Macro-RAFT agents for the synthesis of CeO_2-based hybrid latexes

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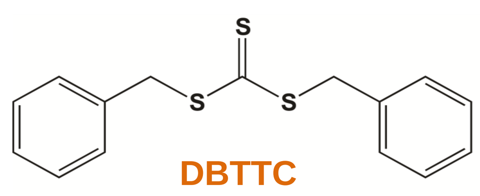
Introduction

Cerium oxide-based materials have been extensively studied for applications in various fields owing to their excellent properties (as engine exhaust catalysts [1], polishing agents [2], UV filters [3] or solid electrolytes [4]). Additional features may be obtained when ceria is employed in nanoparticle form [5], including an enhanced carbon monoxide oxidation rate [6] and ultraviolet blue shifts in UV filters [3]. Therefore emulsion polymerization processes carried out in the presence of nanoceria are of great interest in order to obtain hybrid latexes combining the specific properties of cerium oxide nanoparticles and polymeric materials.

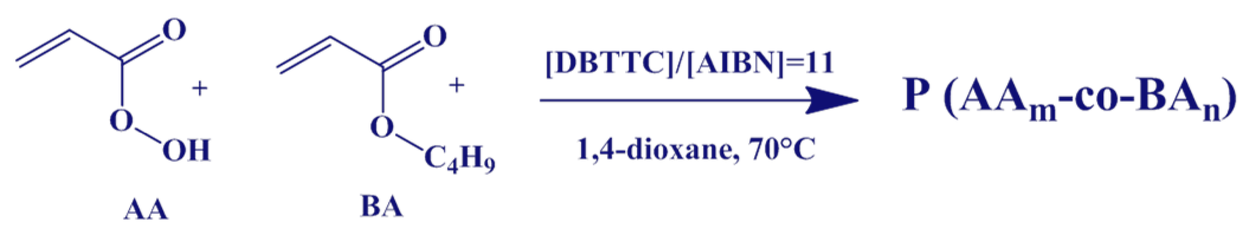
We report here the **synthesis of cerium oxide-based hybrid latexes employing amphiphatic macro-RAFT agents** [7]. The main asset of this technique is that it can be applied to a large range of inorganic particles by tuning the hydrophobic/hydrophilic composition of the macro-RAFT agent. The fact that it **does not require any conventional surfactant** is another remarkable advantage: short emulsifier molecules are indeed likely to migrate, leading to the deterioration of the properties of the final polymeric material.

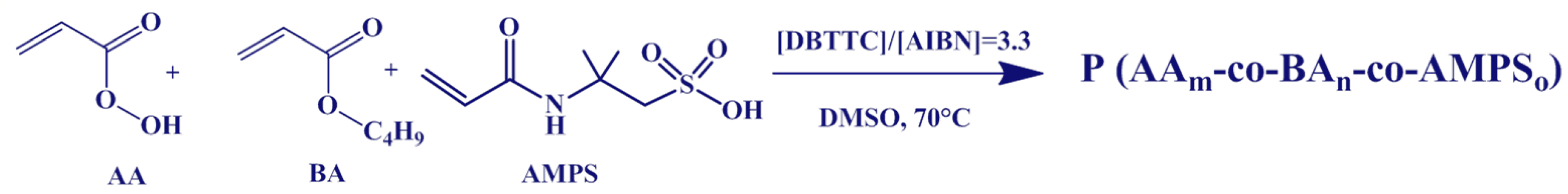
Amphiphatic macro-RAFT agents synthesis

First step: synthesis of amphiphatic random RAFT copolymers:



DBTTC



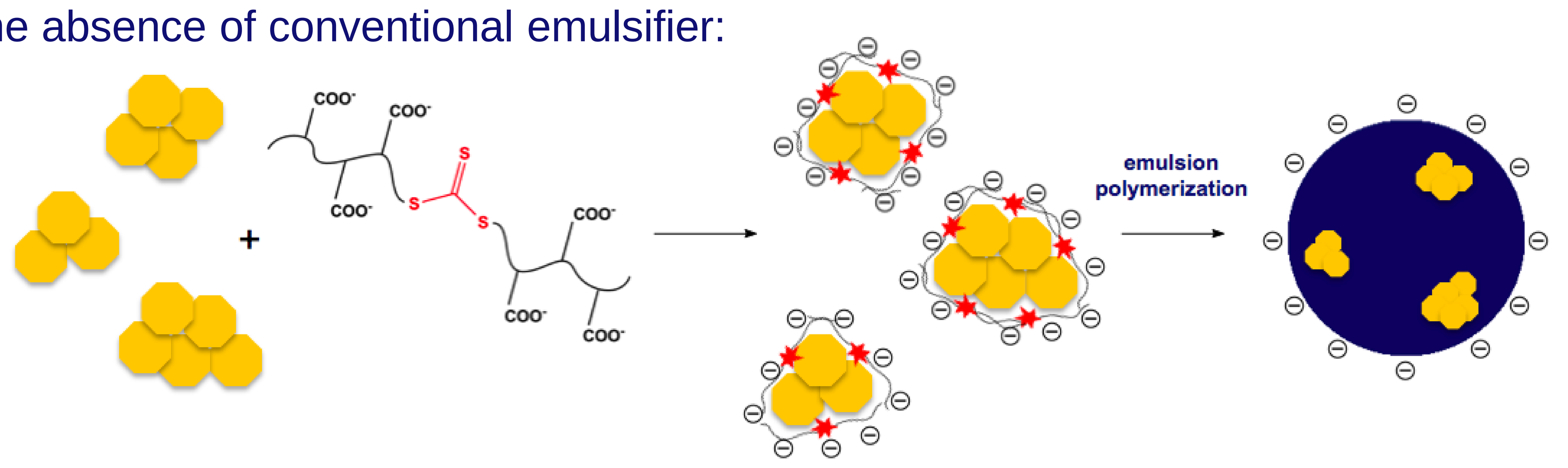


Targeted composition	$M_{n,\ theo}$ ($g.mol^{-1}$)	$F_{AA,\ theo}$	X_M (%)	$M_{n,\ NMR}$ ($g.mol^{-1}$)	$F_{AA,\ NMR}$	$M_{n,\ SEC}$ ($g.mol^{-1}$)	M_w/M_n
$BA_{7.5}$-co-AA_{10}	1940	0.57	97.6	1980	0.58	2060	1.28
BA_5-co-AA_5	1260	0.50	96.0	1300	0.51	1570	1.28

Targeted composition	$M_{n,theo}$ ($g.mol^{-1}$)	$F_{AA,th}$	$F_{AMPS,th}$	X_{BA} (%)	X_{AA} (%)	X_{AMPS} (%)	$M_{n,NMR}$ ($g.mol^{-1}$)	$F_{AA,NMR}$	$F_{AMPS,NMR}$
$BA_{7.5}$-co-AA_{10}-co-$AMPS_4$	2660	0.47	0.17	99.5	98.3	90.2	2830	0.46	0.17
BA_5-co-AA_5-co-$AMPS_4$	2010	0.36	0.27	99.3	97.5	88.2	2110	0.43	0.21

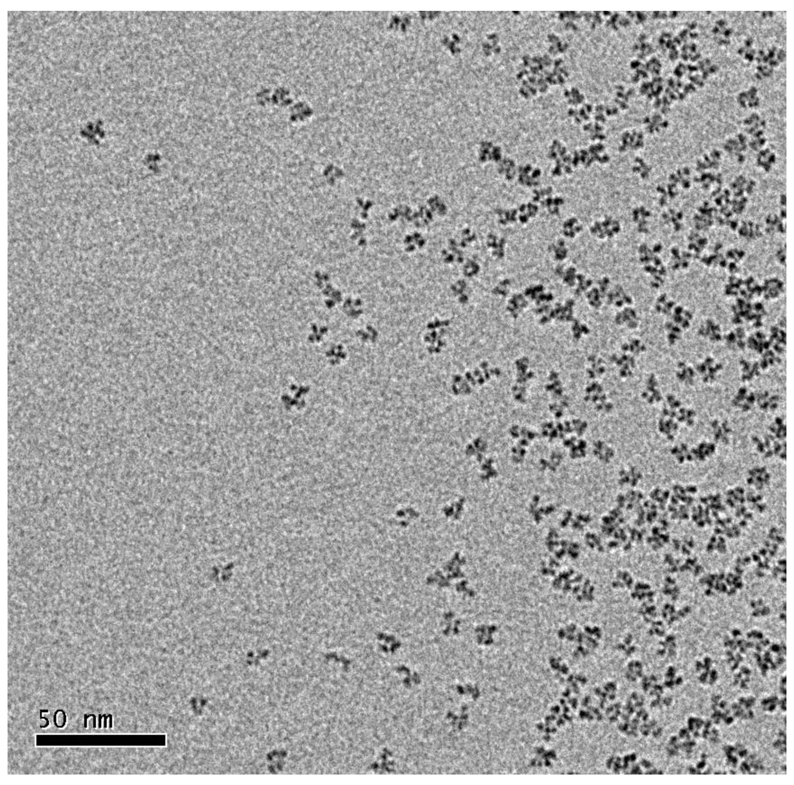
Emulsion polymerization

Second step: emulsion copolymerization of styrene and methyl acrylate in the presence of macro-RAFT oligomers adsorbed at the surface of cerium oxide nanoparticles in the absence of conventional emulsifier:



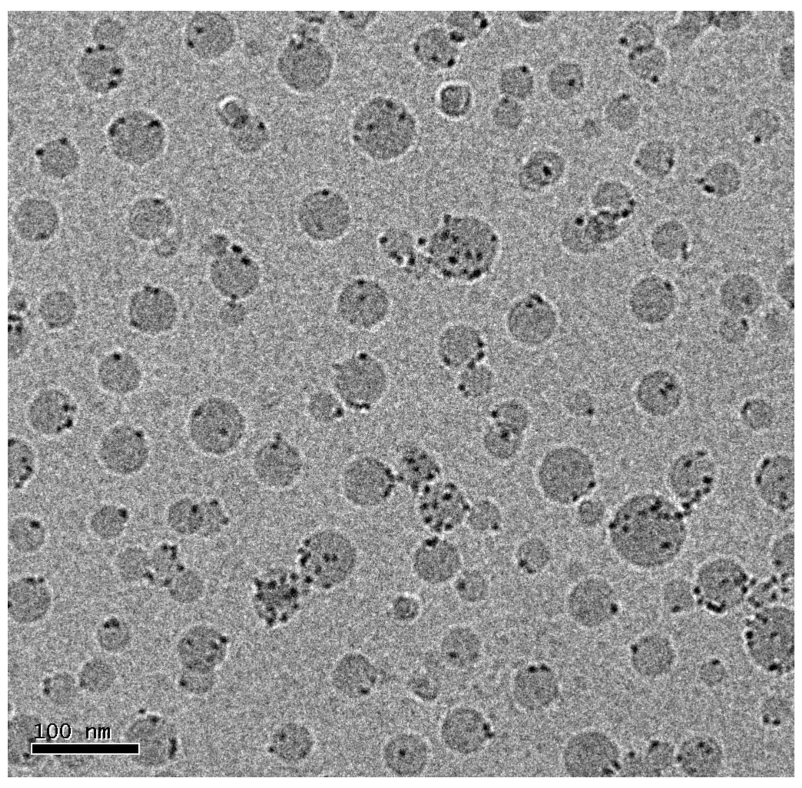
Macro-RAFT agent composition	X_M (%)	D_P (nm)	PDI	$N°_{CeO2}$ ($\times 10^{-16}$)	N^f_P ($\times 10^{-16}$)	$N°_{CeO2}$ / N^f_P
$BA_{7.5}$-co-AA_{10}	91.1	56.05	0.16	20.3	8.74	2.32
BA_5-co-AA_5	86.2	83.48	0.21	20.3	2.51	8.09
$BA_{7.5}$-co-AA_{10}-co-$AMPS_4$	85.22	48.1	0.105	12.6	7.98	1.58
BA_5-co-AA_5-co-$AMPS_4$	84.33	47.7	0.190	12.7	8.08	1.57

Observations



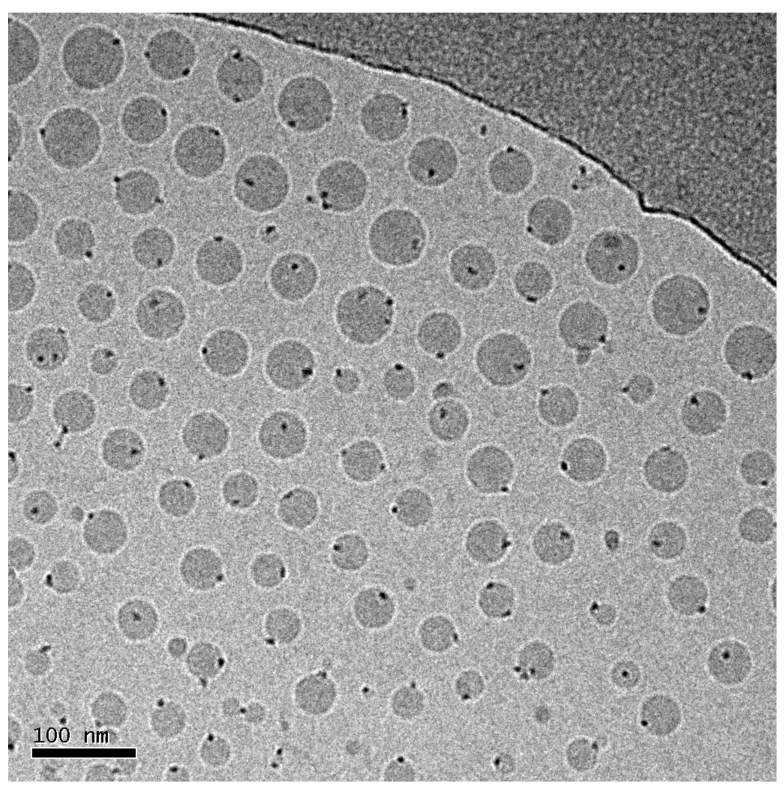
- Clusters of 3 to 4 crystallites of about 3 nm size
- Ammonium citrate strongly adsorbed at the particles surface
→dialysis carried out to remove most of the citrates

TEM picture of nanoceria starting material



Several cerium oxide clusters per polymer particle can be observed

Cryo-TEM picture of hybrid latex employing $BA_{7.5}$-co-AA_{10} macro-RAFT agent



Very uniform distribution of nanoceria between hybrid particles

Cryo-TEM picture of hybrid latex employing BA_5-co-AA_5-co-$AMPS_4$ macro-RAFT agent

Conclusions

- Poly(BA-*co*-AA) and poly(BA-co-AA-co-AMPS) random RAFT oligomers were succesfully synthesized, with a **good agreement between theoretical and experimental molar masses** and **narrow molecular weight distributions**.
- CeO_2-based hybrid latexes were successfully obtained via the macro-RAFT agent route, with a very **high efficiency** of nanoceria incorporation and a very low amount of polymer particles formed by secondary nucleation.
- These latexes present a great potential for use as waterborne polymeric materials with enhanced UV-stability.

Acknowledgements

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