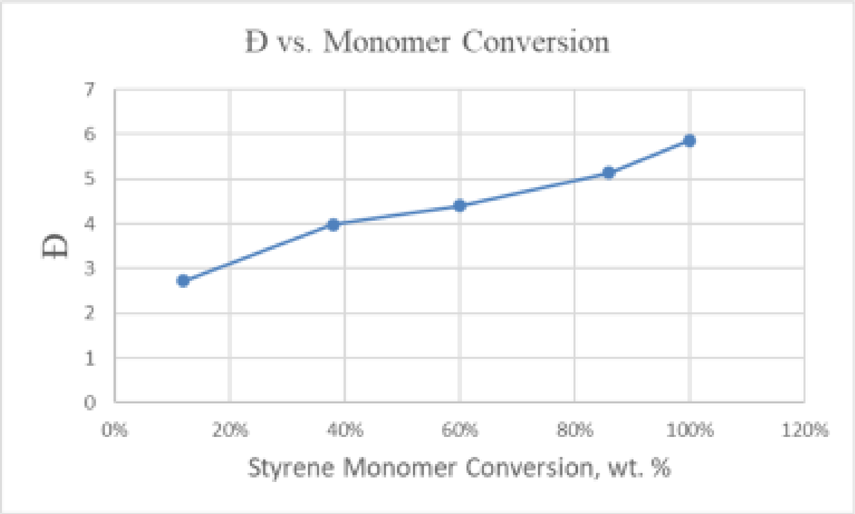
Did you know? January-March series for 2026

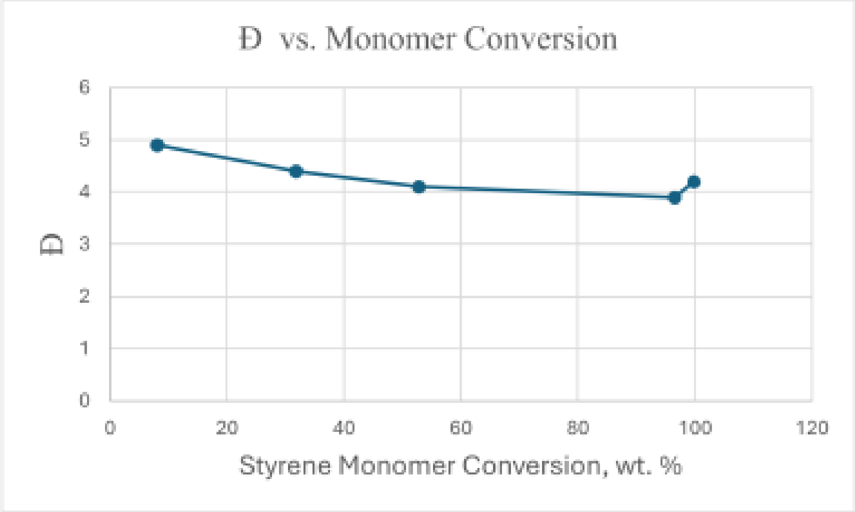
Did you know ……….that polymer molecular weights (MW) produced in emulsion polymerization can be extremely high when no chain transfer agent is used? Did you also know that the type of process used (batch, semi-batch) can significantly affect the polymer MW? This issue of our "Did you know…." presentations is the third in a ***multi-part 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 this issue we address the molecular weight development in **semi-batch** (perhaps starve fed) EP when **no CTA** is used.

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 (termination, 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 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.

A second feature of using semi-batch operation (and especially in the starve fed version) is that the monomer concentration in the particles can be kept almost constant with time during the monomer feed portion of the process. This then avoids the ever-changing monomer concentration during Interval 3 of the batch process and rather naturally results in lower dispersities ($Đ = M_W/M_N$) by way of a simple process change.

The first plot below shows how the dispersity proceeds with time (expressed as conversion of monomer to polymer) for a typical polystyrene **batch** emulsion polymerization at 70 °C when no CTA is used. Note the dramatic rise in Đ as the process advances. The second plot below shows the results for Đ when the **semi-batch** process is used with the same polystyrene recipe and temperature as in the batch process, but where the monomer was fed evenly over 4 hours. Clearly, there is a major difference in dispersity due to this process change. These two plots show that the MW features of emulsion polymers are "a product of process" (i.e. the same formulation can give widely varying polymer properties, depending on exactly how the process is conducted).





As always, we invite your questions and comments by going to ***info@epced.com***.