“Did you know? April-June 2026"

Did you know .... that polymer molecular weights (MWs) produced in emulsion polymerization can be extremely high when no chain transfer agent is used? Did you also know that the type of process used (batch. semi-batch) can significantly affect the polymer MW? This issue of our "Did you know ... ." presentations is the 4th in a **multipart series** that will collectively discuss the molecular weights typically produced in both batch and semi-batch emulsion polymerization (EP) processes. the effectiveness of chain transfer agents (CTA) in both process types, and the possibility of polymer chain branching and cross-linking in the latex particles. In the current issue we address the molecular weight development in **semi-batch** (perhaps starve fed) EP when **CTA** is used.

Note: All of these topics are presented in much greater detail in our upcoming online tutorial on controlling the polymer MW in emulsion polymerization, May 7, 2026. Go to www.epced.com for details and registration.

In general, linear polymer chain lengths produced in free radical polymerizations depend upon the rate of propagation of the polymer radical and the rate at which chain growth is stopped (due to termination or chain transfer). the so-called initiation, propagation, termination sequence. This is certainly true in EP. Here we have latex particles constantly receiving oligomeric radicals (typically containing -3-6 monomer units) from the aqueous phase - some of these radicals grow into high MW polymer and some terminate other polymer radicals already in the particles. In semi-batch operation the monomer is fed. either neat or as a pre-emulsion, at rates determined by the process design and desired product quality. Often this rate is related to heat transfer characteristics of the reactor to maintain temperature control. In the so-called **"starve fed"** mode, the overall reaction rate is essentially equal to the monomer feed rate. This limits the monomer concentration in the latex particles to levels much lower than those in batch EP, especially those in Interval 2 of the batch process. It is no wonder then that the chain lengths produced in this semi-batch process mode are naturally lower than those in the batch mode of operation. While the rate of radical entry from the aqueous phase is likely the same in the semi-batch and batch modes, the chain propagation rate in the particles experiencing semi-batch operation is very much limited due to the lower monomer concentration - thus the lower the polymer MW. So now what happens when some CTA is added to the recipe?

As you would expect, the overall effect is to lower the MW from the value without CTA, but by how much? And is the CTA effectiveness as great as it was in a batch process? To address these questions, we need to consider that by controlling the feed rate (FR) of the monomer to achieve other goals, we have also introduced a new variable effecting the MW characteristics of the polymer. To add a bit more complexity, the so called starve fed (SF) process is conducted in a variety of ways in industry - these include variations in obtaining the seed latex particles prior to (or during) monomer feed (either neat or as a pre-emulsion). Just for a single example, consider the often used process in which a small portion (maybe 10%) of the monomer is added at time zero along with some water, surfactant and initiator and allowed to polymerize for -30-60 minutes. The intent is to nucleate a set number of polymer particles which then grow in size during the monomer feed. This initial stage of the process is a batch reaction that converts nearly all of the first charge of monomer to polymer. and then those particles continuously receive monomer that is fed at some controlled rate. The MW produced in that early portion of the reaction will have the characteristics of any batch reaction (relatively broad MW distribution, i.e. high

dispersity, D) and is then "blended" with the polymer produced in the monomer feed period that has a different MW distribution. Another variable is the monomer feed rate itself, as it can change at times because of productivity increases. new latex recipes, etc. Changing the feed rate alone requires consideration of related changes to the monomer concentration in the latex particles. As we know, the MW produced is highly dependent on the monomer concentration in the particles. Now one has the challenge of determining any necessary CTA level change as the feed rate is altered in order to preserve the MW characteristics prior to the change in the feed rate.

With the limited scope of these "Did you know ... ?" series we are not able to develop answers to the above questions here. as they are quite involved. But as always, we invite your questions and comments by going to rnfo@epced.com.
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