Gradient and Core–Shell Waterborne Polymer Nanoparticles: Effects of Particle Morphology on Coating Performance

Yasemin Fadil,[1] Florent Jasinski,[1] Monique Mballa Mballa,[2] Stuart C. Thickett,[3] William Weaver,[2] Richard H. G. Brinkhuis,[2] Per B. Zetterlund[1]*

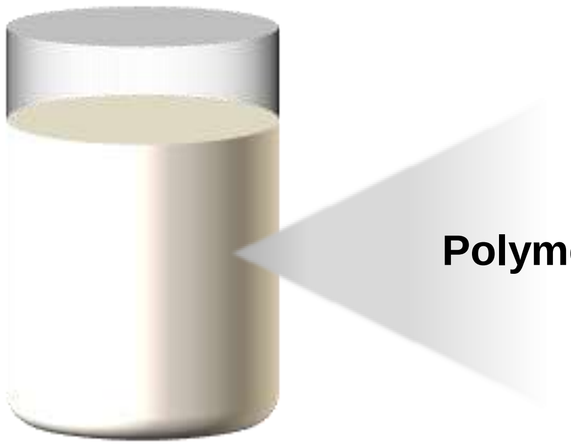
[1]Cluster for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[2]Allnex Corporate Innovation Group, Wageningen 6709 PA, Netherlands
[3]School of Physical Sciences, University of Tasmania, Sandy Bay TAS 7005, Australia

UNSW SYDNEY

Polymeric coatings

Synthetic polymers coatings can be used in a wide range of applications in our daily life such as adhesives, inks, varnishes and automotive or decorative paints

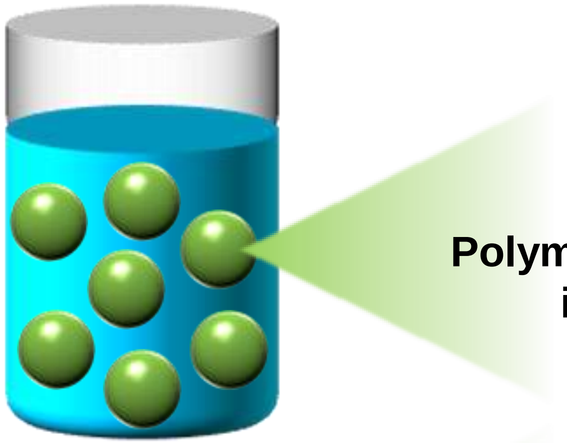
Solvent-borne systems



Polymer dissolved in solvent

Release of volatile organic compounds (VOCs)

Water-borne systems



Polymer dispersed in water

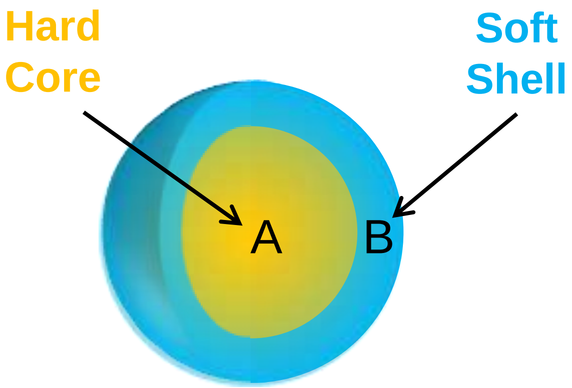
Environmentally friendly

Gradient polymer nanoparticles

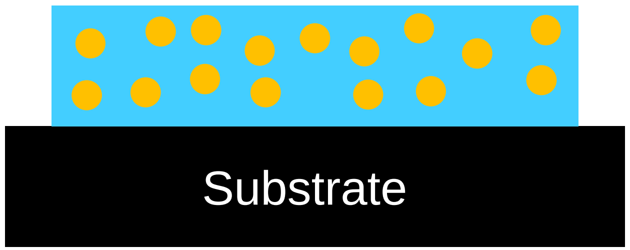
Composite particles

Low T_g → good film formation

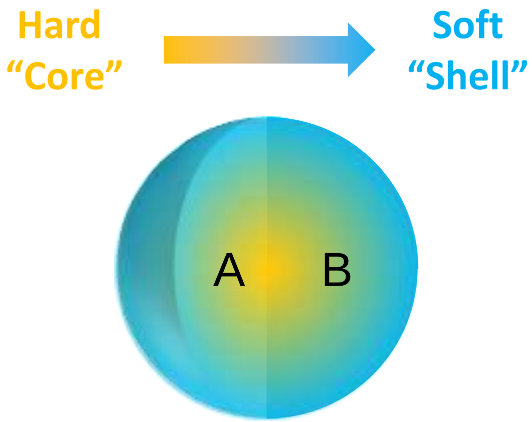
High T_g → hardness/blocking



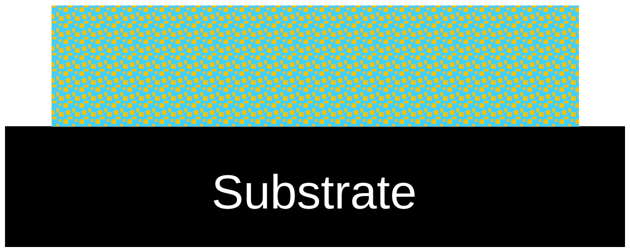
Core-shell morphology[1]
Two distinct particle composition domains



Heterogeneous Film



Gradient morphology[2,3]
Gradual change in particle composition

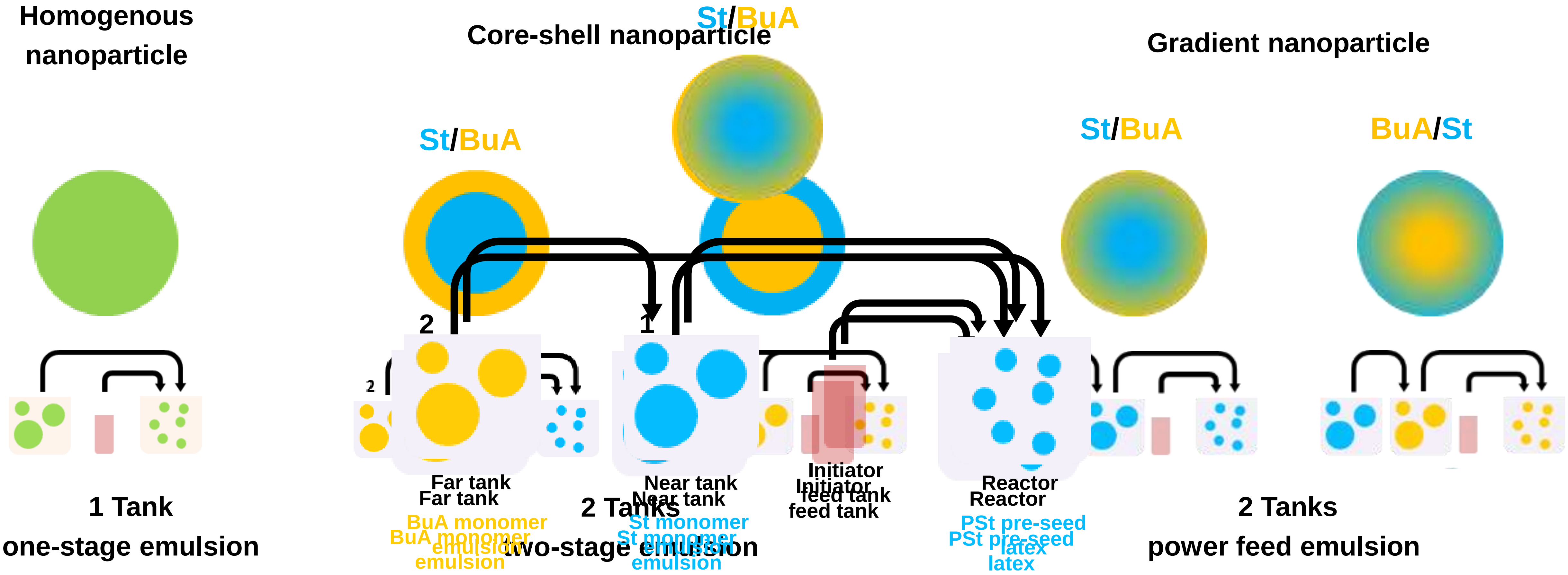


Homogeneous Film

1. Lee, S.; Rudin, A. In *Polymer Latexes: Preparation, Characteristics and Application, ACS Symposium Series* **1992** p 234
2. Hoy, K. L. *J. Coat. Technol.*, **1979** pp 27-41
3. Bakker, P.; Mestach, D. *Surf. Coat. Int. B* **2001,** 84, (4), 271-276

Different monomer feed strategies

Homogenous nanoparticle | **Core-shell nanoparticle** | **Gradient nanoparticle**

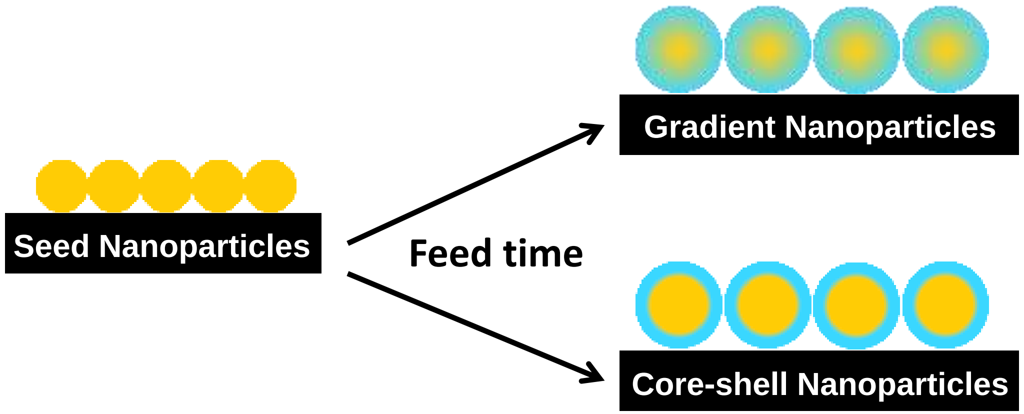


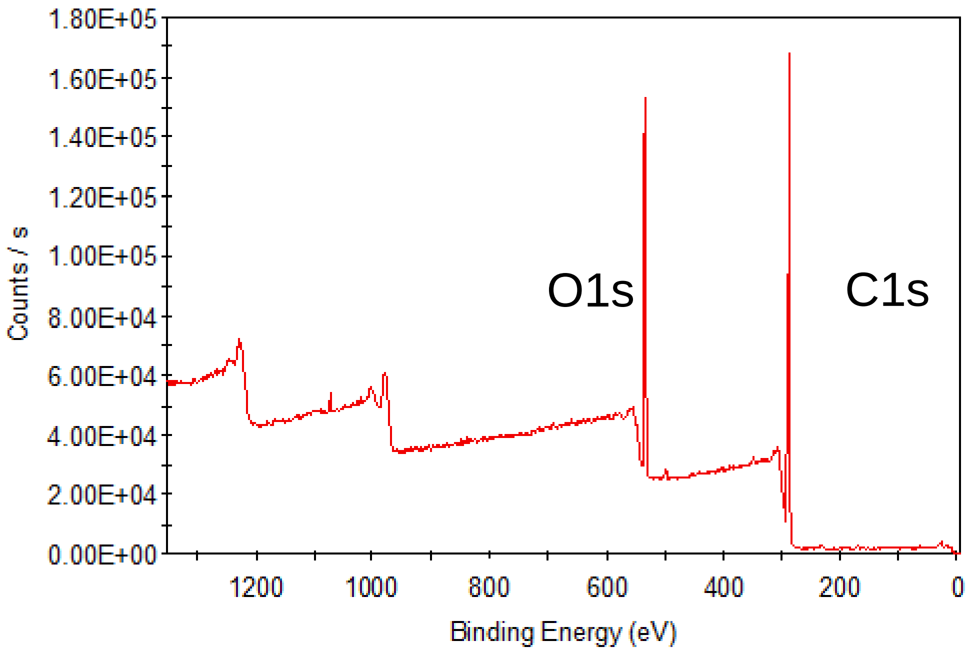
1 Tank one-stage emulsion polymerization (1SEP)

2 Tanks two-stage emulsion polymerization (2SEP)

2 Tanks power feed emulsion polymerization (PFEP)

Particle morphology assessment

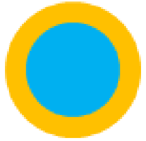




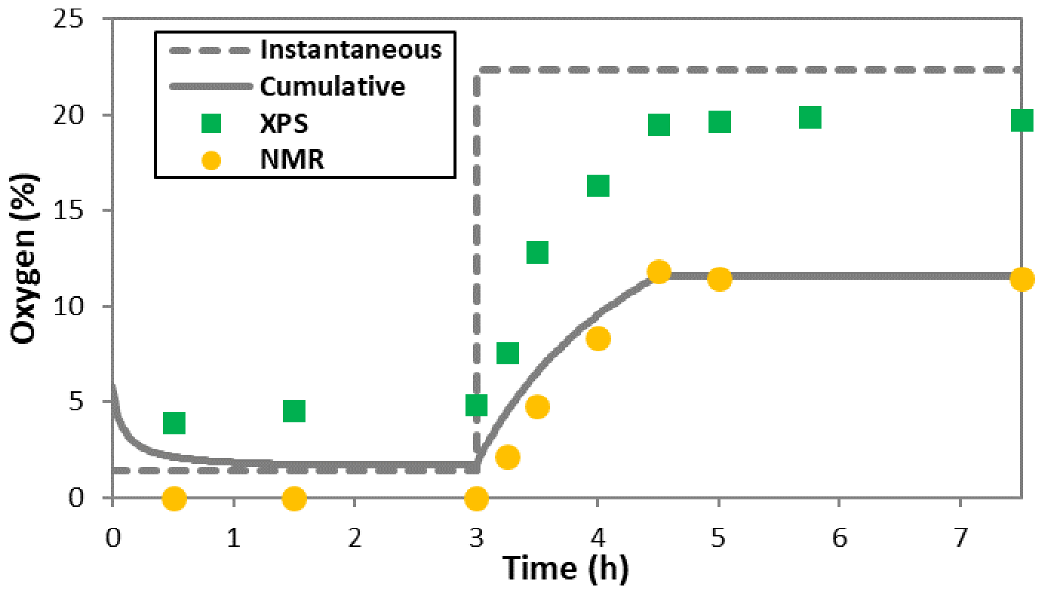
XPS: Evolution of particle surface composition (oxygen is probing element in BuA)

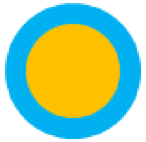
^{1}H NMR: Evolution of overall particle composition

Morphology assessment by XPS and ^{1}H NMR: Core-shell particles

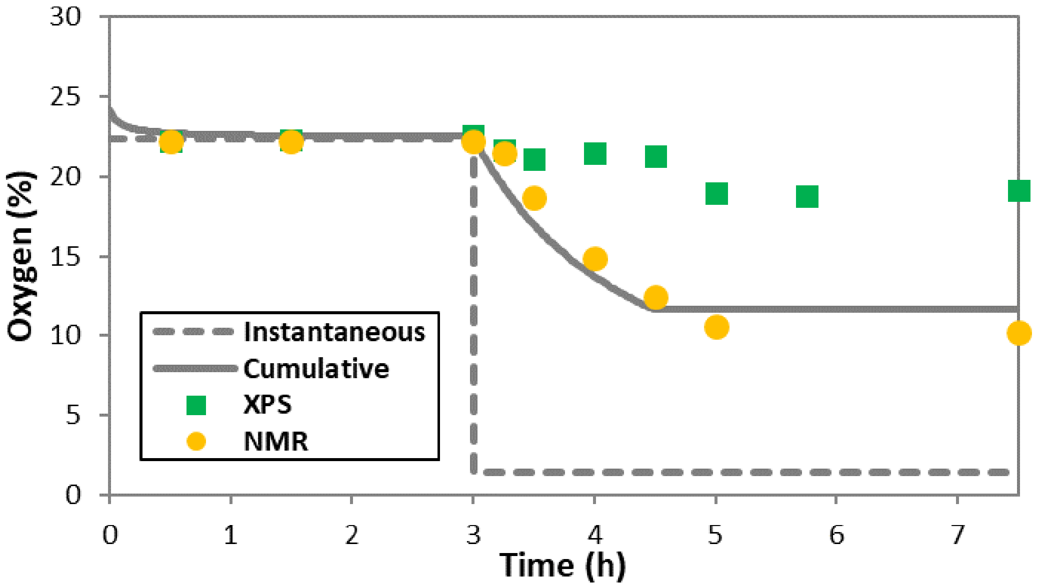


St/BuA Core-shell nanoparticle



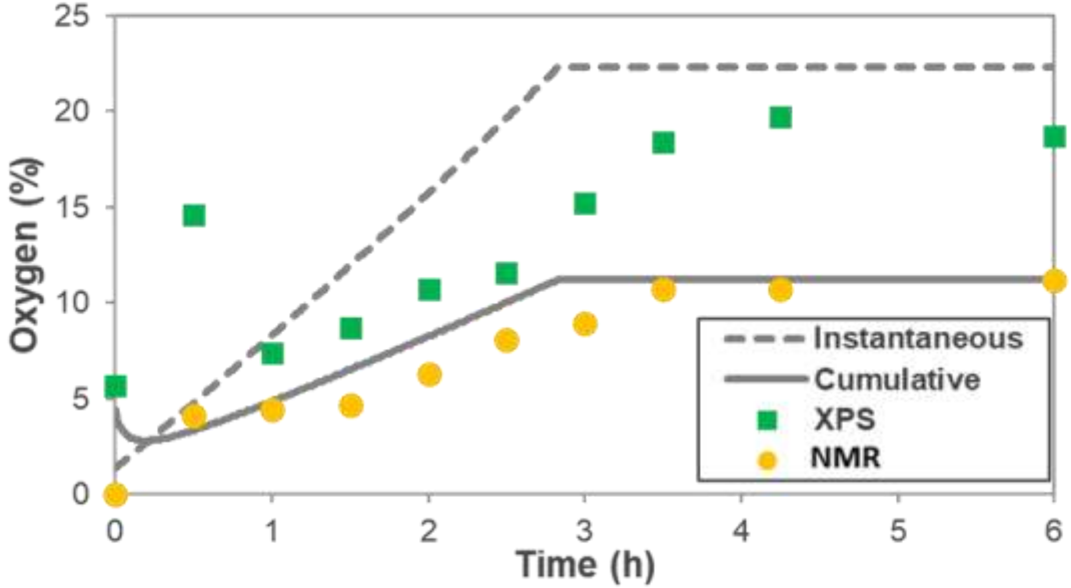


BuA/St Core-shell nanoparticle

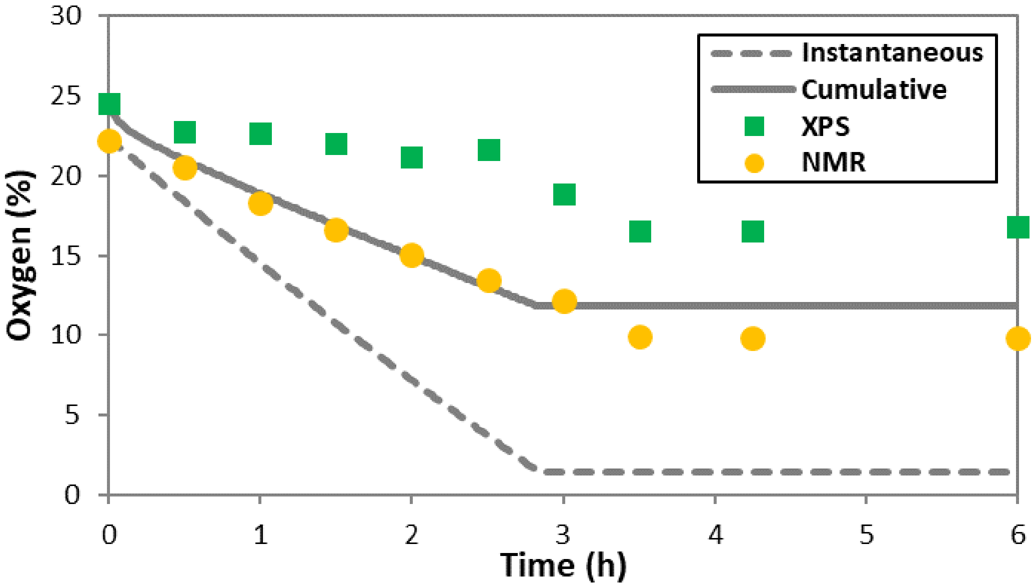


Morphology assessment by XPS and ^{1}H NMR: Gradient particles

St/BuA Gradient nanoparticle



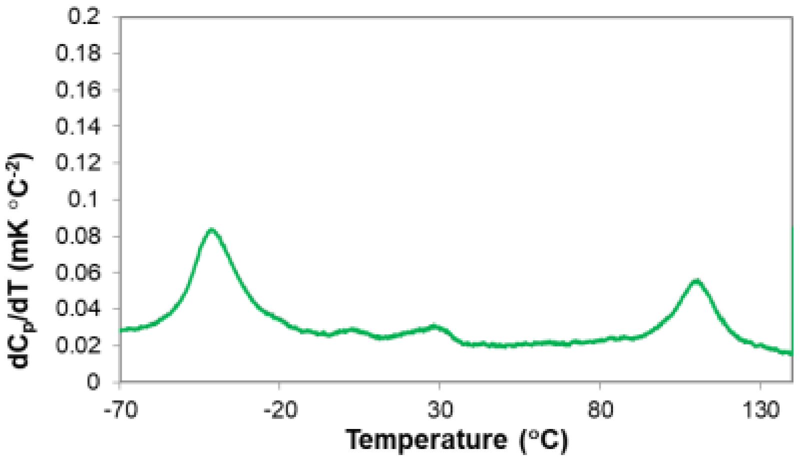
BuA/St Gradient nanoparticle



Morphology assessment by DSC

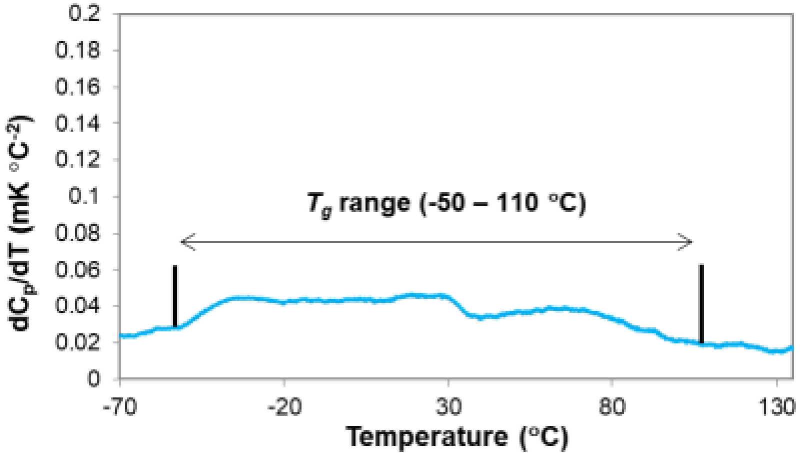
St/BuA 

Core-shell particles



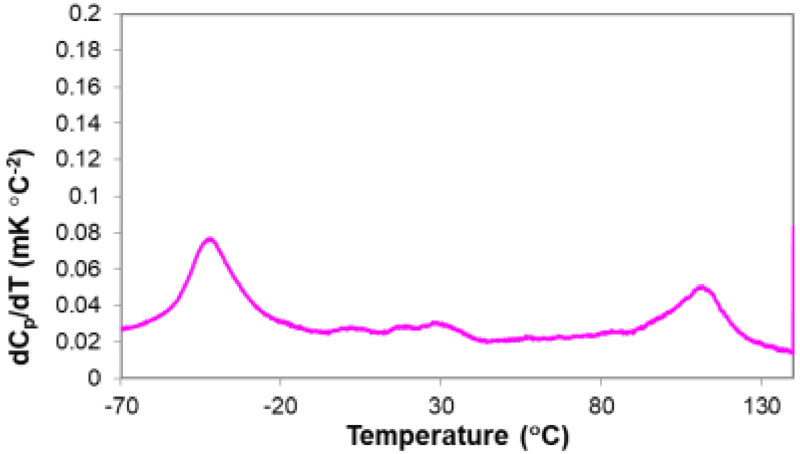
St/BuA 

Gradient particles



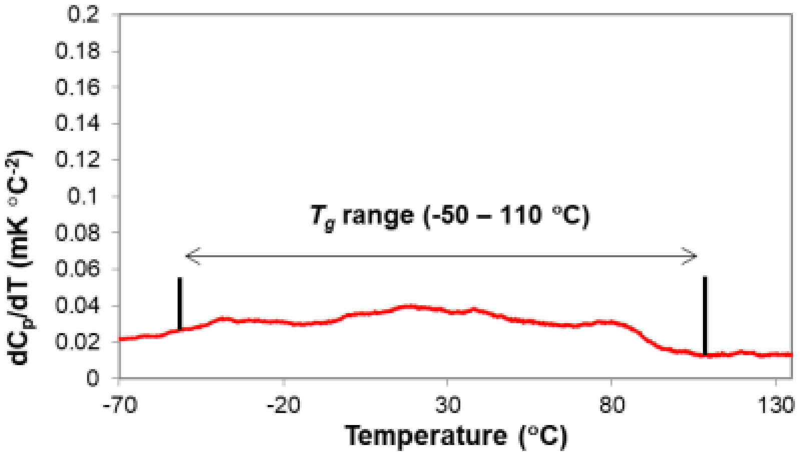
BuA/St 

Core-shell particles



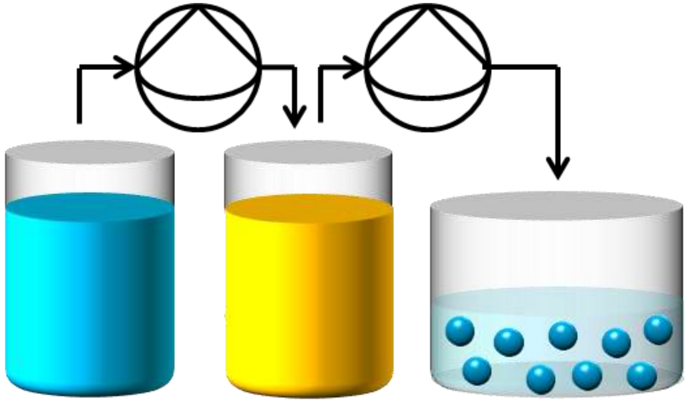
BuA/St 

Gradient particles



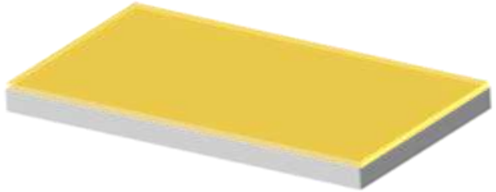
Film properties

Emulsion process



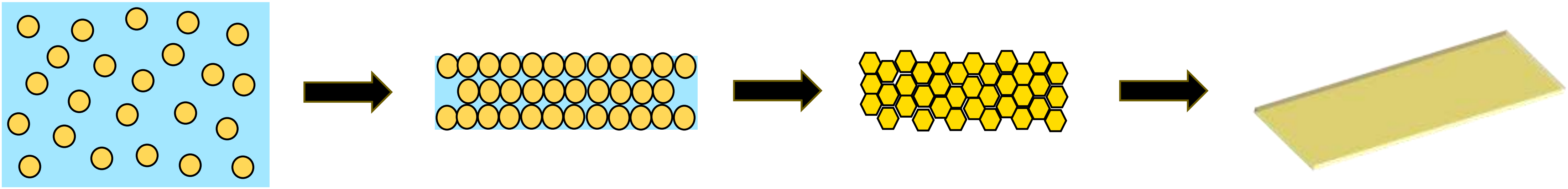
Particle morphology

Film performance



- Minimum film forming temperature
- Hardness

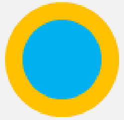
Film properties: Minimum film forming temperature (MFFT)



Temperature when the film became translucent/coherent

MFFT > T_{amb} / MFFT < T_{amb} => Brittle / tacky coating

MFFT ≈ T_{amb} => Balance

Homogenous nanoparticle	St/BuA Core-shell nanoparticle	BuA/St Core-shell nanoparticle	St/BuA Gradient nanoparticle	BuA/St Gradient nanoparticle
				
22 °C	<0 °C	23 °C	5 °C	33 °C

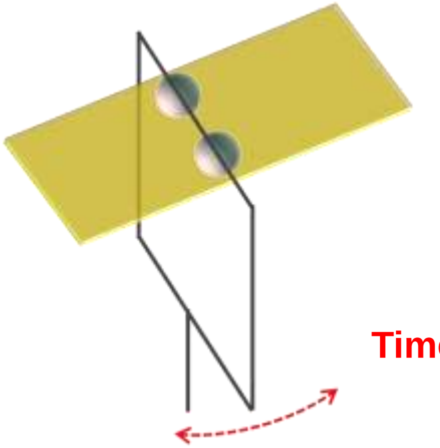
Low T_g P(BuA) at particle surface (core-shell and gradient) leads to low MFFT, and high T_g P(St) leads to high MFFT

Core-shell St/BuA has lower MFFT than gradient due to core-shell having shell with just P(BuA), whereas gradient has gradual change of P(St-BuA) composition

BuA/St core-shell and gradient particles are partially inverted (BuA at the surface). The gradual change in chain composition leads to less driving force for chain rearrangement, which results in more P(St) at the particle surface and higher MFFT for the gradient case.

Film properties: Hardness

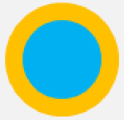
Hardness test (Persoz Pendulum)



Short time => Soft coating

Long time => Hard coating

Time for the oscillation to decrease from 14 to 7°

Homogenous nanoparticle	St/BuA Core-shell nanoparticle	BuA/St Core-shell nanoparticle	St/BuA Gradient nanoparticle	BuA/St Gradient nanoparticle
				
266 s	32 s	48 s	98 s	172 s

Particles with low T_g P(BuA) at the surface (core-shell and gradient) are softer than particles with high T_g P(St)

Core-shell St/BuA is softer than gradient due to core-shell having shell with just P(BuA) whereas gradient has gradual change of P(St-BuA) composition

BuA/St core-shell and gradient particles are partially inverted (BuA at the surface). The gradual change in chain composition leads to less driving force for chain rearrangement, which results in more P(St) at the particle surface therefore harder particles

Conclusions

- Well defined nanocomposite particles with core-shell and gradient morphology were synthesized using seeded starved-feed semibatch emulsion polymerization

- The effect of particle morphology on the film/coating performance has been elucidated
  - Gradient particles with hard core and soft shell (St/BuA) led to reduction of MFFT while maintaining high hardness and flexibility

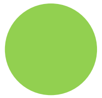
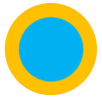
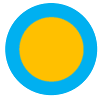
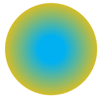
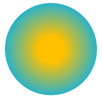
Acknowledgement

University of New South Wales (UNSW)
Prof Per Zetterlund
Dr Florent Jasinski

Allnex Corporate Innovation Group (Netherlands)
Monique Mballa Mballa
William Weaver
Richard H. G. Brinkhuis

University of Tasmania
Assoc Prof Stuart Thickett

Summary of the film properties

System	1SEP Homogeneous	2SEP St/BuA	2SEP BuA/St	PFEP St/BuA	PFEP BuA/St
Targeted morphology					
HNMR BuA: St (wt %)	49:51	57:43	55:45	51:49	46:54
XPS BuA: St (wt %)	61:39	93:7	89:11	87:13	78:22
MFFT (°C)	22	<0	23	5	33
Blocking Resistance (N/cm^2)	0.74	0.5	0.14	3.34	0.9
Persoz hardness (s)	266	32	48	98	172
Flexibility df (cm) at 20°C	12	0	0	0	1.2
Film at T_{amb}	No	Yes	Yes	Yes	No
Haziness	Low	Medium	High	Low	High

Preferred Criteria:

MFFT ≈ T_{amb}

High blocking resistance

High hardness

High flexibility

Form a film at 20°C

Low haziness