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Modeling and Experimental Evaluation of Single Particle Growth in Syndiotactic Polymerization of Styrene

S.R. Sultan, W.J.N. Fernando, and Suhairi A. Sata

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A comprehensive mathematical model and experimental study of single particle growth for styrene polymerization over a silica-supported metallocene catalyst were investigated. The model was developed based on the modification of the well-known multigrain model (MGM) by introducing mesoparticle scale limitations. Thereafter, the model was employed to predict the effects of bulk phase temperature and catalyst properties (initial catalyst active site concentration and initial catalyst particle size) on the polymerization rate, degree of polymerization (DP), and the polydispersity index (PDI) of syndiotactic polystyrene (SPS). The simulation results showed a significant radial distribution of styrene concentration across polymer particle growth at different polymerization conditions. It was found that increasing the initial catalyst concentration and bulk phase temperature resulted in polymerization rate enhancement. In context, the polymerization rate decreased as the initial catalyst particle size increased from 20 to 50 μm. The results revealed that a uniform increase in DP of the polymer was obtained by increasing the initial catalyst concentration and the reaction temperature, while resulting in a decrease of the PDI value. Meanwhile, the DP and PDI values varied inversely under the influence of initial catalyst particle size within a period of time similar to the one needed in the catalyst decay. The simulated results in the study agree well with experimental data of SPS.

Keywords metallocene catalyst, multigrain model, polystyrene, single particle growth, syndiotactic polymerization

1. Introduction

Syndiotactic polystyrene (SPS) is a new polymeric material with high a crystallization rate and a high melting point (270 °C), making this polymer a semicrystalline engineering thermoplastic material with potential industrial applications (Ref 1). SPS was first synthesized by Ishihara (Ref 2) using a soluble titanocene compound, activated by methylalumoxane (MAO). Several styrene polymerizations were carried out with a supported metollocene catalyst, prepared by the reaction of silica gel with MAO and then with a metallocene catalyst (Ref 3-6).

The simplest type of model describes a single catalyst/polymer particle growth based on a spherical layer of polymer particle that is formed around the spherical catalyst particle. Models based on this geometry are commonly called solid core models (SCMs). Monomer diffusion from the polymer shell to the active site on the catalyst surface is the central theme of these models.

Schmeal et al. (Ref 7, 8) and Nagel et al. (Ref 9) used the SCM for olefin polymerization with the aid of heterogeneous Ziegler-Natta catalysts. It was shown that for a single type of active site, this model could not predict broad molecular weight

S.R. Sultan, W.J.N. Fernando, and **Suhairi A. Sata**, School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia. Contact e-mail: saadraheem76@gmail.com

Nomenclature

$D_{ef,M,i}$	Effective macroparticle diffusivity, at the *i*th grid point (cm^2/min)
$D_{ef,s}$	Effective mesoparticle diffusivity (cm^2/min)
$D_{ef,\mu}$	Effective microparticle diffusivity (cm^2/min)
$D_{m,solv}$	Monomer diffusivity in the solvent (cm^2/min)
k_p	Propagation rate constant (L/(mol h))
k_d	Catalyst deactivation rate constant (h^{-1})
k_s	Liquid film mass transfer coefficient (m^2/s)
$[M]_i$	Monomer concentration in the macroparticle, at the *i*th grid point (mol/L)
$[M]_s$	Monomer concentration in the mesoparticle (mol/L)
$[M]_\mu$	Monomer concentration in the microparticle (mol/L)
$[M]_c$	Monomer concentration at the surface of catalyst fragment (mol/L)
$[M]_b$	Bulk monomer concentration (mol/L)
N	Number of shell
r	Radial position at the macroparticle level (m)
R_c	Radius of catalyst subparticles (m)
R_{N+2}	Macroparticle radius (m)
R_o	Initial catalyst particle radius (m)
$R_{h,i}$	Radius of *i*th hypothetical shells
$R_{p,i}$	Rate of reaction per unit volume at the *i*th grid point (mol/(m^3 s))
$R_{overall}$	Overall time-dependent polymerization rate (g SPS/(g cat h))

Greek Letters

η_s	Mesoparticle diffusion effectiveness factor
η_μ	Microparticle diffusion effectiveness factor
λ_{Lk}	*k*th Moment of live polymers
λ_{Dk}	*k*th Moment of dead polymers