HORIBA Scientific

Application Note

Optimization of an Emulsion Polymerization Process

AN226

Optimization of an Emulsion Polymerization Process and Product Through Nanoparticle Concentration Analysis

Introduction

Emulsion polymerization is a commonly used radical polymerization typically involving an emulsion of water, monomer, and surfactant. Polymerization occurs in nanoparticles through complex processes that can be difficult to control. The typical size of particles produced by emulsion polymerization is around 100 nm.

The dispersion resulting from an emulsion polymerization is often called a latex. End products from the emulsion polymerization can be the dispersion itself or just the solid materials which are isolated from the aqueous dispersion. Emulsion polymerization is commonly used to produce several commercially important polymers in many applications including adhesives, paints, paper coating, textile coatings and biotech.

In this note we will cover the history, theory and processes used for emulsion polymerization. We will also examine the importance of measuring the concentration of latex nanoparticles produced by emulsion polymerization for a biotech application developed by the Gianneschi lab at UCSD. The Gianneschi case study includes data from HORIBA's ViewSizer 3000.

History

Prior to World War I, the German company Bayer first conceived the idea of using an emulsified monomer in an aqueous suspension or emulsion for synthetic rubber production. Industrial chemists at the time tried to duplicate the conditions of natural rubber formation at room temperature in dispersed particles stabilized by colloidal polymers. Initial work in this field utilized naturally occurring polymers such as gelatin, egg albumin, and starch to stabilize the dispersion. By modern definitions, these were not true emulsion polymerizations rather they were suspension polymerizations. The first "proper" emulsion polymerizations which used a

Figure 1. The ViewSizer® 3000

surface-active agent and a polymerization initiator were conducted in the 1920s to produce isoprene.

In the 1950s, emulsion polymerization was extended to production of plastics as well as the manufacture of dispersions for latex paints and several other products sold as liquid dispersions. Increasingly sophisticated processes were devised to prepare products that replaced many solvent-based materials thus addressing increased demand for more environmentally friendly products and processes. Ironically, synthetic rubber manufacture turned away from emulsion polymerization as new organometallic catalysts were developed that allowed much better control of polymer architecture.

Theory

Smith, Ewart and Harkins were the first to explain the distinct features of emulsion polymerization in the 1940s. They determined that an ideal emulsion polymerization reaction was an interconnected process that involved three stages.

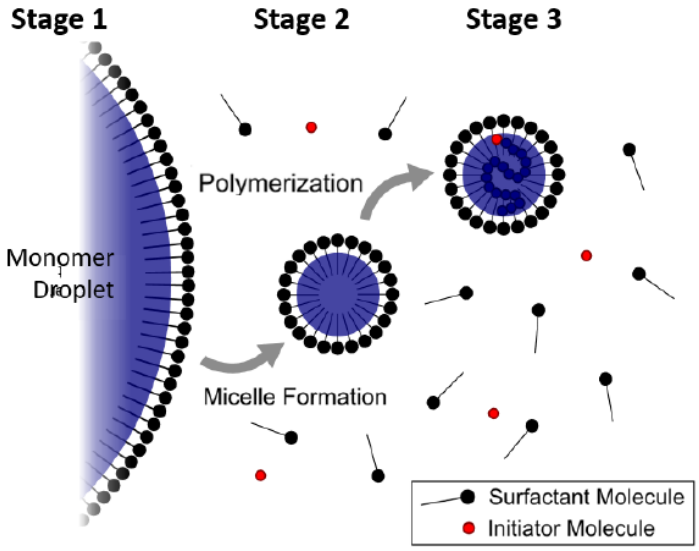

Figure 2. Schematic diagram showing the three stages of emulsion polymerization.

In stage 1, a monomer is dispersed in a solution of water and surfactant which forms large droplets of monomer in water. A water-soluble initiator is added which leads to the formation of micelles. This is different than suspension polymerization where an oil-soluble initiator dissolves in the monomer, followed by polymer formation in the monomer droplets themselves.

In stage 2, excess surfactant continuously creates micelles in the aqueous solution. The combined surface area of the micelles is far greater than that of the larger, but much fewer, monomer droplets. As a result, the initiator preferentially reacts in the micelles rather than the monomer droplets. Monomers in the micelles polymerize rapidly and the growing chain terminates when the monomer-swollen micelle has turned into a polymer particle.

In stage 3, eventually the free monomer droplets are depleted and all remaining monomer is located in the micelle particles.

The final product of the process is typically referred to as a polymer colloid, a latex, or commonly and inaccurately as an 'emulsion.'

An emulsion polymerization involves complex chemistry including polymerization and particle formation kinetics, which lead to significant process control challenges.

Common Processes & Key Properties

Depending on desired properties and economics, emulsion polymerizations can be performed in batch, semi-batch, and continuous processes. Styrene-butadiene rubber has been made with true batch processes where all ingredients added at the same time to the reactor. Partial-batch methods typically include a controlled feed of monomer to the reactor to enable a starve-fed reaction that improves distribution of monomers into the polymer backbone. Vinyl acetate is made from a continuous emulsion polymerization processes.

Colloidal stability is a key factor in the design of an emulsion polymerization process. End products sold as a dispersion also need a high degree of colloidal stability. Colloidal properties such as particle size, particle size distribution, particle concentration as well as viscosity are critically important to the performance of these dispersions. The ViewSizer 3000 provides effective measurements for each of these properties.

Case Study

Gianneschi *et al*.[1] have developed novel latex nanoparticles for retrograde neural tracing which is an important tool for the mapping of brain architecture. These neural-tracing nanoparticles are synthesized with emulsion polymerization methods. The resultant nanoparticles can be conveniently tagged with fluorophores and gadolinium-based MRI contrast agents allowing multiple modes of detection.

Compared to most other polymerization methods, such as atom-transfer radical-polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT), and ring-opening metathesis polymerization (ROMP), emulsion polymerization cannot be controlled in a precise stepwise fashion. In this emulsion polymerization application, a mixture of monomers containing similar functional groups are copolymerized somewhat randomly following initiation.

Therefore, it is difficult to determine the degree of monomer incorporation, polymerization rate, particle molecular weight, and other important factors involved in particle formation. Moreover, without the methods discussed here, it is impossible to quantify the extent to which fluorophores or contrast agents are incorporated into the nanoparticles during polymerization.

As of early 2016, a facile means for measuring the number of particles in a solution generated by emulsion polymerization and other methods did not exist on the market. However, by using the ViewSizer 3000, routine, accurate and reproducible analysis of particle concentration (particles per mL) are now possible. These measurements have enabled a greater understanding of various aspects of the reaction and the properties of the resultant particles.

By measuring the particle concentration of the dispersion, the process yields can be determined. Due to inherent randomness in the copolymerization of the mixed monomers used by Gianneschi *et al*. in their emulsion

polymerization, it was not possible to determine process yields prior to using the ViewSizer 3000. Enhanced process economics are now achievable with this new and accurate method for yield analysis.

Furthermore, product performance was improved through better understanding of the incorporation of imaging agents. Specifically, for particles that are labeled with fluorophores, knowing the number of particles for a given volume of solution allows for calculation of the per-particle dye incorporation.

Similarly, for particles that are tagged with gadolinium-based MRI contrast agents, by knowing the number of particles in the solution, the gadolinium concentration per particle can be determined and used for each batch. Gadolinium concentration can be used as a reference to instruct *in vivo* studies and MRI assays, therefore a correlation between gadolinium concentration in the tissue and contrast in the MRI image can be achieved.

Test Methods and Example Data

The ViewSizer 3000 characterizes nanoparticles by analyzing their movements in Brownian motion and larger, micron-sized particles are analyzed by tracking their settling motion (driven by gravity). The system leverages innovative illumination and detection techniques that enable video recording of scattered light from wide-ranging sizes of individual particles simultaneously. A schematic of the ViewSizer 3000 optical system is shown in Figure 3.

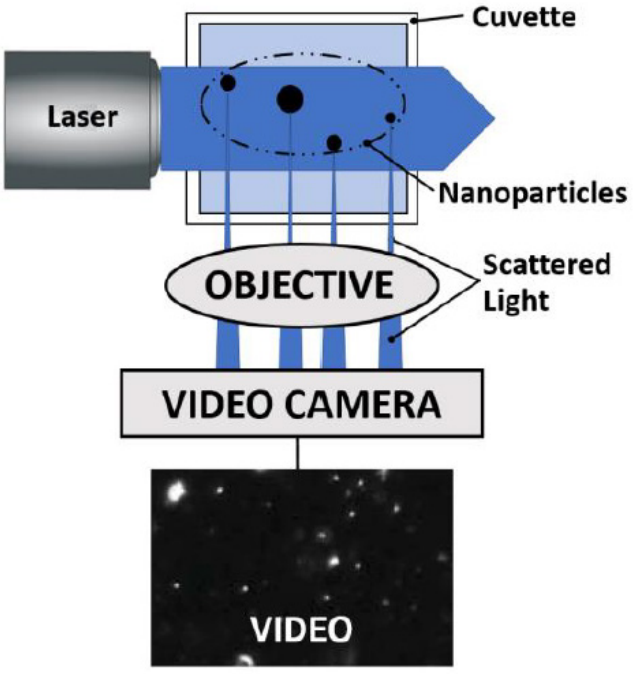

Figure 3. Schematic diagram of the ViewSizer® 3000 optical system.

A key advancement of this system is its ability to address the very large dynamic range of scattered light intensity from differently sized nanoparticles coexisting in polydisperse colloids. Test results from other light scattering techniques typically have significant artifacts and uncertainties that result from this massively disproportionate scattered light intensity. The issue being, very intense scattered light from larger particles overwhelm traditional detection systems and obscure the analysis of other particles in the sample.

Samples produced by Gianneschi, *et al*. by their emulsion polymerization process were diluted with Mili-Q water prior to analysis. The diluted samples were transferred to the ViewSizer 3000 in a cuvette. The only inputs needed for the experiments are temperature, which is controlled at 22°C, and viscosity which the ViewSizer 3000 automatically calculates for water at the controlled temperature. For each experiment, the instrument records 25 seven-second-long videos of particle motion. The instrument stirs the sample between each video, which improves sampling statistics by ensuring that a fresh aliquot of sample is used for each video.

The ViewSizer 3000 provides particle size distribution (PSD) in histogram or cumulative formats. The PSD density histogram of a typical latex sample from the Gianneschi group is shown in Figure 4.

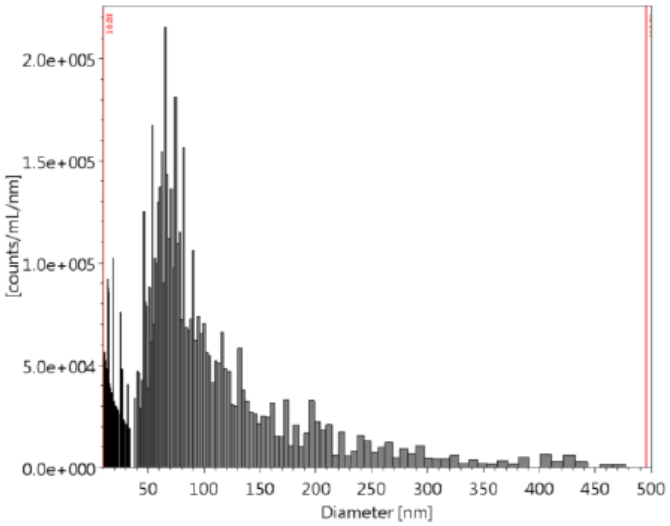

Figure 4. Density of particle size distribution of a typical emulsion polymerized latex produced by Gianneschi *et al*.

For this emulsion polymerization process, the most valuable information provided by the ViewSizer 3000 is particle number concentration. The instrument reproducibly determined particle number concentrations from the dispersion to be 2.3 E+12 particles/mL. Other data of interest are the average and D50 particle sizes of 118 nm and 90 nm respectively.

With the ViewSizer 3000, the PSD data are supplemented by particle visualization whereby images of scattered light from each particle can be viewed in real-time. Such video images provide a desirable visual qualitative validation of the mix of particles in the sample. The videos also provide insights into sample stability. For one batch of latex particles, it was possible to identify unwanted particles of around 10 µm that were settling out of the dispersion. One such large particle can easily be seen in Figure 5.

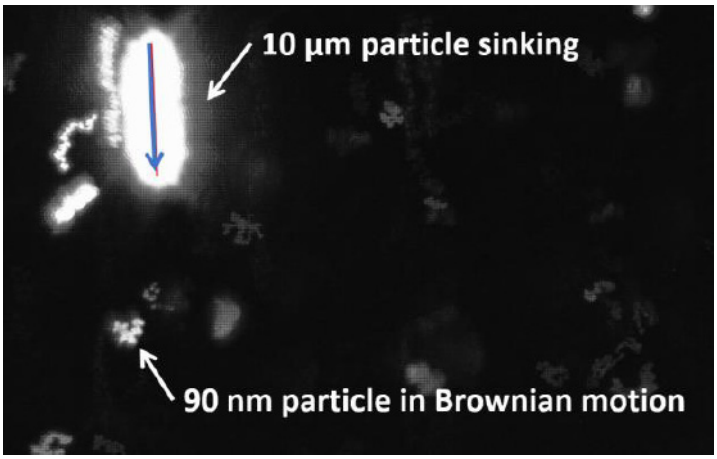

Figure 5. Superimposed video frames of nanoparticles in Brownian motion and a particle of ~10 µm in diameter settling due to gravity.

Summary

Emulsion polymerization processes are complex. It is often difficult to optimize the process and the resultant dispersions. Insights from the ViewSizer 3000 are beneficial for products produced by emulsion polymerization. Specifically, accurate and reproducible measurements of nanoparticle concentrations are used to determine yields and monomer incorporation which can be useful in: i) the characterization of particles synthesized with imaging agents such as fluorophores and MRI contrast agents, as well as ii) optimizing the emulsion polymerization process.

References

[1] more information on the Gianneschi *et al*. process can be found at:
http://gianneschigroup.ucsd.edu/publications.htm