
Abstract

Nonisothermal, uncontrolled polymn., conducted in varying mixing regimes, offered a facile methodol. to evaluate the influence of several important process development factors such as mixing, reaction exotherm, and thermal perturbations on the catalytic activity and kinetic stability, polymn. performance, and properties of the resulting polymers. Ethylene was homo- and copolymd. with hexene-1 under varying impeller speeds (hence, thermal perturbations), using Ind2ZrCl2 and Et(Ind)2ZrCl2 and the MAO cocatalyst. The reaction exotherm profiles, tracing the polymn. history, qual. represented the kinetic profile and the catalytic stability. The unbridged Ind2ZrCl2 was shown to be more stable than the bridged Et(Ind)2ZrCl2. With change in the level of stirring from a diffusion-controlled regime to a nondiffusion-controlled, external gas-liq. mass-transfer resistance-free one, the reaction exotherm and the run time-av. catalytic activity increased. So far as the influence of the chiral vs. the achiral zirconocene structure is concerned, the copolymer compn. distribution and sol. fraction generated by chiral Et(Ind)2ZrCl2 were more sensitive to the mixing conditions and thermal perturbations than were those produced by achiral Ind2ZrCl2. Et(Ind)2ZrCl2 produced higher mol. wt. backbones, incorporated more hexene-1 and chain branching, and introduced less crystallinity in the copolymers than did Ind2ZrCl2. The influence of Ind2ZrCl2 on higher-wt. homopolymer backbones was opposite to that of Et(Ind)2ZrCl2. Incorporation of hexene-1 significantly decreased the av. mol. wts. and d. and increased the run-time-dependent av. catalyst activity. A pos. comonomer effect took place. The bulk polymer properties did not critically depend on the mixing state. Thermal perturbations broadened the polydispersity index.