Surfactant-free Emulsion Polymerization Based on Cellulose Nanocrystals (CNC)

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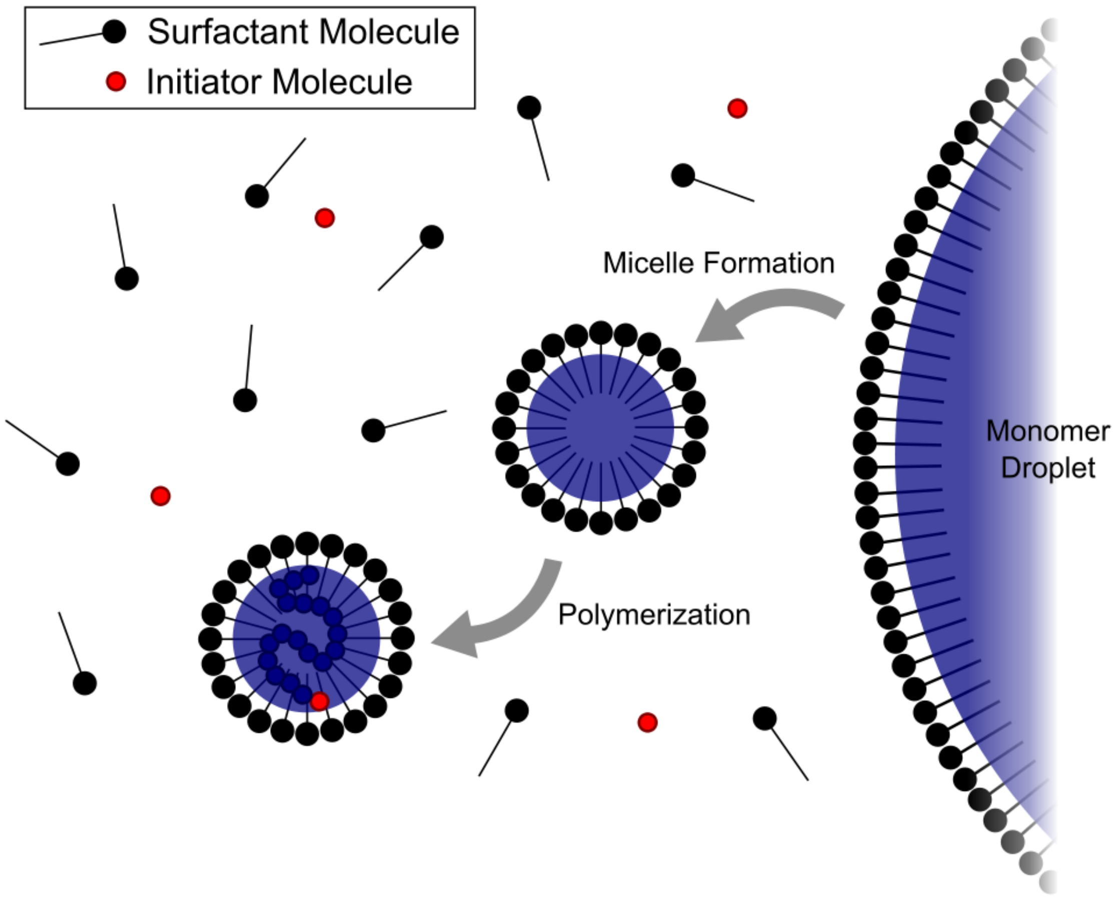
TAPPI NANO DIVISION

Conventional Emulsion Polymerization

- Conventional emulsion polymerization system
  - Monomer
  - Water
  - Surfactant
  - Water-soluble initiator
- Applications of polymer emulsions
  - Synthesis of plastics and rubbers
  - Paint and coatings
  - Adhesives
  - Cosmetics

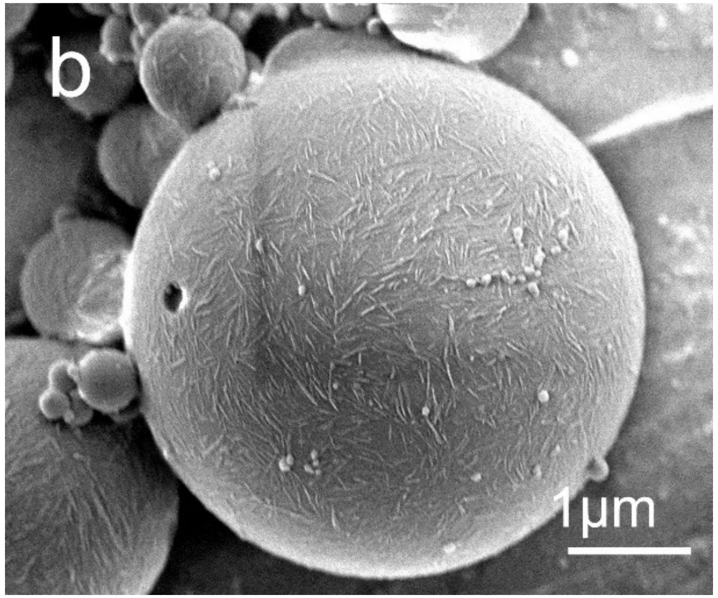


https://en.wikipedia.org/wiki/Emulsion_polymerization

Other Types of Emulsion Polymerization

- Inverse emulsion polymerization
  - Water-in-Oil
  - Polymerization occurs in the aqueous phase
- Mini emulsion polymerization
  - Initiation started in monomer micelles
  - Typically require costabilizer
- Pickering emulsion polymerization
  - Stabilized by solid particles
- CNC in emulsion polymerization
  - Pickering emulsion
  - *In-situ* with conventional emulsion polymerization
  - Modified surface properties

Polymerized Pickering emulsion stabilized with CNCs



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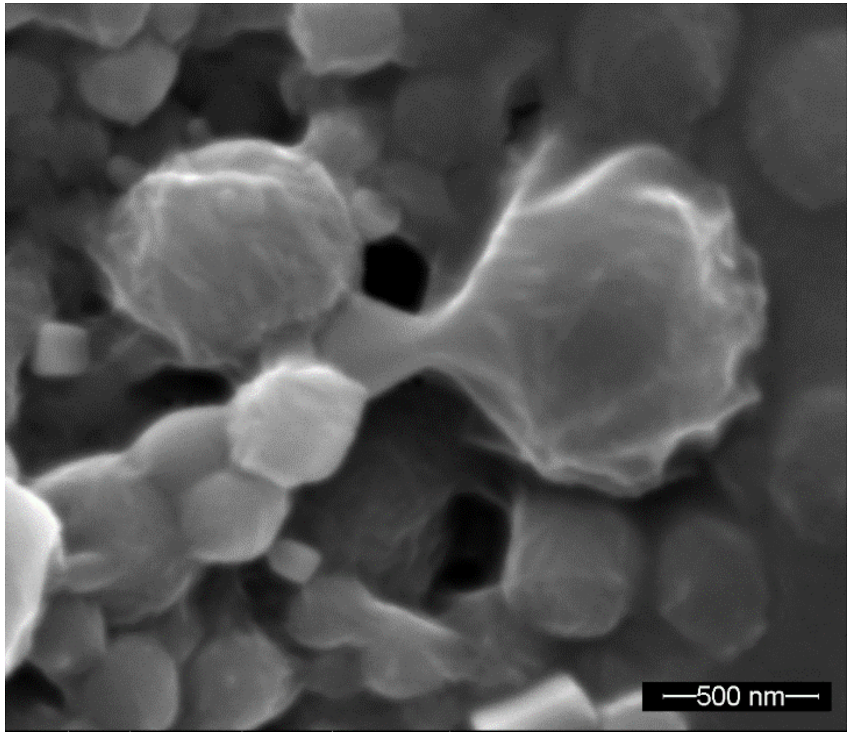
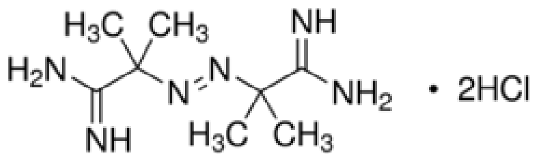
CNC-stabilized Surfactant-free Emulsion Polymerization

- A Simple and versatile process
  - Can be carried out in the same setup for conventional emulsion polymerizations
  - No need for intense shearing treatment, e.g. homogenization and ultrasonication
  - Easy to scale-up
- A wide variety of vinyl monomers can be polymerized through such a process
  - Acrylic monomers
    - Methyl methacrylate (MMA)
    - Butyl acrylate (BA)
    - Ethyl acrylate (EA)
  - Styrene
  - Vinyl acetate
  - Mixture of monomers
- Tunable emulsion properties
  - Monomer content: 10-30 wt. % of total emulsion
  - CNC content: 1-4 wt. % in the aqueous phase

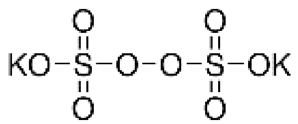


Initiators

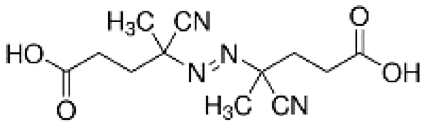
- Cationic water-soluble free radical initiator is critical
  - AIBA (2,2′-Azobis(2-methylpropionmidine) dihydrochloride)



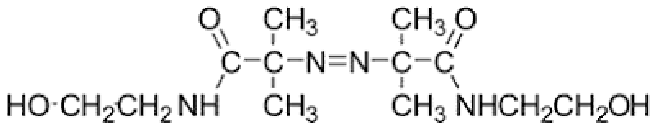
  - Other types of initiator do NOT work



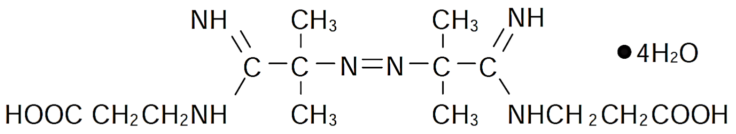
KPS
Anionic



ACVA
Anionic



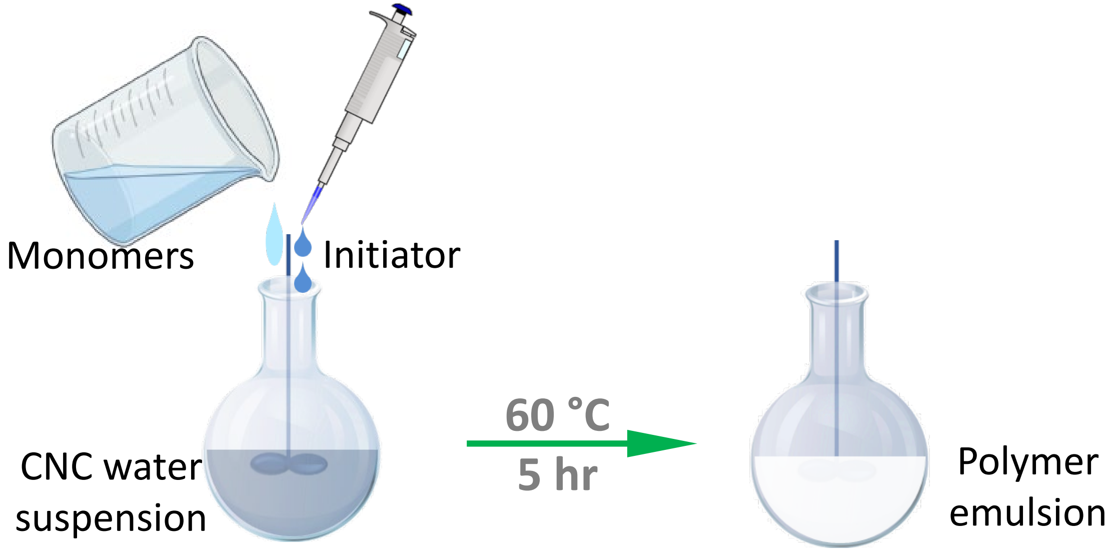
VA-086
Non-ionic



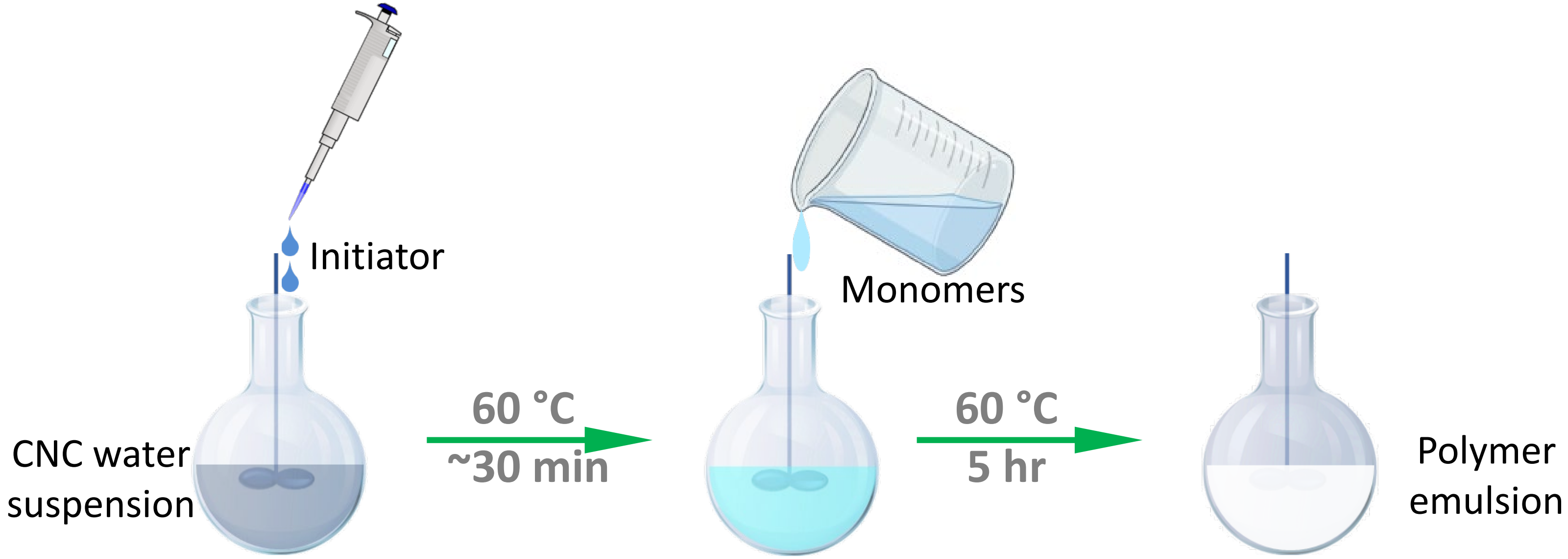
VA-057
Zwitterionic

Two Polymerization Processes

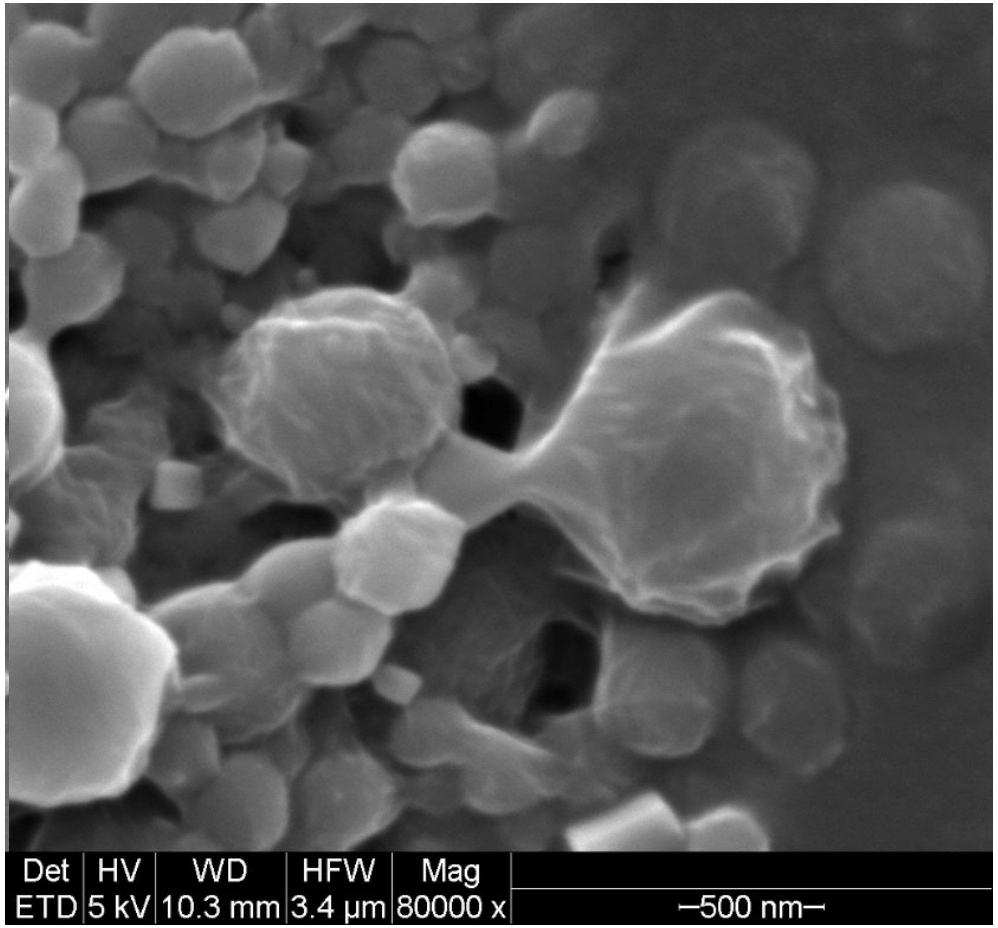
Non-preheated



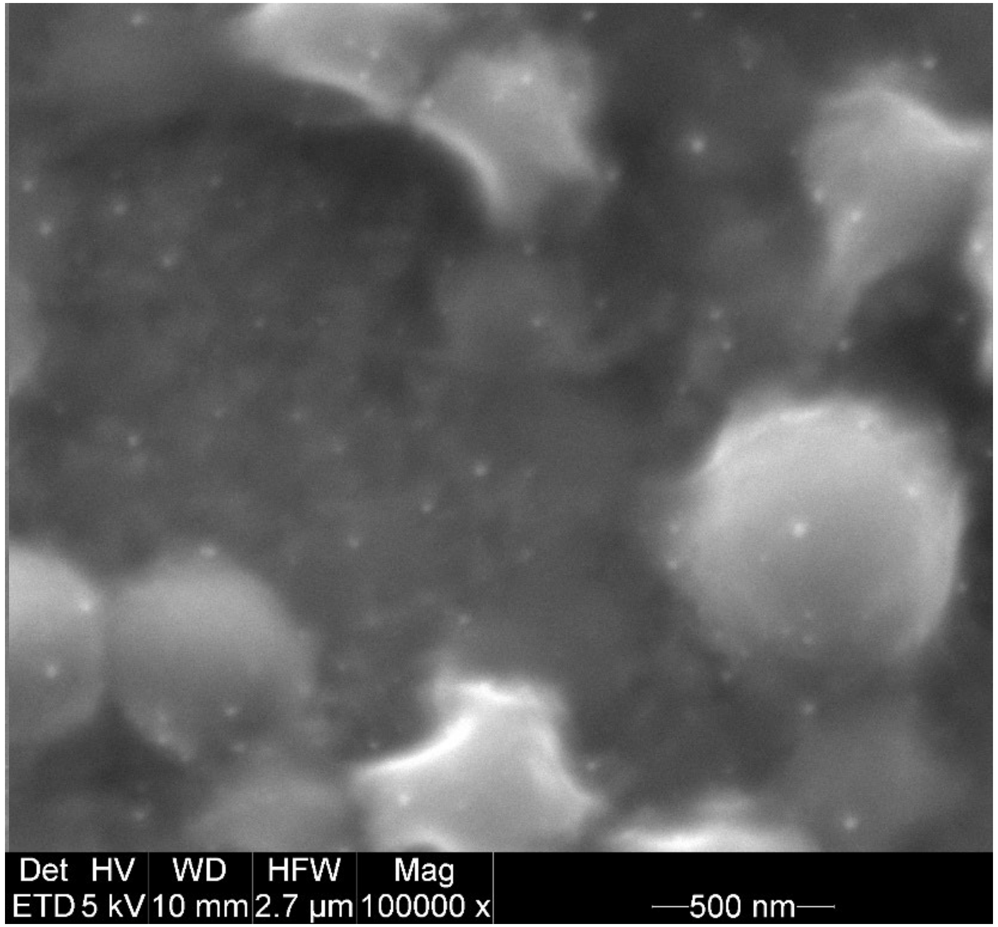
Preheated



Different Morphology of Latex Particles



Preheated Process



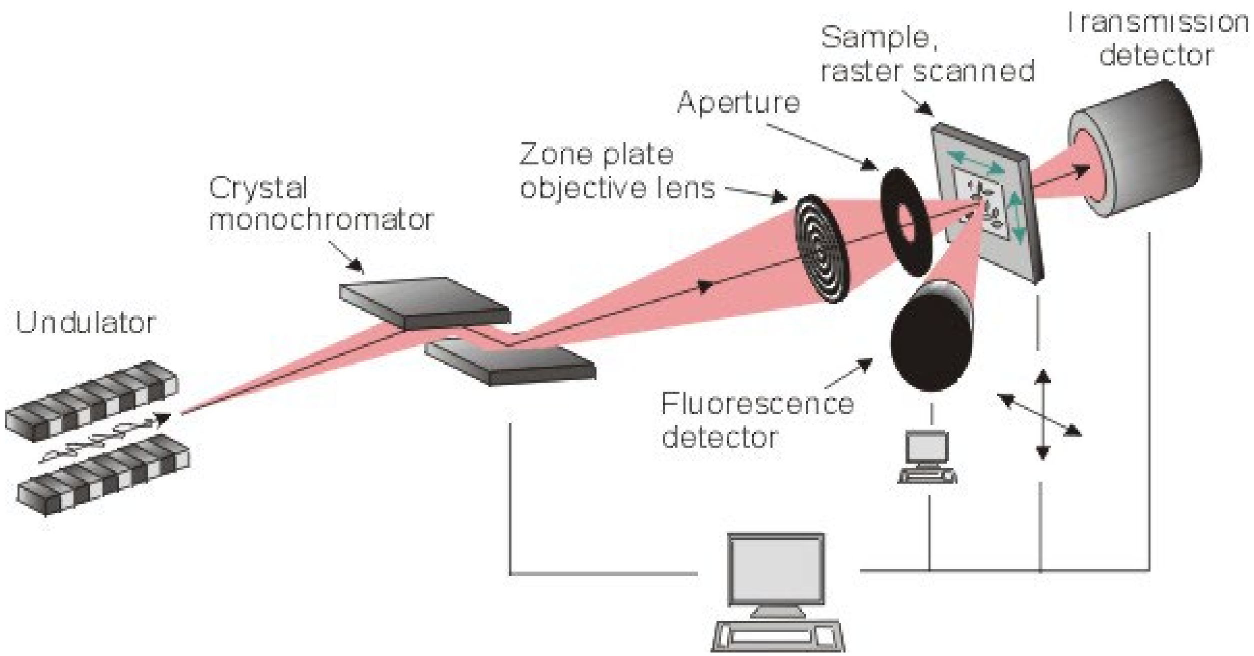
Non-Preheated Process

Mechanism Study – Approaches

- Scanning transmission X-ray microscopy (STXM)
  - CNC distribution inside CNC/polymer emulsion particles
  - In collaboration with Canadian Light Source (CLS)
- Polymerization kinetic study
  - Monomer conversion degree
  - Particle size
  - Zeta potential

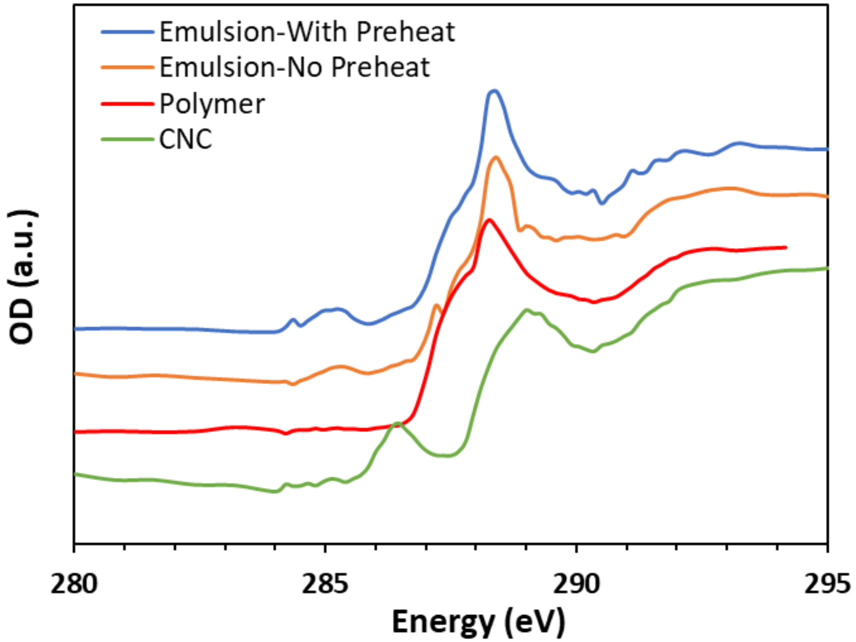
Investigation of Latex Particle Structures

- Scanning transmission X-ray microscopy (STXM)

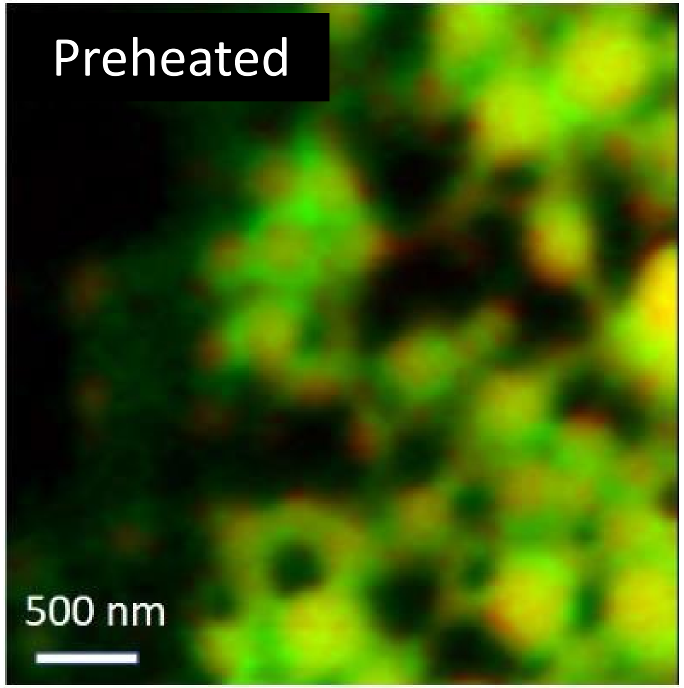


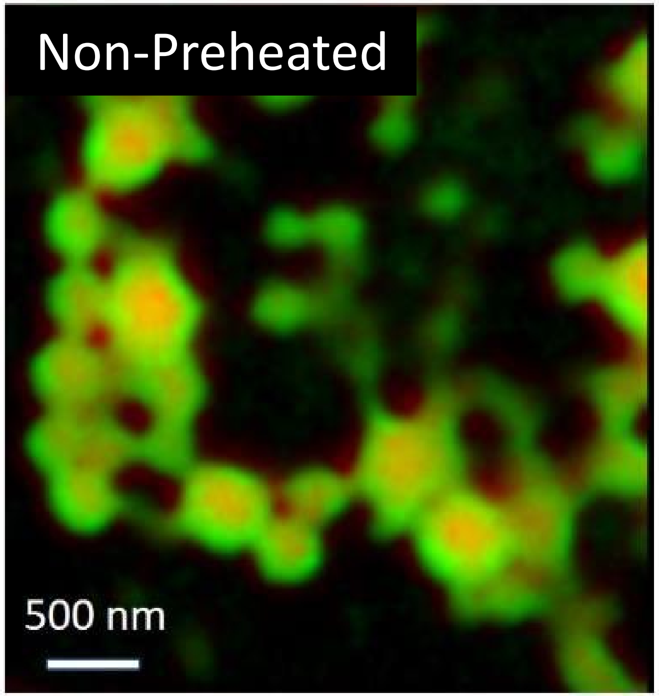
- CNC and polymer distribution can be plotted based on C K-edge absorption

STXM of Latex Particles (C K-edge)



CNC – Green   Polymer – Red





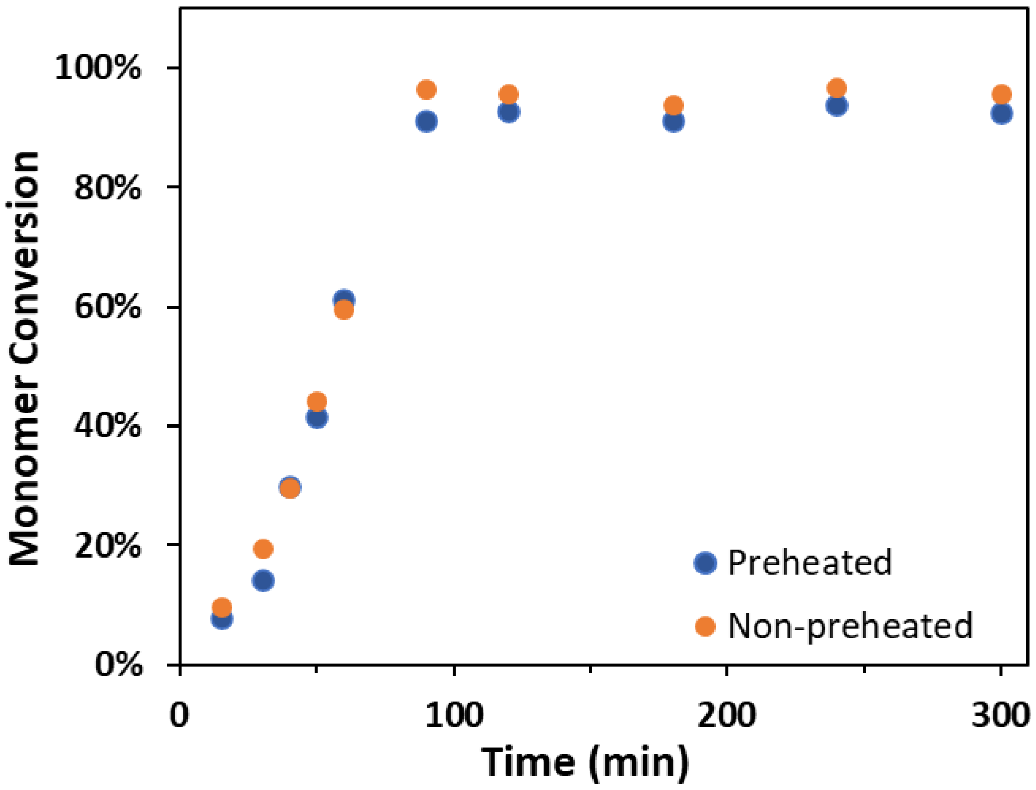
- CNC and polymer were distinguished in C K-edge spectra
- Distinct CNC distribution inside emulsion particles:
  - More uniform for the emulsion polymerized with preheat
  - Higher concentration near the shell when polymerized without preheat

Emulsion Polymerization Kinetics

- Reaction conditions:
  - Monomers
    - A mixture of methyl methacrylate (MMA) and butyl acrylate (BA) (weight ratio 1:1)
    - 10 wt. % of emulsion
  - Initiator
    - AIBA
    - 1 wt. % of monomers
  - CNC suspension
    - [CNC] = 2 wt. %
  - Polymerization at 60 °C

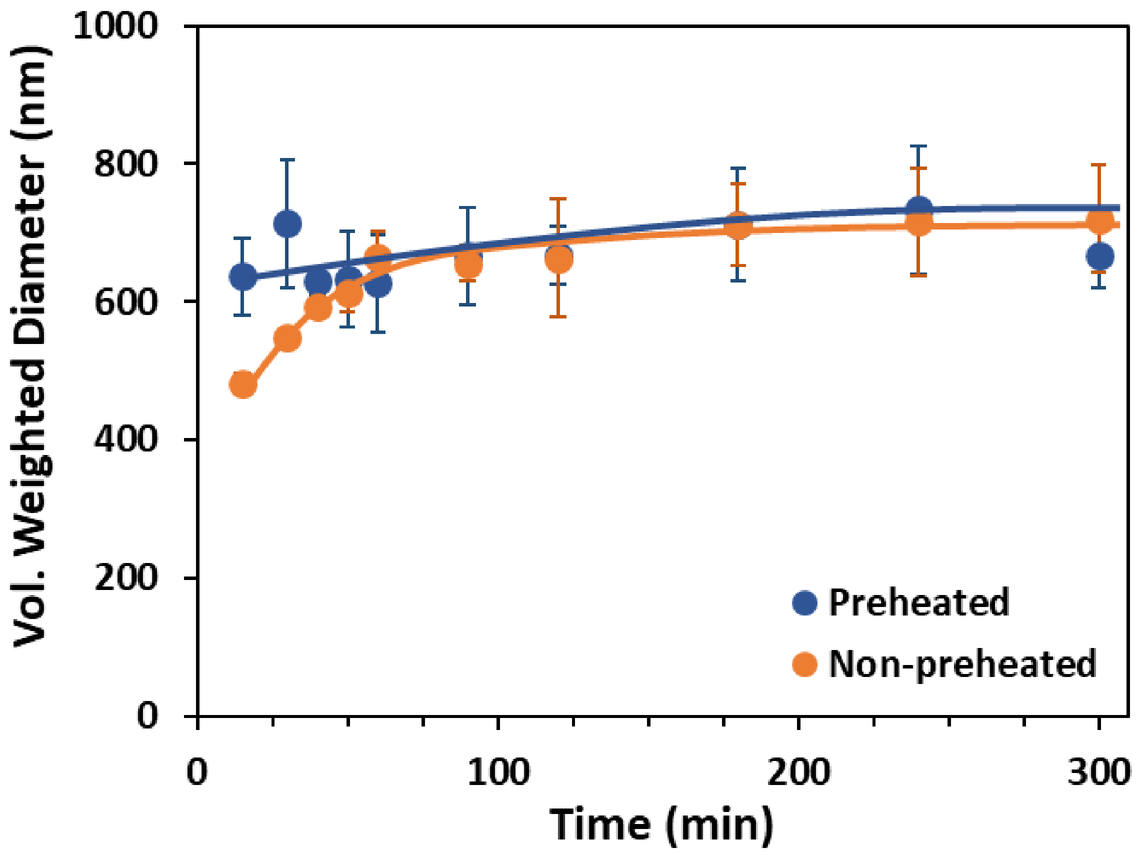
- Two reaction methods
  - With preheat
  - No preheat
- Samples were taken at:
  - 15, 30, 40, 50, 60, 90, 120, 180, 240, 300 min
  - Quenched in ice water bath and MeHQ was added

Monomer Conversion



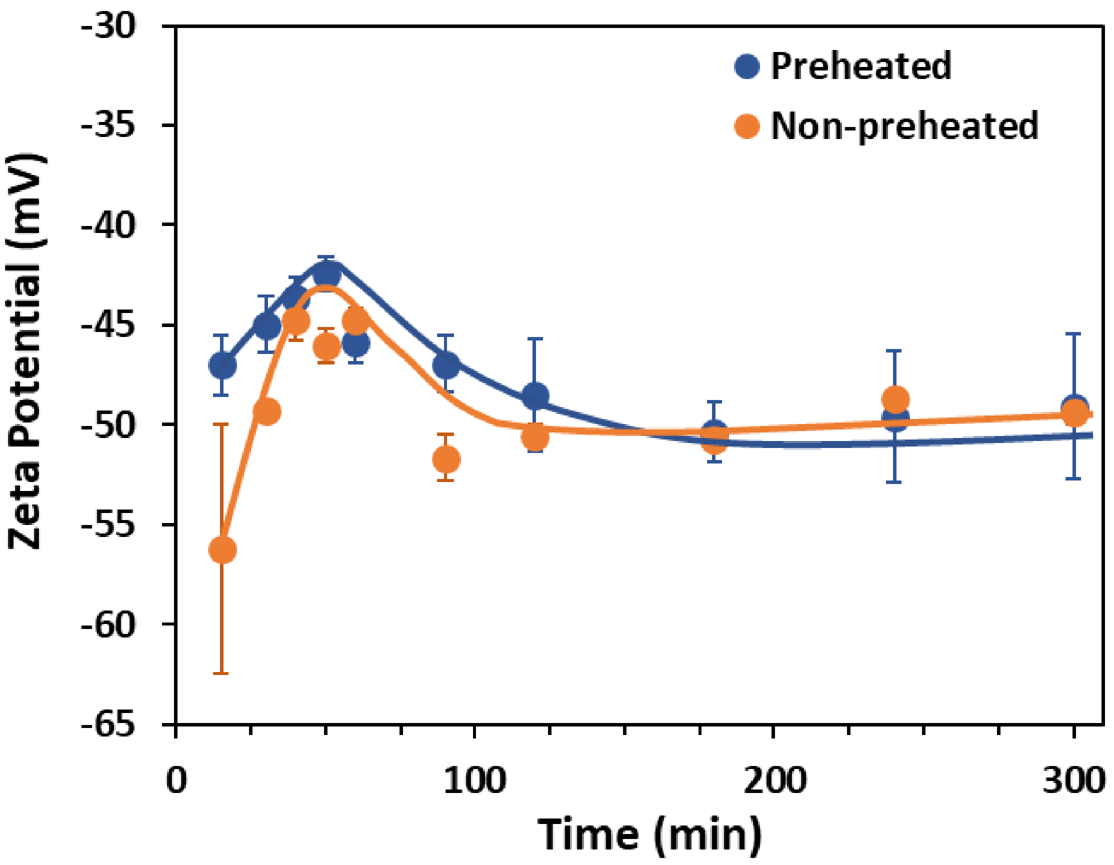
- Calculated by comparing the theoretical and measured solid content
- Decomposition rate of initiator was not affected by the difference in polymerization method

Evolution of Latex Particle Size



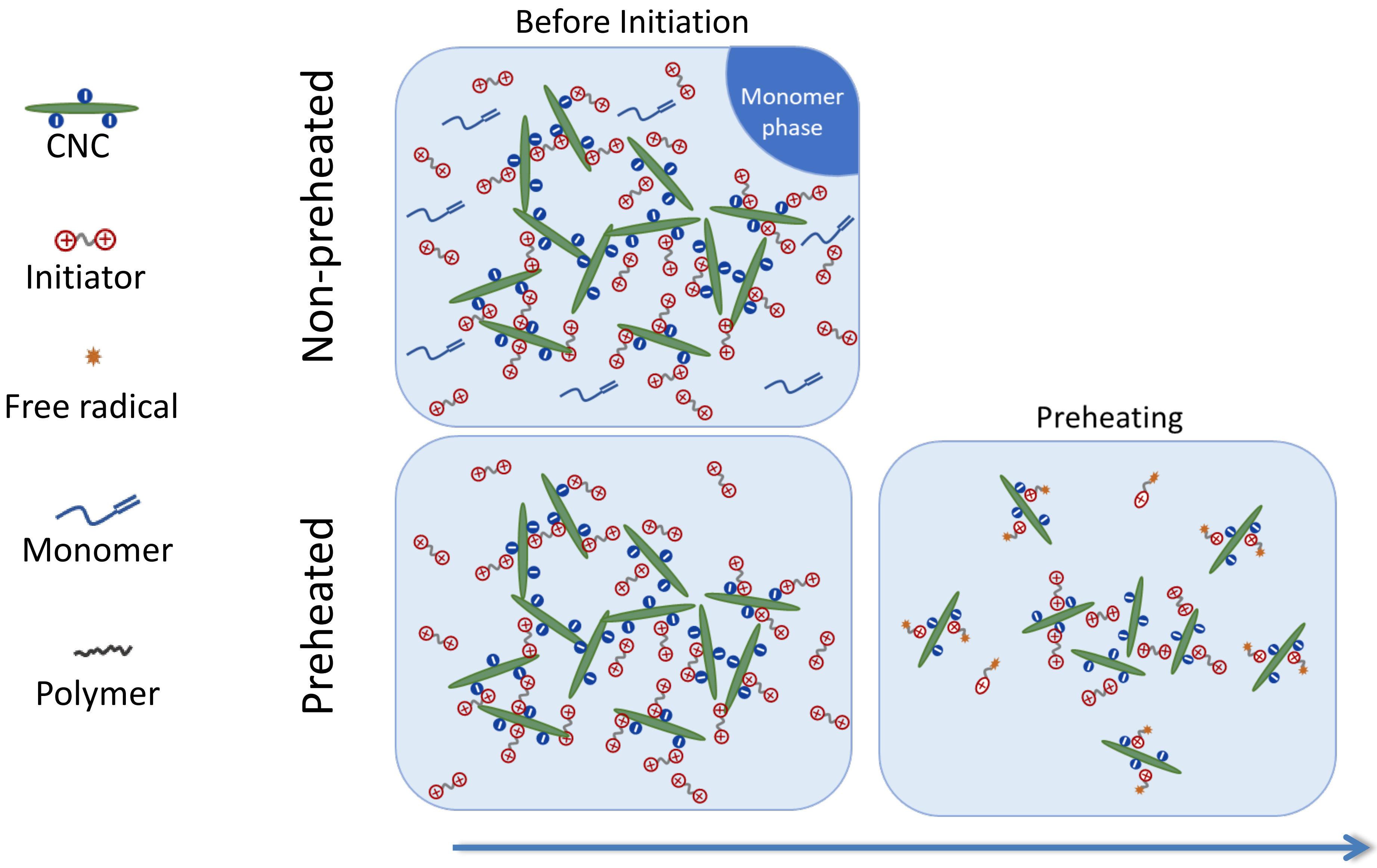
- Preheated reaction
  - Particle size does not have significant change from the beginning to the end of reaction
- Non-preheated reaction
  - A period of size increase in the first 50 min of polymerization, and slight increase after that
- Similar particle size at the end of reaction
- Implications
  - Different particle formation mechanisms
  - Polymerization occurred inside particles once they are formed

Evolution of Latex Particle Surface Charge

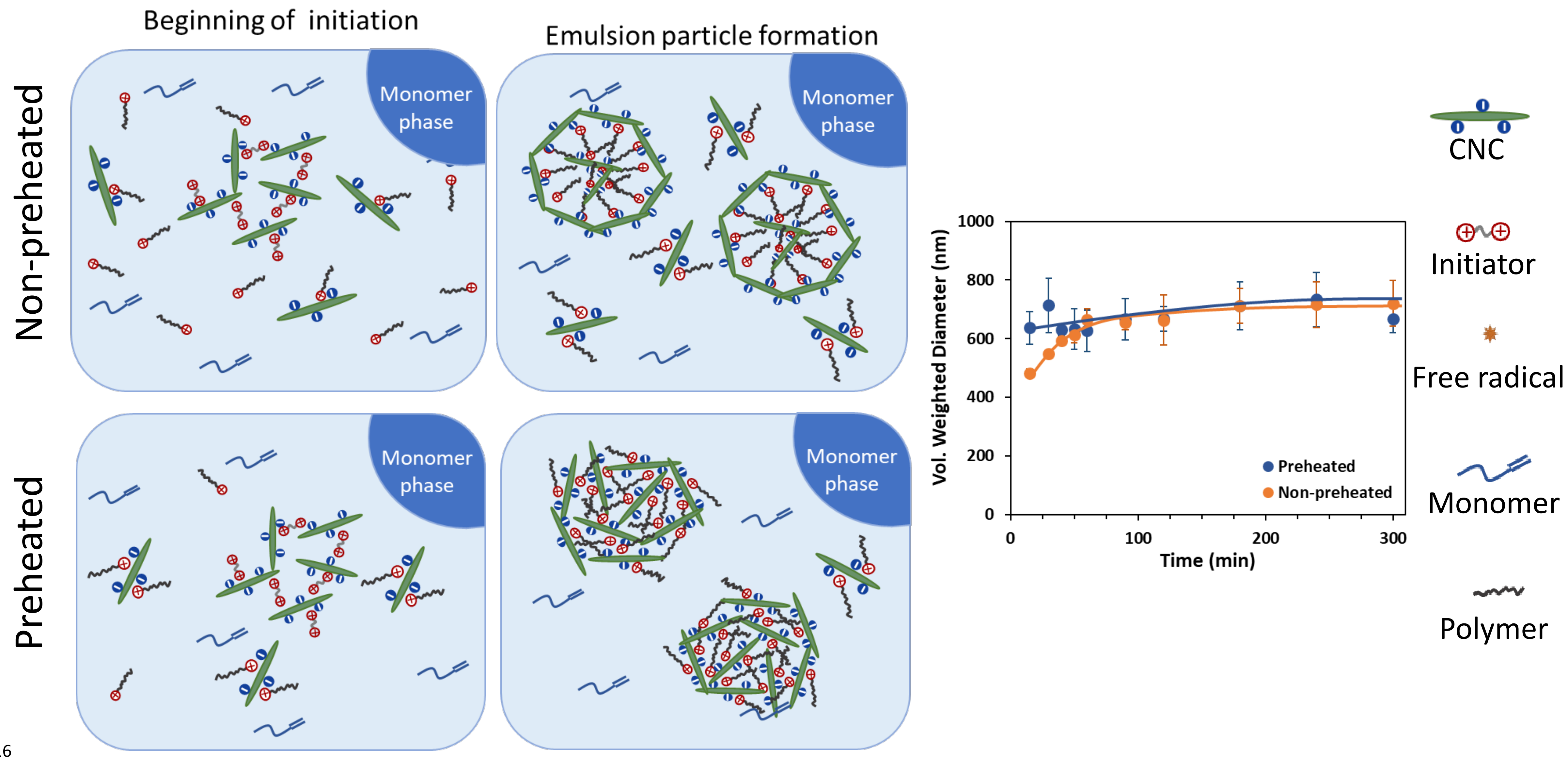


- Zeta potential of CNC/AIBA mixture was -45 mV
- Both reactions showed peak of zeta potential at ~50 min of polymerization
- Similar zeta potential at the end of reactions

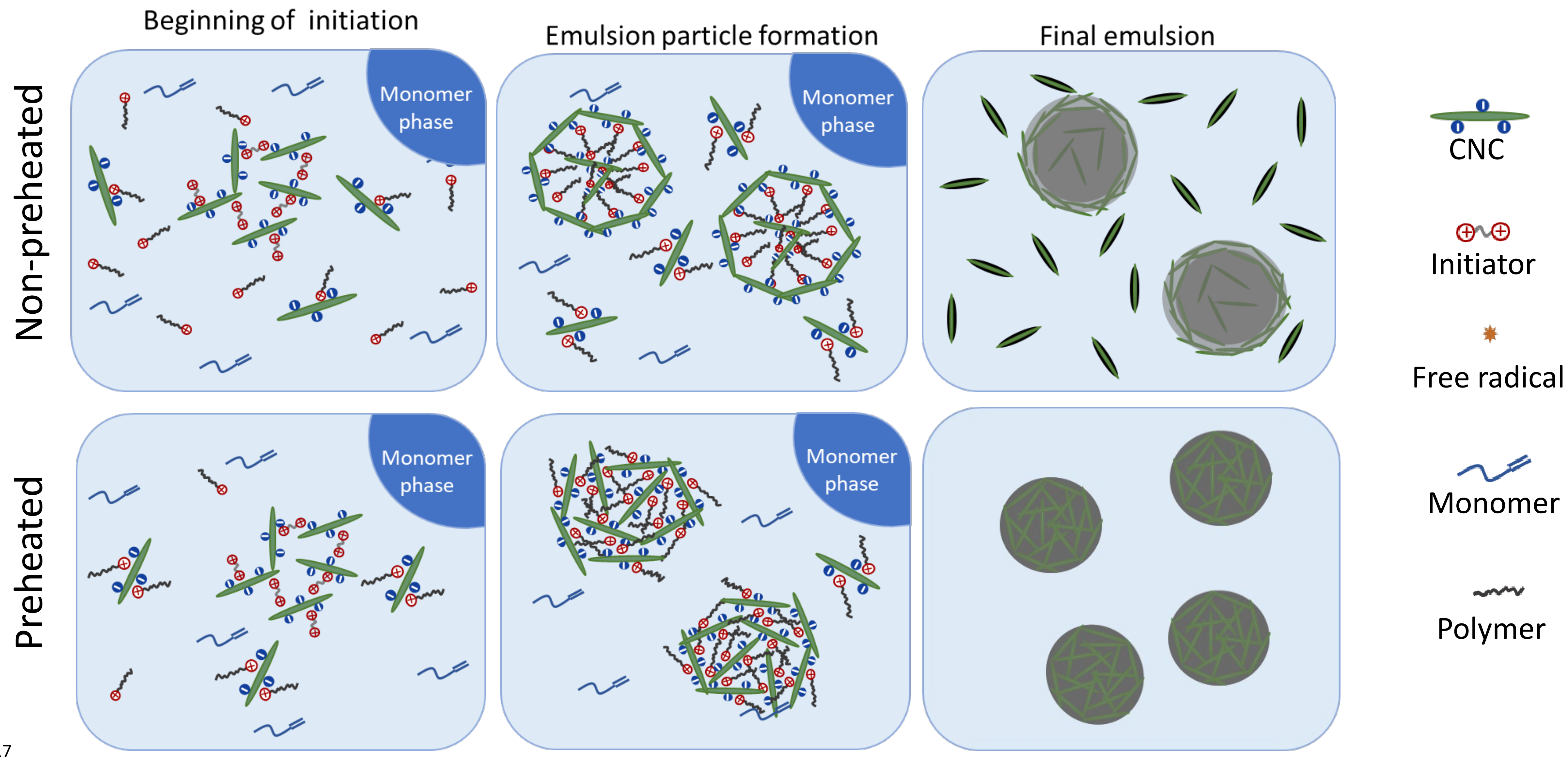
Proposed Polymerization Mechanisms (1/3)



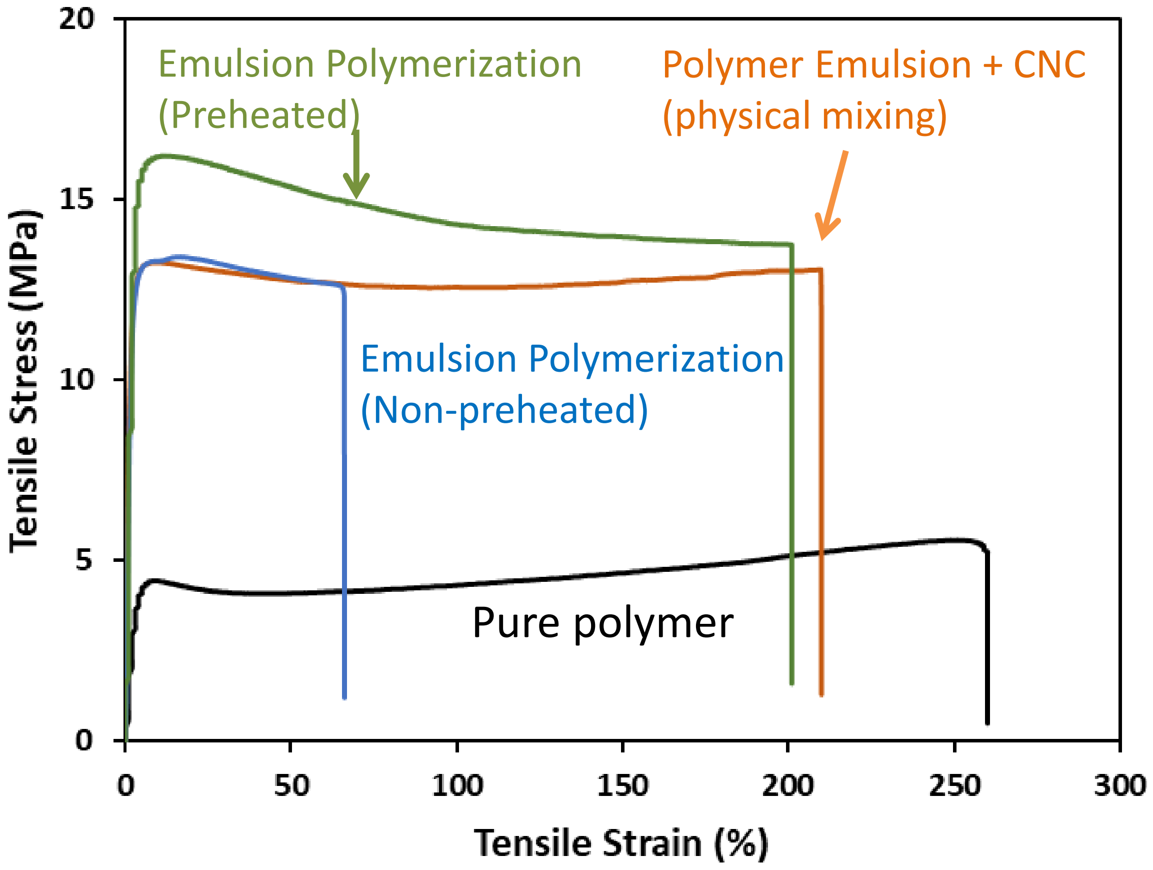
Proposed Polymerization Mechanisms (2/3)

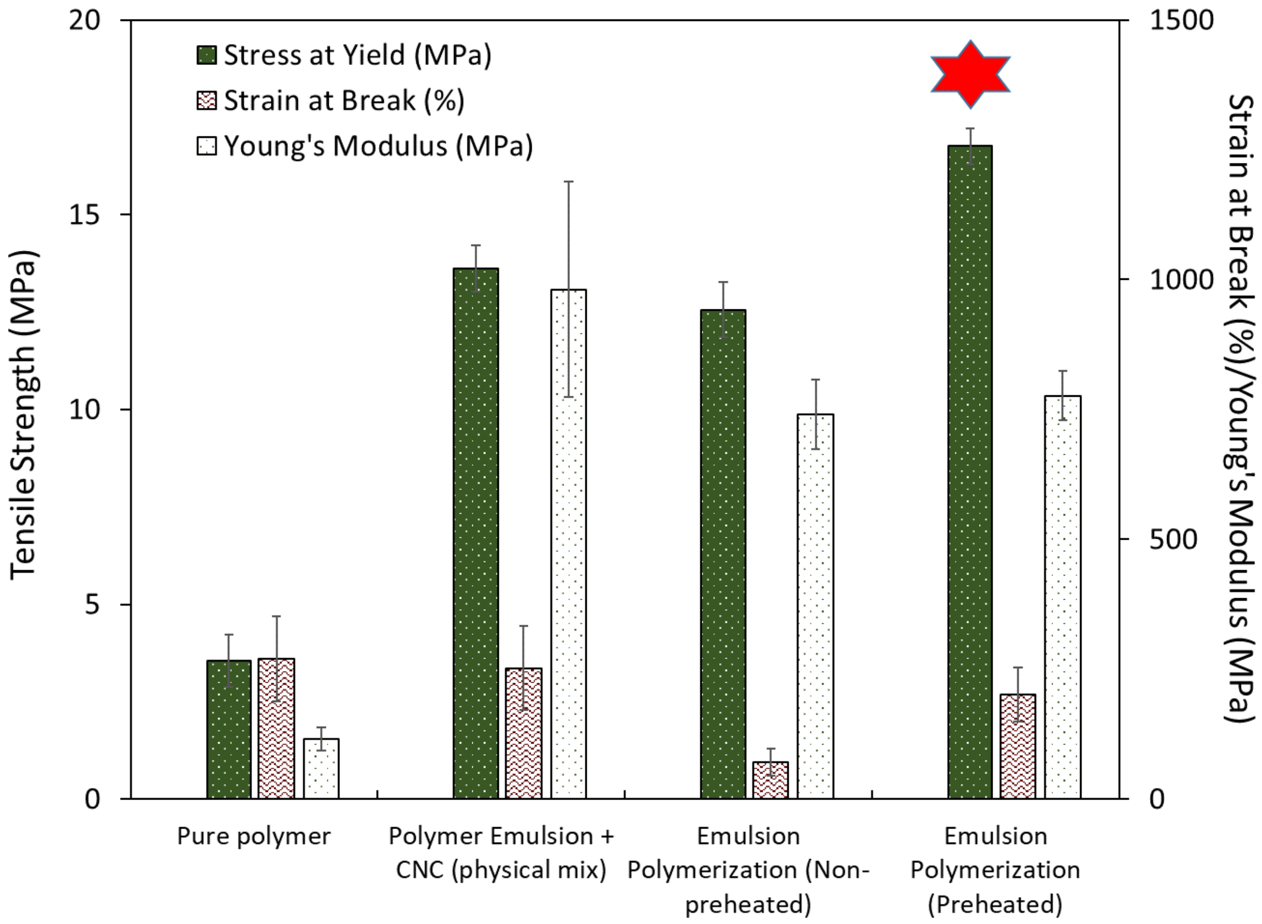


Proposed Polymerization Mechanisms (3/3)



Mechanical Properties of Cast Films





Conclusions

- The structure-process-property relationships of CNC-stabilized emulsion polymerization was studied
  - Difference in polymerization method → particle formation mechanism → morphology of emulsion particles → performance of CNC/polymer nanocomposites
- CNC-stabilized emulsion polymerization mechanisms were proposed
- The nanocomposite films prepared via the preheated emulsion polymerization method have good mechanical performance
- Potential applications
  - Directly in paint and coatings, adhesives, engineering
  - Compatibilization CNC with polymer matrices

Acknowledgement

- Natural Resources Canada (NRCan)

Natural Resources Canada Ressources naturelles Canada

Canada

- British Columbia Ministry of Forest, Lands, Natural Resource Operations and Rural Development (BC-FLNRORD)

BRITISH COLUMBIA Ministry of Forests, Lands, Natural Resource Operations and Rural Development

- Canadian Light Source

Canadian Light Source Centre canadien de rayonnement synchrotron

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Thank You for Your Attention!