Secondary nucleation of styrenated hydroxyl-functionalized latexes

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Background

2-Hydroxyethyl methacrylate (HEMA) is one of the most widely used functional monomers in acrylate/styrene latexes. With hydroxyl groups incorporated by HEMA, resulting emulsion polymers can cross-link with hardeners such as melamine-formaldehyde (MF) resins and isocyanates, thus significantly boosting the coating performance. However, it has been previously reported that limited water solubility of HEMA-rich oligomers results in homogeneous secondary nucleation, leading to an uncontrollable bimodal particle distribution, which is undesirable for latex quality control. It is vital to investigate the conditions where secondary nucleation occurs in HEMA-rich latexes. In this work, the effects of HEMA content on secondary nucleation in butyl acrylate/styrene (BA/St) latexes were investigated.

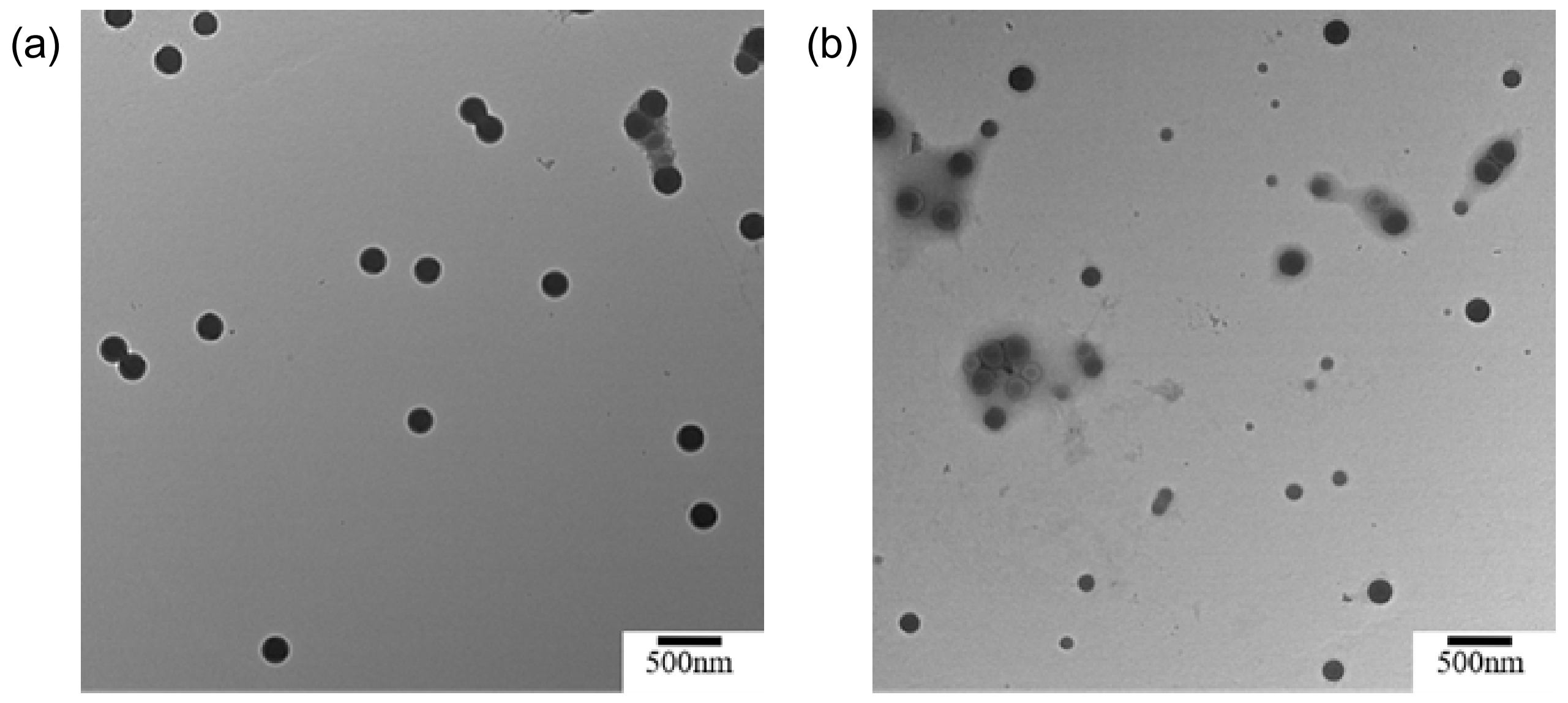


Fig. 1. Comparison of (a) normal latex and (b) latex with secondary nucleation.

Objective

- ❖ Prepare BA/St latexes (BA:St=1:1 by mole) with different HEMA content (0, 10, 20, 30, 40 mol%).
- ❖ Charactize resulting latexes and analyze the phenomenon of secondary nucleation.

Synthesis and Characterization

Latex synthesis:

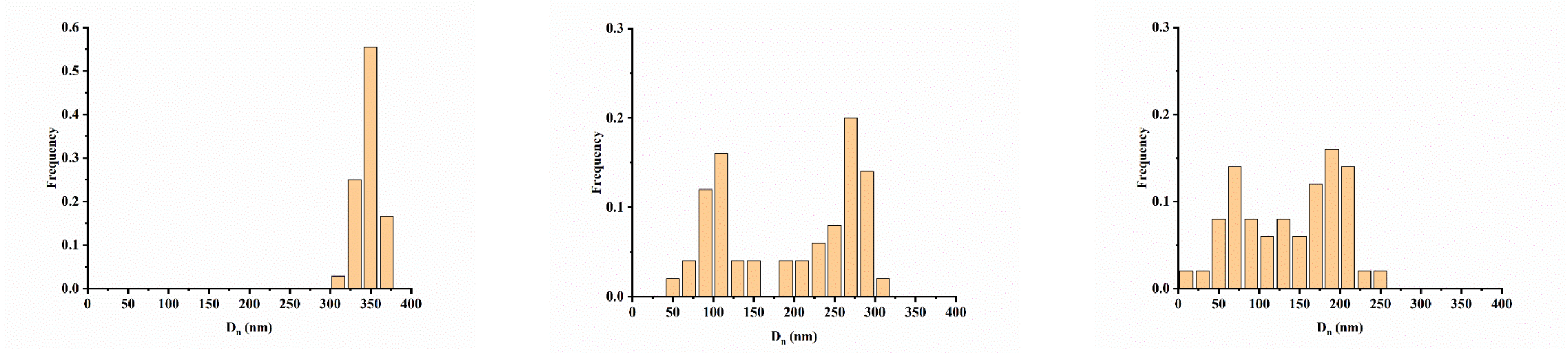
- ❖ Seeded semi-batch emulsion polymerization

Characterization:

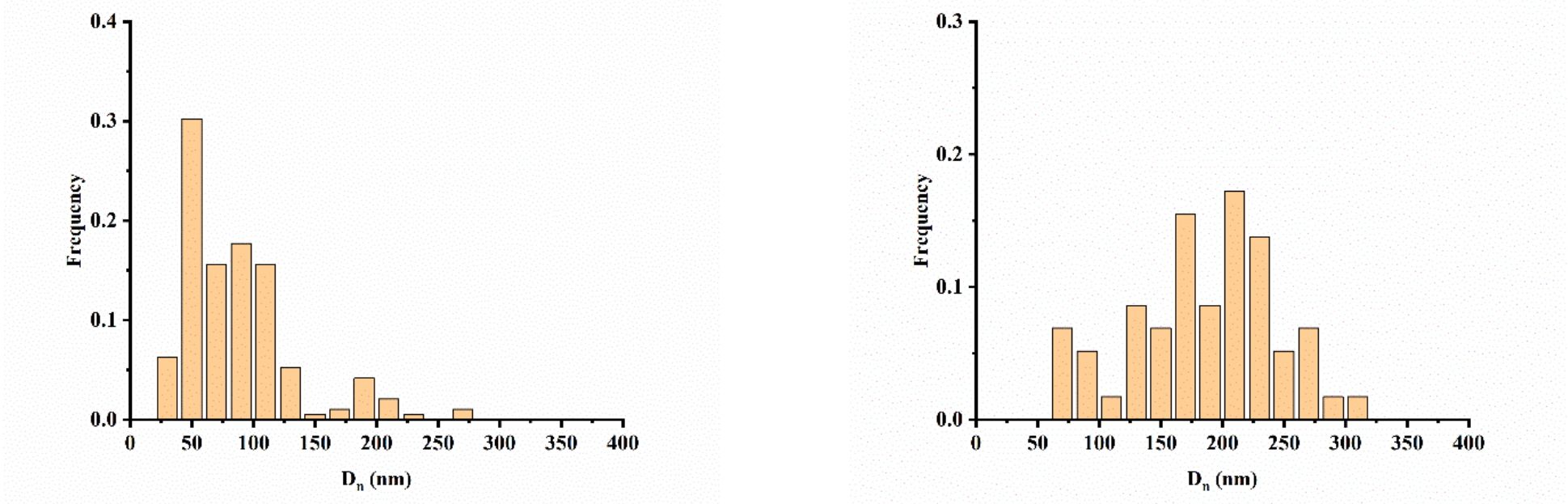
- ❖ Polymerization kinetics
- ❖ Average particle size and particle size distribution (PSD)
- ❖ Glass transition temperature
- ❖ Surface tension

Key Result

- ❖ PSDs are narrowly monodispersed until HEMA is incorporated.



Control　　10 mol% HEMA　　20 mol% HEMA



30 mol% HEMA　　40 mol% HEMA

Fig. 2. Number-based PSDs based on transmission electron microscope (TEM) images.

- ❖ With the increment of HEMA content from 10 to 30 mol%, particle number is found to increase, while it decreases at higher HEMA concentration (40 mol%). On the other hand, size of secondary particle keeps increasing from 10 to 40 mol% HEMA.

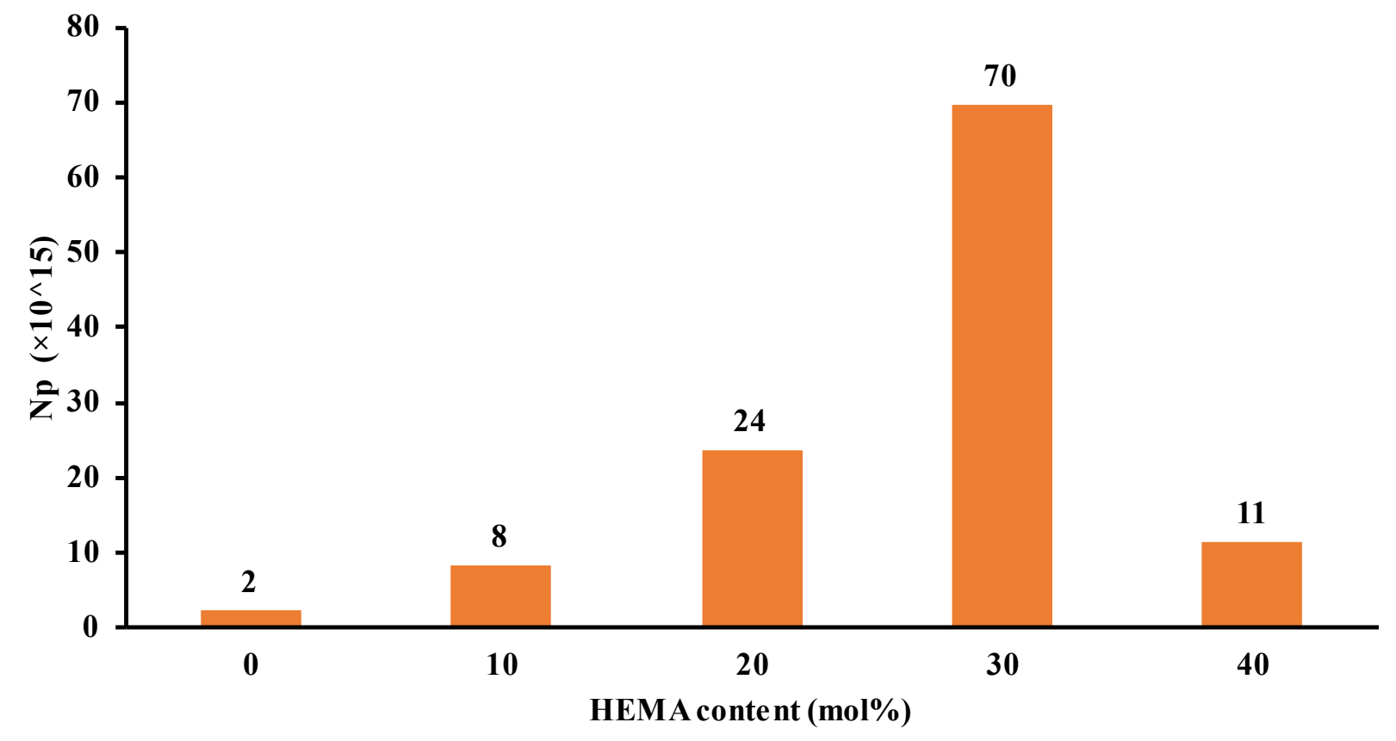


Fig. 3. Particle number N_p evolution with increasing HEMA content based on TEM data.

- ❖ HEMA significantly accelerates the increase of instantaneous conversion as feed process proceeds. The period before reaching monomer-starved conditions (monomer-flooded conditions, t_{m-f}; x_{inst}<80%) is found to be shortened when more HEMA is used.

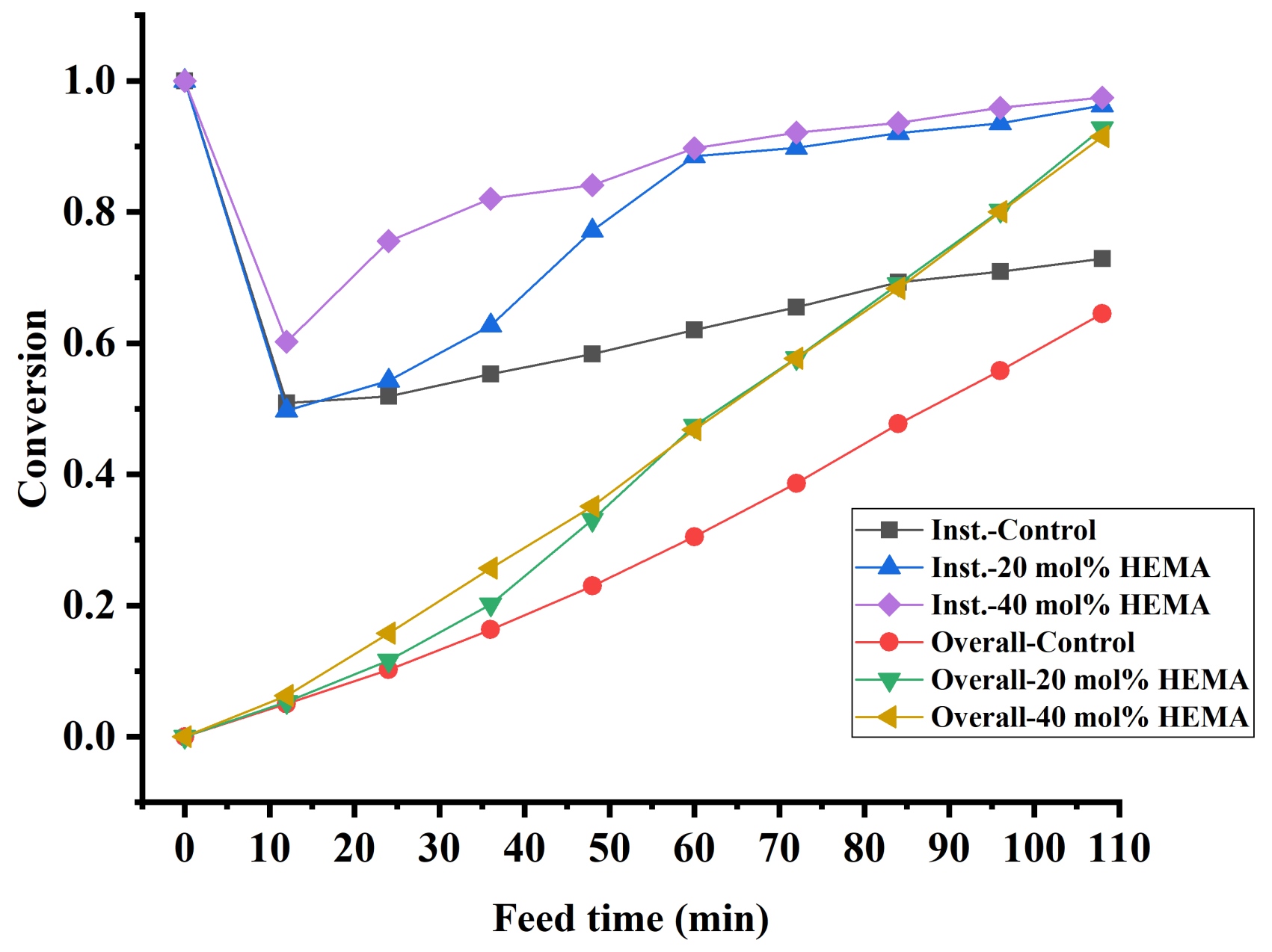


Fig. 4: Instantaneous and overall conversion evolution during the feed.

- ❖ Since all of latexes have a final surface tension > 35 dyne/cm, the absence of micelle is proven, suggesting any secondary nucleation can only be induced by homogeneous nucleation mechanism.

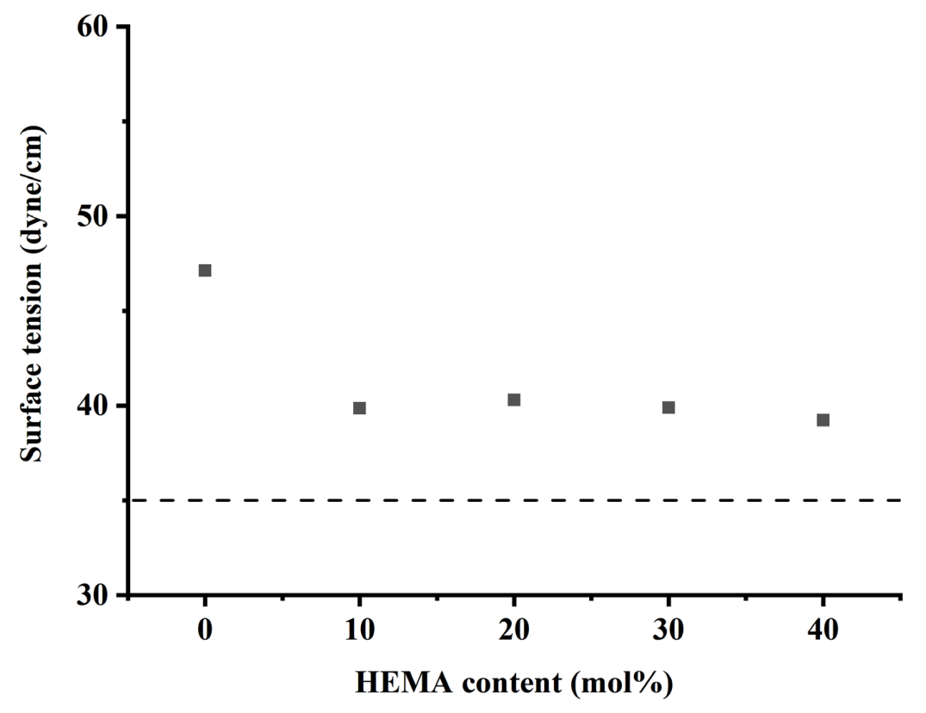


Fig. 5: Surface tension. Dash line represents the surface tension at critical micelle concentration (CMC) of sodium dodecyl sulfate (used as surfactant in this work).

Discussion

- ❖ Based on collected data and previous reports, secondary nucleation is believed to occur under monomer-flooded conditions only and to follow the inequation below:

$$\boldsymbol{R_{p,\,aq} \gg R_{entry,\,particle} + R_{t,\,aq}} \Leftrightarrow$$

$$\Delta = \boldsymbol{R_{p,\,aq} - (R_{entry,\,particle} + R_{t,\,aq}) \gg 0}$$

$R_{p,\,aq}$ = Overall aqueous propagation rate of oligo-radical
$R_{entry,\,particle}$ = Overall radial entry rate
$R_{t,\,aq}$ = Overall aqueous termination rate

- ❖ Since t_{m-f} is shortened with increasing HEMA content, the time for HEMA-rich oligo-radical formation is longer at lower HEMA content. However, at low HEMA content (10 mol%), averagely, less monomer units are needed for a HEMA-rich oligo-radical to become surface-active, leading to a relatively small Δ. In this case, only a small number of secondary particles can be produced. In other words, Δ is the major factor for the occurrence of secondary nucleation while t_{m-f} is the minor factor. It exhibits long t_{m-f} but relatively small Δ at 10 mol% HEMA, medium t_{m-f} and medium Δ at 20 and 30 mol% HEMA, and short t_{m-f} and relatively large Δ at 40 mol% HEMA. In this way, the ascending scale of number of secondary particles produced is 10 mol% HEMA < 40 mol% HEMA < 20, 30 mol% HEMA, which is consistent with the results obtained.
- ❖ It is postulated that with increasing HEMA content, the overall surface area of secondary particles increases, leading to higher probability of monomer entry, which results in larger size of final secondary particles.

Conclusion

The increasing HEMA content can affect the polymerization kinetics and thus the occurrence of secondary nucleation. The number and size of secondary particles are determined by the HEMA content.