Producing Tailor-Made Polymers at the Commercial Scale

Today's modern lifestyle demands highly functional products — from water-wicking fabrics and age-defying beauty products to patient-specific medicines and high-tech electronics — many of which rely on polymers. In turn, to meet these demands, manufacturers are asking for the ability to design and produce polymers with precise control over composition and architecture. Such sophisticated control, however, is not possible with the dominant incumbent technology, free-radical polymerization.

Thanks to a process developed by Carnegie Mellon Univ. spin-out ATRP Solutions, creating the perfect polymer with exactly the right composition, size, and shape just got much easier.

At the foundation of the new process is atom-transfer radical polymerization (ATRP) — a type of "living" polymerization discovered in 1995 by Krzysztof Matyjaszewski at Carnegie Mellon. ATRP uses a special catalyst to add one or several monomers at a time to a growing polymer chain. The catalyst (an alkyl halide initiator and a copper-halide/amine ligand) regulates the growth of the polymer by establishing equilibrium between dormant chains and active chains in the polymerization system. The uniform growth of polymer chains results in well-defined polymers, *i.e.*, polymers with narrow polydispersities.

Because the chain ends are active, ATRP makes it possible to produce a variety of polymer architectures. The technology is extraordinarily powerful in that polymers can be custom-designed with predetermined, highly specific structures that contain tailored functionalities.

In conventional ATRP, the rate of polymerization is predominately determined inside the reactor by the ever-changing ratios of the reagents driving the ATRP equilibrium. Once the reaction starts, very little can be done to control and influence the quality of the polymer produced (*e.g.*, polydispersity, conversion, extent of coupling, type of chain ends, and activity). In addition, these polymerization reactions are exothermic, which presents significant temperature-control challenges when scaling up reactor systems. Although traditional ATRP can produce highly functional polymers at the laboratory scale, such engineering challenges have limited the use of ATRP at the commercial scale. That is, until now.

With funding from the National Science Foundation, scientists at ATRP Solutions have adapted ATRP, enabling it to be scaled to commercial-size reactors. The key feature of the adapted process, called Ultimate ATRP, is sophisticated control of the reaction chemistry and kinetics to allow operators to conveniently adjust both the number of active chains and the amount of active catalyst in the reaction medium during polymerization.

Here's how it works: ATRP proceeds as it normally would, with the polymer chain growing one unit at a time. However, unlike in conventional ATRP, where the entire amount of catalyst activator is added at the beginning of the reaction, in Ultimate ATRP the catalyst activator is fed a little bit at a time throughout the entire process. Thus, as the polymerization proceeds, radical-radical termination reactions "turn off" the catalyst in the reactor, reducing the total amount of available catalyst. More activator is then added, which converts the deactivated catalyst to its activated form, while avoiding the buildup of activator. Because only small amounts of activator are present at any time in the reactor, the reaction stops as soon as the feeding of activator stops. Thus, the activator feed rate can be used to control the rate of polymerization.

"We can regenerate the metal catalyst at a rate commensurate with the rate of radical-radical termination reactions and have exceptional control over the reaction rate," says Patrick McCarthy, CEO of ATRP Solutions.

By controlling the chemistry from outside the reactor, the operator can exert sophisticated control over the polymerization kinetics and reaction temperature. For instance, the feed of activator can be adjusted to slow down, stall, or even stop batches in progress, for example, to check product quality. These batches can be restarted without loss of livingness or broadening the product's polydispersity. Other benefits of the Ultimate ATRP process, which result from operating at high temperatures, include shorter reaction times, higher conversions, and reduced solvent consumption.

ATRP Solutions developed the Ultimate ATRP technology in 2008 and has now validated it for the production of linear, block, and star polymer architectures made of acrylates, methacrylates, and styrenes. The company has carried out reactions in conventional 200-gal glass-lined reactors and has plans to further scale up the process over the next three years, with the goal of producing 10 million lb/yr in a U.S.-based, manufacturing facility.

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