Did you know? series for July-September 2025

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 first 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. We start by addressing the molecular weight development in simple, batch 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 radicals from the aqueous phase – some grow into high MW polymer and some terminate other polymer radicals already in the particles. During the first two time intervals in batch EP (particle nucleation and particle growth), the monomer concentration in the particles (the driver of chain length growth) is essentially constant and the polymer radical chains grow at a constant rate. The stopping event happens when a second free radical enters a particle that contains a growing polymer chain and terminates the growing chain. That radical entry rate is relatively fast during the first interval where new particles are continually being nucleated. In the second interval it is nearly constant (since there is a constant number of growing particles) so that the MWs produced in interval II are expected to be high and have a relatively narrow and monomodal molecular weight distribution (Mw/Mn~2-4).

During the third time interval in batch EP, the monomer concentration in the particles constantly falls, just as in a classic batch bulk or solution polymerization processes. With a nearly constant radical entry rate to the particles, the result is that the MW of the polymer formed during that third interval continually decreases from that of the polymer produced during the first two intervals. Thus, the overall breadth of the distribution of MWs accumulating in the latex particles progressively increases. This is why the dispersity, Đ (Mw/Mn), for emulsion polymers produced in batch EP without CTA is often in the range of 5-6, or even higher. The plot below shows how the MW distribution broadens with time (expressed as conversion of monomer to polymer) for a typical polystyrene batch emulsion polymerization at 70 °C.