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Tracking droplet nucleation in seeded semibatch miniemulsion polymerization

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“Tracking droplet nucleation in seeded semibatch miniemulsion polymerization ”

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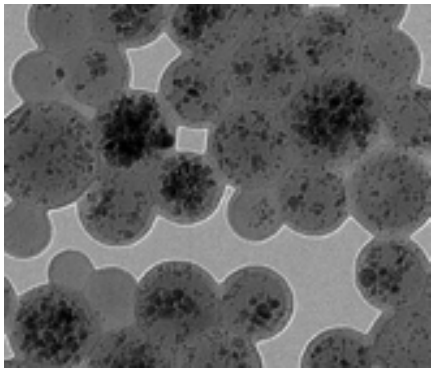
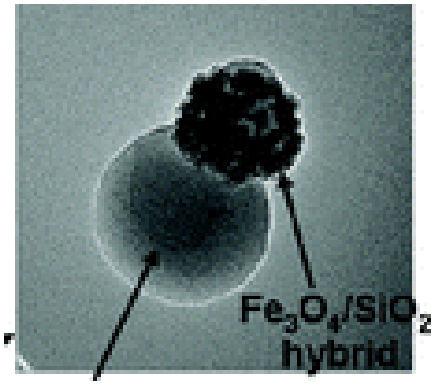
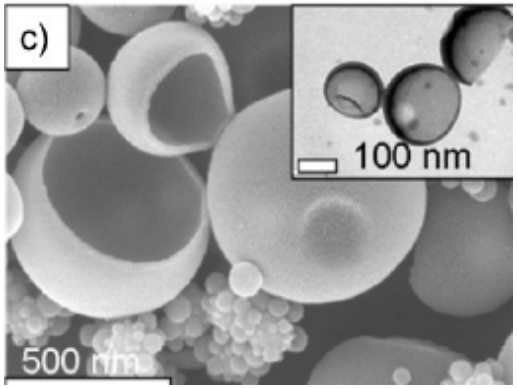
1. Introduction and motivation



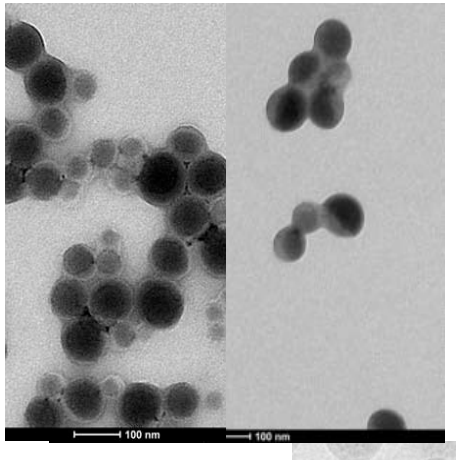
Ramos, Langmuir 2011, 27, 7222

Wang, Langmuir 2011, 27, 7207



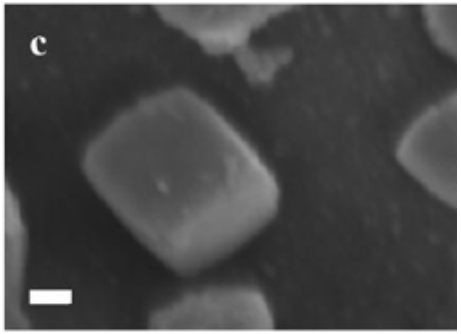


Ge, Macromol Rapid Commun, 2011, 32, 1615

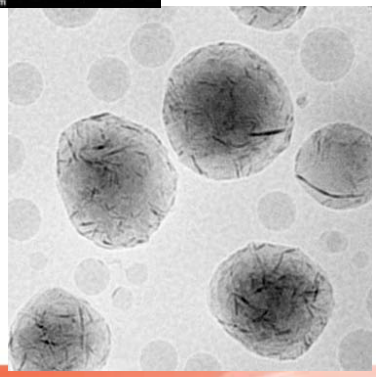


Goikoetxea, Polymer, 2009, 50, 5892

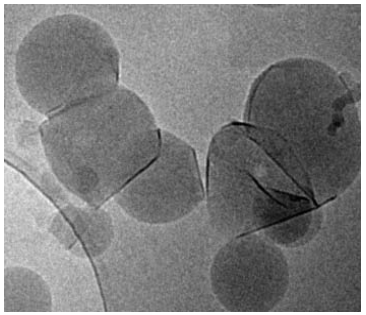
McHale, Chem Commun, 2010, 46, 4574



Véronique Mellon, PhD Thesis, 2009, CNRS/CPE Lyon

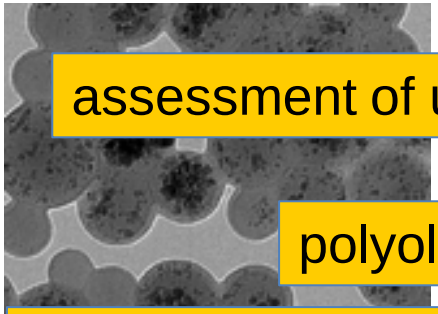


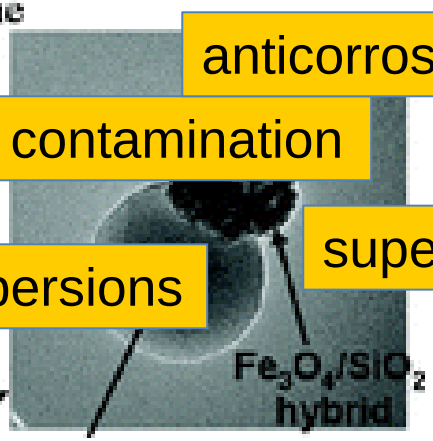
Audrey Bonnefond, Langmuir 29, 2397-405 (2013)

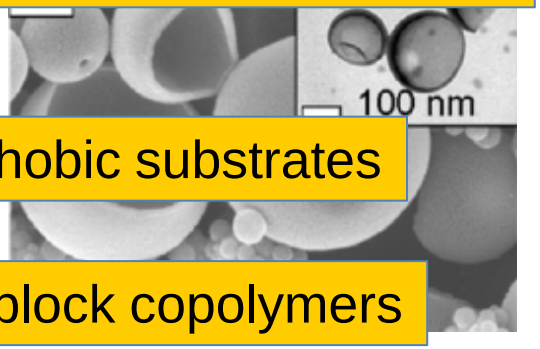


anticorrosive and anti-molding coatings

assessment of uranium contamination







superhydrophobic substrates

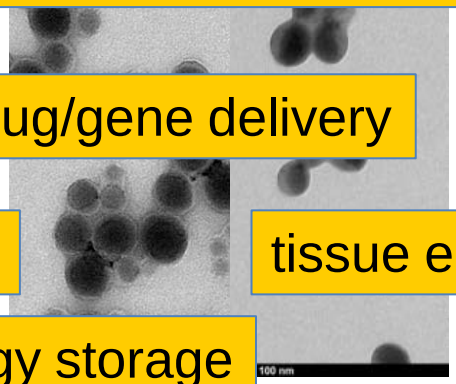
polyolefin dispersions

catalyst supports

multiblock copolymers

photoswitchable fluorescent particles

encapsulation



drug/gene delivery

light emitting diode

anticounterfeiting

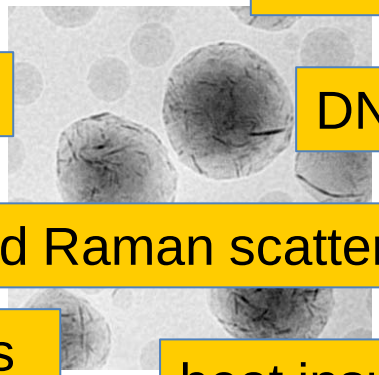
tissue engineering

adhesives

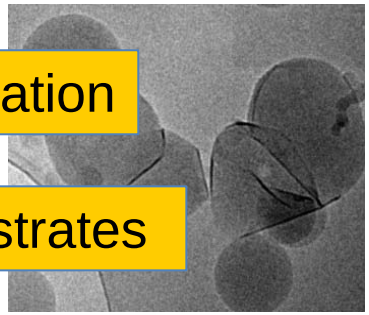
energy storage

coatings

glass and ceramics coatings



DNA separation



surface –enhanced Raman scattering substrates

low viscosity high solids dispersions

heat insulating coatings

POLYMAT

1. Introduction and motivation

Miniemulsion polymerization

Synthesis of complex materials that cannot be produced otherwise.

Incorporation of “preformed” “water”-insoluble materials to “waterborne” dispersed particles

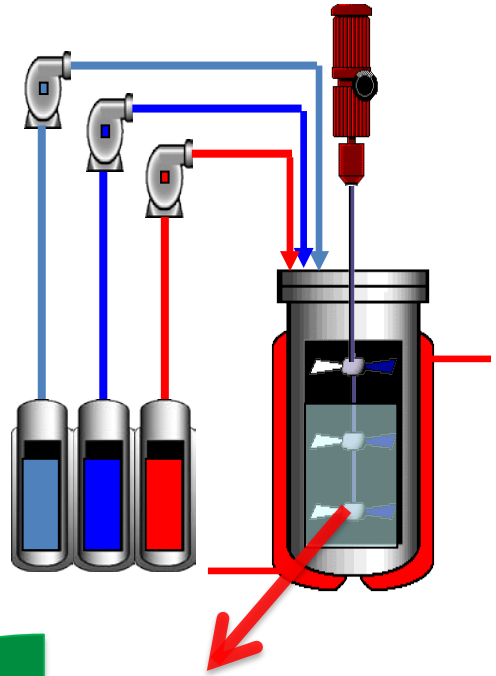
Product-by-Process:

1) To form composite droplets of controlled size and composition, making them colloidally stable (and against Ostwald ripening)
2) To polymerize most of the droplets avoiding other nucleations and coagulations
3) To achieve high conversion minimizing residual monomer
4) To control polymer architecture and achieve adequate morphology

1. Introduction and motivation

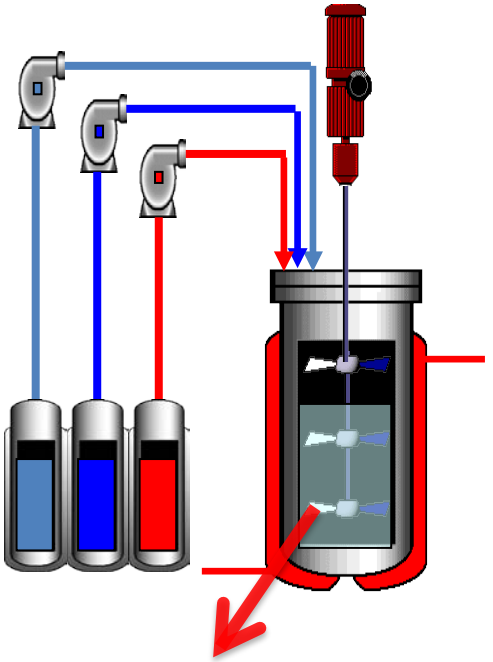
High tonnage productions required semibatch processes

Feed:
All water transportable reagents



Seed: Hybrid Miniemulsion
(all water insoluble species)

Feed:
Remaining Hybrid Miniemulsion



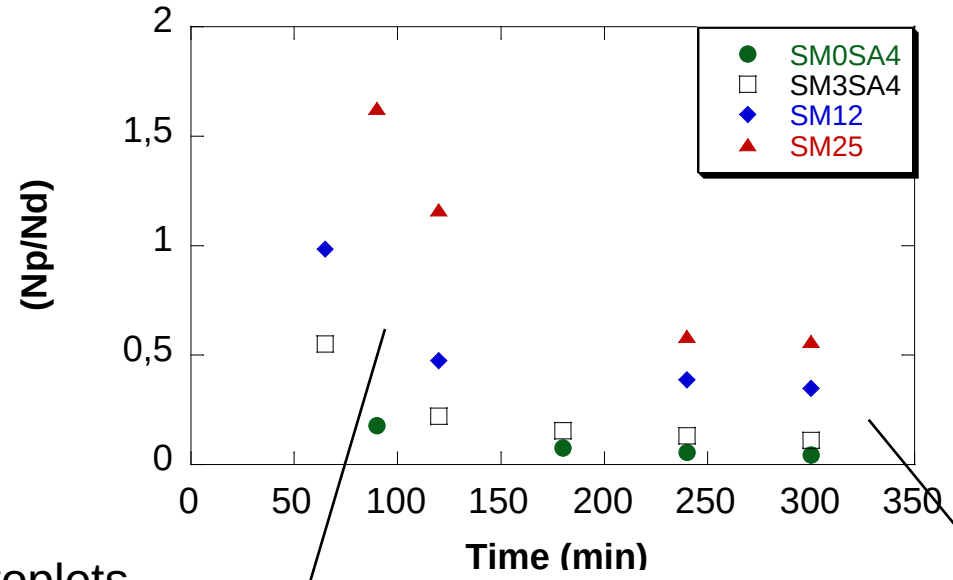
Seed: Fraction of Hybrid Miniemulsion

Seeded semibatch emulsion polymerization

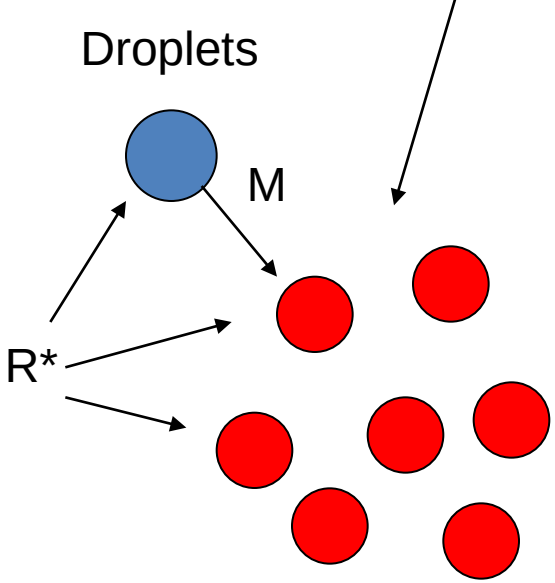
1. Introduction and motivation

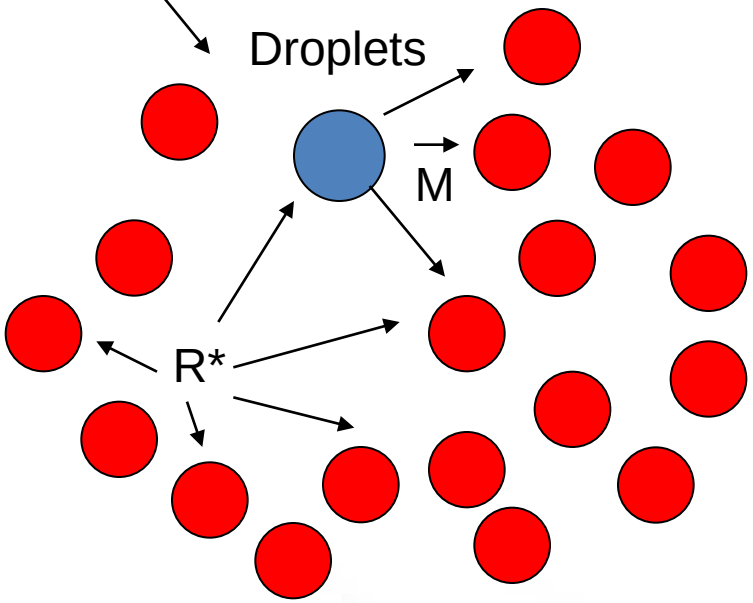
Previous attempts to analyze droplet nucleation

Rodríguez, Macromolecules 2007, 40, 5735



Particle Nucleation
Miniemulsion Addition





1. Introduction and motivation

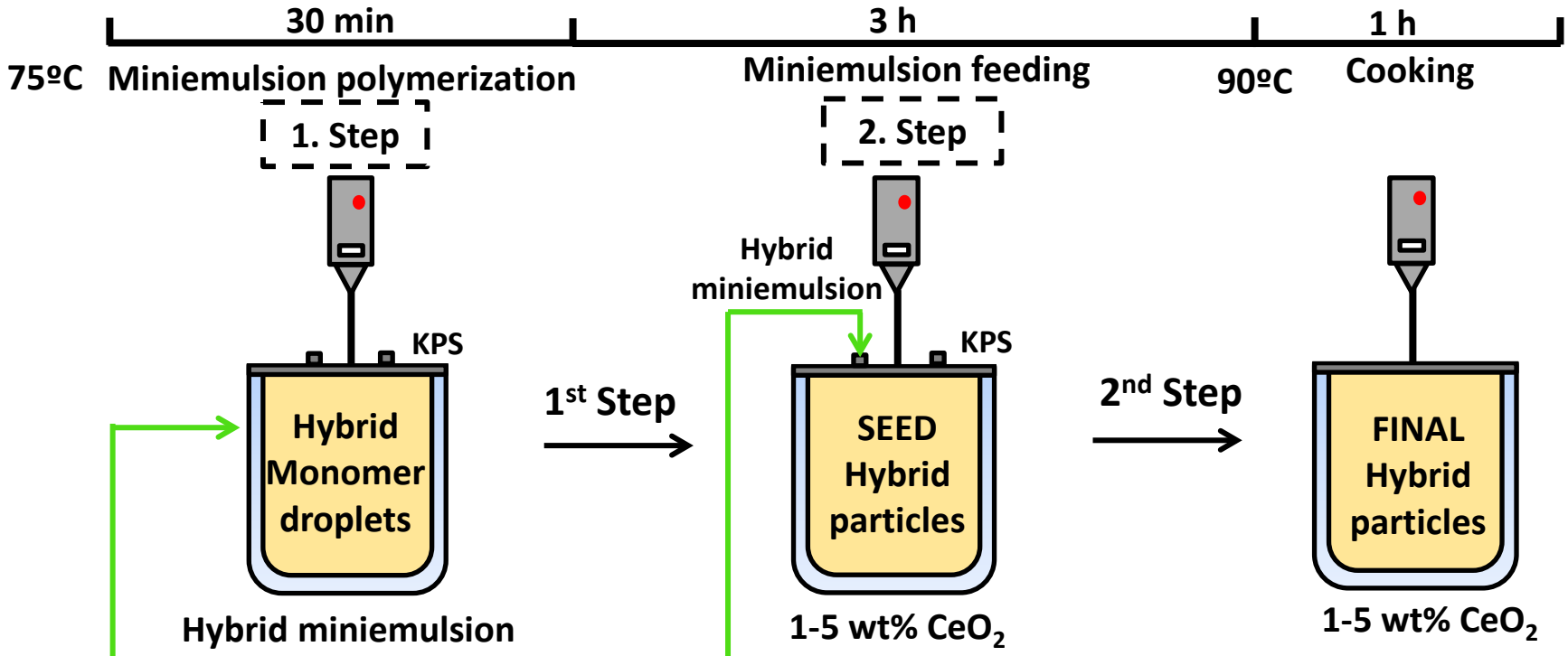
Previous attempts to analyze droplet nucleation

Rodríguez, Macromolecules 2007, 40, 5735

Goal:
To track unambiguously droplet nucleation in miniemulsion feeding semibatch processes

2. Results

Approach: Use CeO_2 nanoparticles as marker



	Component	Wt %
Organic Phase	MMA	19.8
	BA	19.8
	AA	0.4
	Stearyl Acrylate*	4
	Poly(MMA-co-BA-co-AA)*	10
	CeO_2*	2-5
Water Phase	Dowfax*	2
	Water	60

M. Aguirre et al., Polymer, 2014, 55, 3, 752.;
J. Mat. Chem A., 2014, 2, 20280-20287
Aguirre et al. WO2014/005753 A1

*With respect to the monomer

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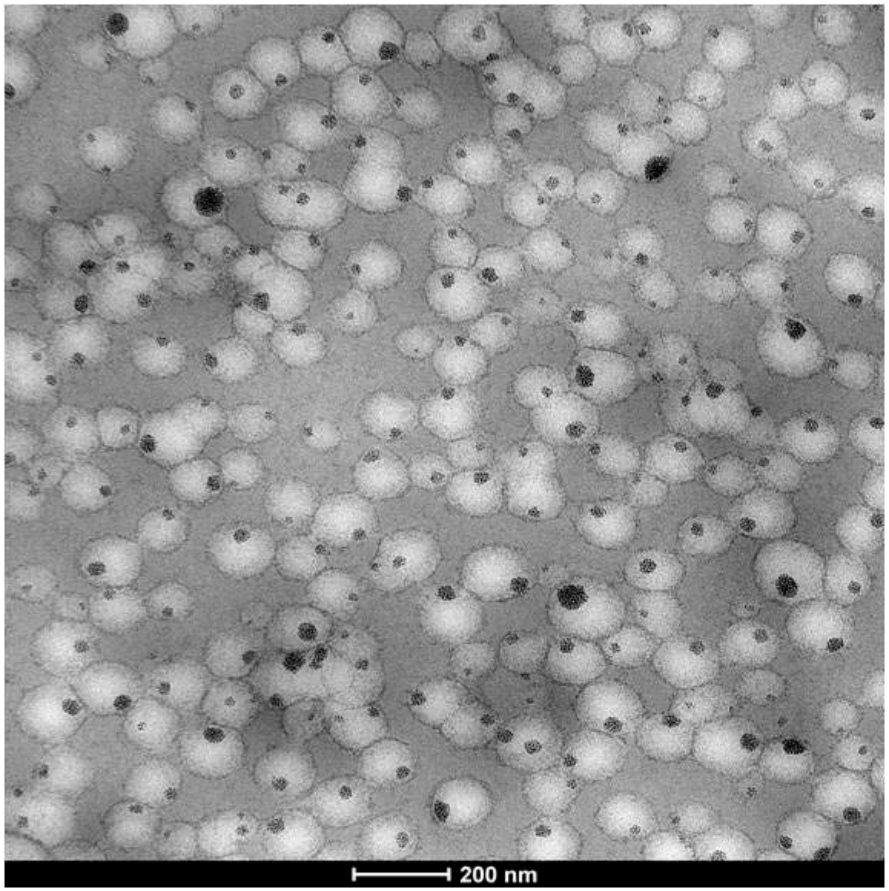
2. Results

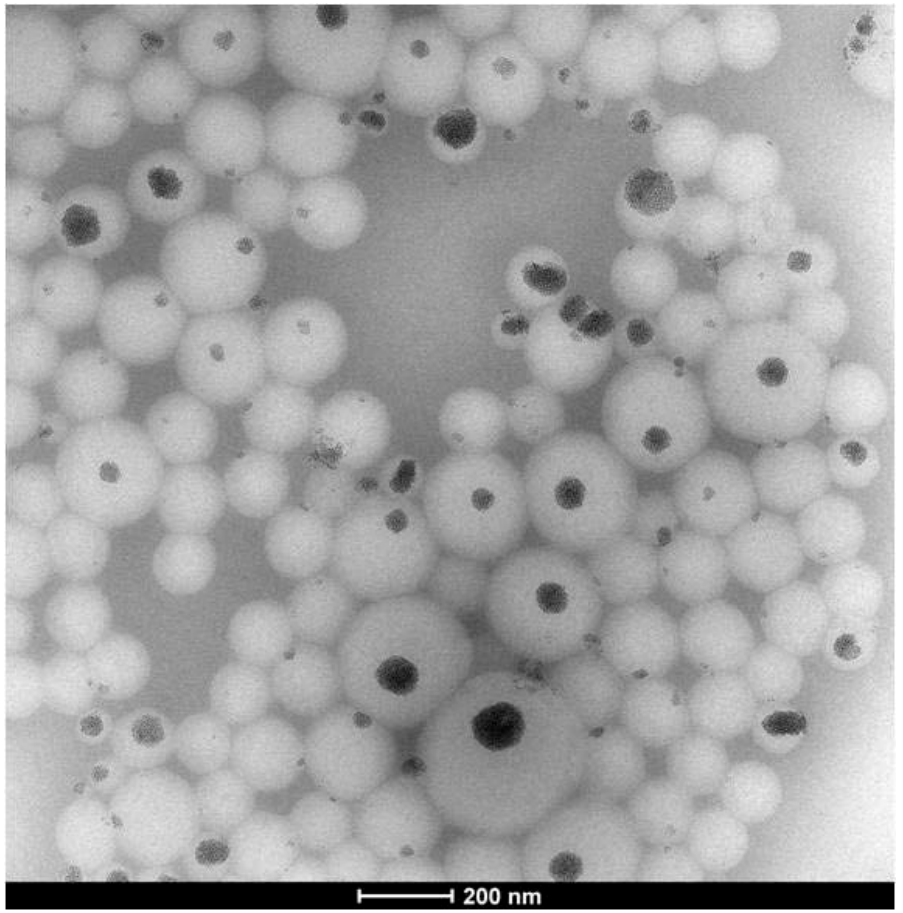
New approach: Using CeO_2 nanoparticles as marker

Model System: acrylic/CeO_2 latexes

Batch Miniemulsion



Seeded Semibatch: Miniemulsion feed



M. Aguirre et al., Polymer, 2014, 55, 3, 752.;J. Mat. Chem A., 2014, 2, 20280-20287

2. Results

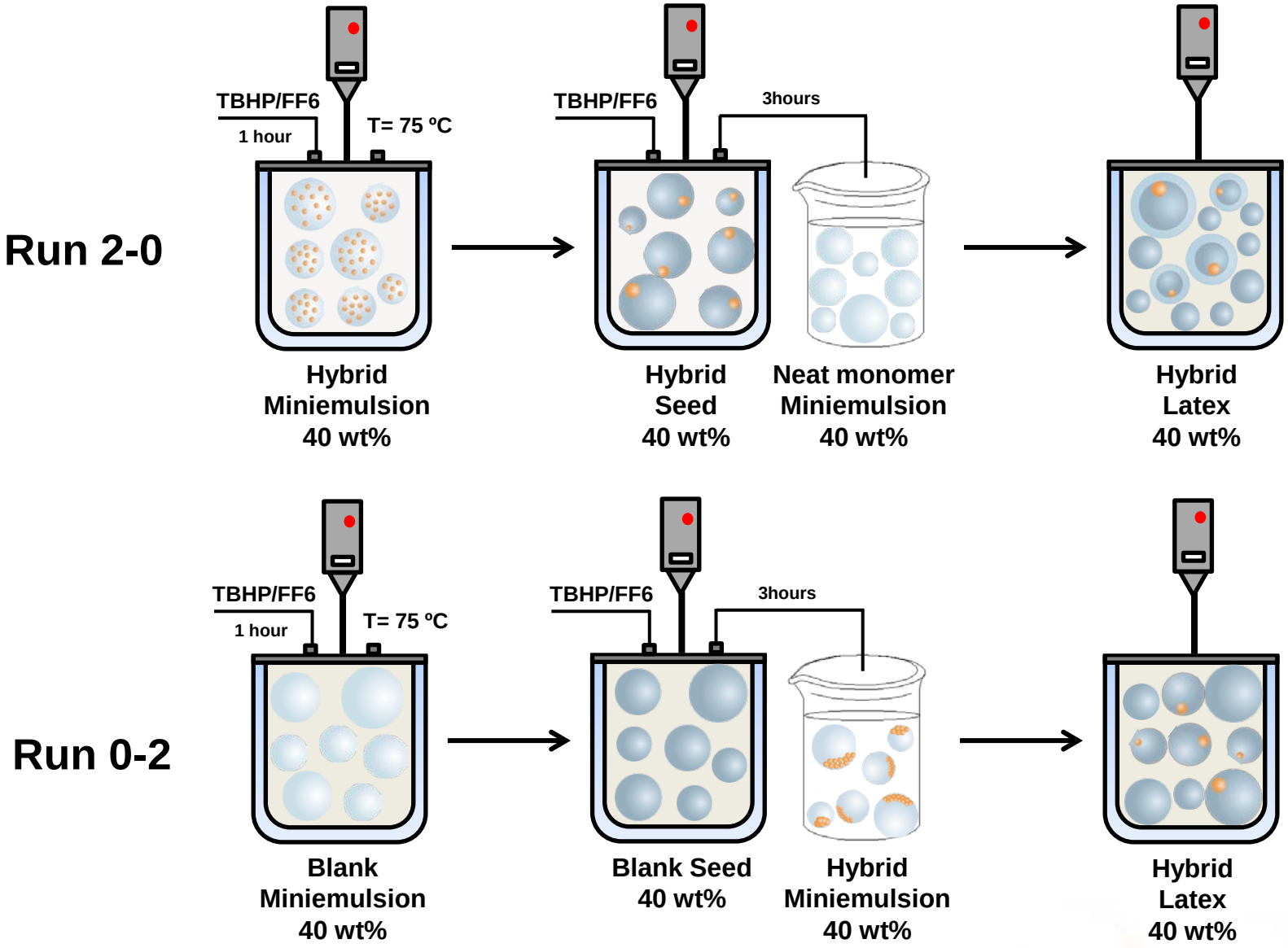
New approach: Using CeO_2 nanoparticles as marker

Model System: acrylic/CeO_2 latexes

- Particles without nanoceria negligible.
- No particles in the aqueous phase.
- CeO_2 nanoparticle size did not change from seed to final latex.
- Polymer particles with and without CeO_2 easily traceable by TEM.
- Possible to design semibatch experiments to track droplet nucleation unambiguously

2. Results

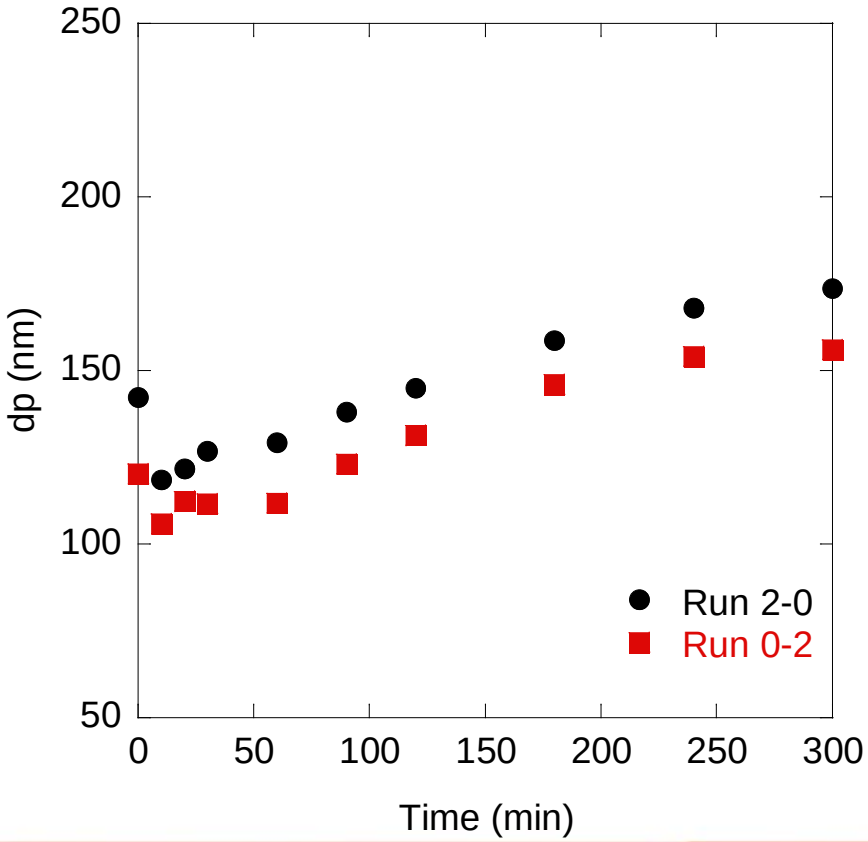
Tracking of droplet nucleation: model experiments

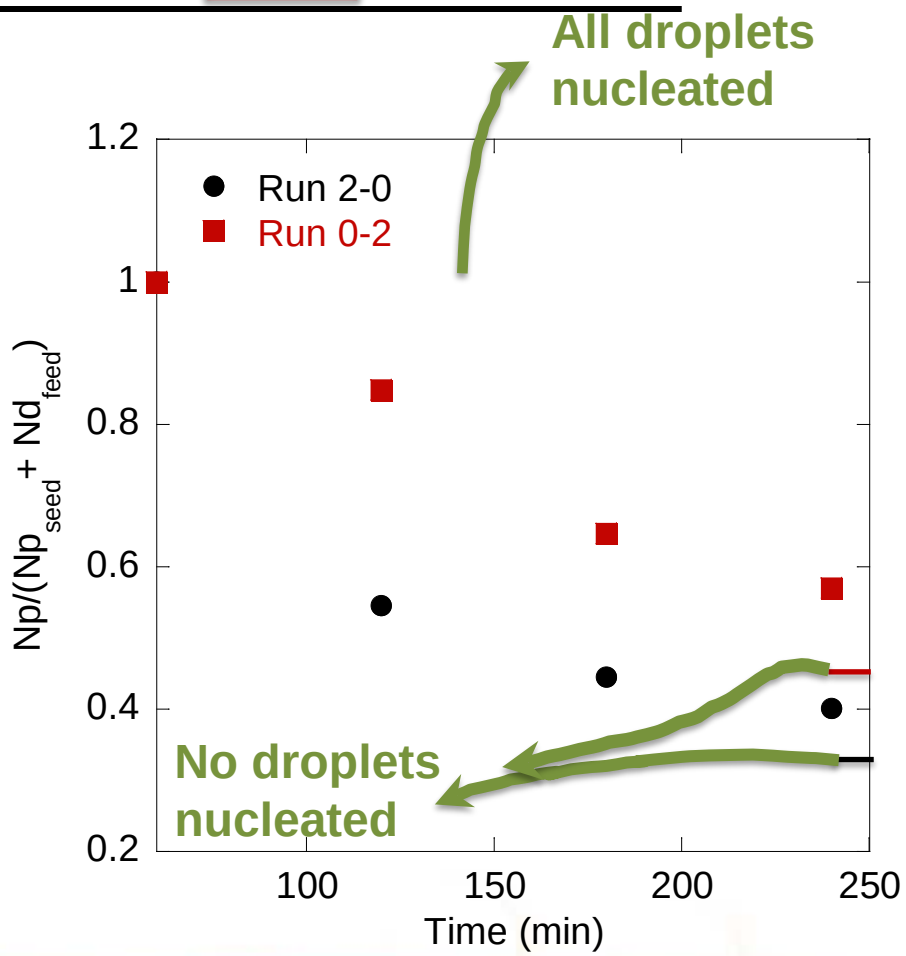


2. Results

Tracking of droplet nucleation: model experiments

	Conv. (%)	$Dd_{initial}$ (nm)	Dp_{seed} (nm)	$Dd_{feeding}$ (nm)	Dp_{final} (nm)
Run 2-0	99	142	129	138	174
Run 0-2	100	120	112	145	156

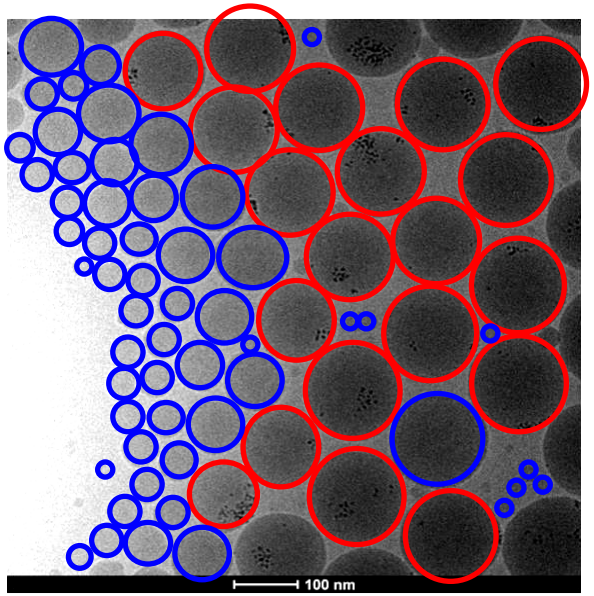




2. Results

Tracking of droplet nucleation: model experiments

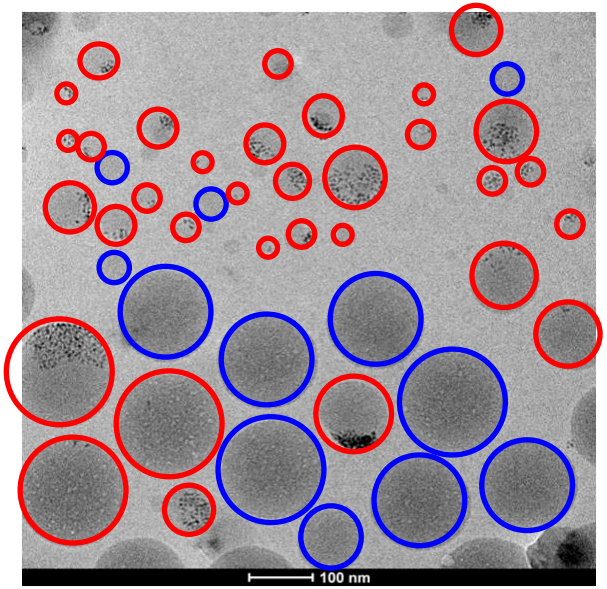
Run 2-0



Particles without CeO_2

Particles with CeO_2

Run 0-2



Qualitative observation:

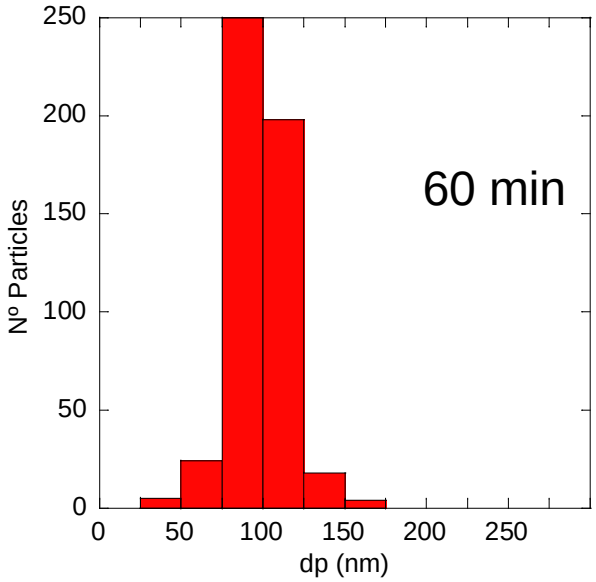
Run 2-0. Particles with CeO_2 are larger. Neat particles are smaller; which indicates that monomer from droplets has diffused out to the seed particles.

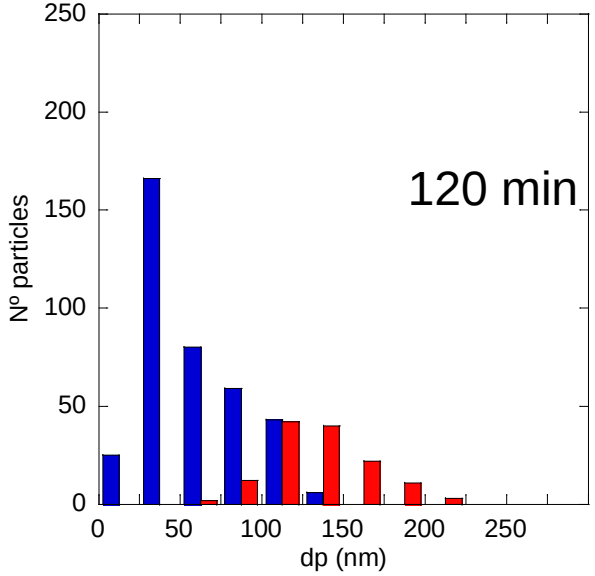
Run 0-2. The feed droplets nucleated at different stages; there are big and small particles containing CeO_2.

2. Results

Tracking of droplet nucleation: model experiments

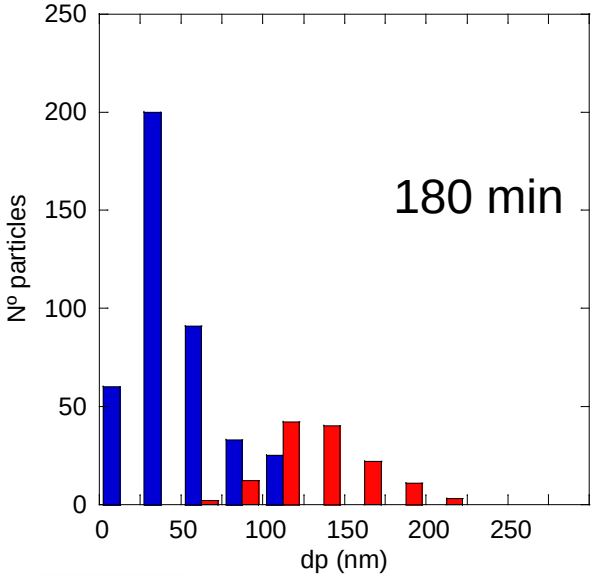
Run 2-0

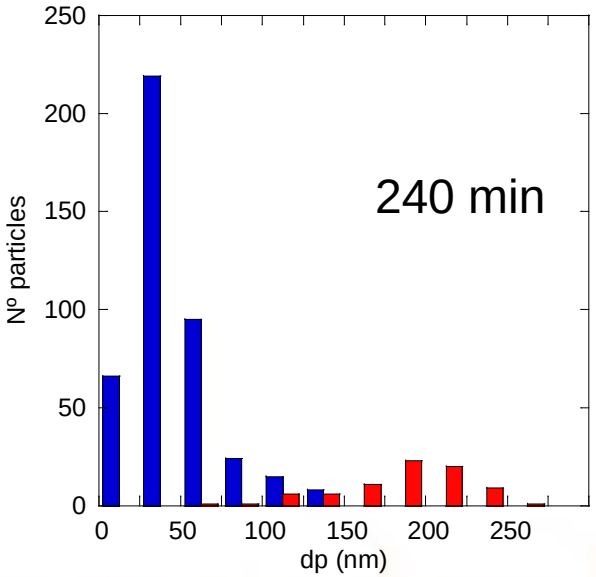




Particles without CeO_2

Particles with CeO_2

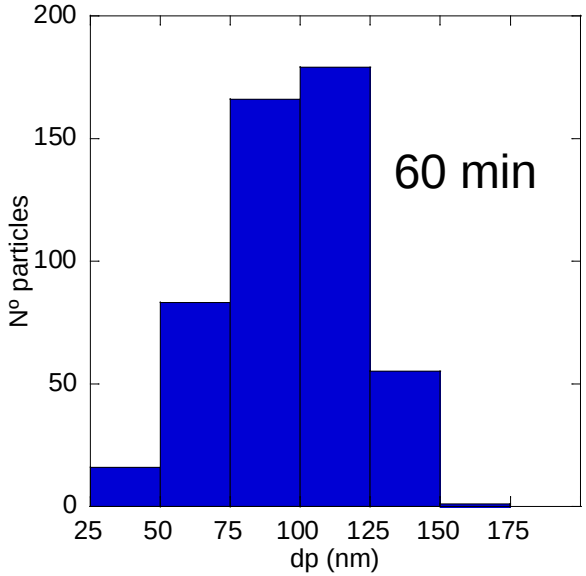


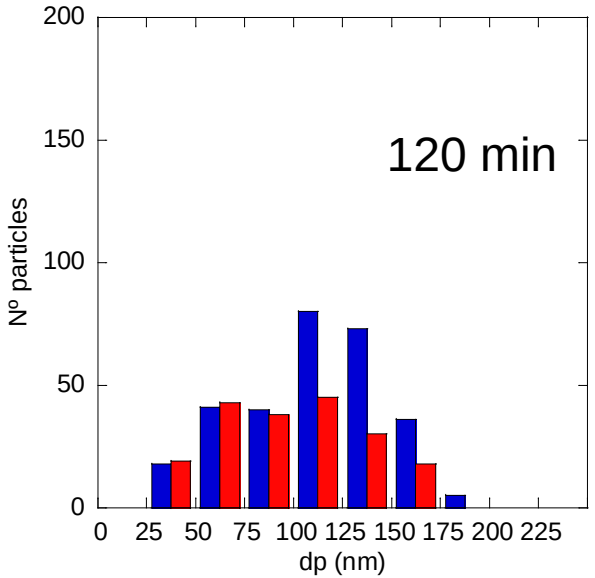


2. Results

Tracking of droplet nucleation: model experiments

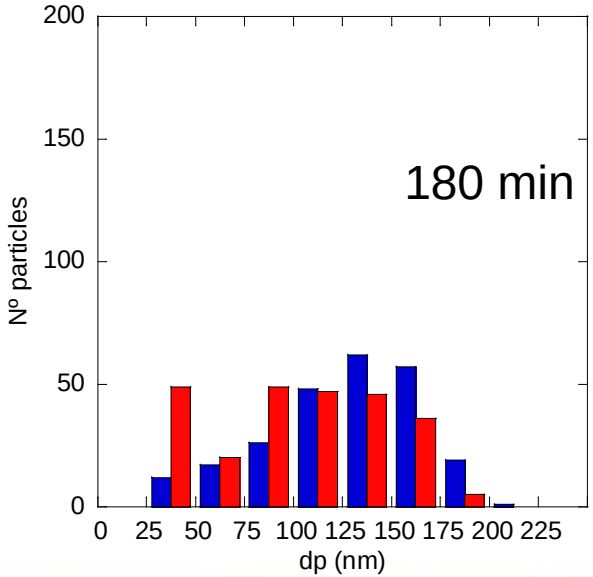
Run 0-2

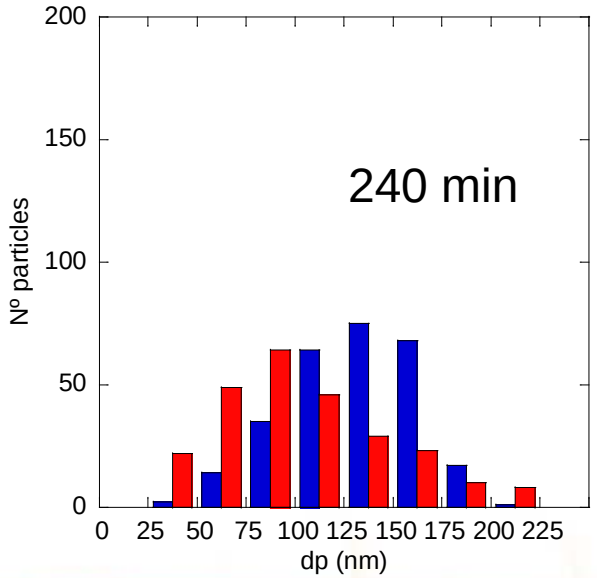




Particles without CeO_2

Particles with CeO_2





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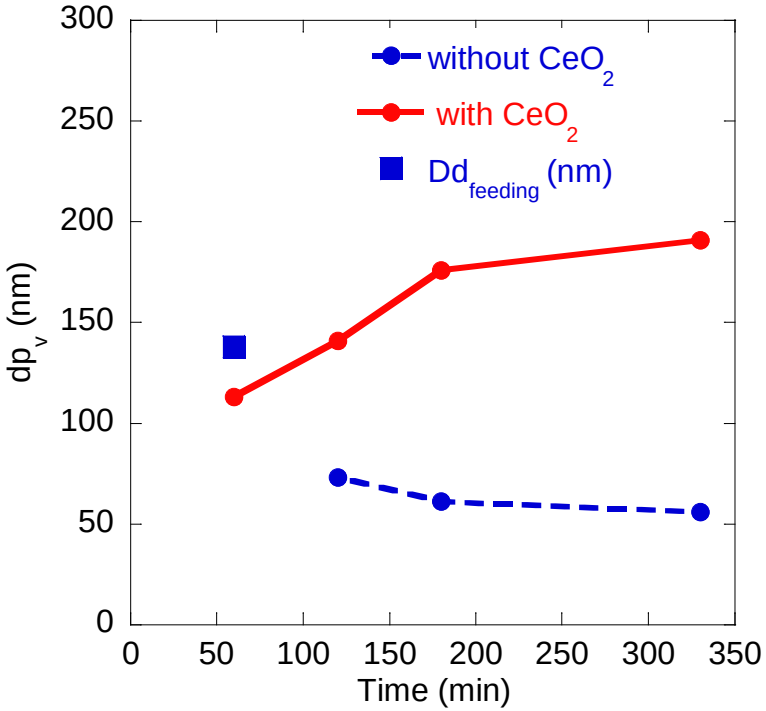
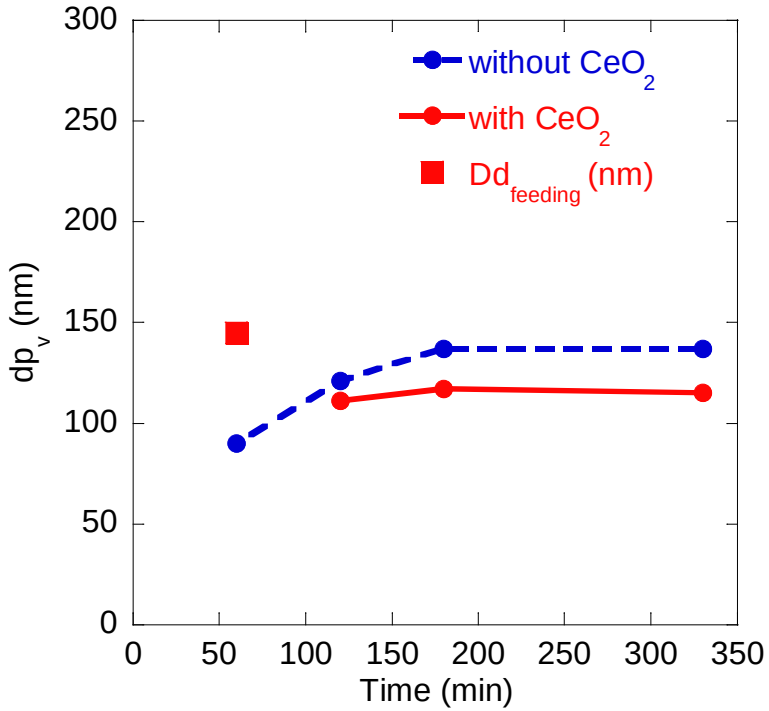
2. Results

Tracking of droplet nucleation: model experiments

Run 2-0



Run 0-2



If all entering droplets nucleate

Np/Np$_{seed}$	Run 2-0	Run 0-2
Theoretical	3.0	2.2
Exp. Cryo-TEM	3.1	2.6

3. Conclusions

Efficiency of droplet nucleation:

CeO_2 nanoparticles coupled with TEM proved to be a powerful technique to understand droplet nucleation efficiency in semibatch miniemulsion polymerization

Stability of the miniemulsion feed is more important than the radical capturing efficiency of the droplets (Ndroplets vs Nparticles)

Bimodal distributions are not due to homogeneous or micellar nucleation, but to late nucleation of droplets that have depleted most of their monomer ⇨most of the droplets nucleate!!

Thank you for your kind attention!!!

Woodlife project (FP7-NMP-2009-SMALL-246434)

Eusko Jaurlaritza (*Ikertzaileak prestatzeko eta hobetzeko laguntzak)*

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GOBIERNO VASCO

woodlife

eman ta zabal zazu
Universidad del País Vasco
Euskal Herriko Unibertsitatea

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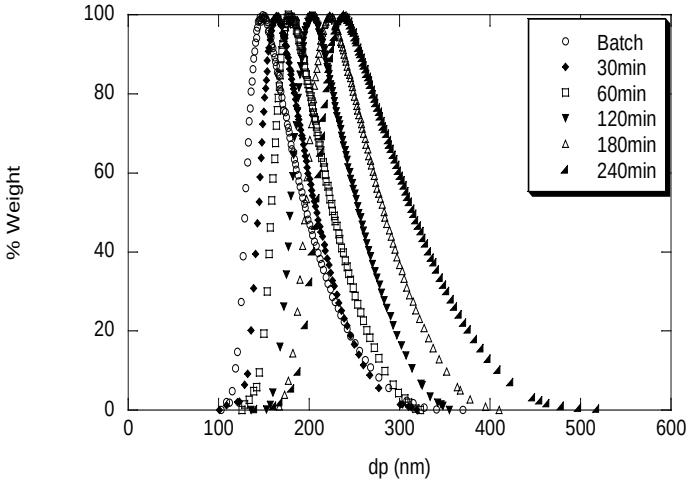
1. Introduction and motivation

Previous attempts to analyze droplet nucleation

Rodríguez, Macromolecules 2007, 40, 5735

4% SA
d_d=83 nm



50 wt% solids
Disc Centrifuge

3%PDMS; 4%SA
d_d=94 nm