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Modeling Study on Effects of Liquid Propylene in Horizontally Stirred Gas-Phase Reactors for Polypropylene

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Summary: Modeling study was carried out for JPP-HORIZONE, which has horizontally stirred gas reactors in which the heat of polymerization is removed by vaporization of liquid propylene (LPP). The effects of LPP were estimated by the model which has a couple of continuous stirred bed reactors different in propylene form, gas of liquid, combined with a less stereospecific catalyst as a probe. LPP affects isotacticity further than catalyst efficiency in the developed model. Observed isotacticity was lower than that estimated by the model without LPP, which can be explained only by the presence of LPP.

Keywords: modeling; polypropylene

Introduction

JPP-HORIZONE has been developed by Chisso and Japan Polypropylene Corp., which has horizontally stirred gas reactors in which the heat of polymerization is removed by vaporization of liquid propylene (LPP). Schematic process flow is shown in Figure 1. Plug-flow profile of mixing is achieved by horizontal reactors with a mild mechanical agitation, so it is suitable for production of impact copolymer because of the sharp residence time distribution. The heat removal system contributes to a compact process package. JPP-HORIZONE provides high quality materials in good productivity.

On the other hands, modeling study is effective to understand and to improve a process. Several authors reported a model of horizontally stirred bed reactors (HSBRs) using some continuous stirred tank reactors (CSTRs) in series.[1–4] But, effects of LPP have not been considered even in the process where LPP is used as a coolant as well as a monomer. In such a process, LPP is usually added to the reactor through spray nuzzles. Small LPP particles contact to the agitated powder bed and vaporized by the heat of vaporization. Because the vaporization has a limited rate, some of LPP is present in the polymer particles. Because active sites are dispersed all over the particle, some of them should be eventually in LPP atmosphere. Therefore, we have developed a model which includes polymerization in LPP as well as in propylene gas.

The objective of this study is to investigate the effects of LPP in JPP-HORIZONE by modeling. We focused on the less stereospecific catalyst because of its sensitivity to the polymerization atmosphere.

Polymerization Kinetics

Polymerization was conducted with the less stereospecific grade of JPP catalysts which is suitable for film application. Both of gas and LPP slurry polymerization were conducted in 3L-A/C under various conditions in a stirred bed or in LPP slurry, respectively. Obtained polypropylene (PP) was analyzed by temperature rising elusion fractionation (TREF). In this study, the

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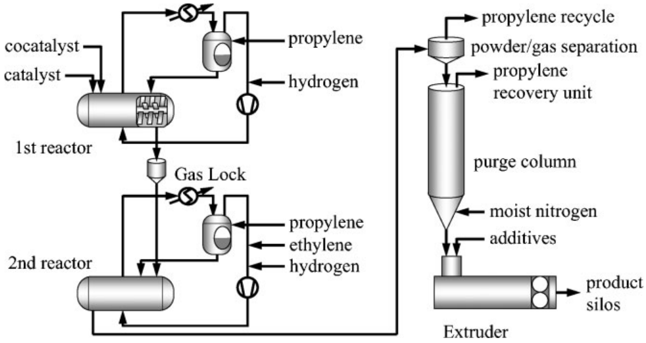

Figure 1.
Schematic process flow of JPP-Horizone.

fraction soluble under 40C-defree in TREF was defined as atactic PP (aPP) and the remaining fraction was defined as isotactic PP (iPP). First order decay assumption was employed to determine kinetic parameters for isospecific sites. Decay constant was larger in LPP slurry polymerization than in gas-phase polymerization. First order decay assumption combined with first order initiation assumption was employed for aspecific sites, however, eventually no decay was observed in LPP slurry polymerizaiton. Initiation reaction was necessary because catalyst efficiency for aPP increased by time. The authors believe that some of isospecific sites were transformed into aspecific sites during polymerization. A pair of an activation energy and a steric factor was also determined for each kinetic parameter by Arrhenius plot. The obtained parameters for gas-phase polymerization at 2.2 MPa of propylene and those for LPP slurry polymerization were shown in Tables 1 and 2, respectively.

Table 1.
Kinetics parameters for gas-phase polymerization.[a)]

		High Si-donor conc.		Low Si-donor conc.	
		ISO	ATA	ISO	ATA
V_o $dE^{\ddagger}$	[kJ/mol]	8.4	2.6	19	30
log [A]	–	−3	1.0	−3	12
k_d $dE^{\ddagger}$	[kJ/mol]	0	37	0	0
log[A]	–	5.5	12	9.1	−2.4
k_i $dE^{\ddagger}$	[kJ/mol]	–	14	–	0
log [A]	–	–	3.1	–	−2.3

[a)] Polymerizaiton was carried out at 2.2 MPa.

Table 2.
Kinetics parameters for LPP slurry polymerization.

		High Si-donor conc.		Low Si-donor conc.	
		ISO	ATA	ISO	ATA
V_o $dE^{\ddagger}$	[kJ/mol]	34	58	31	64
log[A]	–	15	20	14	23
k_d $dE^{\ddagger}$	[kJ/mol]	16	–	34	–
log [A]	–	2.9	–	9.7	–
k_i $dE^{\ddagger}$	[kJ/mol]	–	−35	–	−56
log [A]	–	–	−14	–	−21

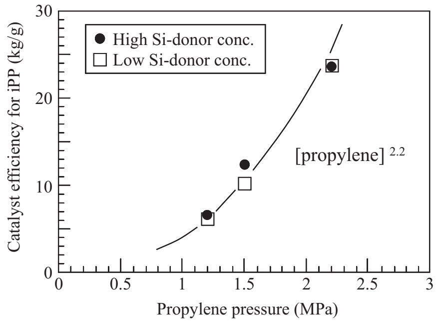

Figure 2.
Pressure dependence of catalyst efficiency for iPP; polymerizaiton conditions: 65°C-degree, 2 h.

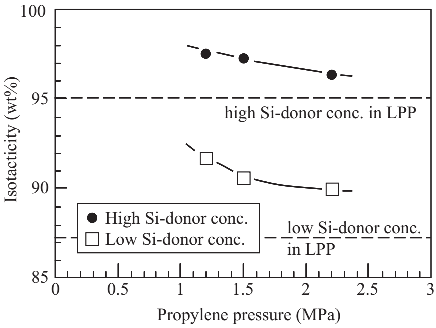

Figure 4.
Pressure dependence of isotacticity; polymerizaiton conditions: 65°C-degree, 2 h.

Figures 2 and 3 show the pressure dependence of catalyst efficiency for iPP and aPP, respectively. Catalyst efficiency for iPP is independent of the Si-donor concentration. On the contrary, catalyst efficiency for aPP depends on it, which implies that more aspecific sites were deactivated at higher Si-donor concentration. Pressure dependence of catalyst efficiency is higher for aPP than for iPP.

Isotacticity strongly depends on the propylene pressure in gas-phase polymerization because of the difference degree of dependence between isospecific and aspecific sites (Figure 4). Isotacticity is lower in LPP slurry polymerization than in gas-phase polymerization at any pressure. It is probably because of the higher monomer concentration in LPP slurry than in gas. The sensitivity of the catalyst on monomer concentration is one of the specific features of less stereospecific catalysts, as far as we know. This is the reason why we chose it for the model of HSBR to estimate the effects of LPP.

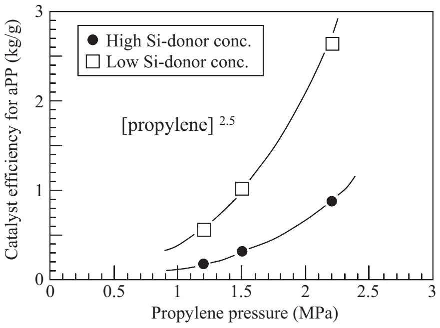

Figure 3.
Pressure dependence of catalyst efficiency for aPP; polymerizaiton conditions: 65°C-degree, 2 h.

Model development

JPP-HORIZONE has two HSBRs, however, only the 1st reactor was divided into 3 zones because the preliminary study showed 1 HSBR corresponding to approximately 3 CSTRs in series. Supplied LPP intrudes into a particle from the surface and consumed by polymerization or vaporization by the polymerization heat as schematically shown in Figure 5.

Active sites located in the shell from the surface to some depth were modeled as in the LPP slurry reactor. The other sites were modeled as in the gas-phase reactor. For this purpose, we modified the model by replacing a CSTR with a couple of CSTRs in parallel which were different in the polymerization atmosphere, that is, gas or LPP (Figure 6).

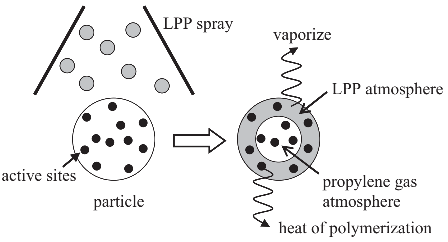

Figure 5.
Plausible model of polymerization atmosphere.

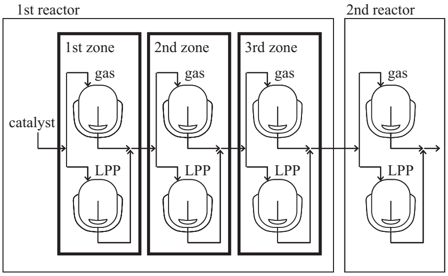

Figure 6.
Reactor allignment of the model.

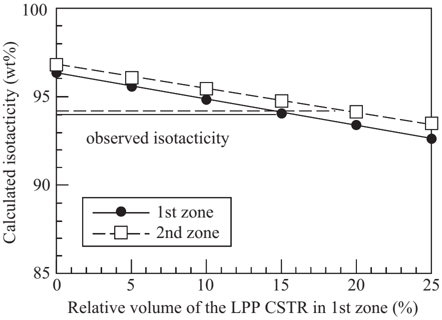

Figure 7.
Effect of LPP on isotacticity.

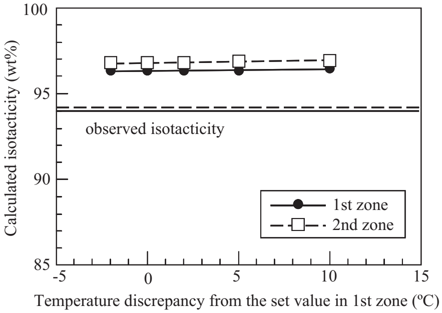

Figure 8.
Effect of termperature discrepancy from the set value on isotacticity without LPP.

Catalyst was supplied to gas and LPP CTSRs in the 1st zone according to the arbitrarily determined volume ratio of them. In both CSTRs, polymerization was independently simulated with the sets of parameters determined by the conditions or arbitrary input. Polymerization unit time of 0.01 h was employed. Active site concentration and production amounts of iPP and aPP were calculated. Increased amounts of PP were discharged from the CSTR to keep the level. Parameters of the discharged PPs from the gas and the LPP CSTRs were averaged and charged into the 2nd zone. Calculation for the 2nd zone to the 2nd reactor was similar. Calculation was repeated until the results converged.

Effects of LPP

The effects of LPP in JPP-HORIZONE were investigated by the model developed above. Calculation results were compared with the results of the pilot plant trials. Especially, we were interested in isotacticity, because we had sometimes found too lower values to be explained only by gas-phase polymerization. One of pilot trials was tried to be reproduced with various amounts of LPP or various temperatures as shown in Figures 7 and 8, respectively. Observed isotacticity can be explained if 15 to 20% of the 1st zone has the LPP atmosphere. Temperature is not effective to change isotacticity. Therefore, even if there is part having different temperature from the set value somewhere inside the reactor, isotacticity does not be affected.

Catalyst efficiency is also affected by the amount of LPP, but not so sensitive as isotacticity. The amount of LPP can be estimated by comparing the observed isotacticity and catalyst efficiency with calculation results with various amounts of LPP.

Conclusion

We successfully showed the importance of the LPP amount for HSBR. The amount of LPP can be estimated by the modeling study using a couple CSTRs different in propylene form, gas or liquid, combined with a less stereospecific catalyst as a probe. LPP affects isotacticity more strongly than catalyst efficiency in the developed model. Observed isotacticity was lower than that estimated by the model without LPP, which can be explained only by the presence of LPP. Temperature is not effective to change it. We believe that our procedure to use a less stereospecific catalyst as a probe and to develop a model using couples of CSTRs different in propylene form in parallel is effective for the deep understanding of the real polymerization environment in actual reactors.

[1] M. Caracotsios, *Chem. Eng. Sci.* **1992**, *47*, 2591.
[2] N. P. Khare, B. Lucas, K. C. Seavey, T. A. Liu, *Ind. Eng. Chem. Res.* **2004**, *43*, 884.
[3] A. B. Gorbach, S. D. Naik, W. H. Ray, *Chem. Eng. Sci.* **2000**, *55*, 4461.
[4] C. Dittrich, S. Mutsers, abstract of ECOREP III **2005**, 31.