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Sorption Studies of Propylene in Polypropylene Polymerized with Novel Ziegler-Natta-Catalysts in Liquid and Gas Phase

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Summary: Polypropylene was produced in gas phase and liquid phase using different supported Ziegler-Natta-catalysts. Sorption behaviour of propylene in polymer particles was studied gravimetrically. The analyzed polymer fractions have average diameters between 250 and 875 μm. Generally it was found that the effective diffusion coefficient is increasing with increasing size of polymer particles. With electron microscopy a change of polymer particle morphology with particle size and type of catalysts was observed.

Keywords: diffusion coefficient; polypropylene; sorption; Ziegler-Natta-Catalyst

Introduction

Sorption and desorption of low molecular weight components such as monomers, hydrogen and diluents play an important role in gas-phase and slurry reactors. The sorption of sparingly soluble penetrants can be modeled by Henry's law because the sorbed amount is sufficiently small so that the polymer matrix does not undergo any swelling strain [1]. Otherwise high soluble penetrants can swell and plasticizing the polymer. This can even change the morphology of the polymer [2]. It is known that the morphology of a polymer particle is a replica of the original catalyst particle. Thus the morphology of catalyst plays an important role in the growth of polymer particles.

Sorption studies were performed in a magnetic suspension balance. This sorption method was also used by other groups like Garmatter [3], Bartke [4] , by Schabel et al. [5], Weickert et al.[6], Svejda et al. …[7], Sato et al. [8] and Kosek et al [9].

Experimental

Propylene (Merck, 3.5) without further purification was polymerized in gas and liquid phase with novel Ziegler-Natta catalysts developed by BOREALIS Polymers Oy (Finland) [10,11,12,13].

In this work three different catalysts (Cat. A, Cat.B, Cat.C, details in Table 1) were used for propylene polymerization.

Cat. A was made by a new emulsion technique described in[10] without external support, so called self-supported catalyst. Particles of Cat. A are perfect spherically shaped and nonporous. Cat. B was produced by same emulsion technique but with SiO_2 as external support. Cat. C was produced by a conventional technique with $MgCl_2$ as external support. The external support leads to porous particle morphologies with much larger surface area compared with Cat. A.

All polymerizations were performed in a 100 ml stirred tank reactor (Premex, Switzerland). The catalyst was activated with a solution of triethylaluminum (TEA) as cocatalyst in pentane and dicyclopentylmethoxysilane (D-Donor) as an external donor. The molar ratio Al/Ti was 250:1 and the Al/D-Donor was 10:1. More details about catalyst activation and polymerization process were published in [14].

The final polymer powder was sieved to obtain different fractions with average particle diameters ranging from 250 to 825 μm. The polymer sample was placed in a magnetic suspension balance

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Table 1.
Specification of catalysts.

Catalyst	Content			Surface area (m^2/g)	d_{Cat} (μm)
	Ti (wt%)	Mg (wt%)	support		
Cat. A	3.5	12.3	self-supported	1–2	35
Cat. B	2.7	6.0	SiO_2*-supported	150	58
Cat. C	2.1	21	$MgCl_2$-supported	>300	70

* Grace Davison; SYLOPOL® 55SJ, surface area 350 m^2/g.

(Rubotherm Präzisionsmeßtechnik GmbH; Germany) and then evacuated to remove residual monomer. Sorption process was studied by adding propylene in range of one to 10 bars at different temperatures.

Results

Table 2 gives an overview about polymer samples analyzed in this work with polymerization conditions and used catalyst.

The isotacticity, measured with FTIR, of polypropylene range from 92 to 99 %. The crystallinities of polymer estimated by DSC (Perkin Elmer, DSC-7) are 32 % related to the first melting peak.

At studied sorption conditions the solubility of propylene in polypropylene can be described by Henry's law[14]. The diffusion of propylene in spherical polypropylene particles can be described by Fick's law. Based on [15], solution of Fick's law for spherical particle yields :

$$\frac{m_M(t)}{m_{M,Equi}} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp(-D_{eff}n^2\pi^2 t/r^2_{Particle})}{n^2} \tag{1}$$

with m_M = mass of absorbed propylene, $m_{M,Equi}$ = mass of propylene absorbed at equilibrium, D_{eff} = effective diffusion coefficient, r = average particle radius, t = time of sorption.

Effective diffusion coefficients were estimated by fitting of eq. (1) to measured sorption curve. Figure 1 shows a fitted sorption curve for polymer particles.

The dependency of diffusion coefficients on particle size for different polymer samples is summarized in Table 3. With increasing particle size the effective diffusion coefficients is increasing. The differences in effective diffusion coefficients of same particle size for different polymerization catalysts are smaller than differences of D_{eff} between different particle sizes. In case of gas phase polymer the diffusion in polymer particles up to 400 μm produced by supported catalysts seems to be faster than diffusion in polymer particles produced by self-supported catalyst. Due to higher porosity of supported catalyst, polymer particles should also have a higher porosity which can accelerate the mass transport.

Table 2.
Polymer samples prepared for sorption measurements.

Polymer Sample	Catalyst	Polymerization Process	Polymerization Conditions		
			$T_{Polym.}$ (°C)	$p_{Propylen}$ (bar)	$t_{Polym.}$ (h)
PP 136	Cat. A	gas phase	55	5	4
PP 146	Cat. A	gas phase	70	5	5
PP 127	Cat. A	liquid phase	70	p_{vapor}	1
PP 150	Cat. A	liquid phase	70	p_{vapor}	1
PP 162	Cat. B	liquid phase	55	p_{vapor}	1
PP 229	Cat. B	gas phase	55	5	3
PP 293	Cat. B	gas phase	55	10	3
PP 195	Cat. C	liquid phase	55	p_{vapor}	1
PP 230	Cat. C	gas phase	55	5	3

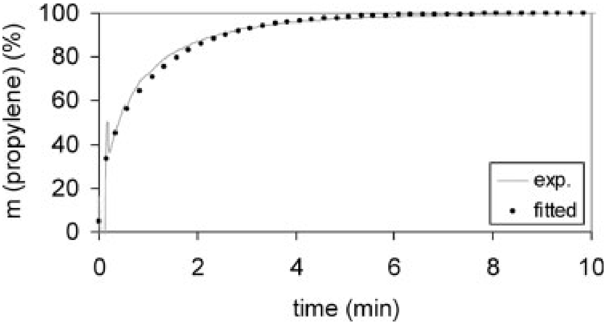


Figure 1.
Dynamic absorption characteristics of polymer particles (PP 150, 625 μm fraction) at 70 °C and 5 bar propylene.

The influence of polymerization process on effective diffusion coefficient is shown in Table 4. In case of Cat. A the effective diffusion coefficients of polymer powder produced in liquid propylene are larger than the diffusion coefficients of a gas-phase product. For Cat. C the opposite was found.

Morphology of Propylene Particles

The morphology of polymer particles was studied using scanning electron microscopy (Hitachi S 2700). Polymer particles polymerized with Cat. A are characterized by spherical shapes and can have compact or broken structures depending on polymerization method. Most of polymer particles produced in gas phase were observed to be more compact (Figure 2, PP146) than polymer particles produced in liquid phase (Figure 2, PP150). Large polymer particles produced in gas phase or in liquid phase are observed to have much more broken structures than smaller ones. Particle morphology is in agreement with increasing of effective diffusion coefficient with increasing particle size.

Polymer particles polymerized with silica-supported Cat. B are not perfect spherically shaped and their morphology does not depend on the polymerization process, shown in Figure 3. The particle surface is rough and seems to be porous. More details of polymer morphology can be seen in cross sectioned polymer particles (Figure 5).

The polymerization with $MgCl_2$ supported catalyst Cat. C gives spherically shaped polymer particles. The polymer morphology also does not depend on polymerization process.

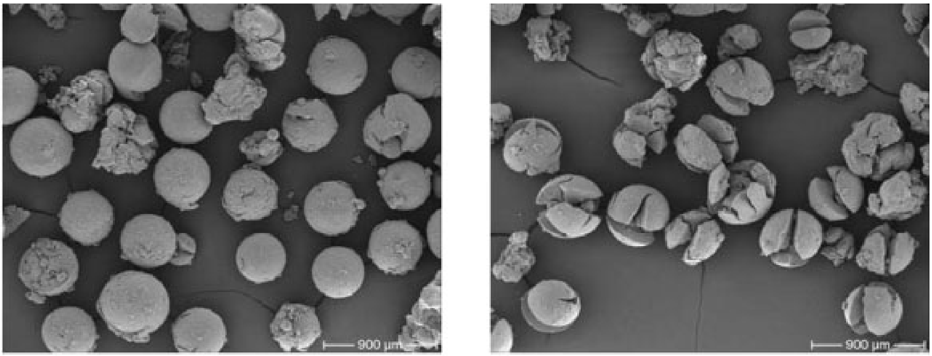
Scanning electron microscopy of cross-sectional cuts of polymer particles was used to study the internal structures of polymer particles, shown in Figure 5. As expected catalysts with external support produces porous polymer particles. Mass transport in polymerization process will be affected by different particle porosities, which are increasing with growing polymer particles.

Table 3.
Dependency of diffusion coefficients on particle diameter for different polymer samples polymerized in gas phase.

Polymer Sample (gas phase)	$D_{eff} \times 10^{11}$ (m^2/s) (measured by 55°C and 5 bar)		
	250 μm	450 μm	625 μm
PP136 (Cat. A)	1.5	2.7	—
PP146 (Cat. A)	1.1	2.4	—
PP293 (Cat. B)	1.5	3.9	7.6
PP230 (Cat. C)	—	2.9	8.7

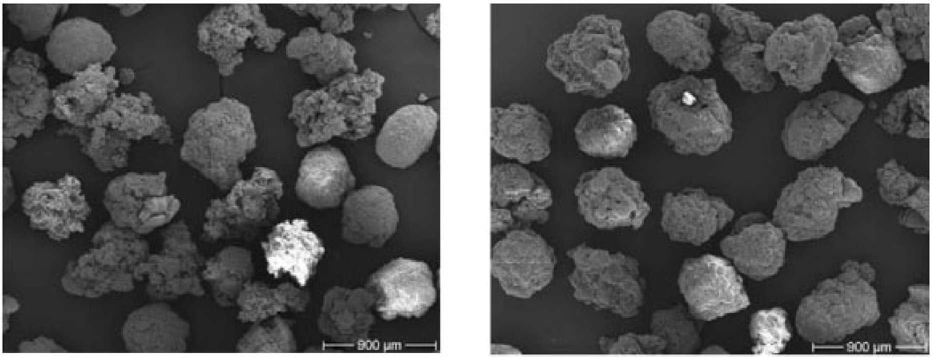
Table 4.
Dependency of effective diffusion coefficients on particle diameter for different polymer samples.

Polymer sample	Particle Size (μm)	$D_{eff} \times 10^{11}$ (at 5 bar) (m^2/s)
PP146 (Cat. A)	250	2.1 (70°C)
(gas phase)	450	4.0 (70°C)
PP127 (Cat. A)	250	2.6 (70°C)
(liquid phase)	450	5.3 (70°C)
PP230 (Cat. C)	625	8.7 (55°C)
(gas phase)	875	23.0 (55°C)
PP195 (Cat. C)	625	6.6 (55°C)
(liquid phase)	875	14.0 (55°C)



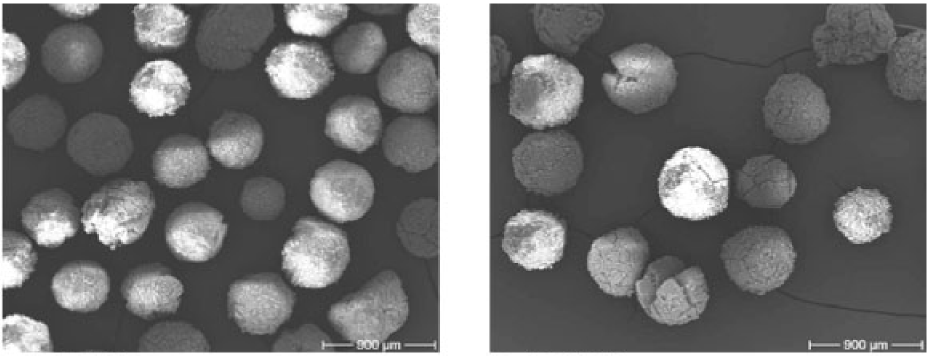
A (PP146)   B (PP150)

Figure 2.
SEM images of polymer particles polymerized with Cat. A in gas phase A and in liquid phase B.



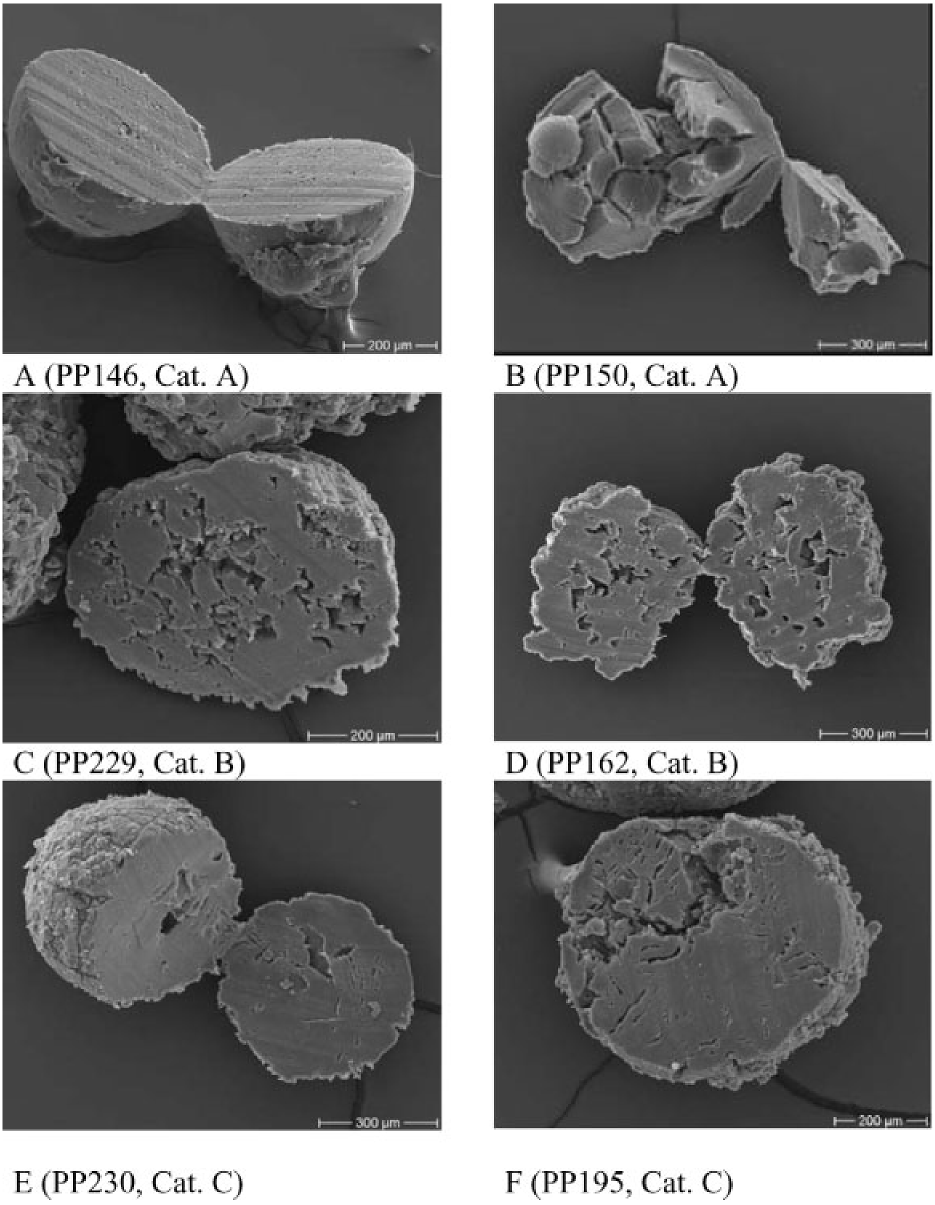
A (PP229)   B (PP162)

Figure 3.
SEM images of polymer particles polymerized with Cat. B in gas phase A and in liquid phase B.



A (PP230)   B (PP195)

Figure 4.
SEM images of polymer particles polymerized with Cat. C in gas phase A and in liquid phase B.



A (PP146, Cat. A)

B (PP150, Cat. A)

C (PP229, Cat. B)

D (PP162, Cat. B)

E (PP230, Cat. C)

F (PP195, Cat. C)

Figure 5.
Cross-sectional SEM images of polypropylene particles polymerized in gas phase (A, C, E) and liquid phase (B, D, F).

The different effective diffusion coefficients of different polymer samples can be related to the different polymer particle morphologies observed. Using Cat. A the larger values of effective diffusion coefficients observed in case of large polymer particles produced in liquid phase can be explained by their open structure due to the high degree of rupturing. The particle rupturing reduces the effective diffusion length in polymer material. Polymer particles of the same size produced in gas phase with Cat. A had smaller effective diffusion coefficients due to the more compact structure.

In this case the effective diffusion length can be better correlated to the polymer particle radius.

Using Cat. B the larger values of effective diffusion coefficients related to particles polymerized with Cat. A can be explained by distinct particle porosities. The observed macro pores reduce the effective diffusion length and is causing a faster mass transport. Polymer particles produced with $MgCl_2$-supported catalyst Cat. C have a different porosity compared with silica-supported catalyst Cat. B. Many particles with voids inside and with cracks in particle surfaces areas have been observed. The change of polymer particle morphology with increasing particle size has more influence on mass transport than different morphologies, of the catalyst used.

Conclusion

The increase of effective diffusion coefficients with increasing polymer particle size is probably due to the decrease of the effective length of diffusion within the polymer particle. This may be caused by the formation of voids, cracks or pores in the polymer particles during the course of polymerization. Polymer particles formed by polymerization with self supported catalysts in liquid phase of monomer seem to be less compact than particles formed by polymerization in gas phase at same reaction conditions. One reason may be the higher rate of polymerization in case of liquid pool polymerization leading to higher mechanical tension within the growing particles. Furthermore, differences in micro structure of polymer may also have to be considered. In case of polymerization with supported catalysts the initial porosity inside growing particles can reduce particle rupturing.

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