

Title	重合初期段階における不均一系チーグラマー・ナッタ触媒の物理・化学的变化
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Abstract

An improved stopped-flow (SF) technique was employed to clarify the origin of kinetics in propylene polymerization with a $\text{Mg}(\text{OEt})_2$ -based Ziegler-Natta catalyst. Polymerization in the range of 0.1-5 s exhibited kinetic transition from a linear development to a build-up-type development of the yield. It was found that a lower alkylaluminium concentration led to a lower activity in the linear regime, while the extent of the activation became greater in the build-up regime. The origin of these kinetic behaviors was studied using scanning electron microscopy (SEM) for catalyst/polymer particles and cross-fractionation analyses for polymer structures. It was found that the kinetic transition mainly arose from the fragmentation of the catalyst particles and resultant increase in the active site concentration. The fragmentation manner strongly depended on the alkylaluminium concentration, which affected not only the amount but also the placement of initial polymer formation. The nature of active sites varied as a result of an ageing effect with alkylaluminium: their stereospecificity, propagation rate constant and tolerance for chain transfer reaction increased as the polymerization progressed.

Keywords: Ziegler-Natta catalyst, alkylaluminium, polypropylene, kinetics, morphology