CeO_2/PVDC hybrid latex mediated by a phosphonated macro-RAFT agent

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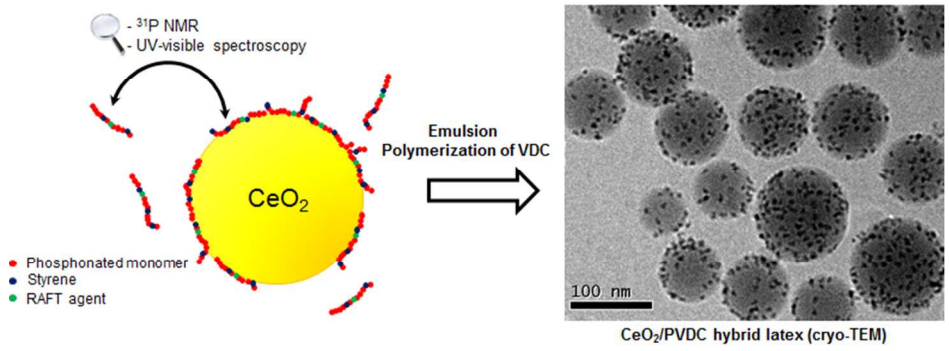

CeO_2/PVDC hybrid latex (cryo-TEM)

ABSTRACT: A poly(vinylidene chloride-*co*-methyl acrylate) hybrid latex comprising CeO_2 nanoparticles was successfully obtained by emulsion polymerization employing a water-soluble phosphonated macro-RAFT agent. A poly(vinylbenzylphosphonic diacid-*co*-styrene) statistical copolymer was first synthesized, using dibenzyl trithiocarbonate as controlling agent, and adsorbed on ceria nanoparticles. UV-visible and ^{31}P NMR spectroscopy proved to be efficient and complementary techniques to assess the extent of interactions between the copolymer and the ceria nanoparticles, leading to a better understanding of the adsorption of phosphonated copolymer chains on the inorganic particles. Then, these functionalized-CeO2 nanoparticles were used to mediate the emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of a very low amount of emulsifier. Cryo-transmission electron microscopy (cryo-TEM) confirmed the hybrid structure of the latex and the absence of either free ceria nanoparticles or free PVDC latex particles.

Combining the organic matter with divided inorganic matter (nanoparticles, clays, nanofibers...) is one of the main current trends to bring about new properties to polymer films[1]. More specifically, emulsion polymerization allows the elaboration of waterborne hybrid films by incorporating mineral fillers into polymer particles to create hybrid latexes. Hence, when such latexes are directly applied as a coating, mineral entities are well distributed within the polymer matrix.

Cerium oxide nanoparticles possess valuable properties, such as a catalytic oxidation activity[2-3] and a relatively high ionic conductivity[4-5]. In this paper, nanoceria (8 nm) have mainly been considered for their high potential as UV stabilizers in polymeric materials, owing to their excellent absorption of UV radiations.

However, to benefit from the specific properties provided by nanoceria, a preliminary step is required in order to compatibilize the mineral phase with the polymer phase.

Recently, hybrid latexes comprising nanoparticles of CeO_2 were synthesized by emulsion polymerization[6-7] according to the original strategy of Nguyen et al., initial-

ly designed to encapsulate particles of TiO_2 or pigments for paint applications[8-9]. This method employs living random amphiphatic copolymers, containing acrylic acid (AA) and n-butyl acrylate (BA) units, synthetized by reversible addition-fragmentation chain transfer (RAFT). Thus, due to the affinity of carboxylic groups towards the cerium oxide surface, living copolymers could be adsorbed on the nanoceria and, by chain extension, promote the growth of polymer domains starting from the cerium oxide surface.

The present paper describes the synthesis of another class of amphiphatic macro-RAFT agent bearing phosphonic acid groups instead of carboxylic acids. Indeed, phosphonic acids are well known for their strong interactions with a large range of inorganic materials[10-13].

To study the adsorption of the phosphonated RAFT copolymer at the surface of cerium oxide nanoparticles, we took advantage of the presence of phosphorous atoms in the macro-RAFT chain that could play the role of probes of the complexation process via ^{31}P NMR spectroscopy. Combined with UV-visible spectroscopy, based on the specific absorption of the C=S double bond of each macro-RAFT polymer chain, a picture of the adsorption of the macro-RAFT agent at the cerium oxide surface can be proposed.

Finally, the functional CeO_2 sol was used to mediate the emulsion copolymerization of vinylidene chloride and methyl acrylate, resulting in a very promising CeO_2/poly(VDC-co-MA) hybrid latex. The combination of these two materials could indeed bring about new properties to poly(vinylidene chloride) (PVDC), a high performance polymer already known for displaying a good resistance to a wide variety of solvents and an extremely low permeability to water, oxygen[14] and aroma[15] owing to its high degree of crystallinity[16-17]. Hence, after having already developed nanostructured composite PVDC latexes with enhanced thermal stability thanks to the use of poly(glycidyl methacrylate)-based seeds[18], we now report the elaboration of CeO_2/PVDC hybrid latexes in view to enhance the UV-stability of the resulting material.

The phosponated copolymer was prepared in two steps using vinylbenzyl phosphonyl diethyl ester (VBPDE) as monomer, synthesized according to Ribaut et al.[19]. First, the RAFT copolymerization of styrene (St) and VBPDE was carried out in α,α,α-trifluorotoluene (TFT) at 75°C, employing azobisisobutyronitrile (AIBN) as radical initiator and dibenzyl trithiocarbonate (DBTTC) as controlling RAFT agent. Secondly, to cleave the ester groups and get the targeted poly(vinylbenzylphosphonic diacid-*co*-styrene) copolymer, a silylation with trimethylsilyl bromide was carried out on poly(VBPDE-co-St), followed by a methanolysis. The ^1H NMR spectrum of the resulting poly(VBPDA-co-St) copolymer showed that the protons corresponding to the diester of the phosphonic acid -C_6H_4-CH_2-P(O)(O$C\underline{H}_2C\underline{H}_3$)$_2$ disappeared. The composition of the copolymer poly(VBPDA$_{10}$-*co*-St$_{2.5}$) ($M_{n,NMR}$=2500 g.mol^{-1}) was determined by ^1H NMR in DMSO. Molecular weight distribution was determined by size exclusion chromatography in THF before the cleavage of the ester groups to avoid the interactions between phosphonic acid units and the chromatographic column: the value of M_w/M_n = 1.19 is typical of a controlled radical polymerization.

The evolution of the monomer conversions (St and VBPDE) versus time was also determined by ^1H NMR to confirm that these monomers copolymerized randomly (see the Supporting Information). Thus, in water, the statistical distribution of the hydrophilic (VBPDA) and hydrophobic (St) monomer units along the copolymer chain will prevent the self-assembly of the copolymer into micelles that could lead to an undesirable secondary nucleation during the emulsion polymerization process. Also, a low molecular weight was targeted for the macro RAFT agent in order to obtain a high number of chain transfer agents per inorganic particle and promote the growth of polymer domains from the surface of the ceria nanoparticles.

Cerium oxide nanoparticles employed for this work are composed of clusters of 3 to 4 crystallites of about 3 nm size and display an isoelectric point of about 7.9. Nonetheless, due to an extremely high surface energy, the colloidal stability of the bare nanoparticles is confined to a narrow range of pH and ionic strengths. For this reason, the commercial dispersion used in our case contained citrate, a widely employed peptizing agent[20-21]. In this study, the excess of citrate was removed by dialyzing the cerium oxide dispersion four times against a large volume of de-ionized water.

To study the adsorption of the poly(VBPDA$_{10}$-*co*-St$_{2.5}$) copolymer on the ceria nanoparticles in a quantitative way, solutions of the macro-RAFT agent were prepared in the presence of cerium oxide at pH 7 and were ultracentrifuged to examine the aqueous serum phase by UV-visible spectroscopy. Indeed, the C=S double bond in the macro-RAFT copolymer displays an absorption maximum at 317 nm and therefore can be used to follow the concentrations of RAFT copolymer in the supernatant, the complementary part being adsorbed on CeO_2 nanoparticles. The number of macro-RAFT chains (N_{m_RAFT}(ads)) per cerium oxide particle (N_{CeO_2}) could be calculated according to the following equations:

$$N_{CeO_2} = 6\,x\,\frac{m_{CeO_2}}{л \times d_{CeO_2} \times {D_{CeO_2}}^3}$$

$$N_{m-RAFT}(ads) = ([m\_RAFT]_0 - [m\_RAFT]_{serum}) \times NA \,/\, M_n(m\_RAFT)$$

where m_{CeO_2} is the mass of cerium oxide, d_{CeO_2} the apparent density of cerium oxide (d_{CeO_2} = 2.6 g.cm^{-3}), D_{CeO_2} the mean volume diameter of the ceria nanoparticles (D_{CeO_2} = 8 nm), $[m\_RAFT]_0$ the total macro-RAFT agent concentration (g/L) (before ultracentrifugation), $[m\_RAFT]_{serum}$ the macro-RAFT agent concentration (g/L)

in the serum and NA the Avogadro number. In Figure 1, this result is represented versus the copolymer/CeO2 weight concentration ratio.

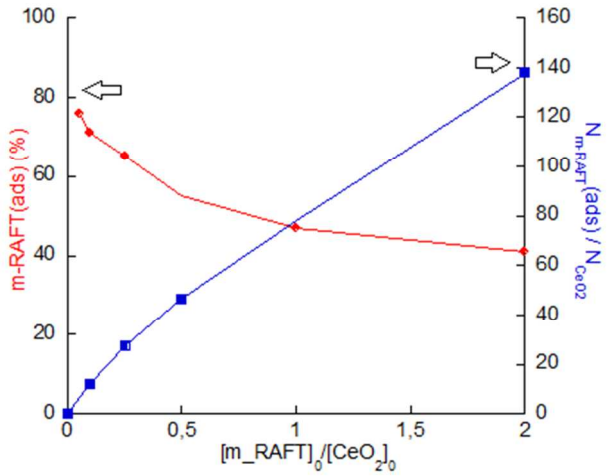

Figure 1. Adsorption of poly(VBPDA$_{10}$-co-St$_{2.5}$) macro-RAFT agent at the surface of cerium cerium oxide particles evidenced by UV-visible spectrometry.

As shown in Figure 1, the adsorption of the macro-RAFT agent at the surface of nanoceria occurred successfully. At low concentration, the adsorption is more efficient (~80% of macro-RAFT were adsorbed) than at high concentration (~40%), given that the surface of the nanoceria becomes less and less accessible. In all cases, however, some copolymers remained in the aqueous phase. Nguyen et al.[9], in the case of a poly(butyl acrylate-*co*-acrylic acid) macro-RAFT agent adsorbed at the surface of titanium dioxide, showed that roughly 75% of the RAFT oligomers remained free in the aqueous phase. Nonetheless, they observed that these aqueous phase macro-RAFT agents did not affect the efficient formation of TiO2/polymer hybrid latexes and hardly led to the formation of free polymer particles by secondary nucleation.

Combined to UV-visible analyses, phosphorous atoms contained in the RAFT copolymer chains were advantageously employed as a probe of the complexation process via ^{31}P NMR. Aqueous solutions of poly(VBPDA$_{10}$-co-St$_{2.5}$) in the presence of nanoceria were prepared at pH 7 and analyzed by ^{31}P NMR. The intensity of the signal at 20.9 ppm, attributed to the phosphorous of VBPDA units present in the copolymer, was calibrated (with capillaries of phosphoric acid in D_2O) to relate back to the concentration of free VBPDA units in solution (the complementary part corresponding to VBPDA units adsorbed on nanoceria). In the presence of nanoceria, a lower signal was observed at 20.9 ppm: the attenuation of the NMR signal is attributed to the fraction of VBPDA units complexed on the surface of the cerium oxide particles[22]. Thus, the percentage of complexed phosphonated units (% VBPDA(cplx)) and the number of VBPDA units complexed were calculated via the equation:

$$\%\,VBPDA(cplx) = 1 - \frac{I(CeO_2)_{20.9}}{I_{20.9}} \times 100$$

$$N_{VBPDA}(cplx) = N_{VBPDA}(total) \times \%\,VBPDA(cplx)$$

where $I_{20.9}$ and $I(CeO_2)_{20.9}$ are the integrals of phosphorous peak in poly(VBPDA$_{10}$-co-St$_{2.5}$) at 20.9 ppm, respectively without and with CeO_2.

In Figure 2, the percentage of phosphonate VBDPA units complexed and the number of VBPDA units complexed per CeO_2 particles is represented versus the weight concentration ratio between copolymer and CeO_2. The same trend is observed as in Figure 1, however giving complementary information compared to the UV-visible study: the percentage of complexed VBPDA decreased with the concentration of copolymer and at high concentration of copolymers only 20% of the VBPDA units were complexed showing a possible saturation of the surface of the CeO_2 particles.

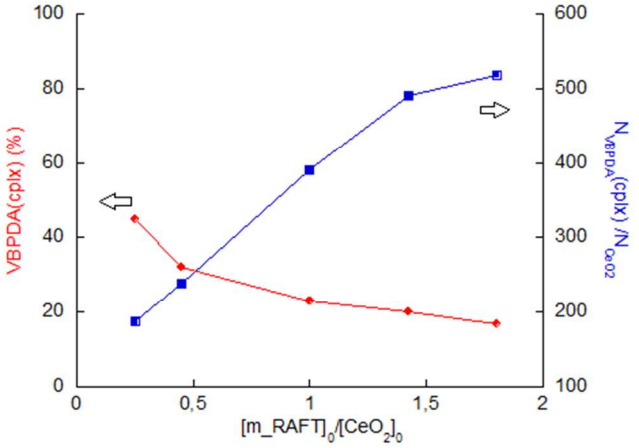

Figure 2. VBPDA complexation of poly(VBPDA$_{10}$-co-St$_{2.5}$) at the surface of cerium oxide particles evidenced by ^{31}P NMR.

UV-visible spectrometry and ^{31}P NMR give respectively the number of macro-RAFT copolymer chains and the number of VBPDA units at the surface of nanoceria. These techniques appear complementary and, for the first time, could be used to propose a picture on how the macro RAFT agent is adsorbed at the surface of CeO_2 nanoparticles (see the Supporting Information). To do so, the average number of VBPDA units complexed on the nanoceria, per macro-RAFT chain, is calculated as a function of the weight concentration ratio between copolymer and CeO_2 (Figure 3).

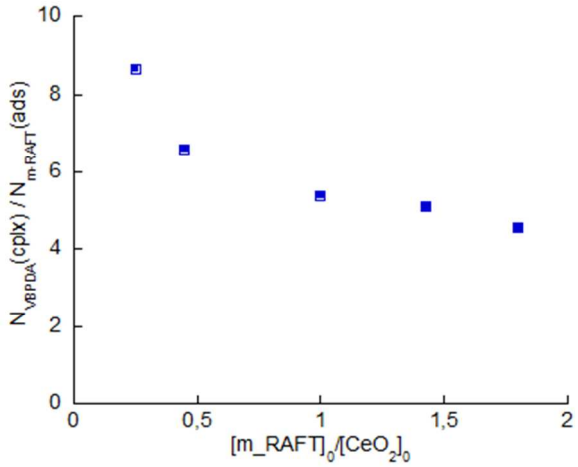

Figure 3. Average number of VBPDA units per poly(VBPDA10-co-St2.5) chain complexed at the surface of cerium oxide particles versus the copolymer/CeO_2 weight concentration ratio.

At low macro-RAFT agent concentrations, an average of 9 VBPDA units per poly($VBPDA_{10}$-co-$St_{2.5}$) chain was complexed on the nanoceria surface: the surface is very accessible and the copolymer chains can find easily a place on the surface of nanoceria. When increasing the concentration of the copolymer, the surface becomes more crowded until an average number of 5 VBPDA units per poly($VBPDA_{10}$-co-$St_{2.5}$) chain are complexed for the highest prepared concentration. At this concentration, it seems that the active sites of CeO_2 are saturated by the phosphonic functions. Interestingly, d'Alençon et al. who also employed nanoparticles of CeO_2 of 8 nm in their work estimated a molar ratio of 0.17 between the complexing agent and cerium by thermogravimetric and chemical analyses. In order to compare our results with their value, the VBPDA/Ce ratio was calculated and the results are reported in Figure 4. At high RAFT copolymer concentration, a value of 0.17 was actually reached, confirming a saturation of the cerium oxide active sites by VBPDA units.

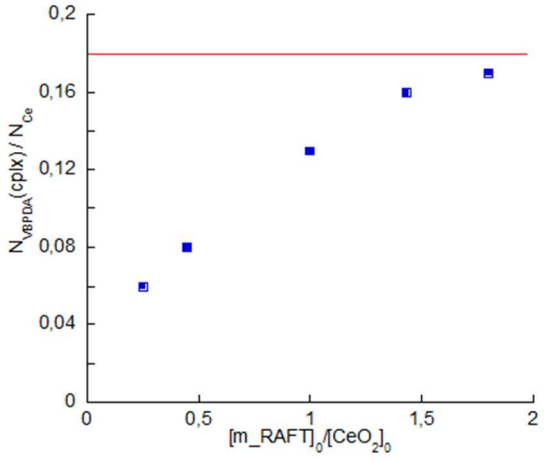

Figure 4. Number of VBPDA units complexed at the surface of CeO2 particles per number of cerium atoms.

Finally, the synthesis of cerium oxide/poly(VDC-*co*-MA) hybrid latexes was carried out by semi-continuous emulsion copolymerization of vinylidene chloride and methyl acrylate (in a 9:1 mass ratio) in the presence of ceria nanoparticles employing the poly($VBPDA_{10}$-co-$St_{2.5}$) macro-RAFT agent (Supporting Information). The monomers and tetrasodium pyrophosphate (TSPP, playing the roles of buffer and deflocculant) were injected as a pre-emulsion in water, stabilized by a very low amount of sodium dodecyl benzene sulfonate (SDBS) surfactant. A solid content of 25 wt% and a cerium oxide content of 4 wt% (respective to the dry polymer) were targeted. A 1:2 macro-RAFT agent:CeO_2 mass ratio was employed and a zwitterionic radical initiator (VA-057) was used to initiate the polymerization.

A stable latex of mean average diameter D=143 nm was obtained with a high monomer conversion (98%) and a relatively high molecular weight poly(VDC-co-MA) ($M_{n,SEC}$ = 71500 g•mol^{-1}). The rather broad molecular weight distribution (M_w/M_n = 1.9) measured for the copolymer latex reflects our main intension to use the macro-RAFT agent as a compatibilizer offering a possibility of chain extension rather than as a molecular weight controller.

Surface tension measurements performed on the CeO_2/poly(VDC-*co*-MA) latex showed that the colloidal dispersion displayed a high surface tension of 64 mN.m^{-1}: this feature is particularly interesting for coating applications, as the latex surface tension could be easily tuned by controlled post-addition of surfactants depending on the substrate to be coated.

Cryo-TEM observations (Figure 5) carried out on this latex showed hybrid particles decorated with several ceria nanoparticles. This result is in line with a mechanism of aggregation of poorly stable hybrid particle precursors, containing a single cerium oxide cluster, into larger mature hybrid particles comprising several nanoceria. In the present case, the rather high solid content of about 25% could have further encouraged the coagulation process of the hybrid particle precursors. Furthermore, the particles morphology consists in CeO_2 particles located at the hybrid particles surface. Actually, with a mass ratio of 1:2 macro-RAFT agent:CeO_2, we showed by ^{31}P NMR and UV visible measurements (Figure 4) that only 47% of the CeO_2 active sites were covered with the macro-RAFT agent, some citrates remaining adsorbed on the cerium oxide surface. Therefore, ceria nanoparticles remain highly hydrophilic, leading to their partial engulfment by the latex polymer phase. However, remarkably, neither free ceria nanoparticles remain in the aqueous phase nor latex particles exempt of ceria were observed (note: the other objects visible on the picture correspond to artifacts originating from the cryo-TEM sample preparation), proving the efficiency of the poly($VBPDA_{10}$-co-$St_{2.5}$) macro RAFT agent to promote the affinity of the polymer latex towards the metal oxide surface.

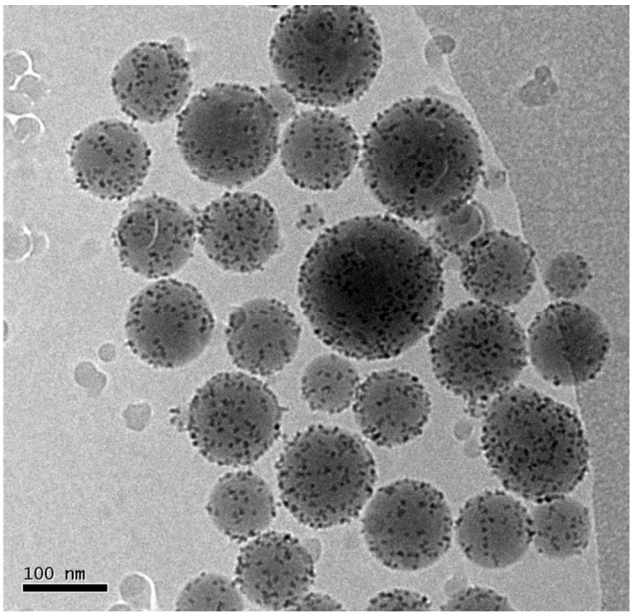

Figure 5. Cryo-TEM picture of a CeO_2/poly(VDC-co-MA) hybrid latex obtained in the presence poly(VBPDA10-co-St2.5).

In conclusion, the synthesis of an hybrid CeO_2/PVDC latex was successfully carried out, via the functionalization of CeO_2 nanoparticles by a phosphonated macro-RAFT agent, with a very high incorporation efficiency of nanoceria.

^{31}P NMR combined with UV-visible spectroscopy proved to be simple and efficient techniques to characterize the surface functionalization of the cerium oxide nanoparticles by the phosphonated macro-RAFT agent. By this way, a better understanding of the macro-RAFT agent adsorption on the nanoceria was achieved, supporting the partial engulfment of cerium oxide nanoparticles by the PVDC latex phase.

This hybrid latex, obtained by emulsion polymerization with reasonably high solid content (25%), is a good candidate for the elaboration of high performance coatings. Film formation and film characterization is now under investigation. Furthermore, the use of such hybrid latexes as templates for the preparation of functional organic or inorganic porous materials with CeO_2 nanoparticles (or other nanoparticles) evenly distributed in the porous matrix is also considered[23].

ASSOCIATED CONTENT

A list of materials, experimental techniques and detailed experimental procedures are provided as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org."

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