# Automatic Control of Free Radical Polymerization Reactions

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Automatic control of various aspects of free radical homo- and copolymerization has been achieved based on continuous model-free measurements of weight average molecular weight $M_w$, and concentrations of comonomers A and B, $C_A$ and $C_B$, respectively. For this purpose a Control Interface was integrated into ACOMP (automatic continuous online monitoring of polymerization reactions) to create an ACOMP/CI platform. A controller was developed to follow target trajectories for conversion, molecular weight, and copolymer composition, as well as to produce multimodal polymer populations. ACOMP furnishes real-time $M_w$, $C_A$ and $C_B$, derivatives of which yield instantaneous weight average molecular weight $M_{w,inst}$ and instantaneous fractional composition of monomers A and B in copolymers, $F_{inst,A}$ and $F_{inst,B}$. The proportionality constant, p, between $M_{w,inst}$ and total polymer concentration $C_p$ can be experimentally measured throughout the reaction, as well as conversion rates, $\alpha_A$ and $\alpha_B$, for comonomers A and B, respectively. The experimentally, periodically re-measured p, $\alpha_A$ and $\alpha_B$, are sufficient to allow the controller to pilot a reaction along an established target trajectory of molecular weight and/or composition, by using semi-batch flows of comonomers into the reactor from a reservoir. The approach, hence, does not depend on a detailed kinetic model and no knowledge of kinetic parameters, such as propagation, termination, and initiator decomposition rate constants, initiator efficiency, reactivity ratios, etc. is needed. The controller is quite robust as a result of this and also works when factors such as reaction temperature are changing, since changes in p, $\alpha_A$, and $\alpha_B$ are constantly re-measured as they change.

The system is demonstrated via aqueous phase polymerization of acrylamide and styrene sulfonate. Several demonstrations of controlled molecular weight and composition trajectories are given using semi-batch (co)monomer flows. Multi-modal populations were automatically produced using combined flows of monomer and chain transfer agent. Using histograms of $M_{w,inst}$ obtained during the reaction, together with well-known expressions for instantaneous molecular weight distributions (MWD) it was possible to build up the MWD during a reaction, arriving at the full MWD for the final product at the end of the reaction.

Active manual control is also demonstrated using initiator flow and oxygen flow into the reactor. Early results on control of inverse emulsion polymerization at high monomer concentration (~30%) are presented. Preliminary results with a 60 MHz NMR coupled to the ACOMP system are also shown.

Automatic production of a trimodal molecular weight distribution using the ACOMP/CI platform