

# Nonisothermal, Uncontrolled Homo- and Copolymerization of Ethylene Using Selected Zirconocenes

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**ABSTRACT:** Nonisothermal, uncontrolled polymerization, conducted in varying mixing regimes, offered a facile methodology 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, polymerization performance, and properties of the resulting polymers. Ethylene was homo- and copolymerized with hexene-1 under varying impeller speeds (hence, thermal perturbations), using  $\text{Ind}_2\text{ZrCl}_2$  and  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  and the MAO cocatalyst. With respect to the effects of the above process development factors, the following was observed: The reaction exotherm profiles, tracing the polymerization history, qualitatively represented the kinetic profile and the catalytic stability. The unbridged  $\text{Ind}_2\text{ZrCl}_2$  was shown to be more stable than the bridged  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ . With change in the level of stirring from a diffusion-controlled regime to a nondiffusion-controlled, external gas-liquid mass-transfer resistance-free one, the reaction exotherm and the run time-average catalytic activity increased. So far as the influence of the chiral versus the achiral zirconocene structure is concerned, the copolymer composition distribution and soluble fraction generated by chiral  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  were more sensitive to the mixing conditions and thermal perturbations than were those produced by achiral  $\text{Ind}_2\text{ZrCl}_2$ .  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  produced higher molecular weight backbones, incorporated more hexene-1 and chain branching, and introduced less crystallinity in the copolymers than did  $\text{Ind}_2\text{ZrCl}_2$ . The influence of  $\text{Ind}_2\text{ZrCl}_2$  on higher-weight homopolymer backbones was opposite to that of  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ . Incorporation of hexene-1 significantly decreased the average molecular weights and density and increased the run-time-dependent average catalyst activity. A positive comonomer effect took place. The bulk polymer properties did not critically depend on the mixing state. Thermal perturbations broadened the polydispersity index. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 137–147, 1998

**Key words:** zirconocene catalyst; nonisothermal olefin polymerization; CRYSTAF; comonomer and molecular weight distributions; chain branching; DSC