Materials Science - Polymers

Emulsion Polymerization on the Chemspeed AutoPlant

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Introduction

Free-radical emulsion polymerization is a process that involves the emulsification of monomers in a continuous aqueous phase, and stabilization of the initial droplets and final latex particles by a surfactant such as sodium dodecylsulfate (SDS). Surfactants have a large influence on the latex product properties, e.g. particle size distribution, molecular weight and rheological properties. Stirred tank reactors are commonly employed for the synthesis of such latexes.

Optimization of emulsion polymerization conditions is often a very time-consuming process, making them a perfect candidate for the application of high-throughput experimentation. To demonstrate this point, the well-known system of styrene-polymerization was chosen for this study.

Polymerization Platform

Chemspeed's AutoPlant represents a flexible, modular and scaleable fully-automated process research workstation (Figure 1). One parameter that was varied, among others, was the shape of the stirrer inside the reactor and its influence on particle size and size distribution.

Figure 1: Chemspeed AutoPlant (left); reactors with anchor or triple helix stirrers (right).

The AutoPlant reflects all operation modes of the universal tank-reactor technology featuring:
- Individually controlled 100ml reactors
- Independent, simultaneous liquid feeds with downscaled feed rates (down to 10 µL/min)
- Exchangeable overhead stirrer designs
- Integration of different in-situ probes, such as NIR and pH
- Intuitive software with on-line visualization of all process parameters, manual control, and interface for the customized integration with any third-party software

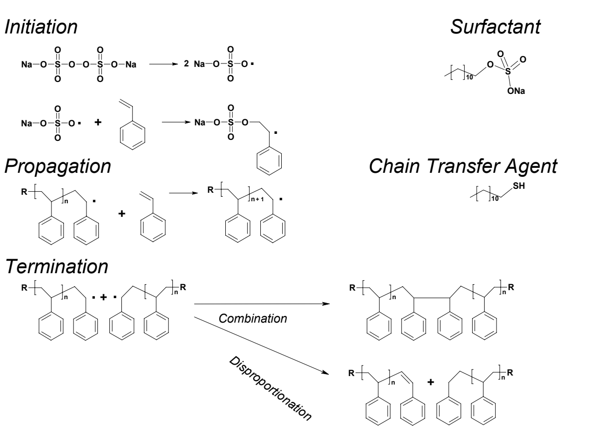

Figure 2: Reaction mechanism for the radical-induced styrene-polymerization

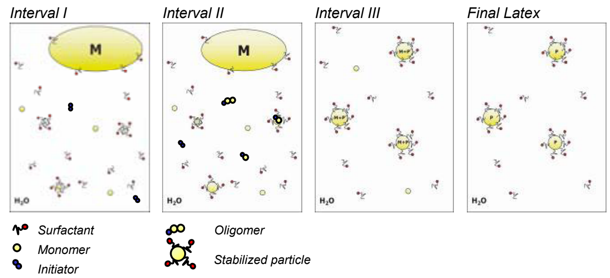

Figure 3:
- *Interval I:* Water insoluble monomer in aqueous solution containing a surfactant resulting in large monomer droplets and micelles with small amounts of monomer.
- *Interval II:* Primary free radicals from the initiator react with monomer in aqueous phase to produce oligomeric radical species that subsequently diffuse into monomer-swollen micelles.
- *Interval III:* Propagation within micelles is supported by diffusion of monomer from the aqueous phase. Micelles grow and incorporate other surfactants from micelles which were not initiated.
- *Final Latex:* Whole monomer is consumed and termination occurs within the micelles.

Analysis of Particle Sizes

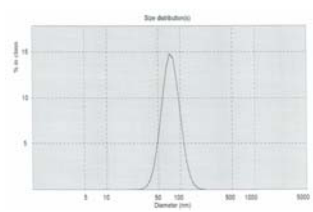

Figure 4: Particle size distribution measured by dynamic light scattering (DLS) techniques from a polystyrene emulsion polymerization (20 wt-%) with an anchor stirrer.

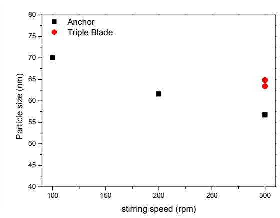

Figure 5: Effect of stirring speed on the particle size for the anchor and triple blade stirrers.

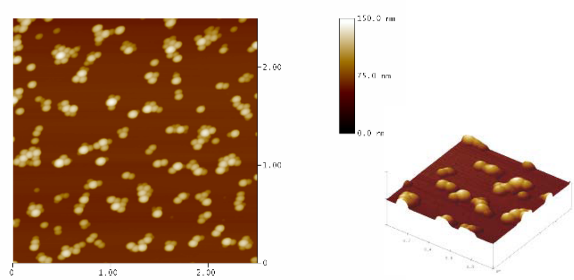

Figure 6: Atomic force microscopy (AFM) images of polystyrene particles from an emulsion polymerization performed on the AutoPlant (20 wt-%) equipped with an anchor stirrer

Conclusions

- As demonstrated, it is possible to perform emulsion polymerizations in an automated parallel process and achieve narrow monomodal particle size distributions.
- The use of the anchor stirrer reveals slightly smaller particles compared to the triple blade stirrer.
- Increasing stirring speed results in slightly smaller particle sizes.

***All scientific data are courtesy of DPI**

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