition: here phase separation occurs throughout the particle without energy barrier. It is favored for low monomer feed rates (corresponding to starving conditions) and high $T_g$ seed polymers.

In particular cases, phase separation might not occur and the final morphology then consists in gradient or mixed phase structures.

**Step 3 – Phase rearrangements:**

The phase separation occurring between the seed and the second stage polymers results in the formation of clusters (in the case of a mechanism of nucleation) or large domains (for spinodal decomposition) that will experience migration, growth or shrinkage according to the following processes\cite{91,99,100}:

- Phase migration: this process is ensured by van der Waals forces occurring between the second stage polymer domains. However, the motion of these domains is limited by viscosity that may originate from the seed polymer glassy state (for a high $T_g$ polymer) or the low second stage monomer concentration in the particle (especially at monomer-starved conditions and at high monomer conversions)
- Ostwald ripening: this phenomenon occurs by the growth of large domains at the expense of smaller ones by diffusion of polymer chains from small domains to larger ones.
- Cluster growth: nucleated clusters may grow by absorption of newly formed macro-radicals/polymer chains entering the particle.

Based on the kinetic and thermodynamic considerations summarized in the preceding pages, Stubbs et al.\textsuperscript{[86]} have developed a diagram (Fig.1.7) as a systematic approach to determine the final morphology expected for a given composite particle. It clearly illustrates that kinetic control prevails prior to thermodynamic control. The equilibrium morphology can indeed only be obtained if the three processes of penetration, phase separation and phase rearrangement are possible, i.e. can proceed on finite timescales.

![Diagram for the prediction of composite latex particle morphology](image)

\textbf{Fig.1.7.} Diagram for the prediction of composite latex particle morphology (reproduced from reference\textsuperscript{[86]} with permission from Elsevier).
PVDC-based composite latexes:

Only a few references deal with the synthesis of PVDC-based composite latexes via two-stage emulsion polymerization processes. Brown et al. reported the synthesis of poly(butyl acrylate)/poly(vinylidene chloride-co-acrylonitrile) composite latexes\textsuperscript{[101]} and studied the gas permeability of the resulting composite films\textsuperscript{[102]}. The authors observed an increase of the film permeability to oxygen and carbon dioxide when increasing the fraction of the poly(butyl acrylate) seed latex. Correa et al.\textsuperscript{[103]} synthesized poly(butyl methacrylate)/poly(vinylidene chloride-co-butyl methacrylate) composite particles to prepare waterborne films consisting of such structured core-shell particles dispersed in a poly(butyl methacrylate) matrix. Those films, obtained by blending the core-shell latex with a poly(butyl methacrylate) latex, were employed as a model to study gas permeation phenomena in composite systems.

1.3.4. Synthesis of hybrid latexes by emulsion polymerization in the presence of inorganic nanoparticles

The incorporation of inorganic particles inside a polymer matrix is of great interest, as these particles may provide specific properties to the final polymeric material, such as, among others, mechanical properties, scratch resistance, magnetic properties, UV absorption, opacity or color when employed as pigments. Nevertheless, the synthesis of inorganic/organic hybrid latexes is generally not as straightforward as the synthesis of fully organic composite latexes depicted in the previous part of this chapter. Polymerization processes are indeed rarely favored at the surface of inorganic particles and usually require a preliminary step of modification of the mineral particles surface. Therefore much focus has been devoted to
the improvement of the compatibility between inorganic and organic phases and to polymerization reactions carried out in the presence of mineral particles. This part of the chapter will present some strategies of surface modification of inorganic particles applicable in aqueous media.

**Inorganic and organic phases – incompatible by nature:**

Inorganic particles are by nature hydrophilic due to the presence of e.g. -OH groups at their surface. Furthermore, when these particles are dispersed in water, hydroxyl functions may be electrically charged, depending on the pH and the ionic strength of the medium. For a given mineral compound, an isoelectric point value\(^{[104]}\) (IEP) can be defined: it corresponds to the pH at which the particle surface displays no net electrical charge. For a pH of the aqueous phase below the IEP, the particle surface exhibits a positive surface potential, originating from the protonation of hydroxyl groups. For pH values higher than the IEP, the surface potential is negative, due to the deprotonation of hydroxyl groups (Fig.1.8).

![Fig.1.8. Effect of the pH on the electrical charge at the surface of inorganic particles (according to reference\(^{[105]}\)).](image-url)
Their hydrophilic nature and the presence of charges at their surface therefore tend to make bare mineral particles by nature incompatible with an organic phase. As a consequence, emulsion polymerization reactions carried out in the presence of bare inorganic particles result generally in a complete segregation between mineral and polymer particles. If such a latex is considered for coating applications, we may expect an aggregation of mineral particles to occur during the film-formation, resulting in a bad dispersion inside the final polymer matrix. The size of mineral objects dispersed in a polymer matrix should indeed be minimized in order to achieve a good film transparency, given that the intensity of scattered light increases as a function of the size of inorganic domains, as described by Rayleighs law\cite{54}:

\[
\frac{I}{I_0} = \exp\left[-\frac{3\Phi_P x r^3}{4\lambda^4} \left(\frac{n_P}{n_m} - 1\right)\right]
\]  

(7),

where \(I_0\) is the intensity of incident light, \(I\) the intensity of transmitted light, \(r\) the radius of dispersed domains (assuming a spherical shape), \(n_P\) the refractive index of dispersed domains, \(n_M\) the refractive index of the polymer phase, \(\lambda\) the wavelength of the light, \(\Phi_P\) the volume fraction of particles and \(x\) the optical path length.

Therefore a preliminary step is often required in order to enhance the compatibility between the mineral and polymer phases. It generally involves surface modification processes that may be classified as follows (Fig.1.9):

1) Adsorption of surfactant molecules.
2) Grafting of coupling agents.
3) Adsorption of small reactive molecules.
4) Adsorption of macromolecules (bearing reactive functions or not).

Fig. 1.9. Strategies for the surface modification of inorganic particles (based on reference [106]).

Some physical processes, such as heterocoagulation or Pickering emulsion, and strategies based on miniemulsion polymerization can also be employed to incorporate inorganic particles in hybrid latexes. However these techniques will not be discussed in this section. For more information about methods for the synthesis of inorganic/organic hybrid latexes, the reader may be referred to review articles [107-109].

1) Adsorption of surfactant followed by admicellar polymerization

Significant improvements of the compatibility between inorganic and polymer phases can be achieved by the use of admicellar polymerization [110-113]. At low surfactant concentrations (well below the CMC), emulsifier molecules tend to self-organize in thin bilayers at the surface of mineral particles. Adsolubilization of a monomer into these
admicelles and addition of a liposoluble initiator can then result into the formation of a thin polymer layer (Fig.1.10). Polymer encapsulation of silica\textsuperscript{[112]}, aluminium\textsuperscript{[114]}, titanium\textsuperscript{[110,115-118]} and iron\textsuperscript{[111,119,120]} oxides employing this method were also reported.

The main parameter to control in these processes is the surfactant concentration. Indeed at too low concentrations, incomplete coverage of the inorganic particles surface will occur, while at too high concentrations oxide-free polymer particles will be formed by secondary nucleation. This rule generally applies to emulsion polymerization reactions carried out in the presence of inorganic particles, regardless of the type of surface-modification employed to improve the compatibility between the mineral and the polymer.

![Fig.1.10: Typical process of polymerization of a monomer adsolubilized in surfactant bilayers adsorbed on silica particles (reproduced from reference\textsuperscript{[113]} with permission from John Wiley & Sons, Inc.).](image)

The use of surfactant molecules bearing reactive functions (also referred to as "surfmers") has also been reported for the synthesis of hybrid
latexes by admicellar polymerization. Nagai et al.\cite{121,122} employed alkyl bromide salts of 2-dimethylaminoethyl methacrylate, cationic surface-active monomers, for the encapsulation of silica particles by homopolymerization and copolymerization with styrene. Following a similar approach, Qu et al.\cite{123} studied the combination of an anionic reactive surfmer with a non-ionic surfactant for the synthesis of silica/fluorocopolymer hybrid latexes and obtained variable morphologies depending on the silica particle concentration and the molar ratio between anionic and non-ionic surfactant. Although oleic acid has been claimed by Ding et al.\cite{124} to be able to copolymerize with styrene via its C=C bond, we may assume that it behaves as a conventional surfactant due to its low reactivity in free radical polymerization. Nevertheless, oleic acid has been widely employed for the successful synthesis of silica and iron oxide-based hybrid latexes.

2) Grafting of coupling agents

The grafting of coupling agents enables to decrease the surface tension of inorganic particles and thus to enhance the affinity between inorganic and organic phases. Furthermore the polymerization reaction at the particle surface is expected to be favored when these coupling agents contain reactive functions. This technique employs RₓMₓ4₋ₓ-type molecules, where M is a metal or semi-metal (Si, Ti, Al…), X a hydrolyzable group (OCH₃, Cl), R a hydrophobic chain or a reactive function (vinyl, methacrylate, thiol, azo-initiator, nitroxide, RAFT or ATRP agent…) and x is typically comprised between 1 and 3. Most coupling agents employed for the functionalization of mineral particles are organosilanes or organotitanates. These compounds react with hydroxyl functions present at the particles surface and form oxometallate bridges that bind them covalently to the particle surface.
Trialkoxysilanes $\text{R-Si(OR')}_3$ are by far the most employed type of coupling agents. Their hydrolysis in water or water/organic solvent mixtures leads to the formation of silanols $\text{R-Si(OH)}_3$ (Fig. 1.11) which are reactive towards $-\text{OH}$ groups present at the surface of mineral particles$^{[125,126]}$. However, silanols are also subjected to self-condensation (homocondensation), which may result in a lower grafting efficiency at the surface of oxide particles. It is thus important to develop experimental conditions for which the hydrolysis of alkoxy silanes is favored while preventing condensation reactions.

**Fig. 1.11:** Mechanism of hydrolysis, condensation and grafting of alkoxy silanes at the surface of mineral particles (adapted from reference$^{[125]}$).
The kinetics of hydrolysis and condensation reactions are influenced by various parameters, such as the nature and concentration of the alkoxy silane, the temperature, the pH and the concentration of water (in the case of water/solvent mixtures)\cite{127-134}. In purely aqueous systems, the pH and the nature and concentration of silane are the main parameters that control the processes of hydrolysis and condensation of silanes. These reactions exhibit different pH dependencies\cite{128,129} as presented in Fig.1.12. At alkaline conditions, the condensation reaction is predominant, while an acidic pH ensures a fast hydrolysis of alkoxy silanes and a much slower condensation reaction. The latter conditions should thus be employed for an efficient grafting in aqueous conditions.

![Graph showing the influence of pH on the rates of hydrolysis and condensation of alkoxy silanes](image)

**Fig.1.12:** Influence of the pH on the rates of hydrolysis and condensation of alkoxy silanes (from reference\cite{132}).

Aqueous solutions of silanols $\text{R-Si(OH)}_3$ formed by hydrolysis of alkoxy silanes are homogeneous and clear due to the high solubility of these compounds in water. However, a haze may develop as soon as they start to condense to oligomeric siloxanes and phase-separate. Plueddemann could thus study the effect of the concentration and pH on the stability of trimethoxyvinyl silane (TMVS) in water by simply measuring
the time for a haze to appear in the solution\textsuperscript{[126]}. Self-condensation of TMVS was decreased by working at low concentrations of silane and at a pH comprised between 2 and 4, resulting in a better stability of the solution (up to 11h). Note that at neutral pH, the haze appeared only after a few seconds. This observation confirms that an acidic pH should be maintained when the grafting of alkoxy silanes is carried out in aqueous media.

Silica has been so far the main oxide employed as a model material to study the synthesis of inorganic/organic composite latexes\textsuperscript{[135]} and the use of organosilanes has often been involved in the preliminary surface-modification step. Emulsion (co)polymerization processes carried out in the presence of surface-modified silica can be described as follows\textsuperscript{[136]}, and may also be generalized to other types of hydrophobized mineral particles: the decomposition of the initiator occurring in the water phase leads to the formation of radicals that will further react with aqueous phase monomer molecules to form oligoradicals. These oligoradicals may then:

- Undergo aqueous phase termination.
- Enter a micelle (depending on the surfactant concentration).
- Precipitate once they reach a critical length.
- Be transferred to the surface of silica particles.

If the surface of silica particles is sufficiently hydrophobic, the latter event will be favored and lead to the formation of polymer sites that will further capture oligoradicals and encourage the polymerization reaction at the oxide surface.

Therefore the nature (hydrophobicity, presence of reactive functions or not) and grafting density of the organosilane and the size and concentration of silica particles are the main parameters affecting the emulsion polymerization process and the final morphology of the
silica/polymer composite particles. For instance, in the case of silica modified by MPTMS (methacryloxy propyl trimethoxysilane), a reactive organosilane, it was demonstrated that at low grafting densities, segregated polymer domains were formed at the surface of silica particles, resulting in multipod-like morphologies\textsuperscript{[137]}, while at a sufficiently high MPTMS coverage, complete encapsulation of silica particles could be achieved\textsuperscript{[138]}. However, several other factors, among which the nature and concentration of emulsifier\textsuperscript{[136]}, the type of monomer or initiator employed in the recipe and the pH of the medium, were also proved to influence the final morphology of hybrid latexes\textsuperscript{[138,139]}.

The encapsulation of titanium dioxide by MMA (co)polymers employing non-reactive and reactive organotitanates has been described by Caris et al.\textsuperscript{[140]} and Janssen et al.\textsuperscript{[141]} The results of their work provided a good understanding of the parameters influencing the course of emulsion polymerization reactions performed in the presence of inorganic particles. They showed that the surfactant concentration had to be well balanced during the emulsion polymerization process to maintain a good colloidal stability while avoiding the formation of free polymer particles by secondary nucleation. Therefore semi-batch operation should be preferred to batch operation to keep control over the surfactant concentration all along the reaction and obtain a compromise between colloidal stability and optimal encapsulation efficiency. They also established that monomer-starved conditions are often required in order to limit the formation of monomer-swollen micelles and avoid the nucleation of oxide-free polymer particles. Finally the type of initiator was shown to have an influence on the course of the reaction: for instance a better encapsulation efficiency was obtained when ACV-Na, the sodium salt of ACVA (4,4’-azobis(4-cyanovaleric acid), was employed instead of SPS (sodium persulfate), as the latter tended to
favor the formation of micelles. Another explanation could be that ACV-Na, being more hydrophobic than SPS, encouraged the migration of oligoradicals towards the hydrophobized mineral surface.

3) Adsorption of small reactive molecules at the surface of mineral particles

The encapsulation of titanium dioxide by poly(styrene) and poly(methyl methacrylate) via the use of ionic initiators was first studied by Haga et al.\[^{142}\] These authors evidenced the influence of electrostatic interactions between the polymer chain ends and the mineral surface on the “encapsulation” of inorganic particles by varying the pH of the continuous phase and the type of initiator. The best conditions for the “encapsulation” of an inorganic pigment were obtained when the mineral surface and the polymer chain ends exhibit opposite charges. We may, however, question their use of the term “encapsulation” as they did not provide any visual proof of the final morphology of TiO\(_2\)/polymer latexes obtained via this process.

Luna-Xavier et al.\[^{143-145}\] reported the synthesis of polymer/silica hybrid latexes via the adsorption of AlBA, a cationic initiator, at the surface of silica particles. They studied the emulsion polymerization of methyl methacrylate reaction in the presence of silica, AlBA and a non-ionic surfactant NP\(_{30}\) (Fig.1.13) and showed that the process depended on several parameters, such as the pH, the monomer, silica and initiator concentrations.

Qi et al.\[^{146}\] employed the same technique for the synthesis of poly(butyl acrylate)/SiO\(_2\) hybrid particles. In this case the latexes exhibited a “raspberry” morphology with silica particles mainly present at the polymer
surface. However, these authors showed that an additional step of polymerization of methyl methacrylate in the presence of PBA/SiO$_2$ particles and AIBA initiator could lead to the complete encapsulation of silica (Fig.1.14).

Fig.1.13: Schematic principle of the polymerization of MMA at the surface of silica particles via the adsorption of AIBA (reproduced from reference [144] with permission from Elsevier).

Fig.1.14: Encapsulation of PBA/SiO$_2$ hybrid particles by PMMA via the adsorption of AIBA at the surface of silica (reproduced from reference [146] with permission from John Wiley & Sons, Inc.).
Finally Schmid et al.\textsuperscript{[147-150]} applied this method for the synthesis of polymer/silica hybrid latexes to various types of polymers: poly(2-vinylpyridine)\textsuperscript{[147]}, poly(styrene)\textsuperscript{[148]} and poly(styrene-co-butyl acrylate)\textsuperscript{[149,150]}. They reported the formation of “raspberry” morphologies with silica particles present at the polymer/water interface with a high incorporation efficiency. Nevertheless it is important to point out that, although silica particles were mainly situated at the polymer surface, poly(styrene-co-BA)/SiO\textsubscript{2} hybrid latexes exhibited good film-forming properties\textsuperscript{[149]}.

4) Adsorption of macromolecules at the surface of mineral particles

Macromolecules adsorbed on the surface of inorganic particles have been extensively employed to promote the polymerization reaction at the mineral particle surface. A few references deal with the use of non-reactive polymers, such as hydroxyl propyl cellulose as a compatibilizing agent for the encapsulation of silica particles by polystyrene, but macromolecules bearing reactive functions have mainly been employed to achieve the synthesis of hybrid particles.

Reculusa et al. reported the use of a poly(ethylene glycol)-based macromonomer – poly(ethylene glycol) monomethyl ether methacrylate (PEGMA) – to modify the surface of silica particles and to promote the polymerization reaction at their surface\textsuperscript{[151-153]}. Similarly to what could be observed in the case of MPTMS-modified silica, various structures were obtained, from dissymmetrical snowman to multipod-like morphologies, depending on the surface coverage of PEGMA adsorbed on silica. This strategy was later applied by Sheibat-Othman et al.\textsuperscript{[154,155]} to the surfactant-free synthesis of hybrid latexes based on clay and silica.
Amphiphatic random copolymers, among which copolymers containing a random distribution of acrylic acid and a hydrophobic comonomer in the polymer chain, have been widely employed to disperse pigments in commercial polymeric dispersions. Nguyen et al.\textsuperscript{[156,157]} developed an efficient and versatile strategy that enables a good dispersion of inorganic particles and promotes the polymerization reaction at their surface. These authors employed amphiphatic macro-RAFT agents containing a random distribution of acrylic acid and \textit{n}-butyl acrylate units to encapsulate alumina- and zirconia-coated titanium dioxide and phthalocyanine blue\textsuperscript{[157]}, and more recently to synthesize TiO\textsubscript{2}/polymer hybrid nanorattles\textsuperscript{[158]}. In a first step, several macro-RAFT copolymers were synthesized employing different types of RAFT agents and various monomer compositions. The random distribution of hydrophobic and hydrophilic units is important to prevent the macro-RAFT agents from forming micelles during the emulsion polymerization step, which would encourage the formation of a second crop of polymer particles and decrease the encapsulation efficiency. Another critical point is to maintain a low molecular weight of the macro-RAFT agents to minimize the proportion of hydrophilic block that would affect the properties of the final polymer coating and to keep a high number of RAFT units at the surface of the particles. After dispersion of the pigments in the presence of an adequate macro-RAFT agent, the emulsion copolymerization of methyl methacrylate and butyl acrylate was carried out in the absence of additional emulsifier, leading to the successful encapsulation of 100\% of the pigment particles without formation of free polymer particles by secondary nucleation. The main asset of this method is the possible encapsulation of a large variety of pigments by tuning the hydrophobic/hydrophilic composition of the macro-RAFT agent depending on the nature of the material to encapsulate. Ali et al. extended the use of this technique to the synthesis of anisotropic hybrid
latexes starting from gibbsite nanoparticles\textsuperscript{[159]} and polymer nanocapsules starting from self-assembled dimethyldioctadecyl ammonium bromide (DODAB) vesicles\textsuperscript{[160]}.

Following a similar approach, Daigle et al.\textsuperscript{[161]} developed a simpler strategy for the encapsulation of various types of inorganic particles (metal oxides, such as alumina, titanium dioxide, barium titanate, zirconia and copper oxide, metals such as molybdenum and zinc and inorganic nitrides like Si\textsubscript{3}N\textsubscript{4}), using poly(acrylic acid) macro-RAFT agents instead of amphiphatic RAFT oligomers. However, the application of a polyacrylic acid macro-RAFT agent required the presence of conventional surfactant and resulted in the formation of a certain amount of free polymer particles by secondary nucleation.

1.4. Conclusions

Poly(vinylidene chloride) displays outstanding properties, such as a very low permeability towards water, oxygen and aroma and a good chemical resistance to a wide range of solvents. Nonetheless, it suffers from limited heat and UV stabilities that require the use of stabilizers. Both processes of thermal and UV degradations of poly(vinylidene chloride) follow an unzipping process, leading to a release of hydrogen chloride and to the formation of conjugated sequences in the polymer chains, which account for yellowing and a decrease of barrier properties of PVDC.

Epoxy-functional compounds, by scavenging hydrochloric acid evolved from the polymer chains, appear to be very efficient thermal stabilizers when incorporated in PVDC resins. To extend the strategy to waterborne PVDC films, we propose to incorporate an epoxy-functional
core into PVDC composite latexes via a two-stage emulsion polymerization process: in a first step, the synthesis of an epoxy-functional seed latex will be performed, followed by the seeded second-stage emulsion copolymerization of vinylidene chloride and methyl acrylate to obtain composite latexes.

Cerium oxide nanoparticles, with a high absorption of UV radiation, a relatively low refractive index in the visible range and a lower photocatalytic activity compared to titanium dioxide and zinc oxide, are very promising candidates as UV stabilizers of poly(vinylidene chloride). Indeed, improvements of the polymer stability to UV radiation were already reported for waterborne films obtained by direct mixing of nanoceria with PVDC latexes. However, in order to favor a good dispersion of the nanoparticles in the final PVDC film, the synthesis of hybrid latexes should be considered. Emulsion polymerization processes carried out in the presence of inorganic particles often require a preliminary surface-modification step in order to achieve an efficient incorporation of mineral objects into the final polymer latex. Two different routes – the grafting of alkoxysilanes and the adsorption of amphiphatic macro-RAFT agents – will be studied in order to promote the polymerization reaction at the surface of nanoceria, as they were both proved to lead to a high efficiency of hybrid particle formation.

References

[24] J. Heerema (Dow Chemical Co., USA), *US 2482771*, **1949**.
[45] A. W. Hanson, W. C. Goggin (Dow Chemical Co., USA), *US 2273262*, 1942.


Chapter 2. Synthesis of PVDC composite latexes from epoxy-functional seeds

Abstract

This chapter deals with the incorporation of an epoxy-functional seed polymer into PVDC latexes via a two-stage emulsion polymerization process. In a first step the emulsion copolymerization of glycidyl methacrylate (GMA) and n-butyl methacrylate (BMA) was carried out in optimized conditions (low temperature, neutral pH, starved-feed conditions) to both limit the hydrolysis of epoxy groups and obtain small particle sizes (typically 30-50 nm size range). Composite latexes were then obtained via the second-stage seeded copolymerization of VDC and MA in the presence of tetrasodium pyrophosphate to control the pH and reach high molecular weight, leading to partial encapsulation of the seed particles. Thermogravimetric analyses performed on the resulting composite particles showed that the epoxy-functionalized seed polymer behaved as an efficient thermal stabilizer of PVDC, while more simple alternatives, such as blends of latexes or direct emulsion terpolymerization of vinylidene chloride, methyl acrylate and glycidyl methacrylate, were less successful to impart the polymer an enhanced thermal stability.
2.1. Introduction

Epoxy-functionalized compounds have been widely employed for the thermal stabilization of PVDC resins\[^{1,2}\]. They may not only behave as efficient HCl-scavengers, but also as chelating agents for metal chlorides\[^{2}\], which are formed in situ via a reaction between hydrochloric acid and metal ion impurities and behave as catalysts for PVDC dehydrochlorination\[^{3}\]. Glycidyl methacrylate (GMA) is a very common monomer employed to introduce an epoxy functionality in polymer particles\[^{4}\]. These polymer colloids have found applications in various fields, such as biochemistry\[^{5}\], chromatography\[^{6}\] or for the preparation of latexes with a crosslinking reactivity\[^{7-9}\]. Given that their incorporation in PVDC latexes could be performed via conventional emulsion polymerization processes, glycidyl methacrylate monomer and (co)polymers may be considered for the thermal stabilization of waterborne PVDC films.

In this chapter we explore the synthesis of PVDC composite latexes containing an epoxy-functional polymer via a two-stage emulsion polymerization process for use as waterborne barrier films with improved thermal stability. After a brief literature study on parameters influencing the cleavage of epoxy groups during the emulsion (co)polymerization of glycidyl methacrylate, the synthesis of epoxy-functional latexes by emulsion copolymerization of glycidyl methacrylate and \(n\)-butyl methacrylate is presented. Results on the second-stage emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of poly(GMA-co-BMA) epoxy-functional seed latexes are then discussed. The thermal stability of PVDC composites is studied by thermogravimetric analyses, and compared to PVDC reference samples. Finally other systems obtained by blends of latexes and direct emulsion terpolymerization of vinylidene
chloride, methyl acrylate and glycidyl methacrylate are compared with the composite route in terms of thermal stability.

### 2.2. Preservation of epoxy groups from ring-opening reactions

The partial hydrolysis of epoxy groups is a major issue to consider not only during the emulsion polymerization of glycidyl methacrylate, but also while storing the resulting latex. Indeed partial cleavage of the epoxy groups does not only induce lower epoxy contents in PGMA latexes, which is of course not acceptable for further applications. The hydrolysis of glycidyl methacrylate to glyceryl methacrylate, a water-soluble monomer, may also affect the emulsion polymerization process and lead to the formation of some water-soluble polymer.

The pH of the reaction medium is probably the most important parameter to control when performing the emulsion polymerization of epoxy-functionalized monomers: since the hydrolysis of epoxy groups can be either acid or base catalyzed\(^{[10,11]}\) (Fig.2.1), it is required to work at a neutral pH. It has also been reported that the ring-opening of epoxy groups may occur via a “spontaneous” water addition that would not require acidic or basic conditions\(^{[10]}\). Nevertheless, Wurtz\(^{[12]}\) and Nef\(^{[13]}\) showed that the hydrolysis of ethylene oxide, glycidol or epichlorohydrin in the presence of only water was very slow at 100°C. We may therefore reasonably assume that this “spontaneous” water addition process is negligible at lower temperatures\(^{[10]}\).

Temperature still remains an important factor influencing the cleavage of epoxy groups. For instance Okubo et al. showed that the
hydrolysis of epoxy groups could be completely avoided by performing the emulsion (co)polymerization of glycidyl methacrylate at 0-5 °C under UV radiation\cite{7,14,15}. Along the same line, Geurts \textit{et al.}\cite{16} compared the effect of a redox-initiated polymerization (sodium persulfate/sodium hydrogen sulfite/iron sulfate complexed with EDTA, at 20°C) with a thermo-initiated reaction (sodium persulfate, at 60°C) on the hydrolysis of epoxy groups, all experiments being conducted in the presence of sodium hydrogencarbonate as a buffer. The authors showed that in the former case, 95% of epoxy groups were still intact at the end of the polymerization, versus roughly 65% in the latter case.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrolysis.png}
\caption{Hydrolysis of epoxy groups: a) Acid catalysis, b) Base catalysis.}
\end{figure}

Horák \textit{et al.} reported that the initiator nature and concentration may also affect the hydrolysis of epoxy groups during the emulsion polymerization of GMA\cite{17}. Indeed, by comparing two different types of initiators at a reaction temperature of 70°C, they concluded that in the presence of 4,4’-azobis(4-cyanovaleric acid) (ACVA), a high percentage of epoxy groups remained intact at the end of the polymerization, while ammonium persulfate (APS) tended to decrease the epoxy content in the polymer. This effect is more explicit when the APS content was increased. Despite the fact that they did not establish connections between the initiator
nature and the hydrolysis of epoxy groups, we believe that ammonium persulfate may create more acidic conditions when dissociated in water compared to ACVA: therefore the pH could also be the reason for the hydrolysis of epoxides in the APS case, although pH values of the resulting poly(glycidyl methacrylate) latexes were not reported.

All these considerations remain valid concerning the storage of PGMA latexes: indeed one should store PGMA latexes at neutral pH and preferably at low temperature in order to avoid further hydrolysis of epoxy groups.

2.3. Experimental section

2.3.1. Materials

Glycidyl methacrylate (GMA, Aldrich, 97%), n-butyl methacrylate (BMA, Acros, 99%), vinylidene chloride (VDC, Aldrich, 99%) and methyl acrylate (MA, Aldrich, 99%) were distilled under reduced pressure to remove inhibitors. Potassium persulfate (KPS, Aldrich, 99%), sodium metabisulfite (Na2S2O5, Aldrich, 99%), sodium hydrogenocarbonate (NaHCO3, Aldrich,), tetrasodium pyrophosphate (TSPP, Alfa Aesar, 98%), Dowfax 2A1 (Dow, 42 wt% solution in water) were used as received. Water was deionized through an ion-exchange resin (conductivity below 1 μS/cm).

2.3.2. Polymerizations

Emulsion copolymerizations of glycidyl methacrylate and butyl methacrylate (in a 90:10 mass ratio / 90:10 molar ratio) were carried out in a 250 mL double-walled glass vessel, equipped with a mechanical glass
anchor propeller. An aqueous solution of sodium metabisulfite, Dowfax 2A1 and sodium hydrogenocarbonate was charged in the reactor, heated to 30°C and stirred at a speed of 200 rpm. At the beginning of the reaction, 9 mL of a 10 g/L aqueous solution of KPS was injected at once in the reactor followed by a continuous addition of this solution at a rate of 4.5 mL/h for 4 h. At the same time a continuous feed of the monomer solution (90 wt% of GMA, 10 wt% of BMA) was started and maintained for 3 h. Continuous additions were performed with two Perfusor Compact syringe pumps (Braun). The reaction lasted 5 h in total.

Seeded emulsion copolymerization of vinylidene chloride and methyl acrylate (in a 90:10 mass ratio / 89:11 molar ratio) was performed in a 300 mL stainless steel reactor (Parr Instrument Company), equipped with a stainless steel pitched-bladed mechanical stirrer and internal pressure and temperature sensors. Oxygen was removed from the autoclave by purging it via three cycles of vacuum (10⁻² mbar) broken with nitrogen. Vacuum was restored in the reactor before charging an aqueous solution containing the poly(GMA-co-BMA) seed latex and sodium metabisulfite. A 4 bars nitrogen overpressure was then established in the vessel. The speed of agitation was set at 250 rpm and the temperature was raised to 55°C. A stirred pre-emulsion containing tetrasodium pyrophosphate, KPS, Dowfax 2A1, VDC and MA, was then continuously pumped into the reactor at a rate of 24 mL/h for 5 h via a Series III digital HPLC pump (LabAlliance). The overall reaction lasted for 6 h. Residual monomer was stripped by heating the latex for 1 h at 60°C under reduced pressure (0.2-0.4 bar).

The protocol for the synthesis of reference latexes (R1, R1’, R1”) consisted in adding an initial pulse of 15 wt% of the pre-emulsion and 10 mL of a 10 g/L KPS aqueous solution to form a poly(VDC-co-MA) seed in
situ. After 30 min, the pre-emulsion continuous addition was started and maintained at a rate of 24 mL/h for 5 h. The same procedure was employed for the synthesis of the poly(VDC-co-MA-co-GMA) terpolymer latex.

2.3.3. Characterization

**Particle size measurements.** The particle size distributions of the latexes were determined by dynamic light scattering (DLS) with a Nanotrac particle size analyzer (Microtrac Inc.).

**Gel content.** The percentage of gel present in the poly(BMA-co-GMA) copolymers and the poly(VDC-co-MA-co-GMA) terpolymer was determined by continuous extraction of the soluble part with dichloromethane and tetrahydrofuran. A sample of dry polymer ($w_{\text{polymer}}$) was weighted in a cellulose extraction thimble (Whatman) of known mass, placed in a soxhlet and extracted with dichloromethane at reflux for 72 h. At the end of the extraction, the undissolved part of the polymer remaining in the thimble was dried and weighted ($w_{\text{undissolved part}}$). The gel content was then calculated via equation (1):

$$\text{gel content (\%)} = \frac{w_{\text{undissolved part}} \times 100}{w_{\text{polymer}}}$$

(1)

**Titration of epoxy groups.** The determination of the polymer epoxy content is based on the ring-opening of epoxy groups by HBr, generated *in situ* by a reaction between tetraethylammonium bromide and perchloric acid. An accurately known mass of dry polymer (typically 0.1 g for the seed polymer and 1 g for PVDC composite samples) was placed in a beaker and dissolved in 60 mL of dioxane for 5 minutes at 80°C, before adding 60 mL of acetic acid. Once the beaker was back to room temperature, 10 mL of a
0.1 N solution of tetraethylammonium bromide dissolved in acetic acid was added. The titration by a 0.1 N perchloric acid solution in acetic acid was followed by potentiometric titration. In the case of poly(GMA-co-BMA) seed polymers, the contribution of NaHCO₃ on the titration was subtracted (a blank experiment showed than one equivalent of HBr reacted with one equivalent of NaHCO₃). For poly(GMA-co-BMA)/poly(VDC-co-MA) composite samples the contribution of TSPP was subtracted too (a blank experiment showed that 4 equivalents of HBr reacted with one equivalent of pyrophosphate). By comparing the experimental and theoretical epoxy contents (expressed in moles of epoxy groups per 100 g of polymer), the percentage of epoxy groups preserved from hydrolysis during the polymerization could be determined.

**Determination of molecular weights of poly(VDC-co-MA) copolymers and poly(VDC-co-MA-co-GMA) terpolymer.** Molecular weights of second-stage PVDC copolymers were determined by Gel Permeation Chromatography (PL-GPC 50, Varian, Inc.). Freeze-dried samples of composite and reference latexes were dissolved in THF and filtered on 0.2 mm PTFE filters, before being injected in the SEC apparatus. A calibration employing polystyrene standards (K = 14.1 × 10⁻⁵ dL/g and a = 0.7)¹⁸ was employed in combination with Mark-Houwink coefficients determined by Revillon et al.¹⁹ for poly(VDC-co-MA) copolymers with a 80:20 VDC:MA mass ratio (K = 35 × 10⁻⁵ dL/g and a = 0.57) to calculate the polymer molecular weights.

**Transmission Electron Microscopy (TEM).** Composite latexes were diluted as follows: 2 droplets in 100 mL of DI water. The sample was deposited on a copper grid covered by a layer of FORMAR (polyvinyl
formal), then dried at room temperature and in an air atmosphere. Pictures were obtained using a Zeiss EM910 (80 kV) microscope.

**Thermogravimetric analyses.** The thermal degradation of PVDC powders (obtained by freeze-drying of the composite latexes) was analyzed on a TGA apparatus Q50 (TA Instruments). Analyses consisted of a ramp of 20°C/min from room temperature to 160°C, followed by an isotherm for 120 min at 160°C. Unless stated otherwise, the sample, placed in a 100 μL aluminum pan, was subjected to a constant air flow rate of 100 mL/min during the analysis.

**Measurements of oxygen permeabilities on PVDC films.** PVDC films were coated as follows: a 12 μm thick wet film was bare coated on a PET film substrate (12 μm thick, from Terphan, corona treated prior to use) and dried at 23°C under a 50% relative humidity. Oxygen permeabilities were measured on the resulting PVDC/PET films employing an OX-TRAN (model 2/20) apparatus. Films were treated at 40°C prior to the analysis in order to prevent any crystallization effect during the measurements. An average of two measurements was taken to calculate the film permeability to oxygen (expressed in cm³.m⁻².day⁻¹.bar⁻¹) and the result was normalized over the PVDC layer thickness to obtain the intrinsic oxygen permeabilities of the samples (expressed in cm³.μm⁻¹.m⁻².day⁻¹.bar⁻¹). The PVDC layer thickness was measured with a Davinor LayerGauge instrument (average of 10 measurements performed on different areas of the sample): for film samples obtained in this study, the PVDC layer thickness varied from to 2 to 8 μm.
2.4. Results and discussion

2.4.1. First-stage synthesis of epoxy-functionalized seed latexes

On the basis of results reported in the scientific literature, a preliminary study, employing recipes indicated in Table 2.1, was undertaken in order to determine optimal conditions of temperature and pH that enable to limit the hydrolysis of epoxy groups: the influence of thermal and redox initiations and of the pH was investigated.

Table 2.1. Polymerization recipes to study the influence of temperature and pH on the hydrolysis of epoxy groups.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>pH</th>
<th>Na₂S₂O₅ (g)</th>
<th>NaHCO₃ buffer (g)</th>
<th>Dowfax 2A1 (g)</th>
<th>Water (g)</th>
<th>KPS solution feed (4.5 mL/h)</th>
<th>Water (g)</th>
<th>GMA / BMA feed (10.3 g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>60</td>
<td>6.3</td>
<td>0</td>
<td>0</td>
<td>8.04</td>
<td>73.70</td>
<td>0.27</td>
<td>27</td>
<td>27.82 / 3.08</td>
</tr>
<tr>
<td>S2</td>
<td>30</td>
<td>3.4</td>
<td>0.25</td>
<td>0</td>
<td>8.01</td>
<td>73.52</td>
<td>0.27</td>
<td>27</td>
<td>27.85 / 3.06</td>
</tr>
<tr>
<td>S3</td>
<td>30</td>
<td>7.3</td>
<td>0.24</td>
<td>0.09</td>
<td>8.00</td>
<td>72.83</td>
<td>0.27</td>
<td>27</td>
<td>27.71 / 3.10</td>
</tr>
</tbody>
</table>

HBr titrations carried out on freeze-dried samples of latexes confirmed the sensitivity of epoxy groups to temperature and pH (Table 2.2): a high temperature (60°C) and a pH close to neutral point resulted in the loss of about 10% of the polymer epoxy content, while an acidic pH at low temperature (30°C) provoked the hydrolysis of epoxy groups to a similar extent.
The low pH, i.e. pH=3.4, obtained when performing the polymerization reaction at 30°C in the presence of sodium metabisulfite originates from the formation of one to two equivalents of bisulfite radicals (\(\text{SO}_3\text{H}, \text{pKa} \approx 1.9\)) per dissociation event\textsuperscript{[20]} (Equations (2), (2') and (2'')):

\[
\begin{align*}
\text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O} & \rightarrow 2\text{HSO}_3^- \quad (2) \\
\text{S}_2\text{O}_8^{2-} + \text{HSO}_3^- & \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{SO}_3\text{H} \quad (2') \\
\text{SO}_4^{2-} + \text{HSO}_3^- & \rightarrow \text{SO}_4^{2-} + \text{SO}_3\text{H} \quad (2''),
\end{align*}
\]

while the thermal dissociation of potassium persulfate only leads to the formation of low amounts of bisulfate ions (\(\text{HSO}_4^-, \text{pKa} = 2.0\)) originating from the transfer of \(\text{SO}_4^{2-}\) radicals to water\textsuperscript{[20]} (Equation (3)):

\[
\text{S}_2\text{O}_8^{2-} + x\text{H}_2\text{O} \rightarrow (2-x)\text{SO}_4^{2-} + x\text{HSO}_4^- + x\text{HO}^+ \quad (3),
\]

where \(x\) depends on the extent of transfer of \(\text{SO}_4^{2-}\) radicals to water \((0 < x < 2)\).

**Table 2.2.** Influence of the reaction temperature and pH on the hydrolysis of epoxy groups.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>pH</th>
<th>Gel content (%)</th>
<th>Measured epoxy content(^a)</th>
<th>Theoretical epoxy content(^a)</th>
<th>Intact epoxy groups (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>60</td>
<td>6.3</td>
<td>99.0</td>
<td>0.571</td>
<td>0.633</td>
<td>90.2</td>
</tr>
<tr>
<td>S2</td>
<td>30</td>
<td>3.4</td>
<td>98.5</td>
<td>0.557</td>
<td>0.634</td>
<td>87.9</td>
</tr>
<tr>
<td>S3</td>
<td>30</td>
<td>7.3</td>
<td>99.2</td>
<td>0.622</td>
<td>0.633</td>
<td>98.3</td>
</tr>
</tbody>
</table>

\(^a\) The epoxy content is expressed in number of moles of epoxy groups per 100 g of dry polymer.
Hence sodium hydrogenocarbonate NaHCO₃ was employed as a buffer to compensate for the acidity brought about by bisulfite radicals and maintain a pH close to 7 throughout the polymerization reaction. The HBr titration indicated that more than 98% of epoxy groups were preserved from hydrolysis in these conditions of low temperature and neutral pH.

The gel content determined by soxhlet extraction of the polymer soluble part in dichloromethane was close to 99% in all cases, independent of temperature or pH conditions. Geurts et al.¹⁶ established that the high gel content observed in methacrylic latexes containing GMA originated from traces of dimethacrylates present in glycidyl methacrylate. Considering that they obtained very high gel contents (from 92 to 98%) when performing the emulsion copolymerization of GMA and BMA in a 10:90 GMA:BMA mass ratio, it is not surprising to observe even higher gel contents when working with a 90:10 GMA:BMA mass ratio in our case.

Epoxy-functionalized seed latexes with controlled particle size were obtained by starved-feed emulsion copolymerizations of glycidyl methacrylate and butyl methacrylate, following the recipes given in Table 2.3.

A batch reaction was first carried out to follow the monomer conversion versus time (Fig.2.2). Following experiments employed monomer feed rates ($R_{feed} < 16.8$ g/h, i.e. $R_{feed} < 4.3 \times 10^{-4}$ mol.L⁻¹.s⁻¹) much lower than the maximum rate of polymerization observed during the batch experiment ($R_{p \ max} = 1.5 \times 10^{-3}$ mol.L⁻¹.s⁻¹). Instantaneous monomer conversions higher than 90% obtained along the reaction S5 confirmed that monomer-starved conditions were fulfilled for feed rates lower than 16.8 g/h.
**Table 2.3.** Polymerization recipes for the synthesis of epoxy-functionalized latexes at 30°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Na₂S₂O₅ (g)</th>
<th>NaHCO₃ (g)</th>
<th>Dowfax 2A1 (g)</th>
<th>Water (g)</th>
<th>KPS (g)</th>
<th>Water (g)</th>
<th>GMA/BMA feed (g) / (g)</th>
<th>Feed rate (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>0.25</td>
<td>0.10</td>
<td>8.03</td>
<td>73.25</td>
<td>0.27</td>
<td>27</td>
<td>27.06 / 3.04</td>
<td>batch</td>
</tr>
<tr>
<td>S5</td>
<td>0.25</td>
<td>0.09</td>
<td>8.04</td>
<td>73.47</td>
<td>0.27</td>
<td>27</td>
<td>44.86 / 4.72</td>
<td>16.8</td>
</tr>
<tr>
<td>S6</td>
<td>0.25</td>
<td>0.10</td>
<td>8.04</td>
<td>73.23</td>
<td>0.27</td>
<td>27</td>
<td>36.03 / 4.03</td>
<td>13.4</td>
</tr>
<tr>
<td>S7</td>
<td>0.26</td>
<td>0.11</td>
<td>8.01</td>
<td>73.29</td>
<td>0.27</td>
<td>27</td>
<td>30.50 / 3.40</td>
<td>11.3</td>
</tr>
<tr>
<td>S3</td>
<td>0.24</td>
<td>0.09</td>
<td>8.00</td>
<td>72.83</td>
<td>0.27</td>
<td>27</td>
<td>27.71 / 3.10</td>
<td>10.3</td>
</tr>
<tr>
<td>S8</td>
<td>0.25</td>
<td>0.10</td>
<td>8.02</td>
<td>73.52</td>
<td>0.27</td>
<td>27</td>
<td>19.40 / 2.23</td>
<td>7.2</td>
</tr>
</tbody>
</table>

**Fig.2.2.** Monomer conversion time history for the batch emulsion copolymerization of GMA and BMA at 30°C (see Table 2.3).
The seed latex particle size could then be adjusted by varying the monomer feed rate. According to the Smith-Ewart theory\textsuperscript{[21]}, the number of particles formed during the nucleation phase is given by Equation (4):

\[ N_P = k \times (\rho/\mu)^{0.4} \times (a_s \times [S])^{0.6} \]

Where \( \rho \) is the rate of radical generation, \( \mu \) the rate of particle volume growth, \( a_s \) the area occupied by one surfactant molecule and \([S]\) the concentration of surfactant present in the medium in the form of micelles. As a result, reducing the monomer feed rate parameter should decrease the particle volume growth rate and lead to a higher number of particles nucleated, resulting in a lower average particle diameter. Although our system does not strictly obey the model proposed by Smith and Ewart, this tendency is confirmed by values of \( D_P \) (intensity-averaged particle diameter) presented in Table 2.4.

**Table 2.4.** Influence of the monomer feed rate on the number of nucleated particles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer feed rate (g/h)</th>
<th>Final wt% of polymer</th>
<th>Particle diameter ( D_P ) (nm)</th>
<th>Total number of particles ( N_P ) ( \times 10^{17} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5</td>
<td>16.8</td>
<td>31.5</td>
<td>86</td>
<td>1.4</td>
</tr>
<tr>
<td>S6</td>
<td>13.4</td>
<td>26.9</td>
<td>70</td>
<td>2.1</td>
</tr>
<tr>
<td>S7</td>
<td>11.3</td>
<td>23.7</td>
<td>51</td>
<td>4.6</td>
</tr>
<tr>
<td>S3</td>
<td>10.3</td>
<td>22.1</td>
<td>43</td>
<td>6.9</td>
</tr>
<tr>
<td>S8</td>
<td>7.2</td>
<td>16.5</td>
<td>28</td>
<td>17</td>
</tr>
</tbody>
</table>
2.4.2. Second-stage emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of epoxy-functional seeds

Poly(GMA-co-BMA) latexes were then employed as seeds for the second-stage emulsion copolymerization of vinylidene chloride and methyl acrylate. Table 2.5 indicates the amounts of reactants employed for these reactions.

The stability of epoxy groups was still a serious factor to consider when performing the emulsion copolymerization of vinylidene chloride and methyl acrylate since the evolution of hydrochloric acid from PVDC chains to the water phase already started during the polymerization reaction. Tetrasodium pyrophosphate (TSPP) was therefore employed to scavenge HCl molecules and protect epoxy groups from ring-opening reactions. As indicated in Table 2.6, when TSPP was not included in the recipe, the polymerization reactions occurred in acidic conditions (pH of about 2) and at least 80% of epoxy groups were hydrolyzed, while the addition of TSPP enabled to maintain a pH close to 5 all along the reaction and to preserve more than 80% of epoxy groups.

At first sight, the differences between molecular weights (Table 2.6) of poly(VDC-co-MA) polymers synthesized in the presence or absence of TSPP may be striking, considering that similar monomer/initiator ratios were employed in all recipes. However, the pH values measured on final latexes may account for this divergence, given that the dissociation of potassium persulfate is catalyzed by protons in acidic conditions\cite{22-24}.
Table 2.5. Recipes for the seeded emulsion copolymerization of vinylidene chloride and methyl acrylate at 55°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Seed latex</th>
<th>Initial load</th>
<th>Pre-emulsion feed (≈ 32 g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂S₂O₅</td>
<td>Seed latex</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
</tr>
<tr>
<td>C1</td>
<td>S9ᵃ</td>
<td>0.20</td>
<td>4.18</td>
</tr>
<tr>
<td>C2</td>
<td>S9ᵃ</td>
<td>0.18</td>
<td>4.19</td>
</tr>
<tr>
<td>C3</td>
<td>S3ᵇ</td>
<td>0.23</td>
<td>6.60</td>
</tr>
<tr>
<td>C4</td>
<td>S10ᶜ</td>
<td>0.19</td>
<td>8.48</td>
</tr>
<tr>
<td>C5</td>
<td>S7ᵈ</td>
<td>0.20</td>
<td>9.94</td>
</tr>
<tr>
<td>C5'</td>
<td>S11ᵉ</td>
<td>0.19</td>
<td>9.02</td>
</tr>
<tr>
<td>C6</td>
<td>S6ᶠ</td>
<td>0.21</td>
<td>10.34</td>
</tr>
<tr>
<td>R1  (ref)</td>
<td>None</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1' (ref)</td>
<td>None</td>
<td>0.21</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1'' (ref)</td>
<td>None</td>
<td>0.30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Seed polymer content: 22.0%, seed particle diameter: 43 nm, pH=7.5;
ᵇ Seed polymer content: 22.1%, seed particle diameter: 43 nm, pH=7.3;
ᶜ Seed polymer content: 22.0%, seed particle diameter: 50 nm, pH=7.1;
ᵈ Seed polymer content: 23.7%, seed particle diameter: 51 nm, pH=7.4;
ᵉ Seed polymer content: 26.6%, seed particle diameter: 50 nm, pH=5.4;
ᶠ Seed polymer content: 26.9%, seed particle diameter: 70 nm, pH=7.5.
Table 2.6. Characteristics of composite and reference PVDC latexes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>wt%</th>
<th>TSPP</th>
<th>pH</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>(M_w/M_n)</th>
<th>Epoxy content</th>
<th>Theoretical epoxy content</th>
<th>Intact epoxy groups (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.0</td>
<td>yes</td>
<td>6.2</td>
<td>61500</td>
<td>176400</td>
<td>2.87</td>
<td>4.5 \times 10^{-3}</td>
<td>5.6 \times 10^{-3}</td>
<td>80.4</td>
</tr>
<tr>
<td>C2</td>
<td>1.0</td>
<td>no</td>
<td>2.1</td>
<td>12900</td>
<td>36300</td>
<td>2.80</td>
<td>0</td>
<td>5.5 \times 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>C3</td>
<td>1.7</td>
<td>yes</td>
<td>5.4</td>
<td>60300</td>
<td>155600</td>
<td>2.58</td>
<td>9.0 \times 10^{-3}</td>
<td>10.4 \times 10^{-3}</td>
<td>86.5</td>
</tr>
<tr>
<td>C4</td>
<td>2.0</td>
<td>no</td>
<td>2.2</td>
<td>9900</td>
<td>25000</td>
<td>2.52</td>
<td>0</td>
<td>11.2 \times 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>C5</td>
<td>2.5</td>
<td>yes</td>
<td>5.8</td>
<td>67300</td>
<td>182800</td>
<td>2.72</td>
<td>12.7 \times 10^{-3}</td>
<td>14.3 \times 10^{-3}</td>
<td>88.7</td>
</tr>
<tr>
<td>C6</td>
<td>2.9</td>
<td>no</td>
<td>2.5</td>
<td>10600</td>
<td>25300</td>
<td>2.39</td>
<td>2.6 \times 10^{-3}</td>
<td>15.9 \times 10^{-3}</td>
<td>16.5</td>
</tr>
<tr>
<td>R1</td>
<td>0</td>
<td>yes</td>
<td>3.7</td>
<td>50100</td>
<td>135400</td>
<td>2.70</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Indeed, the rate of dissociation of KPS can be expressed by Equation 5 that takes into account the process of acid-catalysis:

\[
k_0 = k_1 + k_2[H^+]
\]  \(5\)

\(k_0\) dramatically increases at low pH, leading to a higher rate of radical generation which explains the lower polymer molecular weights obtained in the absence of TSPP.

Moreover, the average particle diameters measured by dynamic light scattering (Table 2.7) could also account for these significant molecular weight differences. Indeed polymerization runs carried out in the absence of TSPP resulted in larger particle sizes: by comparing the initial and final number of particles \(N_p^0\) and \(N_p^f\) respectively it appears that,
when no TSPP was present, a loss of colloidal stability led to the coalescence of polymer particles into larger particles, as evidenced by the decreasing number of particles during the reaction. This is in agreement with results reported in the literature describing TSPP as a deflocculant\cite{25}. The formation of a lower number of polymer particles when no TSPP was added to the polymerization medium may thus also account for a decrease of the polymer average molecular weight, due to an increase of the flux of entering radicals per polymer particle. Indeed, if one considers the following equation that gives the rate of entry of a radical in a polymer particle ($r_{\text{entry}}$) as a function of the rate of radical generation ($\rho$) and the number of particles ($N_P$):

$$r_{\text{entry}} = \frac{\rho}{N_P} \quad (6)$$

And if it is assumed that an oligoradical propagating in a polymer particle is terminated as soon as a radical enters the particle (case 2 of the Smith-Ewart theory where $\bar{n} = 0.5$), then the rates of initiation ($r_i$), propagation ($r_P$) and termination ($r_t$) per polymer particle will be:

$$r_i = r_t = \frac{\rho}{2 \times N_P} \quad (7)$$

$$r_P = k_P \times [M]_P \times 0.5 / N_A \quad (8)$$

where $k_P$ is the propagation rate constant, $[M]_P$ the monomer concentration in polymer particles and $N_A$ the Avogadro number:

The kinetic chain length ($\nu$) can then be expressed as\cite{26}:

$$\nu = \frac{r_P}{r_t} = \frac{(k_P \times [M]_P \times 0.5 / N_A) / [\rho / (2 \times N_P)]}{(k_P \times [M]_P \times 0.5 / N_A) / [\rho / (2 \times N_P)]} \quad (9)$$
\[ v = k_p \times [M]_p \times N_p \times (\rho \times N_A) \] (9')

Equation (9') illustrates that, when no TSPP was present in the reaction medium, a higher rate of radical generation \( \rho \) and a lower average number of polymer particles \( N_p \) induced a decrease of the polymer average molecular weight.

**Table 2.7.** Average composite particle diameters and evolution of the number of particles during the second-stage emulsion copolymerization of VDC and MA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>wt% seed</th>
<th>TSPP</th>
<th>Monomer conversion (%)</th>
<th>( D_p ) (nm)</th>
<th>( N_p^0 ) (x 10^{16})</th>
<th>( N_p' )</th>
<th>( N_p'/N_p^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.0</td>
<td>yes</td>
<td>95.9</td>
<td>120</td>
<td>2.9</td>
<td>6.3</td>
<td>2.1</td>
</tr>
<tr>
<td>C3</td>
<td>1.7</td>
<td>yes</td>
<td>94.6</td>
<td>120</td>
<td>3.7</td>
<td>5.3</td>
<td>1.4</td>
</tr>
<tr>
<td>C4</td>
<td>2.0</td>
<td>no</td>
<td>97.7</td>
<td>190</td>
<td>3.0</td>
<td>2.1</td>
<td>0.71</td>
</tr>
<tr>
<td>C5</td>
<td>2.5</td>
<td>yes</td>
<td>95.5</td>
<td>127</td>
<td>3.6</td>
<td>5.2</td>
<td>1.5</td>
</tr>
<tr>
<td>C6</td>
<td>2.9</td>
<td>no</td>
<td>99.2</td>
<td>250</td>
<td>1.6</td>
<td>0.71</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The composite latex morphology was another significant feature to consider, as it may affect the properties of the final material. The graphical representation developed by Gonzalez-Ortiz et al.\(^{27}\) provided a thermodynamic prediction of the composite particles structure, by taking into account the surface tensions \( \gamma_{ij} \) at the interfaces of the three phases present in the system (first-stage polymer (1), second-stage polymer (2) and water (w)). The surface tension values of water\(^{28}\), PGMA\(^{29}\) and PVDC\(^{28}\) (as approximation of poly(VDC-co-MA) copolymer) and their corresponding polar and dispersion components \( \gamma_i^P \) and \( \gamma_i^D \) (Table 2.8) were
used to derive the values of \( \gamma_{ij} \) (by applying the harmonic-mean Equation (10) established by Wu\(^{[28]} \)) , \( T \) and \( U \) (Table 2.9). According to this diagram applied to our case (Fig.2.3), a PGMA seed would only be partially engulfed by the second-stage poly(VDC-co-MA) polymer, resulting in a snowman-like morphology.

\[
\gamma_{ij} = \gamma_i + \gamma_j - \left[ 4 \frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \right] - \left[ 4 \frac{\gamma_i^D \gamma_j^D}{\gamma_i^D + \gamma_j^D} \right]
\]  \hspace{1cm} (10)

\[
T = \frac{\gamma_{2w} - \gamma_{12}}{\gamma_{1w}}
\]  \hspace{1cm} (11)

\[
U = \frac{\gamma_{12}}{\gamma_{2w}}
\]  \hspace{1cm} (12)

**Table 2.8.** Surface tension values of water, PGMA, PBMA and PVDC and their corresponding polar and dispersion components.

<table>
<thead>
<tr>
<th></th>
<th>Surface tension ( \gamma ) (N.m(^{-1}))</th>
<th>Polar component ( \gamma^p ) (N.m(^{-1}))</th>
<th>Dispersion component ( \gamma^D ) (N.m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water(^{[28]} ) (w)</td>
<td>72.8</td>
<td>50.7</td>
<td>22.1</td>
</tr>
<tr>
<td>PGMA(^{[29]} ) (1)</td>
<td>40.1</td>
<td>32.7</td>
<td>7.46</td>
</tr>
<tr>
<td>PBMA(^{[30]} ) (1')</td>
<td>31.2</td>
<td>4.93</td>
<td>26.3</td>
</tr>
<tr>
<td>PVDC(^{[28]} ) (2)</td>
<td>45.4</td>
<td>9.08</td>
<td>36.3</td>
</tr>
</tbody>
</table>

**Table 2.9.** Values of \( \gamma_{ij} \), \( U \) and \( T \) calculated from the harmonic-mean equation.

<table>
<thead>
<tr>
<th></th>
<th>( \gamma_{12} ) (N.m(^{-1}))</th>
<th>( \gamma_{1w} ) (N.m(^{-1}))</th>
<th>( \gamma_{2w} ) (N.m(^{-1}))</th>
<th>( U )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA/PVDC</td>
<td>32.36</td>
<td>11.15</td>
<td>32.44</td>
<td>0.998</td>
<td>0.007</td>
</tr>
<tr>
<td>PBMA/PVDC</td>
<td>2.84</td>
<td>38.02</td>
<td>32.44</td>
<td>0.088</td>
<td>0.779</td>
</tr>
</tbody>
</table>
According to the same graphical representation applied to the case of a less polar first-stage polymer such as poly(n-butyl methacrylate) (PBMA)\textsuperscript{30}, the seed particles were expected to be fully encapsulated by the second-stage PVDC polymer, leading to a core-shell morphology. Therefore, we assumed that employing poly(GMA-co-BMA) as the first-stage copolymer would encourage the encapsulation process.

![Graphical representation](image)

**Fig.2.3.** Graphical representation for the prediction of the thermodynamic morphology of PGMA/PVDC and PBMA/PVDC composite particles ($U = \gamma_2/\gamma_w$, $T = |\gamma_2 - \gamma_1|/\gamma_w$). ◯: seed/first-stage polymer, ■: second-stage polymer.

Transmission electron microscopy (TEM) enabled to visualize the structure of poly(GMA-co-BMA)/poly(VDC-co-MA) composite particles. Snowman morphologies observed on pictures (Fig.2.4) showed that poly(GMA-co-BMA) seed particles were partially encapsulated by the second-stage poly(VDC-co-MA) copolymer: thus, the first-stage
copolymeryization of GMA with BMA was not sufficient to favor the encapsulation process.

**Fig.2.4.** TEM pictures of a poly(GMA-co-BMA)/poly(VDC-co-MA) composite latex.
We may also assume that in our case, the high gel content of the seed latex may have affected the final morphology. The final latex structure could indeed mainly result from kinetic limitations, due to a very limited penetration of second-stage oligoradicals into the seed polymer particles. Indeed, the diagram developed by Stubbs et al.\cite{31} applied to the present case (Fig.2.5), supports the formation of a partially encapsulated seed polymer by the second-stage polymer. Snowman morphologies were obtained instead of lobed structures certainly due to the small particle size of the seed poly(GMA-co-BMA) latexes compared to the final size of composite particles obtained in this study.

![Diagram](image)

**Fig.2.5.** Diagram of morphology development applied to the case of poly(GMA-co-BMA)/poly(VDC-co-MA) composite particles (adapted from reference\cite{31}).
2.4.3. Thermal stability of PVDC composites

Powders obtained by freeze-drying of reference and composite latexes were subjected to thermogravimetric analyses to compare their thermal stabilities (Fig.2.6). After a temperature ramp of 20°C/min during 8 min, the variation of the sample mass was measured at 160°C for 120 min in an air atmosphere. The composite particles clearly exhibited a slower degradation than the reference sample, indicating that the presence of epoxy-functionalized seeds was beneficial for the PVDC thermal stability. The impact of poly(GMA-co-BMA) on the polymer degradation appears to be double: it does not only inhibit the period of initiation of dehydrochlorination, but also slows down the propagation step.

Fig.2.6. Thermogravimetric analyses carried out at 160°C for 120 min in an air atmosphere for the composite particles and the reference PVDC powders.
To quantify the effects of epoxy-functionalized seeds on PVDC degradation, first order rate constants of initiation ($k_{\text{init}}$) and propagation ($k_{\text{prop}}$) of the polymer dehydrochlorination\textsuperscript{32-34} were determined via the local slopes of $\ln((w_\infty - w_0)/(w_\infty - w_t))$ versus $t$, where $w_0$ is the initial sample weight, $w_t$ the sample weight at a given time $t$ and $w_\infty$ is the sample weight at infinite time corresponding to the loss of 1 mol of HCl per VDC unit in the polymer ($w_\infty = 0.7238 \times w_0$). The values given in Table 2.10 confirm that the presence of epoxy-functionalized seed polymer in composite latexes resulted in slowing down the evolution of HCl during both initiation and propagation steps of the degradation process.

**Table 2.10.** Rate constants for the dehydrochlorination of composite and reference PVDC powders at 160°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Poly(GMA-co-BMA) content (%)</th>
<th>$k_{\text{init}} \times 10^4$ (s$^{-1}$)</th>
<th>$k_{\text{prop}} \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>2.5</td>
<td>0.87</td>
<td>11</td>
</tr>
<tr>
<td>C3</td>
<td>1.7</td>
<td>1.3</td>
<td>11</td>
</tr>
<tr>
<td>C1</td>
<td>1.0</td>
<td>4.0</td>
<td>9.7</td>
</tr>
<tr>
<td>R1</td>
<td>0</td>
<td>4.7</td>
<td>17</td>
</tr>
</tbody>
</table>

On the contrary, in the case of composites obtained without TSPP, the polymer dehydrochlorination appeared to be faster than for the reference sample. This could originate from the fact that chain ends are believed to be the main defects contributing to the degradation of low molecular weight PVDC copolymers, although conflicting results were reported concerning a possible correlation between molecular weights and dehydrochlorination rates\textsuperscript{35-37}. Furthermore, in this case most epoxy groups (at least 80%) were hydrolyzed during the second-stage polymerization process, and could not contribute to the polymer
stabilization. Thereby both effects may have contributed to a worsened thermal stability.

To verify our assumption that chain ends did take part in the polymer degradation, conventional PVDC latexes were synthesized targeting three different molecular weights. Table 2.11 shows the characteristics of these latexes.

**Table 2.11.** Characteristics of reference PVDC latexes R1, R1’ and R1”.

<table>
<thead>
<tr>
<th>Entry</th>
<th>TSPP</th>
<th>Latex</th>
<th>Monomer conversion (%)</th>
<th>Dp (nm)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1’</td>
<td>yes</td>
<td>2.3</td>
<td>94.4</td>
<td>138</td>
<td>93200</td>
<td>271000</td>
<td>2.90</td>
</tr>
<tr>
<td>R1</td>
<td>yes</td>
<td>3.7</td>
<td>92.5</td>
<td>143</td>
<td>50100</td>
<td>135400</td>
<td>2.70</td>
</tr>
<tr>
<td>R1”</td>
<td>yes</td>
<td>1.3</td>
<td>100</td>
<td>151</td>
<td>31300</td>
<td>113900</td>
<td>3.63</td>
</tr>
</tbody>
</table>

TGA analyses performed on freeze-dried samples of these PVDC latexes tended to confirm our hypothesis (Fig.2.7). Faster dehydrochlorination rates were indeed measured for PVDC copolymers displaying shorter polymer chain lengths. This result is in line with the trend observed when comparing the thermal degradation of PVDC samples synthesized in the presence or in the absence of TSPP.

Additionally, thermogravimetric analyses were carried out on a composite and a reference PVDC powder to study the effect of the air flow rate surrounding the sample on the dehydrochlorination rate. One would usually expect a higher air flow rate to accelerate the degradation process due to a faster replacement of an oxidizing environment. Yet, in the case of poly(vinylidene chloride), higher flow rates tended to slow down the
Synthesis of PVDC composite latexes from epoxy-functional seeds

dehydrochlorination process, as evidenced by the mass loss curves plotted in Fig.2.8.

**Fig.2.7.** Thermogravimetric analyses carried out at 160°C for 120 min under air atmosphere on poly(VDC-co-MA) copolymers of different molecular weights.

This could arise from two different factors:

- A better elimination of evolved hydrochloric acid from the sample environment may limit the indirect catalytic effect played by HCl on the degradation reaction. This argument is strongly supported by the fact that epoxy groups act as thermal stabilizers by scavenging hydrochloric acid released from the polymer.

- PVDC degradation mechanism occurring via a radical process, oxygen could have an inhibiting effect on the dehydrochlorination reaction: this assumption is also in line with results reported by
Hsieh et al., who evidenced an effect of retardation of PVDC dehydrochlorination due to the influence of an oxygen atmosphere\cite{38}.

**Fig.2.8.** Thermogravimetric analyses carried out at 160°C on composite and reference PVDC powders at different air flow rates.

The variations of the rate of degradation induced by changes in the air flow rate justified the fact that all TGA analyses discussed in this chapter were carried out at a constant air flow rate of 100 mL/min.
2.4.4. Thermal stability of other systems

Considering the beneficial role played by epoxy groups in limiting the polymer degradation, the use of more simple systems could also be considered to impart the polymer an enhanced thermal stability. Two types of alternative systems were studied: 1) blends of poly(GMA-co-BMA) seeds and poly(VDC-co-MA) reference latexes and, 2) a poly(VDC-co-MA-co-GMA) terpolymer latex.

Thermal stability of polymer latex blends

Two poly(GMA-co-BMA) latexes (S3 and S7) were mixed to the reference latex R1 so as to obtain latex blends with similar seed contents as composite latexes C5 (2.5%) and C3 (1.7%). These latex blends were then subjected to freeze-drying and resulting powders were analyzed by thermogravimetry (Fig.2.9). The blends exhibited a slower degradation than the reference sample but showed a slightly shorter inhibition period than their respective composite counterparts. This results bring us to the conclusion that the sample nanostructure had an impact on the polymer thermal stability. This effect may originate from the quality of the dispersion of poly(GMA-co-BMA) particles into the poly(VDC-co-MA) matrix. Blends of the two latexes could indeed result in the formation of larger poly(GMA-co-BMA) domains and thus HCl may be scavenged more efficiently by epoxy groups in the case of composite structures due to a more intimate contact between the two polymer phases. Along the same line, one can assume that PVDC films obtained from composite latexes will exhibit a further enhanced stability compared to reference samples, given that an even more intimate contact between the poly(GMA-co-BMA) seed particles and the poly(VDC-co-MA) matrix can be expected in film forming situations.
Fig. 2.9. Mass loss of composite, blend and reference PVDC powders versus time at 160°C under air atmosphere.

Fig. 2.10. Visual comparison of PVDC powders after 120 min of exposure to a temperature of 160°C under air atmosphere.
Pictures of the powders taken at the end of TGA analyses (Fig.2.10) provided a visual confirmation of the stabilizing role of poly(GMA-co-BMA) seeds. PVDC coloration originates from the creation of conjugated polychloroacetylene sequences into the polymer chains upon dehydrochlorination\[37\]. The evolution of color observed on degraded samples is therefore in good agreement with the trends indicated by TGA experiments. These pictures also made clearly visible the better thermal stability of composites compared to their corresponding blends.

**Poly(VDC-co-MA-co-GMA) terpolymer**

A poly(VDC-co-MA-co-GMA) terpolymer latex (with a 90:7.5:2.5 VDC:MA:GMA mass ratio) was synthesized following a similar procedure as the one employed for the synthesis of reference PVDC latexes. To evaluate the terpolymer thermal stability, isothermal TGA analyses were again carried out at 160°C for 2h and compared with results obtained on freeze-dried samples of composite (C5’) and reference (R1’) PVDC latexes of similar characteristics (Table 2.12).

**Table 2.12. Characterization of PVDC composite, reference and terpolymer latexes.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>GMA content (%)</th>
<th>TSPP</th>
<th>pH</th>
<th>Monomer conversion (%)</th>
<th>DP (nm)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mw/Mn</th>
<th>Gel content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5’</td>
<td>2.3</td>
<td>yes</td>
<td>5.1</td>
<td>99.2</td>
<td>121</td>
<td>93100</td>
<td>287700</td>
<td>3.09</td>
<td>ca. 2.5</td>
</tr>
<tr>
<td>R1’</td>
<td>0</td>
<td>yes</td>
<td>2.3</td>
<td>94.4</td>
<td>138</td>
<td>93200</td>
<td>271000</td>
<td>2.90</td>
<td>n.d.</td>
</tr>
<tr>
<td>T1</td>
<td>2.4</td>
<td>yes</td>
<td>5.4</td>
<td>94.7</td>
<td>172</td>
<td>99400</td>
<td>311000</td>
<td>3.12</td>
<td>23.1</td>
</tr>
</tbody>
</table>
According to the mass time history presented in Fig. 2.11, glycidyl methacrylate, as a comonomer of vinylidene chloride, did not impart PVDC an enhanced thermal stability, but actually even promoted the polymer dehydrochlorination.

**Fig. 2.11.** Comparison of the weight loss of composite and reference PVDC and poly(VDC-co-MA-co-GMA) terpolymer versus time at 160°C under air atmosphere.

On the one hand we assume that a high percentage of epoxy groups was hydrolyzed during the emulsion terpolymerization of vinylidene chloride, methyl acrylate and glycidyl methacrylate despite the presence of tetrasodium pyrophosphate in the recipe. Unfortunately the HBr titration did not enable to verify this hypothesis, given that the titration curves did not show any clear equivalence point. On the other hand, the fact that the terpolymer displayed a faster dehydrochlorination rate compared to
poly(vinylidene chloride-co-methyl acrylate) could be explained by the presence of methacrylate units in the polymer chain. Indeed Collins et al. showed that vinylidene chloride – methacrylate copolymers degrade faster than vinylidene chloride – acrylate copolymers when subjected to high temperatures.

Furthermore the terpolymer exhibited a higher gel content (about 23%) compared to the reference and composite PVDC samples: this result was still attributed to the presence of dimethacrylates impurities in the glycidyl methacrylate monomer. This is an important point to consider, given that a higher gel content could result in poorer film-forming properties.

2.4.5. Barrier properties of films obtained from composite latexes and blends

PVDC films were obtained by bare coating of the latexes on poly(ethylene terephtalate) (PET) film substrates. Reference and composite films displayed a good transparency, which suggests that the composite structures did not affect the latex film formation properties. In the case of blends, mixing of the seed and reference latexes induced a poor colloidal stability of the system, which accounts for a slight whitening of the final films.

The results of oxygen permeability measurements performed on PVDC/PET films are given in Table 2.13. A slight increase of the oxygen permeability could be observed between the composite and reference PVDC samples: this is in agreement with results reported earlier by Brown et al. who measured higher oxygen permeabilities on PVDC films.
obtained from poly(butyl acrylate)/poly(VDC-co-acrylonitrile) composite latexes when increasing the fraction of poly(butyl acrylate) seed polymer. Films obtained from direct blends of seed and reference PVDC latexes displayed comparable barrier properties to composites, while PVDC composites obtained in the absence of TSPP showed the highest values of oxygen permeabilities: this could originate from the lower molecular weights of the polymer, resulting in a lower degree of crystallinity and a higher contribution of polar chain ends. Nevertheless, due to the lack of precision on the film preparation by bare coating, these values should be treated with great caution. We may indeed expect to obtain more reliable and reproducible results on PVDC films coated via industrial processes.

Table 2.13. Oxygen permeabilities measured on PVDC films bare coated on PET substrates.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Seed content (%)</th>
<th>TSPP</th>
<th>Permeability to oxygen (cm³.μm⁻¹.m⁻².day⁻¹.bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>/</td>
<td>yes</td>
<td>27.5</td>
</tr>
<tr>
<td>C1</td>
<td>1.00</td>
<td>yes</td>
<td>36.1</td>
</tr>
<tr>
<td>C3</td>
<td>1.65</td>
<td>yes</td>
<td>36.1</td>
</tr>
<tr>
<td>C5</td>
<td>2.54</td>
<td>yes</td>
<td>37.5</td>
</tr>
<tr>
<td>C4</td>
<td>1.99</td>
<td>no</td>
<td>42.3</td>
</tr>
<tr>
<td>C6</td>
<td>2.87</td>
<td>no</td>
<td>39.8</td>
</tr>
<tr>
<td>Blend 1.5%</td>
<td>1.50</td>
<td>yes</td>
<td>35.6</td>
</tr>
<tr>
<td>Blend 2.5%</td>
<td>2.50</td>
<td>yes</td>
<td>38.8</td>
</tr>
</tbody>
</table>

2.5. Conclusions

Poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes were synthesized via a two-stage emulsion polymerization process. The
conditions of temperature and pH were controlled to limit the hydrolysis of epoxy groups during the first-stage emulsion copolymerization of glycidyl methacrylate and butyl methacrylate, while the monomer feed rate could be adjusted in order to control the seed particle diameter. Due to its role of HCl-scavenger, TSPP appeared to be a key component during the seeded second-stage emulsion copolymerization of vinlylidene chloride and methyl acrylate to limit the hydrolysis of epoxy groups, to provide a good colloidal stability and to obtain higher molecular weights.

Isothermal thermogravimetric analyses carried out on freeze-dried samples obtained from poly(GMA-co-BMA)/poly(VDC-co-MA) latexes showed that composites displayed an enhanced thermal stability compared to PVDC reference samples, which confirmed the role played by epoxy groups in the thermal stabilization of PVDC. Blends of poly(GMA-co-BMA) and PVDC latexes showed less satisfactory results than composite samples, but still displayed an enhanced thermal stability compared to conventional PVDC. Finally, the direct terpolymerization of vinlylidene chloride, methyl acrylate and glycidyl methacrylate resulted in a polymer with a poor thermal stability compared to other systems studied.

PVDC films obtained by bare coating of the composite latexes displayed a good transparency. Measurements of oxygen permeability performed on these films showed that the incorporation of poly(GMA-co-BMA) seed polymers into the PVDC matrix resulted in a slight increase of the polymer permeability towards oxygen. Additional characterization should, however, be conducted on more uniformly coated films in order to draw final conclusions on the barrier properties of films obtained from poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes.
Among all the systems studied in this chapter, we may conclude that poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes appear to be the most suitable candidates for use as waterborne barrier films with improved thermal stability.

References

Synthesis of PVDC composite latexes from epoxy-functional seeds


Chapter 3. Synthesis of cerium oxide-based hybrid latexes - The silane route

Abstract

This chapter deals with the synthesis of CeO_2/polymer hybrid latexes employing an alkoxy silane as surface-modifier to promote the polymerization reaction at the surface of nanoceria. In a first step, methacryloxypropyl trimethoxysilane (MPTMS) was reacted with cerium oxide nanoparticles in aqueous acidic conditions. Characterization of the grafting efficiency was attempted via thermogravimetric analyses (TGA) and elemental analyses performed on dry cerium oxide powders. In a second step, emulsion copolymerizations of styrene and methyl acrylate as well as vinylidene chloride and methyl acrylate were carried out in the presence of modified cerium oxide particles. TEM and cryo-TEM observations showed that the resulting polymer particles displayed an anisotropic structure. However, the latter imaging technique appeared to be a more accurate tool to assess the actual latex structure in the dispersed state.
3.1. Introduction

Apart from thermal degradation, the UV degradation of poly(vinylidene chloride) is another major issue to be circumvented as it also leads to yellowing and an increase of the polymer permeability towards gases under exposure to UV radiation. Among the wide range of existing UV absorbers, cerium oxide nanoparticles are very promising candidates as they have already been proven to impart waterborne PVDC films an enhanced UV-stability by direct mixing of aqueous dispersions of CeO\textsubscript{2} nanoparticles with poly(vinylidene chloride) latexes\textsuperscript{[1]}. Nevertheless, we may assume that without a preliminary step of surface-modification of these mineral objects, they might tend to form aggregates in the polymer matrix. This aggregation would result in a decrease of the film transparency and a less efficient UV absorption. Moreover, due to the current lack of knowledge on the toxicity of nanoceria, a link between the oxide and the polymer is preferable to avoid problems of migration of the particles towards the film surface.

This chapter will first provide a short description of the synthesis and properties of nanoceria. After a detailed description of the experimental procedures and the tools employed for this study, results on the grafting of an alkoxysilane at the surface of cerium oxide particles performed in aqueous conditions will be discussed, as well as the subsequent synthesis and characterization of CeO\textsubscript{2}/polymer hybrid latexes carried out in the presence of surface-modified nanoceria.
3.2. Nanometric cerium oxide dispersions – Synthetic routes and properties

Cerium oxide-based materials, owing to their excellent properties, have been studied extensively for application in various fields\(^2\), for instance as engine exhaust catalysts\(^3,4\), polishing agents\(^5,6\), UV filters\(^7-9\) or as solid electrolytes in fuel cells\(^10-12\). In particular cerium oxide nanoparticles have become increasingly attractive as UV blocking agents\(^13-15\) due to their good absorption of UV radiation and a relative transparency in the visible region. Furthermore, their photocatalytic activity may be greatly reduced by doping with calcium oxide or zinc oxide\(^16\), making them suitable for use as additives in polymeric materials. Polymerization processes carried out in the presence of cerium oxide nanoparticles have therefore recently attracted much interest\(^17,18\).

Among the great variety of processes described in the literature to obtain cerium oxide\(^19,20\) (Fig.3.1), the synthesis of aqueous dispersions of nanoceria (with a particle size less than 10 nm) can be achieved by thermohydrolysis\(^21-24\) of an aqueous solution of cerium-IV nitrate salt Ce(NO\(_3\))\(_4\) at relatively high temperatures (70°C) under continuous addition of hydroxide ions (by means of an ammonia solution for instance). This procedure results in the precipitation of a CeO\(_2\) nanoparticles “pulp”. The precipitated nanoparticles contained in the “pulp” can then be easily redispersed by simple dilution. This technique enables to obtain relatively monodisperse CeO\(_2\) particles and a good control of the particle size by adjusting the amount of OH\(^-\) ions added during the hydrolysis step.

According to the theory of Verwey and Overbeek, electrostatic repulsions should not be sufficient to prevent the aggregation of such
nanometric particles due to their low potentials of interaction (less than 15 kT)\[25\]. However, in the specific case of nanoceria obtained via this process, the presence of nitrate counterions adsorbed on the surface of cerium oxide particles enables to maintain their colloidal stability at pH < 3 (well below the point of zero charge of pure cerium oxide situated at a pH of 7.9\[22\]) and at ionic strengths lower than 0.55 M\[22,26\]. Above a pH of 3, reversible precipitation of the sol is observed\[22\], while above a pH of 5 an irreversible precipitation occurs due to the desorption of nitrate ions from the oxide surface. Therefore, to maintain the colloidal stability of the system over a wider range of pH and ionic strengths, several types of dispersants (also called ligands or peptizers) (Fig.3.2), can be employed\[27-30\]. These dispersants consist of polyfunctional compounds, typically citrate\[13,28,29,31\], poly(acrylic acid)\[23,29\], oxalate, phosphates or phosphonates\[30,32\], that can be added during or after the synthesis to form complexes with the oxide surface and increase the electrostatic repulsions between the particles.

**Fig.3.1:** General procedure for the preparation of cerium oxide (from reference\[20\] with permission from Elsevier).
The main consequence of the complexation of the oxide by such dispersants is a change of the range of pH where the colloidal stability of the particles is maintained: for instance in the case of poly(acrylic acid) (or citric acid) coated ceria, the particles become stable at pH > 5, where the carboxylic acid functions are in their anionic form. Actually, the complexation of cerium oxide particles by poly(acrylic acid) occurs through a precipitation-redispersion mechanism\cite{23}: precipitation of the particles at a pH of 1.4 (where poly(acrylic acid is in its neutral form), followed by a redispersion by raising the pH above 7, where the dispersing agent is in its anionic form.

Fig. 3.2: Chemical formulas and pKa values of some typical dispersing agents in their sodium salt form.
3.3. Experimental section

3.3.1. Materials

Styrene (Sty, Aldrich, ≥99%), methyl acrylate (MA, Aldrich, 99%) were purified through columns of inhibitor removers (Aldrich). Vinilidene chloride (Solvay, containing 80 ppm of butylated hydroxytoluene) and methyl acrylate (Arkema, containing less than 20 ppm of 4-methoxyphenol), employed for the synthesis of CeO₂/PVDC hybrid latexes, were used as received. The cerium oxide nanoparticles dispersion (Nanobyk 3810, 18 wt% cerium oxide, 23 wt% solid content, containing triammonium citrate as dispersing agent, BYK Chemie), was used as received. Methacryloxypropyl trimethoxysilane (MPTMS, Aldrich, 98%), sodium dodecylbenzene sulfonate (SDBS, Aldrich, technical grade, 96%, or Disponil LDBS 25, BASF, 50 wt% aqueous solution), tetrasodium pyrophosphate (TSPP, Budenheim) and 2,2'-Azobis[N-(2-carboxyethyl)-2-methylpropionamidine]hydrate (VA-057, Wako, purity >95%) were used as received. Water was deionized through an ion-exchange resin (conductivity below 1 μS/cm).

3.3.2. Surface-modification of cerium oxide nanoparticles

A 2 wt% cerium oxide aqueous solution was prepared by dilution of the commercial cerium oxide dispersion. The pH was adjusted from pH = 7 to the desired value (pH = 5) by addition of the required amount of an aqueous 0.25 N nitric acid solution. The cerium oxide dispersion was placed in a 3-neck double-walled 250 mL reactor equipped with a 6-bladed stainless-steel turbine impeller. A 5 mL syringe (equipped with a tubing and a needle) was filled with the methacryloxypropyl trimethoxysilane solution,
mounted on a KDS270 syringe pump (KD Scientific) and connected to a reactor feed point. If the addition of surfactant was required to provide colloidal stability during the grafting reaction, a 22 g/L aqueous solution of surfactant (SDBS) was prepared in a volumetric flask of 250 mL. A 765 Dosimat dosing pump (Metrohm) was filled with the surfactant solution and the output side of the dosing pump connected to the reactor. After setting the mechanical stirring system at a speed of 500 rpm, the continuous injections of the alkoxysilane (at a rate of 44 μL/h) and the surfactant solution (at a rate of 20.8 μL/min) were started. Once the continuous feedings of the alkoxysilane and the surfactant were completed, the reaction was left for two additional hours before switching off the stirring system.

To characterize the grafting efficiency, two different purification techniques were employed to remove the unreacted silanes from the cerium oxide dispersion:

**Ultracentrifugation.** 12 g of surface-modified cerium oxide dispersions were placed in polyallomer tubes filled with an additional amount of 12 g of deionized water. The closed tubes were placed symmetrically in a rotor 70 Ti in an Optima L-90K (Beckman Coulter) ultracentrifuge. After a cycle of 2 h at 40000 rpm at 20°C, 2/3 of the serum was replaced with deionized water in each tube and the cerium oxide dispersion was redispersed by shaking the tube manually. The same ultracentrifugation procedure was repeated 5 times.

**Dialysis.** 20 mL of silane-grafted cerium oxide dispersion were placed in a Spectra/por 6 dialysis tubing (Spectrum Laboratories, molecular weight cut
off (MWCO) of 1000 g/mol) and dialyzed 4 times against large volumes (about 3 L) of deionized water.

The purified cerium oxide dispersions were then dried overnight at 50°C under vacuum conditions, and the resulting dry crystals were crushed to powders in a mortar. A second drying cycle was performed under vacuum at 90°C for 1 hour to remove excess water from the cerium oxide surface.

### 3.3.3. Polymerizations

The emulsion copolymerization of styrene and methyl acrylate was carried out in the presence of surface-modified cerium oxide particles. The initial load, containing the silane-grafted cerium oxide aqueous dispersion diluted in deionized water, a solution of the monomers (styrene and methyl acrylate in a 90:10 mass ratio / 88:12 molar ratio), a surfactant aqueous solution (SDBS) and a 9.5 g/L initiator aqueous solution (VA-057) were purged separately with argon during 30 min. The initial load was introduced in a 3-neck 250 mL double-walled reactor equipped with a condenser and maintained under argon atmosphere. Continuous stirring of the medium at 250 rpm was ensured by a 6-bladed stainless steel turbine impeller, and the temperature in the reactor was controlled with a continuous flow of thermostated water delivered by a MGW Lauda M3 circulating water bath. Once the reactor had reached the temperature of 60°C, a shot of 10 mL of the initiator solution was injected to the reaction medium and the monomer feed (at a rate of 51.1 μL/min to achieve monomer starved conditions) and surfactant feed (at a rate of 69.4 μL/min) via two Dosimat 765 dosing pumps (Metrohm) were started and maintained for 6 hours. Afterwards the
The reactor was maintained at reaction temperature and under stirring for an additional 2 hours.

The emulsion copolymerization of vinylidene chloride and methyl acrylate was carried out in the presence of surface-modified cerium oxide nanoparticles according to the following procedure. The initial load, containing the silane-grafted cerium oxide dispersion, tetrasodium pyrophosphate and the initiator (VA-057) were injected in a 2L Parr autoclave (model 4534, Parr instruments). After starting the mechanical stirring at a speed of 250 rpm, the reactor was subjected to two cycles of vacuum at a pressure of 0.14 bar. The atmospheric pressure was then restored by injection of nitrogen in the autoclave and the temperature was raised to 60°C with a JULABO thermostated bath connected to the reactor envelope and controlled with an internal PT 100 temperature probe. Continuous feeds of a monomer solution (at a rate of 83.3 g/h, vinylidene chloride:methyl acrylate mass ratio of 90:10 / molar ratio of 89:11) and an aqueous solution of surfactant (Disponil LDBS 25) and TSPP (at a rate of 8.2 g/h) were carried out via two separate LEWA FCKMK2 dosing pumps for 6h. The reaction was maintained for an additional hour after the end of the injections. The latex was then stripped for 1 hour at 70°C under continuous stirring.

3.3.4. Characterization

**TGA analyses.** To characterize the silane grafting efficiency at their surface, cerium oxide powders were analyzed on a TGA apparatus Q50 (TA Instruments). Analyses consisted of a ramp of 10°C/min from room temperature to 90°C, followed by an isotherm of 15 min at 90°C and a ramp
of 10°C/min from 90°C to 580°C. The sample was subjected to a constant air flow rate of 100 mL/min during the analysis.

The grafting efficiency (Eff\textsubscript{grafting}) was then calculated from the equation:

\[
\text{Eff\textsubscript{grafting}} \, (\%) = \frac{\% \text{silane}_{\text{exp}} \times 100}{\% \text{silane}_{\text{theo}}} \quad (1)
\]

where \%\text{silane}_{\text{exp}} and \%\text{silane}_{\text{theo}} correspond to the experimental and theoretical weight percentages of grafted silane:

\[
\% \text{silane}_{\text{exp}} = 10^4 / \left[100 + (100 - ML_0) \times (100 - ML) / (ML - ML_0)\right] \quad (2)
\]

\[
\% \text{silane}_{\text{theo}} = 100 \times \frac{m_{\text{silane}}}{m_{\text{CeO}_2} \times (M_{\text{silane}} / M_{\text{silanol}}) + m_{\text{silane}}} \quad (3)
\]

with $ML_0$ the mass loss (in %) measured between 90 and 580°C for the bare cerium oxide powder, $ML$ the mass loss (in %) measured for the surface-modified cerium oxide, $m_{\text{CeO}_2}$ the mass of cerium oxide engaged in the grafting process, $m_{\text{silane}}$ the mass of silane added, $M_{\text{silane}}$ the molar mass of the alkoxy silane ($M_{\text{silane}} = 248.35 \text{ g/mol}$) and $M_{\text{silanol}}$ the molar mass of the grafted silanol specie ($M_{\text{silanol}} = M_{\text{silane}} - 3 \times M_C - 9 \times M_H = 203.25 \text{ g/mol}$).

**Elemental analyses.** Elemental analyses (carbon and silicon) were sent to Mikroanalytisches Labor Kolbe, Germany.

The grafting efficiency (Eff\textsubscript{grafting}) was calculated via the following equations:

\[
\text{Eff\textsubscript{grafting} (from C)} = \frac{(%C_{\text{exp}} - %C_0) \times 100}{%C_{\text{theo}}} \quad (4)
\]

\[
\text{Eff\textsubscript{grafting} (from Si)} = \frac{(%Si_{\text{exp}} - %Si_0) \times 100}{%Si_{\text{theo}}} \quad (5)
\]
where $\% C_0$ ($\% S_{i0}$) corresponds to the carbon (silicon) content of the bare cerium oxide powder, $\% C_{\text{exp}}$ ($\% S_{i\text{exp}}$) the carbon (silicon) content of the surface-modified cerium oxide powder and $\% C_{\text{theo}}$ and $\% S_{i\text{theo}}$ are the theoretical carbon and silicon contents obtained from the following equations:

$$\% C_{\text{theo}} = 100 \times \frac{m_{\text{silane}}}{m_{\text{CeO}_2} \times \left( \frac{M_{\text{silane}}}{7M_C} + m_{\text{silane}} \right)} \quad (6)$$

$$\% S_{i\text{theo}} = 100 \times \frac{m_{\text{silane}}}{m_{\text{CeO}_2} \times \left( \frac{M_{\text{silane}}}{M_S} + m_{\text{silane}} \right)} \quad (7)$$

The calculations of theoretical carbon and silicon content were performed assuming a complete hydrolysis and condensation of every silane function of MPTMS (Scheme 3.1).

![Scheme 3.1. Chemical formula of methacryloxypropyl trimethoxysilane (MPTMS).](image)

**Particle size and $\zeta$-potential measurements.** Latex particle size distributions and average particle diameters were determined by dynamic light scattering (DLS) with a Zeta Nano ZS particle size analyzer (Malvern Instruments Ltd).
The same instrument was employed for pH-dependent average particle size and \( \zeta \)-potential measurements carried out on the CeO\(_2\) dispersion. A 2 g/L cerium oxide dispersion was prepared at pH 10 by dilution of the commercial dispersion and addition of a 0.1 N sodium hydroxide solution. A 10 mL sample was placed in a MPT-2 autotitrator (Malvern Instruments Ltd) and connected to a folded capillary cell. For each measurement, the pH was automatically measured and adjusted by the instrument by addition of small amounts of 0.1 N HCl and 0.1 N NaOH solutions.

**TEM and cryo-TEM microscopy.** Samples were prepared by 1/100 dilution of CeO\(_2\)/poly(styrene-co-methyl acrylate) latexes in DI water. A 3 \( \mu \)L drop of the sample was deposited on a carbon-coated grid (glow-discharged for 40 s prior to use).

The preparation of samples for cryo-TEM observations involved a vitrification procedure on a FEI Vitrobot Mark 3. A 3 \( \mu \)L sample (about 5 wt\% solid content) was applied to a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; glow discharged for 40 s just prior to use) within the environmental chamber of the Vitrobot and the excess liquid was blotted away. The sample was shot into melting ethane and immediately transferred to a cryoholder (Gatan 626) and observed under low dose conditions at -170 °C.

Both TEM and cryo-TEM pictures were obtained using a FEI Tecnai 20, Sphera TEM microscope (LaB\(_6\) filament, operating voltage of 200 kV).
3.4. Results and discussion

3.4.1. Surface-modification of cerium oxide particles and characterization of the grafting efficiency

Cerium oxide nanoparticles employed for this work were provided as an aqueous dispersion. The particles displayed non-spherical structures, corresponding to clusters of 3 to 4 crystallites of about 3 nm size each (Fig. 3.3).

![Fig. 3.3. TEM picture of cerium oxide nanoclusters.](image)

The CeO$_2$ nanoparticles dispersion contained a certain amount of triammonium citrate, a complexing agent that imparts the dispersion a good colloidal stability above a pH of 4. $\zeta$-potential measurements coupled with particle size analyses were carried out as a function of the pH to evaluate the stability of the dispersion. The results collected in Fig. 3.4 confirmed that
a stability threshold was reached at a pH of 4, below which large aggregates were formed and redispersion was difficult.

Fig. 3.4. Particle size and ζ-potential measurements as a function of the pH (for a constant cerium oxide concentration of 2 g/L).

The poor colloidal stability of the dispersion at low pH was a very limiting factor when performing the grafting of alkoxy silanes at the surface of cerium oxide nanoparticles. Indeed, considering that the rate of condensation of alkoxy silanes is higher than their hydrolysis rate at pH > 7 in aqueous media, the surface-modification should be carried out at a pH as low as possible in order to favor the grafting reaction over the self-condensation of silanes. The surface-modification of cerium oxide nanoparticles was carried out at a pH of 5, employing methacryloxypropyl trimethoxysilane (MPTMS) as coupling agent and a constant cerium oxide concentration of 2 wt%. Furthermore, the alkoxy silane was added slowly to the cerium oxide dispersion to maintain low local concentrations of silane molecules in the medium and attempt to minimize its self-condensation.
Experiments thus consisted in the slow addition of MPTMS to the cerium oxide dispersion at room temperature under vigorous stirring (Table 3.1).

The targeted grafting density (in molecules/nm²) is calculated via the equation:

$$Graft_{theo} = \frac{m_{silane} \times \rho_{CeO_2} \times D_{CeO_2} \times N_A}{6 \times m_{CeO_2} \times M_{silane}}$$  \hspace{1cm} (8)$$

where $m_{CeO_2}$ corresponds to the mass of cerium oxide engaged in the grafting process, $m_{silane}$ the mass of alkoxysilane added, $M_{silane}$ the molar mass of the alkoxysilane, $N_A$ the Avogadro number, $\rho_{CeO_2}$ the density of cerium oxide ($\rho_{CeO_2} = 7.13 \text{ g/cm}^3 = 7.13 \times 10^{-21} \text{ g/nm}^3$), $D_{CeO_2}$ the volume average diameter of cerium oxide particles ($D_{CeO_2} = 8 \text{ nm}$).

Table 3.1. Recipes for the grafting of MPTMS at the surface of cerium oxide nanoparticles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Targeted grafting density (molecule/nm²)</th>
<th>Initial load</th>
<th>Silane</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CeO₂</td>
<td>HNO₃</td>
<td>Water</td>
<td>MPTMS</td>
</tr>
<tr>
<td>G1</td>
<td>1.0</td>
<td>12.02</td>
<td>0.10</td>
<td>94.90</td>
</tr>
<tr>
<td>G2</td>
<td>2.0</td>
<td>12.00</td>
<td>0.10</td>
<td>95.76</td>
</tr>
<tr>
<td>G2'</td>
<td>1.9</td>
<td>12.01</td>
<td>0.09</td>
<td>89.90</td>
</tr>
<tr>
<td>G4</td>
<td>3.8</td>
<td>12.00</td>
<td>0.09</td>
<td>83.96</td>
</tr>
<tr>
<td>G10</td>
<td>9.5</td>
<td>12.00</td>
<td>0.10</td>
<td>86.17</td>
</tr>
</tbody>
</table>

For a low targeted grafting density (1 molecule/nm²), the dispersion remained stable and did not require the addition of any extra stabilizer.
However, when higher grafting densities were targeted (> 1.9 molecules/nm\(^2\)), the cerium oxide dispersion became unstable as evidenced by an increasing turbidity of the medium and confirmed by DLS analyses (Table 3.2). We attributed this loss of colloidal stability to an increase of the hydrophobicity of cerium oxide particles due to their surface-modification by MPTMS. When a surfactant – sodium dodecylbenzene sulfonate (SDBS) – was continuously added during the process, clearer dispersions were obtained, although DLS analyses indicated that aggregation of particles still occurred to a certain extent. Moreover, according to the scientific literature\(^{[34]}\), the presence of a surfactant is recommended to facilitate the dispersion of alkoxysilanes in water and to increase the efficiency of the grating process.

**Table 3.2.** Average particle diameters of silane-grafted cerium oxide particles measured by DLS (\(D_p^I\): intensity mean particle diameter; \(D_p^V\): volume mean particle diameter; \(D_p^N\): number mean particle diameter).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Targeted grafting density (molecule/nm(^2))</th>
<th>CeO(_2) content (wt%)</th>
<th>(D_p^I) (nm)</th>
<th>(D_p^V) (nm)</th>
<th>(D_p^N) (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.95</td>
<td>2.0</td>
<td>10</td>
<td>7.8</td>
<td>6.4</td>
<td>0.13</td>
</tr>
<tr>
<td>G2</td>
<td>1.95</td>
<td>2.0</td>
<td>65</td>
<td>7.9</td>
<td>6.5</td>
<td>3.6</td>
</tr>
<tr>
<td>G2'</td>
<td>1.90</td>
<td>2.0</td>
<td>60</td>
<td>8.2</td>
<td>6.9</td>
<td>0.33</td>
</tr>
<tr>
<td>G4</td>
<td>3.81</td>
<td>2.0</td>
<td>160</td>
<td>8.4</td>
<td>7.0</td>
<td>0.27</td>
</tr>
<tr>
<td>G10</td>
<td>9.51</td>
<td>2.0</td>
<td>770</td>
<td>33</td>
<td>8.3</td>
<td>0.72</td>
</tr>
</tbody>
</table>

To characterize the grafting efficiency, surface-modified cerium oxide dispersions were purified via two procedures, dialysis and ultracentrifugation, to eliminate the unreacted and the self-condensed silanes from the medium. Cerium oxide dispersions were then dried and crushed to powders. Attempts to characterize the grafting efficiency were
then carried out by thermogravimetric and elemental analyses (Tables 3.3 and 3.4).

**Table 3.3.** Characterization of the silane grafting efficiency by TGA analyses.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mass loss (%)</th>
<th>% silane grafted exp</th>
<th>% silane grafted theo</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
<th>Mass loss (%)</th>
<th>% silane grafted exp</th>
<th>% silane grafted theo</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>17.9</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>12.6</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>G1</td>
<td>17.9</td>
<td>0</td>
<td>3.28</td>
<td>0</td>
<td>13.9</td>
<td>1.70</td>
<td>3.28</td>
<td>51.8</td>
</tr>
<tr>
<td>G2'</td>
<td>19.1</td>
<td>1.76</td>
<td>6.36</td>
<td>27.7</td>
<td>15.0</td>
<td>3.09</td>
<td>6.36</td>
<td>48.6</td>
</tr>
<tr>
<td>G4</td>
<td>20.6</td>
<td>3.93</td>
<td>12.0</td>
<td>32.9</td>
<td>18.2</td>
<td>7.30</td>
<td>12.0</td>
<td>61.1</td>
</tr>
</tbody>
</table>

**Table 3.4.** Characterization of the silane grafting efficiency by elemental analyses.

<table>
<thead>
<tr>
<th>Entry</th>
<th>% C (from C)</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
<th>% Si (from Si)</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
<th>% C (from C)</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
<th>% Si (from Si)</th>
<th>Eff&lt;sub&gt;grafting&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>3.10</td>
<td>/</td>
<td>0.10</td>
<td>/</td>
<td>4.33</td>
<td>/</td>
<td>0.31</td>
<td>/</td>
</tr>
<tr>
<td>G1</td>
<td>3.27</td>
<td>14.4</td>
<td>0.20</td>
<td>21.7</td>
<td>5.37</td>
<td>88.1</td>
<td>0.53</td>
<td>47.8</td>
</tr>
<tr>
<td>G2'</td>
<td>4.53</td>
<td>62.5</td>
<td>0.83</td>
<td>82.0</td>
<td>6.21</td>
<td>82.1</td>
<td>0.85</td>
<td>60.7</td>
</tr>
<tr>
<td>G4</td>
<td>5.92</td>
<td>65.6</td>
<td>0.92</td>
<td>48.8</td>
<td>8.51</td>
<td>97.2</td>
<td>1.40</td>
<td>64.9</td>
</tr>
</tbody>
</table>

These contrasting results illustrate the problems encountered to characterize the grafting efficiency of the process. These issues may originate from different factors:
Both purification processes did not enable to eliminate compounds other than silanes – citrates or nitrates for instance – that remained strongly attached to the cerium oxide surface. This is clearly evidenced by TGA and elemental analyses carried out on the “bare” cerium oxide (BC). To calculate grafting efficiencies we assumed that the same amount of impurities were removed from every sample: in reality this may not be the case.

Although the oxide was dried under vacuum prior to thermogravimetric analyses, the samples could have absorbed water while transferred to the TGA instrument. An isothermal step of 15 minutes at 90°C was achieved to dry the samples, but this may not be sufficient to ensure a good reproducibility of TGA analyses.

Elemental analyses detected a non-negligible amount of silicon in the “bare” cerium oxide. We ignore if the commercial cerium oxide already contained silicon or if silicon impurities were captured by the samples during the purification procedures. This number was taken into account in the calculation of grafting efficiencies based on the silicon content of cerium oxide powders.

### 3.4.2. Synthesis of hybrid latexes from silane-modified cerium oxide nanoparticles

Despite the inaccurate determination of the grafting efficiency at the surface of CeO₂ particles, the synthesis of hybrid latexes was attempted from silane-grafted cerium oxide particles.

Styrene was initially employed as a model monomer to study the feasibility of the synthesis for the following reasons:
The monomer is easier to handle and safer than vinylidene chloride and does not require the use of an autoclave as reaction setup.

The observation of polystyrene particles by electron microscopy is more straightforward, due to the high polymer $T_g$ (about 80°C for a poly(styrene-co-methyl acrylate) copolymer with a 90:10 Sty:MA mass ratio$^{35,36}$ vs about 10°C for a poly(vinylidene chloride-co-methyl acrylate) copolymer with a 90:10 VDC:MA mass ratio$^{37}$).

Based on our literature study, we opted for a semi-batch process, with continuous additions of the monomer solution and the surfactant (SDBS) solution, in order to minimize secondary nucleation. For the same reason, a zwitterionic azo-initiator (VA-057) was preferred to anionic persulfates over encourage the migration of oligoradicals towards the negatively charged cerium oxide surface. The polymerization recipes employed for the synthesis of CeO$_2$/poly(styrene-co-methyl acrylate) are collected in Table 3.5.

**Table 3.5.** Recipes for the emulsion copolymerization of styrene and methyl acrylate in the presence of cerium oxide nanoparticles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CeO$_2$ dispersion</th>
<th>Initial load</th>
<th>Monomers</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>H0</td>
<td>commercial</td>
<td>CeO$_2$ dispersion (g)</td>
<td>VA-057 (g)</td>
<td>Water (g)</td>
</tr>
<tr>
<td>H2</td>
<td>G2'</td>
<td>2.09</td>
<td>0.095</td>
<td>87.00</td>
</tr>
<tr>
<td>H4</td>
<td>G4</td>
<td>19.00</td>
<td>0.096</td>
<td>70.00</td>
</tr>
<tr>
<td>H10</td>
<td>G10</td>
<td>19.00</td>
<td>0.095</td>
<td>71.00</td>
</tr>
</tbody>
</table>
Colloidally stable latexes with about 14 wt% solid content were obtained in all cases. Cryo-TEM observations carried out on the hybrid latex H0 obtained in the presence of bare nanoceria showed a complete segregation between polymer particles and cerium oxide particles (Fig. 3.5). It confirmed that a surface-modification step was required in order to promote the polymerization at the surface of the oxide particles.

![Cryo-TEM Image](image)

**Fig. 3.5.** Cryo-TEM image of the CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes H0 (see Table 3.5).

DLS analyses showed that the surface-modification of nanoceria had an influence on the final latex particle diameter (Table 3.6). Indeed the higher the targeted grafting density, the lower the particle size: it suggested that silane-grafted ceria played a role in the formation of polymer particles. Moreover TEM analyses performed on these latexes seemed to show polymer particles displaying non-spherical structures and decorated with...
cerium oxide particles at their surface (Fig.3.6): this result tended to confirm the participation of surface-modified nanoceria in the process of particle formation. However the samples still contained a large amount of cerium oxide particles freely dispersed in the aqueous phase, as well as CeO$_2$-free polymer particles formed by secondary nucleation.

Table 3.6. Characterization of CeO$_2$/poly(Sty-co-MA) hybrid latexes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CeO$_2$ content in dry polymer (wt%)</th>
<th>pH</th>
<th>Conversion (%)</th>
<th>$D_p^I$ (nm)</th>
<th>$D_p^V$ (nm)</th>
<th>$D_p^N$ (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>H0</td>
<td>2.5</td>
<td>6.6</td>
<td>81.2</td>
<td>205</td>
<td>206</td>
<td>184</td>
<td>0.002</td>
</tr>
<tr>
<td>H2</td>
<td>2.1</td>
<td>6.6</td>
<td>97.1</td>
<td>175</td>
<td>172</td>
<td>148</td>
<td>0.02</td>
</tr>
<tr>
<td>H4</td>
<td>2.2</td>
<td>6.7</td>
<td>94.9</td>
<td>108</td>
<td>95</td>
<td>81</td>
<td>0.05</td>
</tr>
<tr>
<td>H10</td>
<td>2.6</td>
<td>6.5</td>
<td>81.8</td>
<td>80</td>
<td>68</td>
<td>58</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Further investigation of the hybrid latexes by cryo-TEM led to a very different conclusion: the samples hardly contained cerium oxide particles attached to the polymer surface (Fig.3.7). We came to the conclusion that the formation of polymer particles mostly occurred by secondary nucleation, and that the grafting of alkoxy silanes on cerium oxide particles was not efficient to promote the polymerization reaction at their surface.

This result also questioned the use of conventional transmission electron microscopy as an effective tool to assess the actual structure of hybrid latexes containing nanometric mineral objects: we assume that, during the latex drying process on the TEM grid, a certain amount of nanoceria deposited on the polymer particles, resulting to the formation of misleading artifacts as observed in Fig.3.5. In that sense, cryo-TEM is a more reliable technique as it provides a picture of the latex sample in its dispersed state.
Questions still remained concerning the decrease of the final latex particle size when increasing the amount of MPTMS added to the cerium...
oxide dispersion, as well as the anisotropic particle shapes observed by electron microscopy. We presume that the alkoxysilane was mainly subjected to self-condensation reactions that led to the formation of silsesquioxanes comprising methacrylate reactive functions that took part in the process of polymer particle formation and influenced the final latex morphology. Indeed the synthesis of such nanometric objects by self-condensation of alkoxysilanes in aqueous media has already been reported in the scientific literature[38,39].

To verify this assumption, a blank experiment was carried out, consisting in the addition of MPTMS to an aqueous medium at similar conditions as those employed for the grafting reaction G4, but in the absence of cerium oxide particles (Table 3.7). For this purpose a sample of commercial cerium oxide dispersion was centrifuged at 40000 rpm for 2 h and a fraction of the serum was collected at the end of the cycle.

**Table 3.7.** Recipe for the blank experiment B1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initial load</th>
<th>Silane</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Serum CeO₂ dispersion (g)</td>
<td>HNO₃ (g)</td>
<td>Water (g)</td>
</tr>
<tr>
<td>B1</td>
<td>9.85</td>
<td>0.10</td>
<td>82.00</td>
</tr>
</tbody>
</table>

Unfortunately, neither DLS nor TEM characterization enabled to identify the presence of such silane-based nano-objects. However, when the blank aqueous sample B1 was introduced in the initial load of a reaction of emulsion copolymerization of styrene and methyl acrylate (Table 3.8), the resulting polymer particles still displayed an anisotropic shape, as evidenced by TEM observations (Fig.3.8).
Table 3.8. Recipe for the synthesis of the poly(Sty-co-MA) blank latex.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initial load</th>
<th>Monomers</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B1</td>
<td>VA-057</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
</tr>
<tr>
<td>BL1</td>
<td>18.62</td>
<td>0.096</td>
<td>70.00</td>
</tr>
<tr>
<td></td>
<td>15.0 / 1.67</td>
<td>0.80</td>
<td>24.33</td>
</tr>
</tbody>
</table>

Fig. 3.8. TEM observations of the poly(styrene-co-methyl acrylate) blank latex BL1.

This result supports our assumption that nanometric species arising from the self-condensation of MPTMS took part in the process of formation of non-spherical polymer particles. These silsesquioxanes could have indeed played the role of seed particles to form SiO₂/poly(Sty-co-MA) hybrid particles at an early stage of the emulsion polymerization reaction. The surfactant concentration at that stage of the reaction may have been insufficient to stabilize the particles during their growth, so their
coalescence led to non-spherical objects. The high polymer $T_g$ of the poly(Sty-co-MA) copolymer (about 80°C for a 90:10 Sty:MA mass ratio$^{[35,36]}$) compared to the reaction temperature (60°C) and the low monomer concentration in the particles (kinetic studies of the reaction indeed showed that starved-monomer conditions were obeyed) did not allow the anisotropic particles to rearrange into spherical objects during their growth. This could explain the non-spherical shape of the final latex particles.

The synthesis of a CeO$_2$/poly(vinylidene chloride-co-methyl acrylate) latexes was attempted in the presence of the modified cerium oxide nanoparticles dispersion, employing the recipe given in Table 3.9 and targeting a solid content of about 50% to meet the industrial requirements for the synthesis of poly(vinylidene chloride) latexes.

**Table 3.9.** Recipe for the emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of cerium oxide nanoparticles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CeO$_2$ dispersion</th>
<th>Initial load</th>
<th>Monomers</th>
<th>Surfactant and TSPP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CeO$_2$ dispersion (g)</td>
<td>TSPP (g)</td>
<td>VA-057 (g)</td>
<td>VDC/MA (g / g)</td>
</tr>
<tr>
<td>HV4 G4$^{a)}$</td>
<td>530</td>
<td>1.00</td>
<td>2.85</td>
<td>450 / 50</td>
</tr>
</tbody>
</table>

$^{a)}$ CeO$_2$ dispersion modified targeting a 4 molecules/nm$^2$ grafting density, 2wt% cerium oxide content.

Characterization of the final latex showed a very broad particle size distribution. Also a very low monomer conversion was achieved (Table 3.10). On-line monitoring of the temperatures inside the reactor and in the thermostated envelope (Fig.3.9) showed that during the first 200 minutes of reaction the temperature of the heating medium was maintained lower than
the reaction temperature to compensate for the exothermic nature of the polymerization reaction. Both temperatures remained equal during the time interval situated between 200 and 400 minutes of reaction. These observations suggest that an inhibition of the polymerization reaction occurred during that period of time. We assume that this inhibition originates from the radical scavenging nature of Ce$^{3+}$ active sites present at the cerium oxide surface. More details about the antioxidant role played by cerium oxide will be provided in Chapter 5. Finally, cryo-TEM observations of the final latex confirmed that the silane modification did not seem to impart a good compatibility between the cerium oxide particles and the polymer phase (Fig.3.10). Although a few CeO$_2$ clusters could be observed in the vicinity of the polymer/water interface, we doubt that a strong chemical interaction occurred between the polymer particles and cerium oxide. Noteworthy, the latex particles displayed spherical shapes: in this case we may reasonably assume that the low glass transition of poly(VDC-co-MA) copolymers (about 10°C for a 90:10 VDC:MA mass ratio$^{[37]}$) compared to poly(Sty-co-MA) copolymers (about 80°C for a 90:10 Sty:MA mass ratio$^{[35,36]}$) and the monomer-flooded conditions (due to the inhibition period observed during the reaction) allowed the particles to rearrange after the coalescence of precursor particles and adopt a spherical structure.

**Table 3.10.** Characterization of the CeO$_2$/poly(VDC-co-MA) hybrid latex HV4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CeO$_2$ content in dry polymer (wt%)</th>
<th>pH</th>
<th>Conversion (%)</th>
<th>$D_p$ (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV4</td>
<td>2.02</td>
<td>5.05</td>
<td>40.1</td>
<td>192.0</td>
<td>0.247</td>
</tr>
</tbody>
</table>
Fig. 3.9. On-line monitoring of temperatures of reaction and inside the thermostated envelope.

Fig. 3.10. Cryo-TEM observations of the CeO$_2$/poly(VDC-co-MA) hybrid latex HV4.
3.5. Conclusions

The synthesis of cerium oxide-based hybrid latexes was attempted, employing an alkoxysilane as a coupling agent to modify the cerium oxide surface. Characterization of the silane-grafting efficiency by thermogravimetric and elemental analyses was problematic, mainly due to the fact that purification processes did not enable to remove impurities such as citrates or nitrates from the commercial cerium oxide samples.

Emulsion copolymerization of styrene and methyl acrylate or vinylidene chloride and methyl acrylate carried out in the presence of “surface-modified” cerium oxide particles hardly led to the formation of CeO$_2$-based hybrid structures, as evidenced by cryo-TEM observations. We assume that the surface-modification step mostly consisted in the formation of silsesquioxanes by self-condensation of the alkoxysilane. These silsesquioxanes comprising methacrylate functions would have then taken part in the process of polymer particle formation and in the development of the anisotropic shape in the case of poly(styrene-co-methyl acrylate) latexes.

We could propose two main explanations for the low efficiency of the process in promoting the polymerization reaction at the cerium oxide surface:

- A pH of 5 was chosen to carry out the grafting reaction, due to the limited colloidal stability of the CeO$_2$ dispersion at lower pH. Such conditions may have favored self-condensation reactions at the expense of the grafting of MPTMS at the oxide surface.
- The presence of citrate molecules strongly attached to CeO$_2$ particles may have rendered the cerium oxide surface hardly
accessible for silane molecules to achieve an efficient grafting reaction.

The main conclusion to be drawn from this study is that the surface-modification of nanoceria by alkoxy silanes in the conditions as described in this chapter is not an efficient strategy to promote the affinity of the polymer towards cerium oxide particles during a subsequent emulsion polymerization reaction. However, we could propose some directions to increase the efficiency of the grafting process. An acidic cerium oxide dispersion could indeed be employed in order to carry out the modification reaction at a lower pH and in the absence of complexing agents at the cerium oxide surface. Nevertheless, special attention should be paid to the colloidal stability of such dispersions during the grafting process and emulsion polymerization reactions, as it is highly sensitive to variations of pH and ionic strength.

References


Chapter 4. Amphiphatic RAFT copolymers for the synthesis of inorganic/organic hybrid latexes

Abstract

This chapter tackles the synthesis of amphiphatic random copolymers via Reversible Addition Fragmentation chain Transfer (RAFT) polymerization for use as compatibilizing agents in emulsion polymerization processes carried out in the presence of inorganic particles. Three types of macro-RAFT agents were synthesized employing different combinations of butyl acrylate as a hydrophobic monomer and acrylic acid and/or 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as hydrophilic monomers. RAFT copolymerization and terpolymerization reactions were carried out and the resulting macro-RAFT agents were characterized by $^1$H NMR, SEC and MALDI-ToF-MS analyses to confirm their structure.
4.1. Introduction

Progress made in the implementation of living/controlled radical polymerization techniques in dispersed media\textsuperscript{[1-3]} enabled the development of novel strategies for the synthesis of inorganic/organic hybrid latexes\textsuperscript{[4]}. In particular Nguyen et al. reported an effective method\textsuperscript{[5]} employing amphiphatic macro-RAFT agents adsorbed on pigments to promote the emulsion polymerization at the particle surface. The main asset of this method is that it can be applied to a large range of inorganic particles by tuning the hydrophobic/hydrophilic composition of the macro-RAFT agent depending on the nature of the material to encapsulate. The fact that it does not require any conventional surfactant is another remarkable advantage: short emulsifier molecules are indeed likely to migrate in waterborne polymer films, leading to a possible deterioration of the properties of the final material.

After a short description of the main principles of controlled radical polymerization and more particularly the RAFT (Reversible Addition-Fragmentation chain Transfer) technique in the first part of this chapter, results on the synthesis and characterization of three types of amphiphatic macro-RAFT agents will be presented and discussed.

4.2. Reversible Addition-Fragmentation chain Transfer (RAFT)

4.2.1. Controlled radical polymerization

In a conventional radical polymerization, the three steps of initiation, propagation and termination occur within a short time interval (typically 1
second), from the appearance of a radical to the formation of a high molecular weight dead chain. Due to the continuous formation of radical species throughout the reaction, the process is repeated till the total consumption of the monomer or the initiator. It results in a broad distribution of molecular weights between all macromolecules constituting the final polymeric materials. It also results in a broad distribution of composition between all the chains in the case of copolymerization of monomers with different reactivities.

The principle of controlled radical polymerization\(^6\) (or reversible-deactivation radical polymerization\(^7\)) consists in maintaining a low radical concentration in the reaction medium, while having a pool of dormant chains, in order to limit irreversible bimolecular termination (dead chains). This may be achieved by adding a compound capable of inducing a reversible de-activation of growing oligoradicals so as to establish an equilibrium between a majority of dormant (non propagating) species and a minority of active (propagating) species. Methods of controlled radical polymerization are based on the two main principles of:

- Reversible termination: techniques belonging to this class are Nitroxide Mediated Polymerization (NMP)\(^8\text{-}10\) and Atom Transfer Radical Polymerization (ATRP)\(^11\text{-}12\).

- Degenerative chain transfer, comprising techniques such as Reversible Addition-Fragmentation chain Transfer (RAFT)\(^13\text{-}16\), Macromolecular Design via Interchange of Xanthates (MADIX)\(^16,17\), Iodine Transfer Polymerization (ITP)\(^18\text{-}21\) and Reverse Iodine Transfer Polymerization (RITP)\(^21\text{-}24\).

By definition a living polymerization is characterized by the absence of irreversible bimolecular termination and irreversible transfer reactions,
which does not necessarily mean that the process leads to a good control of molecular weight. Indeed, a living polymerization may result in the formation of a polymer displaying a broad molecular weight distribution if the rate of initiation is slow compared to the rate of propagation. Experimental criteria to evidence the controlled/living nature of a polymerization reaction are the following:\[3\]:

- \(\ln \left[ \frac{1}{1 - \text{conversion}} \right] = f(t)\) is a linear function of time. It implies a constant concentration of propagating radicals and a first order reaction with respect to the monomer.
- \(M_n = f(\text{conversion})\) is a linear function: a slow initiation or the presence of irreversible termination or transfer reactions would result in a different trend.
- The molecular weight distribution is narrow \((M_w / M_n < 1.5)\) and decreases with conversion following the Poisson equation: \(I_p = 1 + \left\{ \frac{1}{DP_n} \right\}\).
- Polymers with preserved chain-end functionalities (dormant chains) are obtained quantitatively. Therefore, chain extension should be possible and, if the second monomer is different, block copolymers could be obtained.

This last feature is an interesting peculiarity of controlled living radical polymerization, as it enables the preparation of a wide range of polymer compositions and macromolecular architectures\[3,25,26\] (Fig.4.1).

**4.2.2. Reversible Addition Fragmentation chain Transfer (RAFT) polymerization**

The RAFT (Reversible Addition Fragmentation chain Transfer) and the MADIX (MAcromolecular Design via Interchange of Xanthates)
processes were both discovered in 1998, by the group of Rizzardo at the Commonwealth Scientific and Industrial Research Organization (CSIRO)\textsuperscript{[13,15]} and the group of Charmot at Rhodia Chimie\textsuperscript{[17]}, respectively.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Topologies</th>
<th>Functionalities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
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<tr>
<td></td>
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<tr>
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<td>Comb/brush</td>
<td>End-functional groups</td>
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<td></td>
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<td>Star</td>
<td>Telechelic polymers</td>
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<td>Star</td>
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</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="Dendritic/Hyperbranched" /></td>
</tr>
</tbody>
</table>

**Fig.4.1.** Polymer compositions and architectures accessible via controlled/living radical polymerization (reprinted from reference\textsuperscript{[3]} with permission from Elsevier).

These techniques rely on the principle of degenerative (or reversible) chain transfer and more particularly on the use of transfer agents with the general formula $Z\text{-C}(=\text{S})\text{-SR}$, where $Z$ is the “stabilizing
group” and R the “leaving group”. It is now generally admitted that the mechanism of the RAFT/MADIX process can be described as follows (Scheme 4.1)[14]: radicals are generated by dissociation of the radical initiator and form oligoradicals via propagation reactions with monomer molecules. These macroradicals then react with the transfer agent to form an intermediate radical (addition), which may then undergo two types of beta fragmentation events: the first one corresponds to the regeneration of the initial radical, while the second results in the formation of a radical $R^\circ$ capable of initiating a new polymer chain. As a result an equilibrium is obtained between active species (propagating radicals) and dormant chains (thiocarbonylthio-terminated chains) that can be reactivated, contrary to dead polymer chains obtained via termination or irreversible transfer. This equilibrium (degenerative, i.e. same chemical species on both sides of the equilibrium) accounts for the control of the polymerization.

Several criteria need to be fulfilled in order to obtain a good control throughout the polymerization reaction[14]:

- Polymer chains should be initiated within a short time, close to the ideal case of a living polymerization.
- To achieve a uniform growth of polymer chains, the number of monomer units added onto an oligoradical for each active/dormant cycle (kinetic chain length between each activation / de-activation cycle) should be low.
- Bimolecular termination and irreversible chain transfer reactions leading to the formation of dead polymer chains should be minimized.
For a given monomer, the control of the polymerization relies mostly on the RAFT agent structure (nature of \(Z\) and \(R\) groups), as it will influence the efficiency of the addition-fragmentation reaction. During the last decades, great efforts have thus been dedicated to the design of a large variety of transfer agents by tuning the nature of \(Z\) and \(R\) groups in order to control more or less specifically the polymerization of a wide range of monomers\(^{14,27,28}\). The most common groups of RAFT agents are dithioesters\(^{13}\), trithiocarbonates\(^{29-31}\), xanthates\(^{32}\) (specific to the MADIX technique), dithiocarbamates\(^{32,33}\) and phosphoryl dithioformates\(^{34}\) (Fig.4.2).
Another remarkable advantage of the RAFT process is its good tolerance towards polar solvents, which enables to apply the technique to polymerization processes in dispersed media\cite{1-3,35-38}. It opened the way to innovative strategies for the synthesis of polymer colloids with controlled morphologies\cite{4}. Among them, the use of amphiphatic macro-RAFT agents is a very efficient and versatile technique that enables the encapsulation of many types of inorganic particles\cite{5}. While the ratio between the hydrophilic and hydrophobic monomer units of such oligomers controls their adsorption at the surface of a given mineral object, their thiocarbonylthio-functionality enables chain extension and promotes the polymerization reaction at the surface of the inorganic particle.

4.3. Experimental section

4.3.1. Materials

Butyl acrylate (BA, Aldrich, ≥99%) and acrylic acid (AA, Aldrich, 99%) were purified through inhibitor removing columns. 2-Acrylamido-2-methyl propane sulfonic acid (AMPS, Aldrich, 99%) was used as received.
2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was purified by recrystallization in methanol. Sodium sulfide (Aldrich, hydrate form, 30wt%), carbon disulfide (Fluka 99%), tetrabutylammonium bromide (Aldrich, 99%), benzyl chloride (Aldrich, 99%), ethanol (Biosolve), methanol (Biosolve), 1,4-dioxane (Merck), dimethyl sulfoxide (DMSO, Carlo Erba), tetrahydrofuran (THF stabilized with butylated hydroxytoluene, Biosolve) and acetic acid (Sigma-Aldrich, >99%) were used as received.

4.3.2. Synthesis of dibenzyl trithiocarbonate (DBTTC)

The synthesis of the DBTTC RAFT agent involved a phase-transfer catalysis mechanism and followed a protocol published in earlier literature[39]. Sodium trithiocarbonate was first obtained by reacting sodium sulfide (hydrate form, 30 wt%, 70.08 g, 269 mmol) with carbon disulfide (22.1 g, 291 mmol) at room temperature for 1h in water (89.75 g) in the presence of tetrabutylammonium bromide (2.05 g). In a second step benzyl chloride (63.91 g, 0.505 mmol) was added dropwise to the solution for 30 min. The reaction was performed at room temperature for 3h, followed by a period of 1h at 70°C. Once the reaction medium was back to room temperature, an additional charge of tetrabutylammonium bromide (2.36 g) dissolved in water (4.73 g) was added. The solution was then stirred overnight to complete the reaction. After separation of the organic and aqueous phases, DBTTC was obtained by precipitating the organic phase in 150 mL cold ethanol. The resulting yellow crystals were then filtered and rinsed with cold ethanol on a sintered glass filter, and dried in a vacuum oven at 30°C. Mass of DBTTC obtained: 59.91 g. Yield: 82 %. Purity (by °H NMR in CDCl3): 98%.
4.3.3. Polymerizations

**Synthesis of poly(BA-co-AA) RAFT oligomers.** Poly(BA-co-AA) random copolymers with different compositions were synthesized by copolymerization of butyl acrylate and acrylic acid in 1,4-dioxane at 70°C, employing AIBN as initiator and DBTTC as RAFT agent. A DBTTC:AIBN molar ratio of 11 was employed in order to favor the transfer to the RAFT agent and achieve a good control over the polymerization reaction. To obtain the macro-RAFT agents in their dry form for further analyses and emulsion polymerization reactions, a portion of each polymer solution was dried overnight in a vacuum oven at 50°C. Stock aqueous solutions of poly(BA-co-AA) macro-RAFT agents were obtained by dissolving 0.5 g of oligomer in 100 mL DI water, in the presence of sodium hydroxide to achieve a neutral pH.

**Synthesis of poly(BA-co-AMPS) and poly(BA-co-AA-co-AMPS) RAFT oligomers.** Poly(BA-co-AMPS) random copolymers with different compositions were synthesized by copolymerization of butyl acrylate and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) in dimethylsulfoxide (DMSO) at 70°C, employing AIBN as initiator and DBTTC as RAFT agent. A DBTTC:AIBN molar ratio of 3.3 was employed in order to achieve a good control over the polymerization reaction. For the syntheses of poly(BA₅-co-AMPS₅) and poly(BA₁₀-co-AMPS₂₀) RAFT oligomers, time-resolved $^1$H NMR analyses were performed in parallel on 0.6 mL samples of the reaction medium placed in a NMR tube with 3 capillaries containing deuterated benzene C₆D₆ and analyzed for 10 hours at 70°C in a 250 MHz Bruker NMR spectrometer.

To obtain the macro-RAFT agents in their dry form for further analyses and emulsion polymerization reactions, a portion of each polymer
solution was dried in a rotary evaporator and then overnight in a vacuum oven at 60°C. To remove the unreacted AMPS, copolymers were dissolved in 50mL water and dialyzed against a large volume (3L) of DI water in a Spectra/por 6 dialysis tubing (Spectrum Laboratories, MWCO 1000). The dry copolymer was then obtained by drying the solution in a rotavap and overnight in a vacuum oven at 50°C. Stock aqueous solutions of poly(BA-co-AMPS) macro-RAFT agents were obtained by dissolving 0.5 g of oligomer in 100 mL DI water, in the presence of sodium hydroxide to achieve a neutral pH. The same synthesis and purification procedures as for poly(BA-co-AMPS) were followed for the RAFT terpolymerization of butyl acrylate, acrylic acid and AMPS.

**4.3.4. Characterization**

**Molecular weight determination.** For poly(BA-co-AA) RAFT copolymers, size exclusion chromatography was performed on a system equipped with a Waters 1515 isocratic HPLC pump, a Waters 2707 autosampler, a Waters 2414 refractive index detector (35°C) and a PSS SDV 5μ guard column followed by 2 SDV 5μ, 500 Å (8 × 300 mm) columns in series at 40°C. Tetrahydrofuran with 1 vol% acetic acid was used as eluent at a flow rate of 1.0 mL.min⁻¹. The molecular weights were calculated against polystyrene standards (Polymer Laboratories, Mᴾ = 580 g.mol⁻¹ up to Mᴾ = 21000 g.mol⁻¹). ¹H NMR analyses performed on a Varian 400 MHz spectrometer were employed to determine monomer conversions (with the crude reaction products diluted in DMSO-d₆) and the oligomers average molecular weights and compositions (with the dry copolymers dissolved in DMSO-d₆).
For poly(BA-co-AMPS) copolymers, sulfonic acid groups were protected prior to the analysis: 40 mg of sample was dissolved in dimethylformamide (DMF) and an excess of trimethoxysilyl diazomethane was added (about 0.5 mL of a 2.0 M solution in heptane). The reaction was maintained for 3 hours in total. SEC with DMF as eluent, calibrated with poly(methyl methacrylate) standards from Polymer Laboratories, was run with a Varian Prostar (model 210) pump at a flow rate of 0.8 mL.min⁻¹ using two 300 mm long, mixed-D PL-gel 5 μm columns (molecular weight range: 2 × 10² – 4 × 10⁵ g.mol⁻¹ from Polymer Laboratories) thermostated at 70°C, connected to a Shodex (model RI-101) refractometer detector. ¹H NMR analyses were carried out on a Brüker 400 MHz NMR spectrometer to determine monomer conversions (with the crude reaction products diluted in DMSO-d₆) and experimental molecular weights and compositions (with the dry copolymers dissolved in deuterium oxide, D₂O).

**Matrix Assisted Laser Desorption Ionization - Time of Flight – Mass Spectrometry (MALDI-ToF-MS).** MALDI-ToF-MS analyses were performed on a PerSeptive Biosystems Voyager-DE Biospectrometry Workstation.

Poly(BA-co-AA) oligomer samples were prepared as follows: a 40 mg/mL trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] (DCTB) matrix sample and a 5mg/mL potassium trifluoroacetate sample were prepared in tetrahydrofuran. A 1 mg/mL oligomer solution was prepared in THF and mixed with the matrix and cationization agent solutions in a 4:4:1 volume ratio (oligomer : matrix : potassium trifluoroacetate). A 3 μL drop was deposited and dried on a V700666 sample plate SS (Applied Biosystems). Analyses were carried out in positive reflector mode, with a total of 1000 shots per measurement.
Poly(BA-co-AMPS) macro-RAFT agent samples were prepared as follows: a saturated solution of α-Cyano-4-hydroxycinnamic acid (HCCA) matrix was prepared in ethanol. A 1 mg/mL oligomer solution was prepared in ethanol and mixed with the matrix solution in a 20:1 volume ratio (oligomer : matrix). A 3 μL drop was deposited and dried on a V700666 sample plate SS (Applied Biosystems). Analyses were carried out in linear negative mode, with a total of 1000 shots per measurement.

4.4. Results and discussion

4.4.1. RAFT copolymerization of \( n \)-butyl acrylate and acrylic acid

Poly(BA-co-AA) amphiphatic oligomers with various compositions were synthesized by RAFT copolymerization of \( n \)-butyl acrylate and acrylic acid in 1,4-dioxane at 70°C in the presence of AIBN as initiator and DBTTC as chain transfer agent (Table 4.1). According to the scientific literature, acrylic acid and butyl acrylate are expected to give random copolymers\(^5\). Indeed Paxton determined reactivity ratios of \( r_1 = 1.07 \) and \( r_2 = 0.58 \) for the butyl acrylate (1) / acrylic acid (2) system\(^{[40]}\), while Vollmert gave a different estimation for the same system: \( r_1 = 0.78 \) and \( r_2 = 1.15 \)\(^{[41]}\). They showed that the consumption of the two monomers followed a linear curve, which suggested that the monomers copolymerized randomly in both cases. A random sequence of hydrophilic and hydrophobic units is of great importance to achieve a high efficiency of hybrid particle formation, given that more structured copolymers (e.g. block copolymers) would tend to self-organize into micelles during the emulsion polymerization reaction and favor the formation of a second crop of cerium oxide-free polymer particles. Another key point was to maintain a low molecular weight of the macro-
RAFT agents to minimize the proportion of hydrophilic moieties that would affect the properties of the final polymeric material and to keep a high number of RAFT units at the surface of the particles.

**Table 4.1.** Polymerization recipes for the synthesis of poly(BA-co-AA) amphiphatic macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Targeted macro-RAFT agent composition</th>
<th>BA (g)</th>
<th>AA (g)</th>
<th>DBTTC (g)</th>
<th>AIBN (g)</th>
<th>1,4-dioxane (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>poly(BA_{5-co-AA_{10}})</td>
<td>9.76</td>
<td>11.30</td>
<td>4.40</td>
<td>0.224</td>
<td>25.22</td>
</tr>
<tr>
<td>A2</td>
<td>poly(BA_{2.5-co-AA_{10}})</td>
<td>6.00</td>
<td>13.61</td>
<td>5.52</td>
<td>0.281</td>
<td>27.80</td>
</tr>
<tr>
<td>A3</td>
<td>poly(BA_{7.5-co-AA_{10}})</td>
<td>12.10</td>
<td>9.12</td>
<td>3.65</td>
<td>0.196</td>
<td>25.29</td>
</tr>
<tr>
<td>A4-1</td>
<td>poly(BA_{5-co-AA_{5}})</td>
<td>10.60</td>
<td>6.03</td>
<td>4.80</td>
<td>0.238</td>
<td>24.95</td>
</tr>
<tr>
<td>A4-2</td>
<td>poly(BA_{5-co-AA_{5}})</td>
<td>10.60</td>
<td>6.00</td>
<td>4.80</td>
<td>0.238</td>
<td>22.00</td>
</tr>
<tr>
<td>A5</td>
<td>poly(BA_{15-co-AA_{20}})</td>
<td>13.24</td>
<td>9.95</td>
<td>1.99</td>
<td>0.103</td>
<td>25.51</td>
</tr>
<tr>
<td>A6</td>
<td>poly(BA_{10-co-AA_{20}})</td>
<td>10.61</td>
<td>11.90</td>
<td>2.41</td>
<td>0.132</td>
<td>25.37</td>
</tr>
</tbody>
</table>

Theoretical molecular weights were calculated via the following equation:

\[
M_{n,th} = M_{DBTTC} + \left[ (m_0^{BA} \times X_{BA} + m_0^{AA} \times X_{AA}) / n_0^{DBTTC} \right] \quad (1)
\]

where \( m_0^{BA} \) and \( m_0^{AA} \) are the initial masses of butyl acrylate and acrylic acid, respectively, \( X_{BA} \) and \( X_{AA} \) the monomer conversions, \( n_0^{DBTTC} \) the initial moles of RAFT agent and \( M_{DBTTC} \) corresponds to the RAFT agent molecular weight.

\(^1\)H NMR spectra acquired on a Varian 400 MHz spectrometer (Fig.4.3) on the crude reaction product and the dry copolymers were employed to determine the monomer conversions and the number average
molecular weight ($M_n,_{\text{NMR}}$) and average molar composition ($F_{AA,\text{NMR}}$) of the copolymers. Molecular weights were calculated assuming that all polymer chains were terminated by two benzyl groups originating from the RAFT agent fragmentation.

**Fig.4.3.** $^1$H NMR spectrum and corresponding integration peaks of the poly(BA$_5$-co-AA$_{10}$) RAFT copolymers (crude reaction product diluted in DMSO-$d_6$).

Size exclusion chromatography experiments were carried out to obtain additional experimental molecular weight values ($M_n,_{\text{SEC}}$) and polydispersity indices (PDI). THF containing 1 vol% acetic acid was...
employed as eluent in order to minimize interactions between acrylic acid units and the column that would affect the final results.

Comparison of characterization results collected in Table 4.2 showed that experimental molecular weights were in general in good agreement with targeted values. However, some molecular weight discrepancies were observed concerning Size Exclusion Chromatography results, possibly due to interactions between carboxylic acid units and the SEC column that were not completely avoided by the use of small amounts of acetic acid in the THF eluent. Nevertheless, low PDI values obtained in all cases tended to confirm the controlled character of these polymerization reactions. Average compositions calculated from $^1$H NMR results also matched the targeted values.

**Table 4.2.** Characterization of poly(BA-co-AA) oligomers by $^1$H NMR and SEC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Composition</th>
<th>Theoretical values</th>
<th>$^1$H NMR results</th>
<th>SEC results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_{n,th}$ (g/mol)</td>
<td>$F_{AA,th}$</td>
<td>$X_{BA}$ (%)</td>
</tr>
<tr>
<td>A1</td>
<td>poly(BA$<em>{4.9-}$ co-AA$</em>{10.2}$)</td>
<td>1660</td>
<td>0.67</td>
<td>98.3</td>
</tr>
<tr>
<td>A2</td>
<td>poly(BA$<em>{2.4-}$ co-AA$</em>{9.8}$)</td>
<td>1310</td>
<td>0.80</td>
<td>98.7</td>
</tr>
<tr>
<td>A3</td>
<td>poly(BA$<em>{7.3-}$ co-AA$</em>{9.8}$)</td>
<td>1940</td>
<td>0.57</td>
<td>97.5</td>
</tr>
<tr>
<td>A4-1</td>
<td>poly(BA$<em>{4.8-}$ co-AA$</em>{4.9}$)</td>
<td>1260</td>
<td>0.50</td>
<td>95.8</td>
</tr>
<tr>
<td>A5</td>
<td>poly(BA$<em>{13.6-}$ co-AA$</em>{18.3}$)</td>
<td>3340</td>
<td>0.57</td>
<td>89.9</td>
</tr>
<tr>
<td>A6</td>
<td>poly(BA$<em>{9.1-}$ co-AA$</em>{18.5}$)</td>
<td>2790</td>
<td>0.67</td>
<td>91.3</td>
</tr>
</tbody>
</table>
Amphiphatic RAFT copolymers for the synthesis of hybrid latexes

In order to confirm that butyl acrylate and acrylic acid copolymerized randomly in these experiments, the synthesis of the poly(BA$_5$-co-AA$_5$) macro-RAFT agent was repeated (experiment A4-2) to follow the conversions of both monomers against time. Samples were taken regularly and analyzed by $^1$H NMR. The integration peak $a$ corresponding to aromatic protons of benzyl chain ends was taken as an internal standard and the integrations of peaks $b$ and $c$ (integrating for protons of butyl acrylate and acrylic acid respectively) (Fig.4.3) were used to calculate the conversions of the two monomers as a function of time:

$$X_{\text{BA}, t} (\%) = \frac{(b_{t=0} - b_t) \times 100}{b_{t=0}} \quad (2)$$

$$X_{\text{AA}, t} (\%) = \frac{(c_{t=0} - c_t) \times 100}{c_{t=0}} \quad (3)$$

where $X_{\text{BA}, t}$ and $X_{\text{AA}, t}$ are the conversions of butyl acrylate and acrylic acid respectively at time $t$, $b_{t=0}$, $c_{t=0}$ the integration values of peaks $b$ and $c$ at initial time and $b_t$ and $c_t$ are the integration values of peaks $b$ and $c$ at time $t$.

From these calculations, the conversions of the two monomers could be plotted as a function of time and as a function of the total monomer conversion (Fig.4.4). Although butyl acrylate seemed to be incorporated slightly faster than acrylic acid into the RAFT polymer chains at the initial stage of the reaction, we may still conclude that overall the two monomers copolymerized randomly. We may thus expect a very low proportion of blocky structures in poly(BA-co-AA) macro-RAFT agents synthesized in these conditions, which is a prerequisite to minimize the formation of free polymer particles during emulsion polymerization.
reactions carried out in the presence of these RAFT copolymers adsorbed at the surface of inorganic particles.

![Graph](image1.png)

**Fig. 4.4.** Butyl acrylate and acrylic acid conversions as a function of time (top) and as a function of the total monomer conversion (bottom).

MALDI-ToF-MS analyses were performed on the poly(BA<sub>5</sub>-co-AA<sub>5</sub>) macro-RAFT agent to verify the chain-end functionality of the copolymer (Fig. 4.5).
As expected, the interval between peaks of a same series are equal to the isotopic masses of the two monomers ($M_{BA} = 128.08$ g/mol and $M_{AA} = 72.02$ g/mol). The main series (a) was attributed to the structure of the macro-RAFT agent associated with a potassium cation, while the structures corresponding to series (b) and (c) were assumed to be formed by fragmentation of the trithiocarbonate function occurring during the analysis (Table 4.3). Despite a small shift compared to m/z values calculated for these structures, experimental m/z values are in good agreement with theoretical values. From this analysis we may thus conclude that poly(BA-co-AA) RAFT copolymers display the expected functionality: two benzyl groups on each chain end and a trithiocarbonate function at a random position inside the polymer chain. This will allow chain extension of the
macro-RAFT agents to occur during emulsion polymerization reactions carried out in the presence of inorganic particles.

**Table 4.3.** Assignment of the peaks in the enlarged region of the MALDI-ToF-MS spectrum of the poly(BA$_5$-co-AA$_5$) RAFT copolymer.

<table>
<thead>
<tr>
<th>Series and structure</th>
<th>x</th>
<th>y</th>
<th>m/z theo</th>
<th>m/z exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5</td>
<td>4</td>
<td>1257.49</td>
<td>1257.67</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>1297.60</td>
<td>1297.70</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3</td>
<td>1313.56</td>
<td>1313.68</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>14</td>
<td>1261.42</td>
<td>1261.45</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13</td>
<td>1317.48</td>
<td>1317.54</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>15</td>
<td>1333.44</td>
<td>1333.45</td>
</tr>
<tr>
<td>c</td>
<td>6</td>
<td>4</td>
<td>1263.56</td>
<td>1263.48</td>
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<tr>
<td></td>
<td>5</td>
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<td>1279.52</td>
<td>1279.56</td>
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<td>4</td>
<td>8</td>
<td>1295.47</td>
<td>1295.53</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4</td>
<td>1335.58</td>
<td>1335.65</td>
</tr>
</tbody>
</table>

4.4.2. RAFT copolymerization of butyl acrylate and AMPS

Given that the emulsion (co)polymerization of vinylidene chloride may result in a decrease of the pH of the reaction mixture and/or that the
pH of PVDC latexes often decreases upon storage towards values below 3, the use of macro-RAFT agents based on acrylic acid as hydrophilic units may be limited. A loss of colloidal stability could indeed arise from the protonation of the carboxylic acid units for pH < 4. Thus, macro-RAFT agents based on stronger acidic monomers as hydrophilic units, and more particularly monomers bearing a sulfonic acid function, were considered as an alternative to poly(BA-co-AA) RAFT copolymers for the synthesis of PVDC-based hybrid latexes.

Among the two main commercially available monomers comprising a sulfonate or sulfonic acid group – sodium styrene sulfonate (SSNa) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) – AMPS was preferred to SSNa for the following reasons:

- This monomer is commercially available in its sulfonic acid form, which ensures a better solubility in organic solvents compared to sulfonate salts.
- $^1$H NMR spectra of poly(BA-co-SSNa) RAFT copolymers would be difficult to interpret, due to overlapping of the peaks corresponding to aromatic protons of sodium styrene sulfonate and the peaks of aromatic protons of benzyl end groups originating from the scission of DBTTC.
- Vinlylidene chloride copolymers containing styrenic units display poor thermal stabilities$^{[42]}$: the presence of such units adjacent to a poly(vinylidene chloride) block is thus undesired.
- According to calculations of the reactivity ratios of AMPS and butyl acrylate from the Q and e values of the two monomers (Table 4.4) employing Alfrey-Price equations$^{[43]}$, their copolymerization should result in a fairly good alternation of hydrophobic and hydrophilic units (Table 4.5). Results obtained from this simplistic method
should, however, be treated as qualitative, considering that the reactivity ratios depend on several factors, such as, among others, the temperature and the polarity of the reaction medium.

\[ r_1 = \frac{Q_1}{Q_2} \times \exp[-e_1 \times (e_1 - e_2)] \]  
\[ r_2 = \frac{Q_2}{Q_1} \times \exp[-e_2 \times (e_2 - e_1)] \]

**Table 4.4.** Q and e values of butyl acrylate, AMPS, SSNa and styrene.

<table>
<thead>
<tr>
<th></th>
<th>Butyl acrylate (^{[44]})</th>
<th>AMPS (^{[45]})</th>
<th>SSNa (^{[46]})</th>
<th>Styrene (^{[44]}) (Sty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>0.38</td>
<td>0.30</td>
<td>0.44</td>
<td>1.00</td>
</tr>
<tr>
<td>e</td>
<td>0.85</td>
<td>0.45</td>
<td>-0.38</td>
<td>-0.80</td>
</tr>
</tbody>
</table>

**Table 4.5.** Reactivity ratios calculated from Alfrey-Price equations (see equations (4) and (5) and Table 4.4).

<table>
<thead>
<tr>
<th></th>
<th>BA (1)</th>
<th>Sty (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AMPS (2)</td>
<td>SSNa (2)</td>
</tr>
<tr>
<td>( r_1 )</td>
<td>0.90</td>
<td>0.30</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>0.95</td>
<td>0.73</td>
</tr>
</tbody>
</table>

In order to study the reactivity of butyl acrylate and AMPS, a time-resolved \(^1\)H NMR study was employed to follow the course of the copolymerization of the two monomers at 70°C in DMSO, employing DBTTC as RAFT agent and AIBN as initiator. The same method as the one employed previously to plot the conversions of butyl acrylate and acrylic acid as a function of time was applied similarly to the butyl acrylate / AMPS system, based on the integrations of the specific peaks b and c of the two monomers (Fig.4.6).
**Fig. 4.6.** $^1$H NMR spectrum and corresponding integration peaks of the poly(BA$_{7.5}$-co-AMPS$_{10}$) RAFT copolymer (crude reaction product diluted in DMSO-d$_6$).

According to the evolution of the conversion of each monomer as a function of time and of the overall monomer conversion (Fig. 4.7), the system does not qualitatively follow the theoretical calculations based on Alfrey-Price equations, since AMPS reacted slower than butyl acrylate in both experiments.
Nonetheless, the fact that the gradient structure (composition drift along the polymer chain) was not too much pronounced encouraged us to go on with this system for further experiments. Six poly(BA-co-AMPS) copolymers with various compositions and chain lengths were therefore synthesized (Table 4.6). A ratio $[\text{DBTTT}]_0/[\text{AIBN}]_0$ of 3.3 was judged
sufficient to favor the transfer to the RAFT agent and achieve a good control over the polymerization reaction, given that a few preliminary experiments carried out in presence of lower amounts of initiator resulted in too low monomer conversions (BA conversion < 90% and AMPS conversion < 60%).

Table 4.6. Polymerization recipes for the synthesis of poly(BA-co-AMPS) amphiphatic macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Targeted macro-RAFT agent composition</th>
<th>BA (g)</th>
<th>AMPS (g)</th>
<th>DBTTC (g)</th>
<th>AIBN (g)</th>
<th>DMSO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1'</td>
<td>poly(BA5-co-AMPS10)</td>
<td>1.29</td>
<td>4.15</td>
<td>0.583</td>
<td>0.102</td>
<td>54.02</td>
</tr>
<tr>
<td>A2'</td>
<td>poly(BA2.5-co-AMPS10)</td>
<td>0.70</td>
<td>4.49</td>
<td>0.631</td>
<td>0.109</td>
<td>54.31</td>
</tr>
<tr>
<td>A3'</td>
<td>poly(BA7.5-co-AMPS10)</td>
<td>1.73</td>
<td>3.74</td>
<td>0.524</td>
<td>0.090</td>
<td>54.29</td>
</tr>
<tr>
<td>A4'</td>
<td>poly(BA9-co-AMPS5)</td>
<td>1.86</td>
<td>2.98</td>
<td>0.839</td>
<td>0.143</td>
<td>53.99</td>
</tr>
<tr>
<td>A5'</td>
<td>poly(BA15-co-AMPS20)</td>
<td>1.85</td>
<td>3.94</td>
<td>0.284</td>
<td>0.050</td>
<td>54.00</td>
</tr>
<tr>
<td>A6'</td>
<td>poly(BA10-co-AMPS20)</td>
<td>1.37</td>
<td>4.38</td>
<td>0.312</td>
<td>0.051</td>
<td>54.02</td>
</tr>
</tbody>
</table>

Theoretical molecular weights of poly(BA-co-AMPS) copolymers were estimated from the equation:

\[
M_{n,\text{th}} = M_{\text{DBTTC}} + [(m_0^{\text{AMPS}} \times X_{\text{AMPS}} + m_0^{\text{BA}} \times X_{\text{BA}} / n_0^{\text{DBTTC}}]
\]  (6)

where \(m_0^{\text{AMPS}}\) and \(m_0^{\text{BA}}\) are the initial masses of AMPS and butyl acrylate respectively. \(X_{\text{AMPS}}\) and \(X_{\text{BA}}\) are the AMPS and BA conversions, \(n_0^{\text{DBTTC}}\) is the initial molar amount of RAFT agent and \(M_{\text{DBTTC}}\) corresponds to the RAFT agent molecular weight.
1H NMR analyses carried out on the dry poly(BA-co-AMPS) copolymers dissolved in deuterium oxide (D$_2$O) were employed to determine their average molecular weights and compositions (Table 4.7).

Table 4.7. Characterization of poly(BA-co-AMPS) oligomers by 1H NMR and SEC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Composition</th>
<th>Theoretical values</th>
<th>1H NMR results</th>
<th>SEC results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_n, \text{th}$ (g/mol)</td>
<td>$F_{\text{AMPS,th}}$</td>
<td>$X_{\text{BA}}$ (%)</td>
</tr>
<tr>
<td>A1'</td>
<td>poly(BA$<em>{4.9}$-co-AMPS$</em>{7.9}$)</td>
<td>2520</td>
<td>0.62</td>
<td>98.2</td>
</tr>
<tr>
<td>A2'</td>
<td>poly(BA$<em>{2.4}$-co-AMPS$</em>{7.6}$)</td>
<td>2130</td>
<td>0.76</td>
<td>95.5</td>
</tr>
<tr>
<td>A3'</td>
<td>poly(BA$<em>{7.2}$-co-AMPS$</em>{7.6}$)</td>
<td>2740</td>
<td>0.52</td>
<td>95.8</td>
</tr>
<tr>
<td>A4'</td>
<td>poly(BA$<em>{4.9}$-co-AMPS$</em>{3.8}$)</td>
<td>1690</td>
<td>0.44</td>
<td>97.8</td>
</tr>
<tr>
<td>A5'</td>
<td>poly(BA$<em>{14.5}$-co-AMPS$</em>{14.6}$)</td>
<td>5100</td>
<td>0.52</td>
<td>98.3</td>
</tr>
<tr>
<td>A6'</td>
<td>poly(BA$<em>{9.7}$-co-AMPS$</em>{14.7}$)</td>
<td>4490</td>
<td>0.62</td>
<td>97.3</td>
</tr>
</tbody>
</table>

A fairly good agreement could be observed between the theoretical and experimental copolymer compositions, but observed molecular weights were higher than the predicted values: considering that these RAFT copolymers were purified by dialysis employing membranes with a molecular weight cut-off of 1000 Da, the removal of low molecular weight oligomers cannot be excluded and may account for the differences between experimental and theoretical data. Size exclusion chromatography performed on the oligomers after substitution of sulfonic acid groups by a reaction with trimethylsilyl diazomethane showed that poly(BA-co-AMPS) RAFT oligomers exhibited low polydispersity indices (1.24 < PDI < 1.36),
which evidenced that the DBTTC RAFT agent achieved a fairly good molecular weight control. Although molecular weights determined by SEC did not match theoretical values – as they were calculated against poly(methyl methacrylate) standards – the comparison of theoretical and SEC results followed a coherent trend.

MALDI-ToF-MS analyses were carried out in linear negative mode on a RAFT copolymer with the targeted composition poly(BA$_5$-co-AMPS$_5$) (Fig.4.8).

**Fig.4.8.** MALDI-ToF-MS spectrum of the RAFT copolymer with a BA$_5$-co-AMPS$_5$ targeted composition.

Peaks corresponding to the main series (a) were still attributed to the expected macro-RAFT agent structure, with two benzyl groups as chain ends and a trithiocarbonate function situated inside the polymer chains. A
second structure (series b) was identified as carrying a sulfine end-group that may originate from the fragmentation and oxidation of the trithiocarbonate group during the analysis. For both series a and b, an acceptable agreement could be observed between theoretical and experimental m/z values (Table 4.8).

**Table 4.8.** Assignment of the peaks in the enlarged region of the MALDI-ToF-MS spectrum of the poly(BA5-co-AMPS5) RAFT copolymer.

<table>
<thead>
<tr>
<th>Series and structure</th>
<th>x</th>
<th>y</th>
<th>m/z theo</th>
<th>m/z exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5</td>
<td>1</td>
<td>1136.49</td>
<td>1136.91</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>1166.36</td>
<td>1166.85</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>1215.47</td>
<td>1215.81</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1</td>
<td>1264.58</td>
<td>1264.92</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>1294.44</td>
<td>1294.82</td>
</tr>
<tr>
<td>b</td>
<td>4</td>
<td>2</td>
<td>1109.44</td>
<td>1109.78</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1</td>
<td>1158.55</td>
<td>1159.81</td>
</tr>
<tr>
<td></td>
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<td>1188.42</td>
<td>1188.79</td>
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<tr>
<td></td>
<td>5</td>
<td>2</td>
<td>1237.53</td>
<td>1237.86</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>1286.64</td>
<td>1287.84</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>3</td>
<td>1128.45</td>
<td>1129.00</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0</td>
<td>1147.70</td>
<td>1149.70</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2</td>
<td>1177.56</td>
<td>1181.76</td>
</tr>
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<td></td>
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<td>4</td>
<td>1207.42</td>
<td>1208.91</td>
</tr>
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<td></td>
<td>7</td>
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<td>9</td>
<td>0</td>
<td>1275.78</td>
<td>1277.69</td>
</tr>
</tbody>
</table>
A third structure (c series) was assumed to correspond to the thiol-ended polymer chains, also formed by fragmentation of the trithiocarbonate function and complementary to structure b. However, comparison of theoretical isotopic masses to experimental data tends to question this assumption. Yet it is reasonable to assume that the extensive noise observed in this spectrum may have complicated the attribution of the main isotopic peaks corresponding to the c series.

4.4.3. RAFT terpolymerization of butyl acrylate, acrylic acid and AMPS

The last series of experiments consisted in the RAFT terpolymerization of butyl acrylate, acrylic acid and AMPS (Table 4.9).

Table 4.9. Polymerization recipes for the synthesis of poly(BA-co-AA-co-AMPS) amphiphatic macro-RAFT agents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Targeted macro-RAFT agent composition</th>
<th>BA (g)</th>
<th>AA (g)</th>
<th>AMPS (g)</th>
<th>DBTTC (g)</th>
<th>AIBN (g)</th>
<th>DMSO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1''</td>
<td>poly(BA7.5-co-AA10-co-AMPS4)</td>
<td>2.68</td>
<td>2.00</td>
<td>2.30</td>
<td>0.807</td>
<td>0.137</td>
<td>34.00</td>
</tr>
<tr>
<td>A2''</td>
<td>poly(BA5-co-AA5-co-AMPS4)</td>
<td>2.16</td>
<td>1.19</td>
<td>2.76</td>
<td>0.970</td>
<td>0.164</td>
<td>34.00</td>
</tr>
</tbody>
</table>

Theoretical molecular weights were still calculated according to the following equation:

\[ M_{n,th} = M_{DBTTC} + \left[ \left( m_0^{AMPS} \times X_{AMPS} + m_0^{AA} \times X_{AA} + m_0^{BA} \times X_{BA} \right) / n_0^{DBTTC} \right] \]  

where \( m_0^{AMPS}, m_0^{AA} \), and \( m_0^{BA} \) are the initial masses of AMPS, acrylic acid and butyl acrylate, respectively. \( X_{AMPS}, X_{AA} \) and \( X_{BA} \) are the AMPS, AA
and BA conversions, \( n^0_{DBTTC} \) is the initial molar amount of RAFT agent and \( M_{DBTTC} \) corresponds to the RAFT agent molecular weight.

\(^1\)H NMR analyses carried out on the crude reaction product (Fig.4.9) and the dry terpolymers (in DMSO-\(d_6\) and \(D_2O\), respectively) were employed to determine the monomer conversions and the terpolymer average compositions and molecular weights, respectively (Table 4.10).

**Fig.4.9.** \(^1\)H NMR spectrum and corresponding integration peaks of the poly(\(BA_5\)-co-\(AA_5\)-co-AMPS\(_4\)) RAFT terpolymer (crude reaction product diluted in DMSO-\(d_6\)).
Table 4.10. Characterization of poly(BA-co-AA-co-AMPS) oligomers by $^1$H NMR.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Composition</th>
<th>$M_n,\text{th}$ (g/mol)</th>
<th>$F_{\text{AA},\text{th}}$</th>
<th>$F_{\text{AMPS},\text{th}}$</th>
<th>$X_\text{BA}$ (%)</th>
<th>$X_\text{AA}$ (%)</th>
<th>$X_\text{AMPS}$ (%)</th>
<th>$M_n,\text{NMR}$ (g/mol)</th>
<th>$F_{\text{AA},\text{NMR}}$</th>
<th>$F_{\text{AMPS},\text{NMR}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1&quot;</td>
<td>poly(BA$<em>{7.5}$-co-AA$</em>{9.8}$-co-AMPS$_{3.5}$)</td>
<td>2660</td>
<td>0.47</td>
<td>0.17</td>
<td>99.5</td>
<td>98.3</td>
<td>90.2</td>
<td>2830</td>
<td>0.46</td>
<td>0.17</td>
</tr>
<tr>
<td>A2&quot;</td>
<td>poly(BA$<em>{5.0}$-co-AA$</em>{4.9}$-co-AMPS$_{3.8}$)</td>
<td>2010</td>
<td>0.36</td>
<td>0.27</td>
<td>99.3</td>
<td>97.5</td>
<td>88.2</td>
<td>2110</td>
<td>0.43</td>
<td>0.21</td>
</tr>
</tbody>
</table>

A good agreement was found between theoretical and experimental molecular weights, although the final compositions of each monomer did not completely match the expected values. Time-resolved $^1$H NMR analyses were not carried out to study the terpolymerization of the three monomers. However, based on previous experiments carried out on poly(BA-co-AA) and poly(BA-co-AMPS), we may reasonably assume that the polymers would display a gradient structure (composition drift along the chains), with butyl acrylate/acrylic acid rich “tails” and an AMPS rich “center”.

MALDI-ToF-MS analyses, measured in linear negative mode on the poly(BA$_5$-co-AA$_5$-co-AMPS$_4$) terpolymer were more difficult to interpret due to the higher number of possible structures obtained from different combinations of the three comonomers (Fig.4.10). The main series (a), corresponding to the sulfine-ended polymer chain, was still attributed to the fragmentation and oxidation of the trithiocarbonate function occurring during the analysis (Table 4.11).
Fig. 4.10. MALDI-ToF-MS spectrum of the poly(BA$_5$-co-AA$_5$-co-AMPS$_4$) RAFT terpolymer.

Series b was assigned to the expected RAFT terpolymer structure with two benzyl end groups and a trithiocarbonate function situated inside the polymer chain. A third series (c), still attributed to the thiol-ended fragment, was hardly visible in the spectrum due to overlapping of the isotopic peaks from the two other series.
Table 4.11. Assignment of the peaks in the region 1100 < m/z < 1150 of the MALDI-ToF-MS spectrum of the poly(BA<sub>5</sub>-co-AA<sub>5</sub>-co-AMPS<sub>4</sub>) RAFT copolymer.

<table>
<thead>
<tr>
<th>Series and structure</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>m/z theo</th>
<th>m/z exp</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a</strong></td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1102.49</td>
<td>1103.04</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1125.40</td>
<td>1125.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>1132.35</td>
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<td>1</td>
<td>2</td>
<td>1121.50</td>
<td>1122.01</td>
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</tbody>
</table>

4.5. Conclusions

Three different types of amphiphatic macro-RAFT agents were synthesized, employing butyl acrylate as hydrophobic monomer, acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as hydrophilic monomers and dibenzyl trithiocarbonate as chain transfer...
agent. $^1$H NMR and SEC analyses suggested that a fairly good control of the molecular weights was achieved during the copolymerization reactions, while MALDI-ToF-MS analyses of poly(BA-co-AA), poly(BA-co-AMPS) and poly(BA-co-AA-co-AMPS) macro-RAFT agents confirmed a good preservation of the trithiocarbonate chain-functionality.

Furthermore, an experiment of RAFT copolymerization of $n$-butyl acrylate and acrylic acid followed by $^1$H NMR analyses confirmed that the two monomers copolymerized randomly, which is in agreement with results reported in the scientific literature. The RAFT copolymerization of butyl acrylate and AMPS followed by $^1$H NMR displayed intramolecular composition drifts, as butyl acrylate was incorporated faster than AMPS in the polymer chains. This composition drift may have further consequences in the course of emulsion polymerization reactions carried out in the presence of such gradient poly(BA-co-AMPS) macro-RAFT agents adsorbed at the surface of inorganic particles. A gradient structure of the polymer chains could indeed result in the formation of micelles that would encourage the formation of polymer particles by secondary nucleation. We may expect the same type of gradient structure with AMPS units to occur in terpolymer systems. However this should not be dramatic in this case if we consider that, at neutral pH, these poly(BA-co-AA-co-AMPS) oligomers would contain a more uniform distribution of negative charges along their chains compared to the poly(BA-co-AMPS) system. Fig.4.11 provides an illustration of the structures expected for every type of amphiphatic macro-RAFT agents synthesized in the work described in this chapter.

The performances of these different classes of amphiphatic macro-RAFT agents in emulsion polymerization reactions performed in the presence of cerium oxide nanoparticles will be discussed in chapter 5.
Amphiphatic RAFT copolymers for the synthesis of hybrid latexes

Fig. 4.11. Schematic view of the structures of amphiphatic macro-RAFT agents.

References


Chapter 5. Cerium oxide-based hybrid latexes via the macro-RAFT agent route

Abstract

Three different types of amphiphatic macro-RAFT agents were employed as compatibilizing agents to promote the polymerization reaction at the surface of nanoceria for the synthesis of CeO\textsubscript{2}-based hybrid latexes with enhanced UV-stability. After studying the adsorption of RAFT copolymers and terpolymers at the cerium oxide surface via electrophoretic mobility measurements and UV-visible spectrometry, emulsion copolymerization reactions – employing either styrene and methyl acrylate or vinylidene chloride and methyl acrylate as comonomers – were carried out in the presence of the surface-modified nanoceria. Characterization techniques like Dynamic Light Scattering and cryo-Transmission Electron Microscopy (cryo-TEM) were employed to confirm the hybrid structure of the final CeO\textsubscript{2}/polymer latexes. In most cases, despite the fact that a long inhibition period occurred at the early stage of the reaction, amphiphatic macro-RAFT agents enabled a high incorporation efficiency of cerium oxide nanoparticles in the final hybrid latexes.
5.1. Introduction

Chapter IV described the synthesis and characterization of three groups of amphiphatic macro-RAFT agents. In this chapter we discuss the results of a study on the effect of these RAFT copolymers and terpolymers on emulsion polymerization reactions carried out in the presence of cerium oxide nanoparticles. After detailing the experimental procedures employed for this study, results and discussions will be presented on the adsorption of amphiphatic macro-RAFT agents at the surface of nanoceria and on the synthesis of cerium oxide-based hybrid latexes.

5.2. Experimental section

5.2.1. Materials

Styrene (Sty, Aldrich, ≥99%) and methyl acrylate (MA, Aldrich, 99%) were purified through inhibitor removing columns. Vinylidene chloride (VDC, Aldrich, 99%) was distilled under reduced pressure. 2,2’-Azobis[N-(2-carboxyethyl)-2-methylpropionamidine] hydrate (VA-057, Wako) was used as received. Sodium dodecylbenzene sulfonate (SDBS, technical grade, Aldrich) and tetrasodium pyrophosphate (TSPP, Alfa Aesar, 98%) were used as received. Water was deionized through an ion-exchange resin (conductivity below 1 μS/cm). The commercial cerium oxide aqueous dispersion (Nanobyk-3810, 18 wt%, Byk Chemie) was dialyzed 4 times against deionized water employing Spectra/por 6 dialysis membranes (Spectrum Laboratories, MWCO 1000).
5.2.2. Polymerizations

The emulsion copolymerization of styrene and methyl acrylate was carried out in the presence of amphiphatic macro-RAFT agents and cerium oxide particles according to the following procedure. The initial load containing the dialyzed cerium oxide aqueous dispersion and the RAFT oligomer diluted in deionized water, a mixture of the monomers (styrene and methyl acrylate in a 90:10 mass ratio / 88:12 molar ratio) and an aqueous initiator solution (VA-057, 4 g/L) were bubbled separately with argon during 30 min. The initial load was introduced in a 3-neck 250 mL double-walled reactor equipped with a condenser and maintained under argon atmosphere. Continuous stirring of the medium at 250 rpm was ensured by a 6-bladed stainless steel turbine impeller, and the temperature in the reactor was controlled with a continuous flow of thermostated water delivered by a MGW Lauda M3 circulating water bath. Once the reactor had reached the temperature of 60°C, a pulse of 10 mL of the initiator solution was injected into the reaction medium and the monomer feed via a Dosimat 765 dosing pump (Metrohm) was started and maintained for 4 hours at a rate of 42 μL/min. Afterwards, the reactor was maintained at reaction temperature for an additional 2 hours.

The synthesis of CeO₂/PVDC hybrid latexes was performed by emulsion copolymerization of vinylidene chloride and methyl acrylate (90:10 mass ratio / 89:11 molar ratio) in a 300 mL stainless steel reactor (Parr Instrument Company), equipped with a stainless steel pitched-bladed mechanical stirrer and internal pressure and temperature sensors. Oxygen was removed from the autoclave by purging it via three cycles of vacuum (10⁻² mbar) broken with nitrogen. Vacuum was restored in the reactor before charging an aqueous solution of the macro-RAFT agent and the
dialyzed cerium oxide dispersion. A 4 bars nitrogen overpressure was then established in the vessel. The speed of agitation was set at 250 rpm and the temperature was raised to 60°C. An initial pulse of initiator solution (VA-057) was added to the reactor. A stirred pre-emulsion containing VDC, MA, TSPP and sodium dodecylbenzene sulfonate was then continuously pumped into the reactor at a rate of 20 mL/h for 5 h via a Series III digital HPLC pump (LabAlliance). The overall reaction lasted for 6 h. Residual monomer was stripped by heating the latex for 1 h at 60°C under reduced pressure (0.2-0.4 bar).

5.2.3. Characterization

**Dynamic Light Scattering.** Latex particle size distributions and average particle diameters of CeO₂/poly(Sty-co-MA) hybrid latexes obtained from the poly(BA-co-AA) macro-RAFT agents were determined by dynamic light scattering (DLS) with a Zetasizer Nano ZS particle size analyzer (from Malvern).

Latex particle size distributions and average particle diameters of CeO₂/poly(Sty-co-MA) hybrid latexes obtained from poly(BA-co-AMPS) and poly(BA-co-AA-co-AMPS) macro-RAFT agents and particle size distributions of CeO₂/poly(VDC-co-MA) hybrid latexes were determined with a VASCO-3 particle size analyzer (from Cordouan technologies).

**Electrophoretic mobility measurements.** Electrophoretic mobility measurements performed on a Zetasizer Nano ZS (Malvern) were employed to characterize the adsorption of amphiphatic macro-RAFT agents at the surface of nanoceria at pH 7. Given volumes of dialyzed cerium oxide aqueous dispersion and RAFT copolymer aqueous stock solutions were mixed and diluted in DI water and stirred overnight so as to
obtain samples containing 4 g/L cerium oxide and macro-RAFT agent concentrations varying from 0.4 to 4 g/L. For each sample, the average electrophoretic mobility was calculated by taking an average of three measurements.

**UV-visible spectrometry.** 25 mL aqueous solutions containing 4 g/L cerium oxide and macro-RAFT agent concentrations varying from 0 to 8 g/L were prepared (at pH 7) and stirred overnight in polyallomer tubes. The closed tubes were placed symmetrically in a rotor 70 Ti inside an Optima L-90K (Beckman Coulter) ultracentrifuge. After a cycle of 4 h at 40000 rpm at 20°C, 15 mL of the serum of each sample was collected.

UV-visible spectrometric measurements were performed on an Agilent 8453 UV-visible Spectroscopy System. Spectra were measured between 190 and 1100 nm, employing two different light sources: a deuterium lamp and a low-noise tungsten lamp. A temperature controller (HP Peltier 890904) was employed to maintain a constant temperature of 25°C. For each type of macro-RAFT agent, a calibration curve, giving the maximum absorbance (at 308 nm, specific for the trithiocarbonate function) as a function of the oligomer concentration in water (from 0.005 to 0.3 g/L) was plotted. UV-visible measurements were carried out on the serum solutions, diluted 10 or 100 times in order to fit the range of absorbance of the calibration curve. From this curve, the concentration of the free macro-RAFT agent present in the serum could then be calculated, as well as the mass of RAFT oligomer adsorbed per gram of cerium oxide.

For analyses involving the poly(BA₅-co-AA₅) macro-RAFT agent, due to the incomplete solubility of the copolymer in water, even at neutral pH, a large amount of the stock solution was ultracentrifuged at 40000 rpm for 2 h beforehand in order to eliminate insoluble residues that could affect the adsorption process. ¹H NMR analyses performed on the serum showed
no variation of the RAFT copolymer composition. No preliminary treatment was required when studying poly(BA-co-AMPS) and poly(BA-co-AA-co-AMPS) macro-RAFT agents, due to the complete solubility of these oligomers in water.

**Cryo-TEM observations.** The preparation of samples for cryo-TEM observations involved a vitrification procedure on a FEI Vitrobot Mark III. A 3 μL sample (about 5 wt% solid content) was applied to a Quantifoil grid (R 2/2, Quantifoil Micro Tools GmbH; glow discharged for 40 s just prior to use) within the environmental chamber of the Vitrobot and the excess liquid was blotted away. The sample was shot into melting ethane, immediately transferred to a cryoholder (Gatan 626) and observed under low dose conditions at -170 °C. Cryo-TEM pictures were obtained using a FEI Tecnai 20, Sphera TEM microscope (LaB₆ filament, operating voltage of 200 kV).

**Determination of molecular weights of poly(VDC-co-MA) copolymers.** Molecular weights of PVDC copolymers were determined by Gel Permeation Chromatography (PL-GPC 50, Varian, Inc.). Freeze-dried samples of CeO₂/poly(VDC-co-MA) hybrid latexes were dissolved in THF and filtered on 0.2 mm PTFE filters, before being injected in the SEC apparatus. A calibration employing polystyrene standards ($K = 14.1 \times 10^{-5}$ dL/g and $a = 0.7$) was employed in combination with Mark-Houwink coefficients determined for poly(VDC-co-MA) copolymers with a 80:20 VDC:MA mass ratio ($K = 35 \times 10^{-5}$ dL/g and $a = 0.57$) to calculate the polymer molecular weights (see Chapter 2).

**Surface tension measurements.** Surface tensions of CeO₂-based hybrid latexes were measured at 20°C on a DCAT 11 tensiometer (DataPhysics
Instruments GmbH), employing a PT11 Wilhelmy plate made of platinum-iridium.

5.3. Results and discussion

5.3.1. Adsorption of amphiphatic macro-RAFT agents at the surface of cerium oxide nanoparticles

The cerium oxide dispersion employed for this study was dialyzed 4 times against large volumes of DI water in order to eliminate a major part of citrate molecules that may affect the adsorption of amphiphatic macro-RAFT agents at the surface of ceria. These citrate molecules may indeed decrease the efficiency of hybrid particle formation.

Adsorption of poly(BA-co-AA) macro-RAFT agents

The variations of electrophoretic mobility of cerium oxide particles upon the addition of poly(BA-co-AA) oligomers is plotted in Fig.5.1. Judging by the negative value measured at neutral pH for the dialyzed cerium oxide dispersion (a positive value would be expected for bare ceria at a pH below their point of zero charge (pzc) of 7.9\(^{[1]}\), we could conclude that a residual amount of citrate remained strongly bound to the cerium oxide surface. Despite the presence of residual citrate, the successful adsorption of amphiphatic macro-RAFT agents at the particles surface was evidenced by the evolution of the electrophoretic mobility towards more negative values upon addition of poly(BA-co-AA) copolymers. Besides, no significant variation of the particles hydrodynamic diameter \(D_{\text{CeO}_2} = 8 \pm 2 \text{ nm}\) could be measured by Dynamic Light Scattering when increasing the poly(BA-co-AA) copolymers concentration.
Fig. 5.1. Evolution of the electrophoretic mobility of cerium oxide particles as a function of poly(BA-co-AA) RAFT copolymer concentration (CeO$_2$ concentration kept constant at 4 g/L).

However, these results should only be interpreted as a general trend and absolute values of electrophoretic mobilities should be handled with care, considering that the ionic strength increased upon addition of the macro-RAFT agents. Some attempts to carry out the same measurements at a constant ionic strength indeed led to flocculation and incoherence of the results.

To characterize the adsorption of poly(BA-co-AA) copolymers in a more quantitative way, similar solutions of the poly(BA$_5$-co-AA$_5$) macro-RAFT agent were prepared in the presence of cerium oxide and ultracentrifuged at 40000 rpm for 4h to isolate the supernatant and to plot the corresponding adsorption isotherms via UV-visible spectrometric
measurements performed on the serum (Fig.5.2). We could indeed take advantage of the specific absorption of the C=S bond of trithiocarbonate functions taking place between 265 and 365 nm (with a maximum at 308 nm) to determine the concentration of the macro-RAFT agent remaining in the aqueous phase, and to estimate the mass of RAFT copolymer adsorbed per gram of cerium oxide by means of a mass balance. This calculation required the approximation that the adsorption process was independent of the length and composition of polymer chains, which may in reality not be exactly the case.

![Fig.5.2. Adsorption of poly(BA₅-co-AA₅) macro-RAFT agent at the surface of cerium oxide particles evidenced by UV-visible spectrometry](image)

From Fig.5.2, it can be concluded that, within the studied range of concentrations, the adsorption of the macro-RAFT agent occurred successfully at the surface of nanoceria, but with a large percentage of copolymer – between 50 and 60% – remaining in the aqueous phase.
Similar results were reported by Nguyen et al.\cite{2} in the case of a poly(BA$_5$-co-AA$_{10}$) macro-RAFT agent adsorbed at the surface of titanium dioxide: they showed that roughly 75% of the RAFT oligomer remained dissolved in the aqueous phase. However, they proved that these aqueous phase macro-RAFT agents did not affect the efficient encapsulation of titanium dioxide and hardly led to secondary nucleation.

**Adsorption of poly(BA-co-AMPS) macro-RAFT agents**

Electrophoretic mobilities were measured as a function of the concentration of three poly(BA-co-AMPS) RAFT oligomers in the presence of cerium oxide particles (Fig.5.3).

The general trend of these plots also showed a decrease of the electrophoretic mobility towards more negative values, which also tended to evidence the adsorption poly(BA-co-AMPS) RAFT copolymers at the surface of cerium oxide particles. However, in the case of the poly(BA$_5$-co-AMPS$_5$) macro-RAFT agent, a decrease of the absolute mobility was observed for concentrations higher than 1.5 g/L. Assuming that, similarly to the case of poly(BA-co-AA) macro-RAFT agents, a certain amount of oligomers remains free in the aqueous phase and that increasing the RAFT copolymer concentration will increase the ionic strength of the solution, it is not surprising to observe a decrease of the absolute value of the electrophoretic mobility at high poly(BA-co-AMPS) concentrations. However, the fact that this feature was only observed with one of the three compositions tested remains unanswered.
Fig. 5.3. Evolution of the electrophoretic mobility of cerium oxide particles as a function of poly(BA-co-AMPS) RAFT copolymer concentration (CeO$_2$ concentration kept constant at 4 g/L).

UV-visible spectroscopic analyses carried out on supernatants of ultracentrifugated cerium oxide/poly(BA$_5$-co-AMPS$_5$) dispersions showed a very different trend compared to the case of poly(BA-co-AA) RAFT copolymers (Fig.5.4). Indeed, the macro-RAFT agent mostly remained dissolved in the water phase and hardly any RAFT copolymer appeared to adsorb at the cerium oxide surface. It led us to reconsider the validity of electrophoretic measurements to characterize the adsorption of amphiphatic macro-RAFT agents. The case of poly(BA-co-AMPS) RAFT oligomers indeed showed that a decrease of the average electrophoretic mobility of cerium oxide particles upon the addition of amphiphatic
oligomers does not necessarily evidence their successful adsorption on the inorganic particle surface.

**Fig. 5.4.** Adsorption of poly(BA<sub>5</sub>-co-AMPS<sub>5</sub>) macro-RAFT agent at the surface of cerium oxide particles evidenced by UV-visible spectrometry.

**Adsorption of poly(BA-co-AA-co-AMPS) macro-RAFT agents**

The same experimental procedure involving an ultracentrifugation cycle and UV-visible spectrometric analyses was employed to study the adsorption of the poly(BA<sub>5</sub>-co-AA<sub>5</sub>-co-AMPS<sub>4</sub>) RAFT oligomer at the surface of nanoceria. The adsorption isotherm represented in Fig. 5.5 shows that the incorporation of acrylic acid units in the RAFT terpolymer resulted in a slight increase of the mass of macro-RAFT agent adsorbed per gram of cerium oxide compared to the case of the poly(BA<sub>5</sub>-co-AMPS<sub>5</sub>) RAFT copolymer. Nevertheless, this value remained very low compared to the mass of poly(BA<sub>5</sub>-co-AA<sub>5</sub>) oligomer adsorbed per gram of cerium oxide.
5.3.2. Synthesis of cerium oxide / poly(Sty-co-MA) hybrid latexes

Following the same approach as the one employed to study the synthesis of cerium oxide-based hybrid latexes via the silane route (Chapter III), styrene was initially employed as a model monomer to evaluate the efficiency of amphiphatic macro-RAFT agents at incorporating cerium oxide nanoparticles in polymer latexes.

**Employing poly(BA-co-AA) macro-RAFT agents**

Emulsion copolymerization of styrene and methyl acrylate (in a 90:10 mass ratio) was carried out in the presence of ceria employing different poly(BA-co-AA) macro-RAFT agents compositions (Table 5.1).
Table 5.1. Recipes for the emulsion copolymerization of styrene and methyl acrylate in the presence of nanoceria and poly(BA-co-AA) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>Cerium oxide dispersion (g)</th>
<th>Macro-RAFT agent (g)</th>
<th>VA-057 (g)</th>
<th>Water (g)</th>
<th>Styrene/methyl acrylate (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>poly(BA5-co-AA10)</td>
<td>3.19 a)</td>
<td>0.196</td>
<td>0.0396</td>
<td>70.82</td>
<td>8.16 / 0.91</td>
</tr>
<tr>
<td>B2</td>
<td>poly(BA2.5-co-AA10)</td>
<td>3.16 a)</td>
<td>0.195</td>
<td>0.0395</td>
<td>71.00</td>
<td>8.16 / 0.91</td>
</tr>
<tr>
<td>B3</td>
<td>poly(BA7.5-co-AA10)</td>
<td>3.16 a)</td>
<td>0.195</td>
<td>0.0395</td>
<td>71.00</td>
<td>8.16 / 0.91</td>
</tr>
<tr>
<td>B4</td>
<td>poly(BA5-co-AA5)</td>
<td>3.16 a)</td>
<td>0.195</td>
<td>0.0395</td>
<td>73.00</td>
<td>8.16 / 0.91</td>
</tr>
<tr>
<td>B5</td>
<td>poly(BA15-co-AA20)</td>
<td>3.17 a)</td>
<td>0.209</td>
<td>0.0403</td>
<td>71.02</td>
<td>8.16 / 0.91</td>
</tr>
<tr>
<td>B6</td>
<td>poly(BA10-co-AA20)</td>
<td>3.20 a)</td>
<td>0.202</td>
<td>0.0403</td>
<td>70.96</td>
<td>8.16 / 0.91</td>
</tr>
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</table>

a) CeO₂ content of the dispersion: 12.3 wt%.

In all cases a solid content of 12 wt% and a 4 wt% cerium oxide content (respective to the dry polymer) were targeted. A 1:2 poly(BA-co-AA):CeO₂ mass ratio was employed, which corresponded to a mass of about 0.25 g of oligomer adsorbed per gram of cerium oxide in the case of the poly(BA₅-co-AA₅) composition. A zwitterionic radical initiator (VA-057) was used to initiate the polymerization. High monomer conversions could be achieved in most cases and stable latexes were obtained (Table 5.2).

The initial number of cerium oxide particles (N₀CeO₂) and the final number of hybrid particles (NᶠP) were calculated from volume mean particle diameters via the equations:

\[
N₀CeO₂ = 6 \times \frac{m₀CeO₂}{\pi \times ρCeO₂ \times D_{CeO₂}^3} \quad (1)
\]

\[
NᶠP = 6 \times \frac{[(m₀Sty + m₀MA) \times X_M + m₀RAFT copolymer]}{\pi \times ρ_{polymer} \times D_P^3} \quad (2)
\]
where $m_0^{\text{CeO}_2}$ stands for the initial mass of cerium oxide, $\rho_{\text{CeO}_2}$ for the density of cerium oxide ($\rho_{\text{CeO}_2} = 7.13 \text{ g/cm}^3$), $D_{\text{CeO}_2}$ for the volume mean diameter of ceria ($D_{\text{CeO}_2} = 8 \text{ nm}$) and $m_0^{\text{Sty}}$ and $m_0^{\text{MA}}$ for the initial masses of styrene and methyl acrylate, respectively. $X_M$ is the overall monomer conversion, $m_0^{\text{RAFT copolymer}}$ the initial mass of macro-RAFT agent, $\rho_{\text{polymer}}$ the polymer density (assuming $\rho_{\text{polymer}} \approx \rho_{\text{polystyrene}} = 1.05 \text{ g/cm}^3$) and $D_P$ the hybrid particle volume mean diameter. The contribution of cerium oxide in the calculation of the final number of hybrid particles can be neglected since the dry cerium oxide content did not exceed 4 wt%.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>$X_M$ (%)</th>
<th>$D_P$ (nm)</th>
<th>Polydispersity index</th>
<th>$N_0^{\text{CeO}_2}$ ($\times 10^{-16}$)</th>
<th>$N_f^P$ ($\times 10^{-16}$)</th>
<th>$N_0^{\text{CeO}_2}/N_f^P$</th>
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<tr>
<td>B1</td>
<td>poly(BA$<em>5$-co-AA$</em>{10}$)</td>
<td>68.4</td>
<td>95</td>
<td>0.06</td>
<td>20</td>
<td>1.3</td>
<td>16</td>
</tr>
<tr>
<td>B2</td>
<td>poly(BA$<em>{2.5}$-co-AA$</em>{10}$)</td>
<td>92.3</td>
<td>106</td>
<td>0.08</td>
<td>20</td>
<td>1.3</td>
<td>16</td>
</tr>
<tr>
<td>B3</td>
<td>poly(BA$<em>{7.5}$-co-AA$</em>{10}$)</td>
<td>91.1</td>
<td>56</td>
<td>0.16</td>
<td>20</td>
<td>8.7</td>
<td>2.3</td>
</tr>
<tr>
<td>B4</td>
<td>poly(BA$<em>5$-co-AA$</em>{6}$)</td>
<td>86.2</td>
<td>83</td>
<td>0.21</td>
<td>20</td>
<td>2.5</td>
<td>8.1</td>
</tr>
<tr>
<td>B5</td>
<td>poly(BA$<em>{15}$-co-AA$</em>{20}$)</td>
<td>96.1</td>
<td>99</td>
<td>0.04</td>
<td>20</td>
<td>1.7</td>
<td>12</td>
</tr>
<tr>
<td>B6</td>
<td>poly(BA$<em>{10}$-co-AA$</em>{20}$)</td>
<td>88.1</td>
<td>103</td>
<td>0.002</td>
<td>21</td>
<td>1.4</td>
<td>15</td>
</tr>
</tbody>
</table>

By comparing the final number of particles to the initial number of nanoceria particles employed in the polymerization recipes and assuming a 100% conversion to hybrid structures, we could expect that every latex particle would contain on average from 2 to 16 cerium oxide particles depending on the type of macro-RAFT agent employed. Cryo-TEM observations carried out on CeO$_2$/poly(Sty-co-MA) hybrid latexes confirmed that on average several cerium oxide particles were present in one hybrid particle (Fig.5.6). This feature may originate from the mechanism of hybrid
particle formation during the emulsion polymerization process, and is encouraged by the presence of amphiphatic macro-RAFT agents adsorbed on their surface, cerium oxide particles capture growing oligoradicals to form polymer domains, resulting in the formation of hybrid precursors. Due to the large total surface area developed by all these hybrid precursors, we believe that the available negative charges provided by the acrylic acid units of the amphiphatic moieties are then not sufficient to provide the hybrid particles a complete colloidal stability during their growth. Consequently it leads to their partial coagulation to form larger objects containing several cerium oxide particles.

**Fig. 5.6.** Cryo-TEM picture of the CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes B3 (left) and B4 (right) obtained in the presence of poly(BA$_{7.5}$-co-AA$_{10}$) and poly(BA$_{5}$-co-AA$_{5}$) macro-RAFT agents, respectively.

Besides, the particles morphology seemed to consist of CeO$_2$ particles mainly located at the hybrid particles surface. Although most of the citrates were eliminated by dialysis, some remained strongly bonded to the
cerium oxide surface, as evidenced by electrophoretic mobility measurements. Therefore, we presume that the adsorption of the amphiphatic macro-RAFT agents was not as effective as it would be on bare cerium oxide, and only led to a partial engulfment of cerium oxide particles by the polymer phase. Nonetheless, it is remarkable that in all cases no free cerium oxide particle could be observed in the aqueous phase: it proved the efficiency of the process to increase the affinity of the polymer towards the metal oxide surface. Fig.5.7 provides a tentative schematic description of the mechanism of particle formation occurring during the process.

![Mechanism of particle formation in emulsion polymerization reactions carried out in the presence of nanoceria and poly(BA-co-AA) macro-RAFT agents.](image)

**Fig.5.7.** Mechanism of particle formation in emulsion polymerization reactions carried out in the presence of nanoceria and poly(BA-co-AA) macro-RAFT agents.
Noteworthy, a very low amount of cerium oxide-free polymer particles were formed during the process, as evidenced by further cryo-TEM observations (Fig.5.8).

Fig.5.8. Cryo-TEM picture of secondary nucleated polymer particles observed in the CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes B3 (left) and B4 (right).

Two possible mechanisms could explain the formation of such particles by secondary nucleation:

- Considering that a large amount of poly(BA-co-AA) RAFT oligomers remained free in the aqueous phase, as evidenced by adsorption isotherms (Fig.5.2), their chain extension could have led to the formation of surface active species that stabilized the formation of a secondary crop of polymer particles. Nguyen et al. also reported an extremely low number of particles formed by secondary nucleation when performing the encapsulation of titanium dioxide in the presence of a poly(BA$_5$-co-AA$_{10}$) RAFT copolymer$^{[2]}$. They showed that, for 75% of macro-RAFT agent present in the aqueous phase at
the beginning of the emulsion polymerization reaction, about 19% migrated towards the hybrid particles surface during the process, while the rest did not seem to undergo any chain extension, as evidenced by the almost unchanged molecular weight and molecular weight distribution of the aqueous phase RAFT oligomers during the course of the reaction (determined by mass spectrometry of the macro-RAFT agents present in the supernatant after centrifugation). These results may account for the very low amount of polymer particles formed by secondary nucleation.

- Polymer chain ends resulting from the initiator dissociation could have stabilized a new crop of polymer particles formed by a process of homogeneous nucleation. However, it is unlikely that the overall neutral charge of the zwitterionic initiator employed in this study enabled to provide such particles a sufficient colloidal stability.

Nonetheless, the fact that these secondary nucleated particles remained in large minority compared to hybrid particles suggests that the process of particle formation mostly started from cerium oxide nanoparticles acting as a seed.

Tensiometric measurements performed on CeO₂/poly(Sty-co-MA) latexes (Table 5.3) showed that these colloidal dispersions displayed exceptionally high surface tensions (ST), very close to the value of water (72.86 mN/m at 20°C, according to Pallas et al.[4]). This specific feature, in accordance with the absence of any conventional emulsifier in the polymerization process, is particularly interesting for coating applications, as the latex surface tension could then be easily tuned by a controlled post-addition of a surfactant depending on the substrate to be coated.
Table 5.3. Surface tensions of CeO$_2$/poly(Sty-co-MA) hybrid latexes obtained with poly(BA-co-AA) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Latex</th>
<th>Macro-RAFT agent composition</th>
<th>ST (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>poly(BA$<em>5$-co-AA$</em>{10}$)</td>
<td>72.25</td>
</tr>
<tr>
<td>B2</td>
<td>poly(BA$<em>{2.5}$-co-AA$</em>{10}$)</td>
<td>71.45</td>
</tr>
<tr>
<td>B4</td>
<td>poly(BA$_5$-co-AA$_5$)</td>
<td>71.49</td>
</tr>
<tr>
<td>B5</td>
<td>poly(BA$<em>{15}$-co-AA$</em>{20}$)</td>
<td>72.26</td>
</tr>
<tr>
<td>B6</td>
<td>poly(BA$<em>{10}$-co-AA$</em>{20}$)</td>
<td>72.30</td>
</tr>
</tbody>
</table>

**Employing poly(BA-co-AMPS) macro-RAFT agents**

Emulsion copolymerization reactions were performed in the presence of cerium oxide particles and poly(BA-co-AMPS) macro-RAFT agents, employing the recipes collected in Table 5.4. A solid content of about 12 wt% and a cerium oxide content of 4 wt% in the final dry polymer were still targeted and a poly(BA-co-AMPS):CeO$_2$ mass ratio of 1:2 was employed.

**Table 5.4.** Recipes for the emulsion copolymerization of styrene and methyl acrylate in the presence of nanoceria and poly(BA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>Cerium oxide dispersion (g)</th>
<th>Macro-RAFT agent (g)</th>
<th>VA-057 (g)</th>
<th>Water (g)</th>
<th>Styrene/methyl acrylate (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1'</td>
<td>poly(BA$<em>5$-co-AMPS$</em>{10}$)</td>
<td>2.13$^a$</td>
<td>0.121</td>
<td>0.022</td>
<td>40.05</td>
<td>4.99 / 0.55</td>
</tr>
<tr>
<td>B2'</td>
<td>poly(BA$<em>{2.5}$-co-AMPS$</em>{10}$)</td>
<td>2.15$^a$</td>
<td>0.121</td>
<td>0.029</td>
<td>43.16</td>
<td>5.15 / 0.57</td>
</tr>
<tr>
<td>B3'</td>
<td>poly(BA$<em>{7.5}$-co-AMPS$</em>{10}$)</td>
<td>2.17$^a$</td>
<td>0.120</td>
<td>0.024</td>
<td>43.10</td>
<td>5.15 / 0.57</td>
</tr>
<tr>
<td>B4'</td>
<td>poly(BA$_5$-co-AMPS$_5$)</td>
<td>2.14$^a$</td>
<td>0.120</td>
<td>0.022</td>
<td>40.18</td>
<td>4.99 / 0.55</td>
</tr>
<tr>
<td>B6'</td>
<td>poly(BA$<em>{10}$-co-AMPS$</em>{20}$)</td>
<td>2.16$^a$</td>
<td>0.121</td>
<td>0.015</td>
<td>41.77</td>
<td>5.15 / 0.57</td>
</tr>
</tbody>
</table>

$^a$CeO$_2$ content of the dispersion: 10.9 wt%.
Dynamic light scattering analyses indicated small particle sizes (below 80 nm) in all cases (Table 5.5). Employing equation (2) to calculate $N_{\text{CeO}_2}/N_{\text{f}}$, we could expect a low number of cerium oxide particles per final hybrid particle.

Table 5.5. Characterization of CeO$_2$/poly(Sty-co-MA) hybrid latexes obtained with poly(BA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>$X_M$ (%)</th>
<th>$D_p$ (nm)</th>
<th>Polydispersity index</th>
<th>$N_{\text{CeO}_2}^0$ ($10^{-16}$)</th>
<th>$N_{\text{f}}^0$ ($10^{-16}$)</th>
<th>$N_{\text{CeO}<em>2}/N</em>{\text{f}}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1'</td>
<td>poly(BA$<em>{5}$-co-AMPS$</em>{10}$)</td>
<td>79.4</td>
<td>76</td>
<td>0.07</td>
<td>12</td>
<td>1.9</td>
<td>6.6</td>
</tr>
<tr>
<td>B2'</td>
<td>poly(BA$<em>{2.5}$-co-AMPS$</em>{10}$)</td>
<td>71.8</td>
<td>48</td>
<td>0.23</td>
<td>12</td>
<td>6.7</td>
<td>1.8</td>
</tr>
<tr>
<td>B3'</td>
<td>poly(BA$<em>{7.5}$-co-AMPS$</em>{10}$)</td>
<td>81.1</td>
<td>51</td>
<td>0.15</td>
<td>12</td>
<td>6.5</td>
<td>1.9</td>
</tr>
<tr>
<td>B4'</td>
<td>poly(BA$<em>{5}$-co-AMPS$</em>{5}$)</td>
<td>75.4</td>
<td>50</td>
<td>0.25</td>
<td>12</td>
<td>6.0</td>
<td>2.0</td>
</tr>
<tr>
<td>B6'</td>
<td>poly(BA$<em>{10}$-co-AMPS$</em>{20}$)</td>
<td>82.9</td>
<td>56</td>
<td>0.06</td>
<td>12</td>
<td>4.9</td>
<td>2.6</td>
</tr>
</tbody>
</table>

However, the fact that nanoceria mostly remained in the aqueous phase, as evidenced by cryo-TEM observations (Fig.5.9), suggested that the process did not lead to the incorporation of cerium oxide particles in the polymer latex. This result is in agreement with the adsorption isotherms plotted in the case of a poly(BA-co-AMPS) macro-RAFT agent, which showed that these RAFT copolymers remained free in the water phase and hardly adsorbed on the oxide surface (Fig.5.4). Therefore, in this case, the latex is thought to be mainly formed by secondary nucleation: the ceria nanoparticles do not act as an efficient seed when a poly(BA-co-AMPS) macro-RAFT agent is used, as described schematically in Fig.5.10.
Fig. 5.9. Cryo-TEM observations of CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes B3’ (left) and B4’ (right).

Fig. 5.10. Mechanism of particle formation in emulsion polymerizations carried out in the presence of poly(BA-co-AMPS) RAFT copolymers.
Employing poly(BA-co-AA-co-AMPS) macro-RAFT agents

Poly(BA-co-AA-co-AMPS) RAFT terpolymers were engaged in the emulsion copolymerization of styrene and methyl acrylate in the presence of cerium oxide nanoparticles, employing the recipes indicated in Table 5.6.

**Table 5.6.** Recipes for the emulsion copolymerization of styrene and methyl acrylate in the presence of nanoceria and poly(BA-co-AA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>Cerium oxide dispersion (g)</th>
<th>Macro-RAFT agent (g)</th>
<th>VA-057 (g)</th>
<th>Water (g)</th>
<th>Styrene/methyl acrylate (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1''</td>
<td>poly(BA7.5-co-AA10-co-AMPS4)</td>
<td>2.20 a)</td>
<td>0.165</td>
<td>0.022</td>
<td>41.04</td>
<td>5.15 / 0.57</td>
</tr>
<tr>
<td>B2''</td>
<td>poly(BA5-co-AA5-co-AMPS4)</td>
<td>2.21 a)</td>
<td>0.188</td>
<td>0.033</td>
<td>42.11</td>
<td>5.15 / 0.57</td>
</tr>
</tbody>
</table>

a) CeO₂ content of the dispersion: 10.9 wt%.

Particle size measurements carried out by Dynamic Light Scattering (Table 5.7) also indicated small particle sizes (below 50 nm), and suggested a very low number of cerium oxide particles per hybrid particle (between one and two on average).

**Table 5.7.** Characterization of CeO₂/poly(Sty-co-MA) hybrid latexes obtained with poly(BA-co-AA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>Xₘ (%)</th>
<th>Dₚ (nm)</th>
<th>Polydispersity index</th>
<th>N⁰⁺CeO₂ (x 10⁻¹⁶)</th>
<th>Nₚ'</th>
<th>N⁰⁺CeO₂/Nₚ'</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1''</td>
<td>poly(BA7.5-co-AA10-co-AMPS4)</td>
<td>85.2</td>
<td>48</td>
<td>0.11</td>
<td>13</td>
<td>8.0</td>
<td>1.6</td>
</tr>
<tr>
<td>B2''</td>
<td>poly(BA5-co-AA5-co-AMPS4)</td>
<td>84.3</td>
<td>48</td>
<td>0.19</td>
<td>13</td>
<td>8.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Cryo-TEM observations confirmed an efficient incorporation and a very uniform distribution of nanoceria over the hybrid particles (Fig. 5.11).

**Fig. 5.11.** Cryo-TEM picture of the CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latex B2” obtained in the presence of the poly(BA$_5$-co-AA$_5$-co-AMPS$_4$) macro-RAFT agent.

These results were in line with the tentative mechanism we proposed, involving the coalescence of hybrid precursors at the initial stage of the reaction, when poly(BA-co-AA) macro-RAFT agents were employed. Indeed, in this previous case, a certain fraction of acrylic acid units interacted with the cerium oxide surface by complexation, ensuring a good compatibility between the inorganic and polymer phases, while some pending acrylic acid units provided the system an electrostatic stabilization, yet insufficient to stabilize the growth of a high number of hybrid precursors. When poly(BA-co-AA-co-AMPS) RAFT terpolymers were employed, acrylic acid units still played the same double role, but additional anionic charges
from sulfonic acid groups of AMPS units enabled to support the colloidal stability of the system and prevent the coalescence of hybrid precursors during their growth. As a result, most hybrid particles observed in this case comprised a single cerium oxide nanocluster.

Nonetheless, considering the very low amount of RAFT terpolymer adsorbed at the oxide surface – roughly 5 wt% according to adsorption isotherms determined for this system (Fig.5.5) – such a high efficiency of hybrid particle formation was unexpected. From this result we could conclude that a high degree of adsorption of amphiphatic macro-RAFT agents at the oxide surface was not a prerequisite for a high incorporation efficiency, and led us to reconsider the actual mechanism of formation of hydrophobic domains at the cerium oxide surface when poly(BA-co-AA-co-AMPS) RAFT terpolymers are employed: we believe that, when adding hydrophobic monomer units during the emulsion polymerization reaction, the macro-RAFT agents initially present in the aqueous phase acquire an increasing hydrophobicity and tend to migrate towards the cerium oxide surface where they will undergo further chain extension and promote the growth of polymer domains (Fig.5.12).

The outstanding feature of this process is that these macro-RAFT agents, when adding monomer units, become sufficiently surface-active to promote the polymerization reaction at the oxide/water interface, but not enough to encourage the formation of a second crop of polymer particles by secondary nucleation. Comparing the results obtained between the poly(BA-co-AMPS) (massive renucleation) and poly(BA-co-AA-co-AMPS) (efficient formation of hybrid particles), the differentiation between the two mechanisms seems closely related to the presence of AA monomer units.
able to interact with the ceria nanoparticles at a certain stage of the polymerization.

![Mechanism of hybrid particle formation](image)

**Fig.5.12.** Mechanism of hybrid particle formation in emulsion polymerization reactions carried out in the presence of nanoceria and poly(BA-co-AA-co-AMPS) macro-RAFT agents.

A thorough characterization of the molecular weight distribution of CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes would be useful in order to study the impact of each type of macro-RAFT agent on the polymerization reaction. Unfortunately, attempts to carry out size exclusion chromatography (SEC) measurements on these latexes failed due to the poor solubility of dry CeO$_2$/poly(styrene-co-methyl acrylate) hybrid samples in all types of solvents available for SEC analyses in the laboratory.

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5.3.3. Synthesis of cerium oxide / poly(VDC-co-MA) hybrid latexes

Employing poly(BA-co-AA) macro-RAFT agents

Judging by the high incorporation efficiency of cerium oxide particles obtained when poly(BA-co-AA) RAFT copolymers were employed in the emulsion copolymerization of styrene and methyl acrylate, we decided to apply the same strategy to the emulsion copolymerization of vinylidene chloride and methyl acrylate (Table 5.8).

Table 5.8. Recipes for the emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of nanoceria and poly(BA-co-AA) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>CeO$_2$ dispersion (g)</th>
<th>Macro-RAFT agent (g)</th>
<th>VA-057 (g)</th>
<th>TSPP (g)</th>
<th>SDBS (g)</th>
<th>Water (g)</th>
<th>VDC/MA (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3</td>
<td>poly(BA$<em>{7.5}$-co-AA$</em>{10}$)</td>
<td>14.23 $^a$)</td>
<td>0.782</td>
<td>0.135</td>
<td>+0.19</td>
<td>+0.018</td>
<td>95.03</td>
<td>+25.76</td>
</tr>
<tr>
<td>V4</td>
<td>poly(BA$<em>{5}$-co-AA$</em>{5}$)</td>
<td>14.22 $^a$)</td>
<td>0.781</td>
<td>0.200</td>
<td>+0.15</td>
<td>+0.014</td>
<td>94.89</td>
<td>+20.02</td>
</tr>
<tr>
<td>V4'</td>
<td>poly(BA$<em>{5}$-co-AA$</em>{5}$)</td>
<td>14.20 $^a$)</td>
<td>0.781</td>
<td>0.201</td>
<td>+0.14</td>
<td>+1.74</td>
<td>94.87</td>
<td>+20.01</td>
</tr>
</tbody>
</table>

$^a$)CeO$_2$ content of the dispersion: 10.9 wt%.

A solid content of 25 wt% and a cerium oxide content of 4 wt% (with respect to the dry polymer) were targeted. A poly(BA-co-AA):CeO$_2$ mass ratio of 1:2 was still employed in this series of experiments. Due to experimental constraints, the monomers and tetrasodium pyrophosphate (TSPP) were injected as a pre-emulsion in water via a single reactor entry. Therefore, experiments V3 and V4 contained a very low amount of
conventional surfactant (SDBS) to ensure the formation of the pre-emulsion. In the case of experiment V4’, a higher amount of conventional surfactant was added to the pre-emulsion in order to study its effect on the latex colloidal stability.

The average particle diameters of CeO₂/PVDC latexes determined by DLS were significantly higher than those measured in the case of previous systems based on poly(styrene-co-methyl acrylate) and, accordingly, so were the average numbers of cerium oxide particles per hybrid particle estimated from equation (2), particularly in the case of latexes containing low amounts of conventional emulsifier (Table 5.9).

Table 5.9. Characterization of CeO₂/poly(VDC-co-MA) hybrid latexes obtained with poly(BA-co-AA) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>pH</th>
<th>Xₘ (%)</th>
<th>Dₚ (nm)</th>
<th>Polydispersity index</th>
<th>N⁰₈eo₂ (x 10⁻¹⁵)</th>
<th>N⁰₁₅ (x 10⁻¹⁵)</th>
<th>N⁰₈eo₂/N₁₅</th>
<th>ST (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3</td>
<td>poly(BA₇.₅-co-AA₁₀)</td>
<td>6.5</td>
<td>89.6</td>
<td>95</td>
<td>0.19</td>
<td>814</td>
<td>55.5</td>
<td>14.7</td>
<td>60.17</td>
</tr>
<tr>
<td>V4</td>
<td>poly(BA₅-co-AA₅)</td>
<td>6.9</td>
<td>85.9</td>
<td>187</td>
<td>0.16</td>
<td>814</td>
<td>5.45</td>
<td>149</td>
<td>60.59</td>
</tr>
<tr>
<td>V4’</td>
<td>poly(BA₅-co-AA₅)</td>
<td>6.8</td>
<td>95.4</td>
<td>108</td>
<td>0.22</td>
<td>813</td>
<td>31.1</td>
<td>26.1</td>
<td>36.67</td>
</tr>
</tbody>
</table>

Indeed, cryo-TEM observations carried out on these latexes showed very broad particle size distributions and a certain heterogeneity of hybrid particle structures, the two characteristics appearing to be related to each other: the larger the latex particle size, the higher the number of cerium oxide nanoclusters decorating its surface (Fig.5.10). Again, this result is in line with a mechanism of aggregation of hybrid particle precursors containing a single cerium oxide cluster into larger mature hybrid particles.
comprising several nanoceria. In the present case, the higher targeted solid content could have further encouraged the coagulation process.

**Fig.5.10.** Cryo-TEM pictures of the CeO$_2$/poly(VDC-co-MA) hybrid latex V3 (top) and V4 (bottom) obtained in the presence of poly(BA$_{7.5}$-co-AA$_{10}$) and poly(BA$_5$-co-AA$_5$) macro-RAFT agents, respectively.

Less coalescence occurred when a conventional surfactant was added to the system, as evidenced by cryo-TEM images of latex V4’
(Fig.5.11). However, the addition of higher amounts of SDBS also led to the formation of cerium oxide-free polymer particles by secondary nucleation, which also resulted in a broad particle size distribution.

![Cryo-TEM pictures of the CeO₂/poly(VDC-co-MA) hybrid latex V4’ obtained in the presence of the poly(BA₅-co-AA₅) macro-RAFT agent and conventional emulsifier.]

**Fig.5.11.** Cryo-TEM pictures of the CeO₂/poly(VDC-co-MA) hybrid latex V4’ obtained in the presence of the poly(BA₅-co-AA₅) macro-RAFT agent and conventional emulsifier.

Tensiometric measurements carried out on CeO₂/PVDC hybrid latexes showed lower values compared to those obtained in the case of CeO₂/poly(Sty-co-MA) latexes (Table 5.9), due to the presence of small amounts of surfactant required to stabilize the pre-emulsion continuously injected during the polymerization reaction. Of course, when higher amounts of emulsifier were added in the case of latex V4’, a much lower surface tension was measured.

SEC characterization of CeO₂/poly(VDC-co-MA) hybrid latexes V4 and V4’ (Table 5.10) showed that the average molecular weights and polydispersity indices were in the same range as the results reported in
Chapter 2 in the case of PVDC reference and composite latexes. Therefore, the macro-RAFT agent poly(BA₅-co-AA₅) seemed to have a low impact on the molecular weight distribution of the final poly(VDC-co-MA) copolymer. The polydispersity indices of 2.0 and 2.2 measured for both latexes reflect our main intension to use macro-RAFT agents as compatibilizing agents offering a possibility of chain extension, rather than as molecular weight controllers.

Table 5.10. SEC characterization of CeO₂/poly(VDC-co-MA) hybrid latexes obtained with poly(BA-co-AA) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>pH</th>
<th>Xₘ (%)</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>Mₘ/Mₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>V4</td>
<td>poly(BA₅-co-AA₅)</td>
<td>6.9</td>
<td>85.9</td>
<td>89500</td>
<td>179300</td>
<td>2.0</td>
</tr>
<tr>
<td>V₄'</td>
<td>poly(BA₅-co-AA₅)</td>
<td>6.8</td>
<td>95.4</td>
<td>74700</td>
<td>163200</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Considering the fact that poly(vinylidene chloride) generates a certain acidity upon storage of waterborne PVDC dispersions, the colloidal stability of latexes V4 and V₄' was compared at low pH via a slow addition of a 0.1N HCl solution and was followed by visual inspection and by DLS characterization (Fig.5.12). As suggested by the evolution of the average particle size of latex V4 as a function of the pH and confirmed by visual observations, the irreversible aggregation and flocculation of the colloidal dispersion occurred at about pH 4: the protonation of carboxylate groups, the only functions providing electrostatic stabilization to this system, could account for this loss of stability at low pH. In the case of latex V₄', which contained a higher amount of SDBS, the colloidal stability was maintained at lower pH values. It shows that the conventional surfactant is a key component to prevent the short-term flocculation of CeO₂/PVDC hybrid
latexes obtained via the poly(BA-co-AA) macro-RAFT agent route. However, it should be pointed out that the flocculation of the colloidal dispersion V4’ also occurred within a few days at pH 2. The post-addition of conventional amounts of SDBS at the end of the emulsion polymerization reaction could be a possible solution to overcome instability issues at low pH.

![Graph](image)

**Fig.5.12.** Evolution of the volume average particle diameter of CeO$_2$/poly(VDC-co-MA) hybrid latexes V4 and V4’ as a function of the pH.

**Employing poly(BA-co-AA-co-AMPS) macro-RAFT agents**

As already mentioned in the previous chapter, sulfonated macro-RAFT agents could impart CeO$_2$/PVDC a sufficient colloidal stability at low pH to avoid the use of conventional emulsifier during the emulsion copolymerization of vinylidene chloride and methyl acrylate. Given that poly(BA-co-AMPS) RAFT copolymers failed at promoting the polymerization reaction at the surface of cerium oxide when styrene was employed as a model monomer, this group of amphiphatic macro-RAFT agents was not further tested for the synthesis of CeO$_2$/PVDC hybrid
latexes. Poly(BA-co-AA-co-AMPS) RAFT terpolymers, which showed more encouraging results in the emulsion copolymerization of styrene and methyl acrylate performed in the presence of nanoceria, were therefore applied for the synthesis of CeO$_2$/PVDC latexes (Table 5.11).

**Table 5.11.** Recipes for the emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of nanoceria and poly(BA-co-AA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>CeO$_2$ dispersion (g)</th>
<th>Macro-RAFT agent (g)</th>
<th>VA-057 (g)</th>
<th>TSPP (g)</th>
<th>SDBS (g)</th>
<th>Water (g)</th>
<th>VDC/MA (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3''</td>
<td>poly(BA$<em>{7.5}$-co-AA$</em>{10}$-co-AMPS$_4$)</td>
<td>14.21 a)</td>
<td>1.058</td>
<td>0.138</td>
<td>+0.17</td>
<td>+0.017</td>
<td>88.39</td>
<td>+23.19</td>
</tr>
<tr>
<td>V4''</td>
<td>poly(BA$<em>{5}$-co-AA$</em>{5}$-co-AMPS$_4$)</td>
<td>14.20 a)</td>
<td>1.198</td>
<td>0.206</td>
<td>+0.15</td>
<td>+0.019</td>
<td>87.97</td>
<td>+23.12</td>
</tr>
</tbody>
</table>

a) CeO$_2$ content of the dispersion: 10.9 wt%.

The resulting latexes displayed lower mean particle sizes than with poly(BA-co-AA), but still a broad particle size distribution, according to DLS analyses (Table 5.12).

**Table 5.12.** Characterization of CeO$_2$/poly(VDC-co-MA) hybrid latexes obtained with poly(BA-co-AA-co-AMPS) macro-RAFT agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macro-RAFT agent composition</th>
<th>pH</th>
<th>XM (%)</th>
<th>DP (nm)</th>
<th>Polydispersity index</th>
<th>$N_0$ CeO$_2$ (x 10$^{-15}$)</th>
<th>$N_P$ (x 10$^{-15}$)</th>
<th>$N_0$ CeO$_2$/$N_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3''</td>
<td>poly(BA$<em>{7.5}$-co-AA$</em>{10}$-co-AMPS$_4$)</td>
<td>6.1</td>
<td>82.6</td>
<td>79</td>
<td>0.233</td>
<td>813</td>
<td>80.2</td>
<td>10.1</td>
</tr>
<tr>
<td>V4''</td>
<td>poly(BA$<em>{5}$-co-AA$</em>{5}$-co-AMPS$_4$)</td>
<td>5.9</td>
<td>95.6</td>
<td>129</td>
<td>0.191</td>
<td>813</td>
<td>21.2</td>
<td>38.4</td>
</tr>
</tbody>
</table>
Unfortunately, further characterization was impossible, given that both colloidal dispersions experienced an irreversible flocculation within a few days after their synthesis. The use of conventional emulsifiers may therefore be unavoidable to improve the stability of such hybrid latexes.

5.3.4. Adverse effects of the radical-scavenging role of cerium oxide nanoparticles

Kinetic studies of emulsion copolymerization reactions of styrene and methyl acrylate carried out in the presence of amphiphatic macro-RAFT agents and cerium oxide nanoparticles revealed the occurrence of an inhibition period during the first 60 to 100 minutes of the reaction (Fig.5.14).

![Fig.5.14. Instantaneous monomer conversions as a function of time in emulsion copolymerization of styrene and methyl acrylate in the presence of cerium oxide and amphiphatic macro-RAFT agents.](image)
Accordingly, it implied that all emulsion polymerization reactions presented in this chapter were mainly carried out under monomer-flooded conditions, contrary to what we initially targeted when adding the monomers continuously during the process.

We attributed this phenomenon to the radical scavenging effect displayed by cerium oxide, which is directly related to the presence of Ce$^{3+}$ active sites at the cerium oxide surface. Indeed, it is now generally assumed that cerium oxide nanoparticles contain a majority of Ce$^{4+}$, but small amounts of Ce$^{3+}$ may be introduced by formation of oxygen vacancies in their crystal structure, according to the following reaction\cite{5}:

\[
\text{CeO}_2 \rightleftharpoons \text{CeO}_{(2-x)} + \left(x/2\right)\text{O}_2 \tag{3}
\]

also expressed as\cite{6}:

\[
2\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \tag{3'}
\]

Theoretical calculations reported by Sayle et al. confirmed that this reaction is more favored in surface/subsurface layers rather than in the bulk material\cite{5,6}. As a result, higher Ce$^{3+}$ concentrations were measured at the surface of cerium oxide nanoparticles by X-ray photoelectron spectroscopy, and decreasing the size of cerium oxide nanoparticles appeared to increase the concentration of Ce$^{3+}$ sites, due to an increase of their surface to volume ratio\cite{7}. Furthermore, the creation of oxygen vacancies could be facilitated in aqueous conditions\cite{8,9}, given that the adsorption of water molecules at the cerium oxide surface would decrease the energy of formation of active sites\cite{10}. 

The radical scavenging activity of Ce$^{3+}$ sites in cerium oxide, evidenced for several types of radicals, such as superoxide (O$_2^-$)[11], nitric oxide (NO$^+$)[12] or hydroxyl radicals (HO$^+$)[13], has extended the range of applications of cerium oxide to biomedical fields, owing to its high potential in the treatment of degenerative diseases[14] or chronic inflammation[15] induced by radical species. The mechanism presented in Scheme 5.1, involving a reversible switch between the +III and +IV states of CeO$_2$ nanoparticles, was proposed to describe the scavenging of hydroxyl radicals[13]. Concerning the scavenging of superoxide radicals, Korsvik et al. proposed a mechanism[11] that could be described by the cyclic diagram depicted in Scheme 5.2.

Scheme 5.1. Hydroxyl radical scavenging by cerium oxide nanoparticles (adapted from reference[13]).

Scheme 5.2. Scavenging of superoxide radical by cerium oxide nanoparticles (adapted from reference[11]).
Assuming that, in our case, scavenging of free radicals involved a similar reversible switch between the +III and +IV states of cerium oxide accompanied with a release of oxygen, both the oxidation of Ce\(^{3+}\) to Ce\(^{4+}\) and interaction with oxygen could have taken part in the inhibition observed during emulsion polymerization reactions carried out in the presence of cerium oxide nanoparticles. However, the reason why the regeneration of Ce\(^{3+}\) appeared to cease at a certain point, as evidenced by the end of the inhibition period observed in our kinetic studies, remains undetermined. This would require further investigation in order to propose a mechanism for the radical-scavenging process occurring in our case and to identify the factors influencing the length of the initial inhibition period.

The radical scavenging effect of cerium oxide nanoparticles is of course undesirable for emulsion polymerization processes carried out in their presence. Indeed, as evidenced by our kinetic studies (Fig.5.10), the accumulation of monomer during the first 60 to 100 minutes of reaction did not enable to work in monomer-starved conditions. This did not appear to be critical in terms of efficiency of hybrid particle formation, but it could be detrimental when implementing the process on a larger scale. The sudden increase of the rate of polymerization observed at about 120 min of reaction could indeed lead to an exothermic peak and a loss of control over the reaction temperature. A possible solution to circumvent this issue could consist in carrying out the initial step of particle formation in batch at low solid content to form a hybrid seed latex with a controlled particle size at the end of the inhibition period, followed by the continuous addition of monomer in order to gain control over the rate of polymerization and over the particle growth.
5.4. Conclusions

The synthesis of CeO₂-based hybrid latexes was successfully carried out via the macro-RAFT agent route, in most cases with a very high efficiency of nanoceria incorporation and a very low amount of polymer particles formed by secondary nucleation.

UV-spectrometry appeared to be the most reliable and quantitative method to characterize the adsorption of amphiphatic macro-RAFT agents on the cerium oxide surface. It confirmed that a certain amount of oligomers remained free in the aqueous phase at the start of the polymerization despite the successful adsorption of poly(BA-co-AA) copolymers. It was also evidenced that a very poor adsorption of poly(BA-co-AMPS) and poly(BA-co-AA-co-AMPS) macro-RAFT agents occurred at the cerium oxide surface.

Hybrid particle morphologies of CeO₂/poly(Sty-co-MA) latexes obtained from poly(BA-co-AA) macro-RAFT agents, consisting on average of several cerium oxide clusters present at the polymer/water interface, suggested that residual citrates present at the cerium oxide surface prevented their complete encapsulation by the polymer phase. Moreover, negative charges provided by acrylic acid units may not be sufficient to stabilize the growth of hybrid particles precursors, leading to their coalescence to form larger, more stable hybrid particles. This effect was confirmed and even more pronounced in the case of CeO₂/PVDC hybrid latexes, for which particle aggregation occurred to a larger extent. CeO₂/poly(Sty-co-MA) hybrid precursors obtained from poly(BA-co-AA-co-AMPS) RAFT terpolymers appeared to be more stable during their growth, certainly due to the extra contribution of sulfonate groups to their colloidal stability, as evidenced by the large proportion of final hybrid particles
containing a single cerium oxide nanocluster. The high efficiency of hybrid particle formation observed in the latter case, despite the very low amount of RAFT terpolymer initially adsorbed at the cerium oxide surface, suggested that the migration of macro-RAFT agents towards the cerium oxide could occur when adding hydrophobic monomer units during the course of the emulsion polymerization reaction. Finally, we showed that the presence of a conventional emulsifier seemed to be required in order to provide CeO$_2$/PVDC latexes a sufficient colloidal stability at low pH.

Kinetic studies of reactions of emulsion copolymerization of styrene and methyl acrylate in the presence of cerium oxide and amphiphatic macro-RAFT agents showed a long inhibition period attributed to the radical scavenging role of Ce$^{3+}$ sites present at the cerium oxide surface. Therefore, we could conclude that emulsion polymerization reactions described in this chapter still need optimization to control the rate of the polymerization and the growth of the hybrid particles. A possible solution to circumvent the problems related to the radical scavenging effect of cerium oxide could consist in a first step of hybrid particle nucleation taking place in batch conditions at low solid content, followed by a second step of continuous addition of the monomers with a controlled polymerization rate and particles growth. Nonetheless, this route based on the use of amphiphatic macro-RAFT agents is so far the most promising for the synthesis of CeO$_2$/PVDC hybrid latexes.

Efforts are currently dedicated to increasing the solid content of those latexes before proceeding to further scale up of the reaction. Studies of the UV stability of waterborne barrier films obtained from these latexes will also be performed and compared to results obtained in the case of films obtained from classical PVDC latexes and from blends of PVDC latexes with aqueous nanoceria dispersions.
References

Conclusions and perspectives

This thesis work demonstrated the possibilities of synthesis of novel nanostructured poly(vinylidene chloride) latexes with a high potential for use as waterborne barrier films with improved thermal and UV stabilities. A thorough review of the scientific literature, detailed in Chapter 1, enabled us to gain a better understanding of the mechanisms of thermal and UV degradations of vinylidene chloride copolymers, and to identify potential stabilizers that could be incorporated into PVDC latexes via conventional emulsion polymerization processes:

- Epoxy-functional seed latexes, due to their HCl-scavenging role, were considered as thermal stabilizers to be integrated into poly(vinylidene chloride) colloidal dispersions via a two-stage emulsion polymerization process.

- Cerium oxide nanoparticles, owing to their high absorption of UV radiation and low photocatalytic activity, had already been proven to impart waterborne PVDC films an enhanced UV stability (blends of ceria nanoparticles and PVDC latexes). The synthesis of CeO$_2$/PVDC hybrid latexes was thus attempted via two different routes involving the preliminary surface-modification of nanoceria by either alkoxy silanes or amphiphatic macro-RAFT agents.

However, there are still many opened questions regarding more specific details of the dehydrochlorination process, such as the mechanism(s) of formation of the first degree of unsaturation in the polymer
Conclusions and perspectives

chains and degradation mechanism(s) involving hydrochloric acid as an indirect catalyst, which have not yet been reported in the literature. This could justify a more detailed analysis of PVDC degradation processes in order to propose new strategies of thermal and UV stabilization of vinylidene chloride copolymers.

As discussed in Chapter 2, poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes were synthesized via a two-stage emulsion polymerization process. In a first step, the synthesis of epoxy-functional seed latexes was carried out by emulsion copolymerization of glycidyl methacrylate and butyl methacrylate. After optimization of the reaction conditions, such as the temperature and pH of the aqueous medium, we showed that a high percentage of epoxy groups could be preserved from ring-opening reactions. A good control of the seed latex particle size was also achieved by tuning the rate of continuous addition of the monomers. In a second step, the seeded emulsion copolymerization of vinylidene chloride and methyl acrylate was performed in the presence of poly(GMA-co-BMA) epoxy-functional seed latexes. Tetrasodium pyrophosphate, a common additive employed to control the pH during the synthesis of PVDC latexes, appeared to be a key component during this step, not only to prevent the hydrolysis of epoxy groups, but also to maintain the latex colloidal stability and to control the polymer molecular weight. Poly(GMA-co-BMA)/poly(VDC-co-MA) composite particles displayed snowman morphologies, in agreement with theoretical calculations that predicted the partial encapsulation of the epoxy-functional seed by the second-stage PVDC polymer. Kinetic limitations due to the high gel content of the seed polymer could also account for the final latex morphology.
Thermogravimetric analyses carried out at 160°C in an air atmosphere and visual observations of the degraded samples showed that the resulting PVDC composites exhibited an enhanced thermal stability compared to a classical poly(vinylidene chloride-co-methyl acrylate) sample taken as a reference. Bare coating of the poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes on a PET substrate resulted in a homogeneous film with a good transparency. Measurements of oxygen permeability performed on these films showed that the composite films displayed a slightly higher permeability towards oxygen compared to the reference PVDC waterborne coating. Nevertheless, we may reasonably conclude that the high barrier properties of the polymer towards oxygen were preserved. In order to observe more accurate trends, future efforts could be dedicated to measurements of oxygen and water vapor permeabilities of PVDC films with a more uniform thickness obtained from industrial coating processes. Of course, this requires implementing the synthesis of PVDC composite latexes at a larger scale, but the fact that stable latexes were obtained with solid contents of about 50 wt% is very encouraging for future scaling up of the process. Further work could also focus on strategies aiming at controlling the final morphology of poly(GMA-co-BMA)/poly(VDC-co-MA) composite latexes. A complete encapsulation of the core polymer by the PVDC shell could indeed be beneficial in terms of preservation of the epoxy groups during the storage of the latex as well as in terms of final properties, such as a lower permeability to gases and a higher HCl scavenging efficiency.

Incorporation of cerium oxide nanoparticles into polymer latexes was attempted via two main routes. The first one, presented in Chapter 3, consisted in the grafting of an alkoxy silane at the inorganic particle surface
Conclusions and perspectives

performed in aqueous conditions. An accurate characterization of the grafting efficiency was difficult to achieve due to the presence of a high amount of water-soluble additives in the commercial cerium oxide aqueous dispersion employed in this study. Emulsion copolymerization of styrene and methyl acrylate performed in the presence of silane-modified dispersions led to the formation of anisotropic polymer particles, with cerium oxide particles fully remaining in the aqueous phase. It suggested that the surface-modification step mostly consisted in the self-condensation of alkoxy silanes, resulting in the formation of silsesquioxanes nanometric objects. They could have then played the role of seed particles during the subsequent emulsion polymerization stage and taken part in the development of anisotropic morphologies. Therefore, the silane-modification of cerium oxide particles in the conditions employed in this study did not appear to be an efficient process for the synthesis of CeO$_2$-based hybrid structures. The use of acidic cerium oxide aqueous dispersions could enable a higher grafting efficiency, as the process could be carried out at lower pH values and in the absence of dispersing agents to promote the grafting reaction at the expense of the silane self-condensation.

The second route for the surface-modification of cerium oxide nanoparticles, explored in Chapters 4 and 5, involved the synthesis and adsorption of amphiphatic macro-RAFT agents. Three types of oligomers were obtained by RAFT copolymerization/terpolymerization of butyl acrylate with acrylic acid and/or 2-acrylamido-2-methylpropanesulfonic acid (AMPS) in the presence of a trithiocarbonate as chain transfer agent:

- For poly(BA-co-AA) macro-RAFT agents, a very good agreement between theoretical and experimental molecular weights was
obtained, as well as polydispersity indices of about 1.3, suggesting that a fairly good control was achieved during the reaction. MALDI-TOF-MS analyses confirmed the expected chain-end functionality, while a study of the reaction kinetics evidenced a random copolymerization of the two comonomers. The adsorption of these copolymers occurred successfully at the surface of nanoceria, as evidenced by UV-visible spectrometric measurements, although a high percentage of macro-RAFT agents (between 50 and 60%) remained free in the aqueous phase. Emulsion polymerization reactions carried out in the presence of poly(BA-co-AA) RAFT copolymers and cerium oxide particles led to the efficient formation of hybrid latexes, as no ceria remained free in the water phase and only few oxide-free polymer particles were formed by secondary nucleation. The final morphology of CeO$_2$/poly(Sty-co-MA) hybrid particles suggested that the coalescence of instable hybrid precursors, obtained by seeded nucleation from nanoceria, resulted in the formation of larger particles displaying several cerium oxide nanoclusters on average per latex particle. This effect appeared to be even more pronounced in the case of CeO$_2$/PVDC hybrid latexes, which comprised large particles with a very high number of cerium oxide particles present at the polymer-water interface. The incomplete encapsulation of nanoceria by the polymer phase was attributed to the presence of residuals citrates at the oxide surface, which could have affected the adsorption of amphiphatic macroRAFT agents at their surface.

- In the case of poly(BA-co-AMPS) RAFT copolymers, a good molecular weight control and the preservation of the chain-end functionality were also evidenced by the same characterization tools. However, low AMPS conversions (80%) were obtained and
composition drifts were observed, since butyl acrylate appeared to be incorporated faster in the polymer chains according to time-resolved $^1$H NMR analyses. UV spectrometry suggested that these copolymers hardly adsorbed at the cerium oxide surface (less than 5%), and emulsion polymerization reactions resulted in the full segregation of nanoceria and final polymer particles: most of the ceria nanoparticles remained free in the water phase and only few hybrid particles were formed. Therefore, it was concluded that this type of macro-RAFT agents did not promote the polymerization reaction at the surface of cerium oxide nanoparticles.

Although poly(BA-co-AA-co-AMPS) macro-RAFT agents were subjected to less extensive characterization, $^1$H NMR and MALDI-ToF-MS analyses tended to confirm the final structure of the terpolymers. Despite the fact that their adsorption at the surface of nanoceria was also very limited, they appeared to increase the polymer affinity towards the oxide surface due to the presence of acrylic acid units, while sulfonic acid groups clearly enhanced the colloidal stability of the system and prevented the coalescence of hybrid precursors, as evidenced by the morphology of the final CeO$_2$/poly(styrene-co-methyl acrylate) hybrid latexes. The high efficiency of incorporation of inorganic particles obtained with these RAFT terpolymers, although they hardly adsorbed at the oxide surface, strongly suggested that the nucleation of hybrid particles employing the macro-RAFT agent route could occur via a dynamic process: the chain extension of the amphiphatic macro-RAFT agents, starting mainly in the aqueous phase, could lead to an increase of their hydrophobicity and to their migration towards the oxide surface, where they could promote the formation of hydrophobic domains. It may however require that, as in the case of
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poly(BA-co-AA-co-AMPS) RAFT terpolymers, the chain-extended macro-RAFT agents do not become too much surface-active otherwise it would encourage the formation of a second crop of polymer particles by secondary nucleation.

The radical-scavenging nature of Ce\(^{3+}\) sites present at the surface of cerium oxide nanoparticles could be a serious issue when implementing the process at a larger scale, since it causes the accumulation of monomer at the beginning of the reaction. This should be the object of further investigation in order to circumvent this issue and gain a better control over the particle nucleation and growth. A possible solution could consist in the synthesis of a low solid content seed hybrid latex by batch copolymerization of vinylidene chloride and methyl acrylate in the presence of cerium oxide nanoparticles and an amphiphatic macro-RAFT agent, followed by the continuous addition of a pre-emulsion of the comonomers to allow a more controlled growth of the hybrid particles.

Finally the film formation of cerium oxide/PVDC hybrid latexes should be studied, as well as the impact of cerium oxide nanoparticles on the UV stability and barrier properties of the resulting films compared to a reference PVDC film. However, it would first require the synthesis of CeO\(_2\)/PVDC hybrid latexes with higher solid contents in order to fulfill industrial requirements for film formation. Tests are currently being carried out to increase the latexes solid content from 25 wt% to 40 – 50 wt% solid content and to implement the process at a larger scale.
Appendix A. Calculation of the grafting efficiency from thermogravimetric analyses

Fig. A.1. Thermogravimetric analyses carried out on dry powders obtained from dialyzed CeO$_2$ dispersions.

% of pure CeO$_2$ in bare CeO$_2$ = 100 – ML$_0$

⇒ Mass ratio impurities / pure CeO$_2$ = ML$_0$ / (100 – ML$_0$)

where ML$_0$ is the mass loss (in wt%) measured in the case of bare CeO$_2$

% of pure CeO$_2$ in grafted CeO$_2$ = 100 – ML

where ML is the mass loss (in wt%) measured in the case of grafted CeO$_2$. 
Assuming that the grafted CeO\textsubscript{2} contains the same mass ratio of impurities/pure CeO\textsubscript{2} as bare CeO\textsubscript{2}:

\[ \text{% of impurities in grafted CeO}_2 = \frac{(100 - ML) \times ML_0}{(100 - ML_0)} \]

\[ \Rightarrow \text{% of silane in grafted CeO}_2 = ML - \text{% of impurities in grafted CeO}_2 \]

\[ = ML - \left[\frac{(100 - ML) \times ML_0}{(100 - ML_0)}\right] \]

\[ = 100 \times \frac{ML - ML_0}{100 - ML_0} \]

\[ \Rightarrow \text{% silane}_{\text{exp}} = \text{% silane} \times \frac{100}{\text{% silane} + \text{% CeO}_2} \]

\[ = \frac{104 \times (ML - ML_0)}{100 \times (ML - ML_0) + (100 - ML)} \]

\[ = \frac{104}{100 + (100 - ML_0) \times (100 - ML) / (ML - ML_0)} \]

Assuming a condensation of every silane molecule with the 3 silanol groups:

\[ \text{% silane}_{\text{theo}} = m_{\text{silane}} \times \left(\frac{M_{\text{silanol}}}{M_{\text{silane}}}\right) / \left[m_{\text{CeO}_2} + m_{\text{silane}} \times \left(\frac{M_{\text{silanol}}}{M_{\text{silane}}}\right)\right] \]

\[ \Rightarrow \text{Eff}_{\text{grafting}}(\%) = \frac{\text{% silane}_{\text{exp}} \times 100}{\text{% silane}_{\text{theo}}} \]

\[ \text{N.A.}: \quad \text{For N-3810 dialyzed: } ML_0 = 17.9\% \]

\[ \text{For G4 dialyzed: } ML = 20.6\% \]

\[ \text{% silane}_{\text{exp}} = \frac{104}{100 + (100 - 17.9) \times (100 - 20.6) / (20.6 - 17.9)} \]

\[ = 3.98 \]

\[ \text{% silane}_{\text{theo}} = 11.96 \]

\[ \Rightarrow \text{Eff}_{\text{grafting}} = 3.98 \times 100 / 11.96 = 32.9\% \]
Appendix B. Characterization of the adsorption of amphiphatic macro-RAFT agents by UV-visible spectrometry

All examples below are given in the case of the RAFT terpolymer poly(BA$_5$-co-AA$_5$-co-AMPS$_4$).

For each type of amphiphatic macro-RAFT agents, a calibration curve, giving the maximum absorbance (at 308 nm, specific for the trithiocarbonate function) as a function of the oligomer concentration in water (from 0.005 to 0.3 g/L), was plotted (Fig.B.1). The calibration curves followed a linear trend for values of absorbance below 2.

![Graph showing calibration curve with equation: y = 5.7125x + 0.0092, R$^2$ = 0.9998.](image)

**Fig.B.1.** Calibration curve obtained with the RAFT terpolymer poly(BA$_5$-co-AA$_5$-co-AMPS$_4$).

Serum solutions, containing the portion of macro-RAFT present in the aqueous phase, obtained after ultracentrifugation of cerium oxide
dispersions, were analyzed by UV-visible spectroscopy (Fig.B.2). Dilutions of 10 or 100 times were required in order to fit the linear range of absorbance of the calibration curve.

**Fig.B.2.** UV-visible absorption curves of serum solutions obtained after ultracentrifugation of cerium oxide dispersions.
From the maximum absorbance measured at 308 nm for each solution, the concentration of macro-RAFT agent could be determined via the calibration curve (Table B.1). The mass of macro-RAFT agent adsorbed per gram of cerium oxide ($m_{\text{macro-RAFT} / g \text{CeO}_2}$) could then be calculated via a mass balance equation:

$$m_{\text{macro-RAFT} / g \text{CeO}_2} = ([\text{macro-RAFT}]_0 - [\text{macro-RAFT}]_{\text{serum}}) / [\text{CeO}_2]_0$$  

(1)

where $[\text{macro-RAFT}]_0$ and $[\text{CeO}_2]_0$ (expressed in g/L) correspond respectively to the macro-RAFT agent concentration and the cerium oxide concentration in the initial CeO$_2$ dispersion (before ultracentrifugation), and $[\text{macro-RAFT}]_{\text{serum}}$ is the macro-RAFT agent concentration in the serum (in g/L).

**Table B.1.** Characterization of the adsorption of the RAFT terpolymer poly(BA$_5$-co-AA$_5$-co-AMPS$_4$) at the surface of CeO2 nanoparticles via UV-visible spectroscopy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CeO$_2$ concentration (g/L)</th>
<th>Macro-RAFT concentration (g/L)</th>
<th>Dilution</th>
<th>Absorbance</th>
<th>Macro-RAFT concentration in serum (g/L)</th>
<th>Mass of macro-RAFT per gram of CeO$_2$ (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2''-0</td>
<td>4.0</td>
<td>0</td>
<td>10 x</td>
<td>0.013</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>A2''-1</td>
<td>4.0</td>
<td>0.2</td>
<td>10 x</td>
<td>0.136</td>
<td>0.23</td>
<td>0.00</td>
</tr>
<tr>
<td>A2''-2</td>
<td>4.0</td>
<td>0.4</td>
<td>10 x</td>
<td>0.244</td>
<td>0.42</td>
<td>0.00</td>
</tr>
<tr>
<td>A2''-3</td>
<td>4.0</td>
<td>1.0</td>
<td>10 x</td>
<td>0.546</td>
<td>0.95</td>
<td>0.01</td>
</tr>
<tr>
<td>A2''-4</td>
<td>4.0</td>
<td>2.0</td>
<td>10 x</td>
<td>1.090</td>
<td>1.90</td>
<td>0.03</td>
</tr>
<tr>
<td>A2''-5</td>
<td>4.0</td>
<td>4.0</td>
<td>100 x</td>
<td>0.205</td>
<td>3.75</td>
<td>0.06</td>
</tr>
<tr>
<td>A2''-6</td>
<td>4.0</td>
<td>8.0</td>
<td>100 x</td>
<td>0.436</td>
<td>7.80</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Given the current increase of the world population, the need for good product quality and longer shelf life and our growing awareness of their environmental impacts, food and pharmaceutical packages should nowadays fulfill a wide range of requirements: not only should they preserve the packed products from external polluting agents, but they must also be innocuous, more energy-efficient and disposable. Barrier polymers have enabled to meet these criteria, by offering alternatives to more energy-consuming and heavier materials like glass or metals, while maintaining a low permeability to water and/or oxygen. Among the large variety of barrier polymers, poly(vinylidene chloride) (PVDC) copolymers provide a more complete protection to external contaminants, due to their extremely low permeabilities towards water and oxygen and a high chemical resistance to a wide range of solvents. Furthermore, the fact that their production is carried out in aqueous media, by suspension or emulsion polymerization, is another remarkable advantage, as these techniques reduce the use of volatile organic compounds.

Nonetheless, PVDC films still suffer from limitations as far as their thermal and UV stabilities are concerned. This effect is even more pronounced in the case of films obtained from latexes, due to the presence of higher amounts of additives that could take part in the polymer degradation. Therefore, the synthesis of poly(vinylidene chloride)-based latexes for use as waterborne barrier films with improved thermal and UV stabilities are of great importance.
PVDC-based composite latexes were first synthesized from epoxy-functionalized seed latexes in order to obtain PVDC films with an enhanced thermal stability. Given that hydrogen chloride displays an indirect catalytic effect on the polymer degradation, epoxy groups were indeed expected to act as thermal stabilizers by scavenging the HCl released by the polymer under thermal stress. In a first step epoxy-functionalized seed latexes were synthesized via the emulsion copolymerization of glycidyl methacrylate (GMA) and butyl methacrylate (BMA): the hydrolysis of epoxy groups was limited by controlling the pH and the temperature of reaction and the latex particle size was controlled by tuning the rate of addition of the monomers. In a second step the seeded emulsion copolymerization of vinylidene chloride (VDC) and methyl acrylate (MA) was carried out in the presence of poly(GMA-co-BMA) seed latexes. Thermogravimetric analyses (TGA) carried out on the resulting poly(GMA-co-BMA)/poly(VDC-co-MA) composites evidenced the thermal stabilization provided by epoxy groups.

The second part of the project focused on the synthesis of cerium oxide-based PVDC hybrid latexes so as to improve the polymer stability to UV radiations. Cerium oxide nanoparticles are indeed very attractive as UV-stabilizers due to their high absorption of radiation in the UV range and a lower photocatalytic activity compared to other inorganic UV-absorbers such as titanium dioxide or zinc oxide. However, due to the intrinsic incompatibility between inorganic and polymer phases, the synthesis of inorganic-organic hybrid latexes is rarely straightforward and requires a preliminary step of modification of the inorganic particles surface.

The grafting of alkoxysilanes onto cerium oxide nanoparticles was first attempted in order to promote the polymerization reaction at the surface of the inorganic particles. An accurate determination of the grafting
efficiency by thermogravimetric and elemental analyses was difficult to achieve, mainly due to the presence of large amounts of additives in the commercial cerium oxide dispersion employed in this study. According to observations by cryo-Transmission Electron Microscopy, latexes obtained via emulsion polymerization reactions carried out in the presence of modified nanoceria dispersions mostly consisted of fully separated polymer particles and cerium oxide nanoparticles. Therefore, it was concluded that this route was unsuccessful at improving the compatibility between the inorganic and polymer phases.

Amphiphatic macro-RAFT agents were finally considered as reactive compatibilizing agents that would enable to direct the polymerization towards the cerium oxide surface. RAFT oligomers were first obtained by co- or terpolymerization reactions in the presence of a RAFT controlling agent. The adsorption of the amphiphatic macro-RAFT agents at the surface of cerium oxide particles was characterized by electrophoretic mobility measurements and UV-visible spectrometry. Surface-modified cerium oxide particles were then engaged in reactions of emulsion polymerization reactions. In most cases, cryo-Transmission Electron Microscopy observations carried out on the resulting latexes confirmed the efficiency of the amphiphatic macro-RAFT agent route for the synthesis of hybrid structures, supported by the fact that no free cerium oxide particles could be found in the aqueous phase and that only few cerium oxide-free polymer particles were formed. Therefore this route appeared so far to be the most promising for the synthesis of cerium oxide/poly(vinylidene chloride) hybrid latexes for use as waterborne barrier films with improved UV-stability.
Curriculum vitae

Jérôme Garnier was born on November 2nd 1984 in Pau, France. At the end of two years of preparatory classes with a specialization in Physics and Chemistry, he entered the Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM), France, in 2004. He completed his last year at the ENSCM as an Erasmus student at the University of Linköping, Sweden, where he attended in parallel a Master programme in Materials Physics and Nanotechnology. He was awarded the French Diplôme d'Ingénieur Chimiste in 2007. After completing his Master thesis project in 2008 in the group of Biomolecular and Organic Electronics, under the supervision of Prof. Olle Inganäs, he was awarded the Swedish degree of Master of Science in Engineering Physics. In October 2008, he started a joint doctoral degree in collaboration between the group "Ingénierie et Architectures Macromoléculaires" (IAM) of the Institut Charles Gerhardt of Montpellier, France, the Polymer Chemistry Group (SPC) of the University of Technology of Eindhoven, The Netherlands, and the Solvay Company (NOH, Brussels, Belgium, and Tavaux, France), under the co-supervision of Dr. Patrick Lacroix-Desmazes (DR-CNRS) and Prof. Alex van Herk.
List of publications

**Patents:**

P.-E. Dufils, J. Garnier, A.M. van Herk, P. Lacroix-Desmazes, J. Vinas, Y. Vanderveken, J. Warnant, Solvay SA (Belgium), CNRS, UM2, ENSCM, filed in December 2011.


**Scientific articles:**


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