Macromol. Symp. **2007**, 259, 327–336 DOI: 10.1002/masy.200751337

Sorption and Diffusion of Propylene and Ethylene in Heterophasic Polypropylene Copolymers

Michael Bartke,[1] Sebastian Kröner,[1] Annette Wittebrock,[2] Karl-Heinz Reichert,[2] Ilias Illiopoulus,[3] Christoph Johannes Dittrich[3]*

Summary: Sorption experiments of ethylene and propylene in different polypropylene powder samples, both homopolymer and heterophasic copolymers with different rubber content, have been carried out in a high-pressure magnetic suspension balance at 10 bars pressure and 70 °C. The gross solubilities measured can be well correlated with the rubber content of the polymer samples. Solubility of ethylene and propylene in the rubber phase differ from solubility in the amorphous fraction of the homopolymer, especially the concentration *ratio* of propylene to ethylene differs significantly between rubber phase and amorphous fraction of the homopolymer. From the slope of monomer uptake, information on kinetics of mass-transfer can be gained. No significant differences were observed in terms of mass-transfer for ethylene and propylene. With increasing rubber content, effective diffusion coefficients increased slightly. By combined sorption studies with powder samples and compressed films, information about both effective diffusion coefficients and the effective length scale of diffusion could be gained. It could be shown, that the particle radius is not the characteristic length of diffusion in the studied powder samples. Mass transfer of nearly all samples could be described by a constant diffusion length of 120 to 130 μm, independently on particle size. This indicates that the effective scale of diffusion in polymer particles is in between microparticle and macroparticle scale used in classical particle modeling.

Keywords: diffusion; ethylene; polypropylene; propylene; sorption

Introduction

Heterophasic polypropylene copolymers are commercially important products produced in at least two-stage processes. In a first stage, either bulk or gas-phase polymerization, a matrix material, polypropylene homopolymer or random copolymer is produced. In the second stage, a rubber-like, ethylene-rich copolymer, which is not miscible with the matrix material, is produced. The elastomeric phase improves high-impact strength and toughness of the material.

The rubber phase is usually produced in gas-phase polymerization. In gas phase polymerization, the reaction takes place at the active sites of the catalyst, in the polymer particles formed. The reaction partners have to be absorbed from the surrounding gas phase and have to be transported through the polymer particle to the active site of the catalyst. Hence phase equilibria gas-polymer and mass-transport

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[1] Polymer Reaction Engineering Group, Institute for Chemistry, Martin-Luther-University Halle-Wittenberg, Heinrich-Damerow-Str. 4, 6120 Halle (Saale), Germany
E-mail: michael.bartke@chemie.uni-halle.de

[2] Polymer Reaction Engineering Group, Institute for Chemistry, Technical University of Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany

[3] Research & Development, Sabic Europe B.V., P.O. Box 319, 6160 AH Geleen, The Netherlands

in the polymer particles are important, both for polymerization kinetics, as well as for polymer degassing after polymerization.

Equilibrium solubilities of ethylene and propylene in semi-crystalline polymers at moderate pressures usually can be described by linear correlations with pressure according to Henry's law. Hutchinson and Ray[1] have reviewed experimental data available and suggested a simple correlation based on Stern equation for estimation of equilibrium solubilities, which is widely used. More sophisticated phase equilibria calculations valid also at higher pressures and taking into account e.g. for co-sorption effects are based on equations of state such as the Sanchez-Lacombe-equation or the PC-SAFT equation. For solubility in heterophasic polypropylene copolymers not much data is published. Tsuboi et al.[2] measured propylene solubility in the rubber phase of heterophasic polypropylene copolymers which was 1,8 times higher compared to the solubility in the amorphous fraction of homo PP.

Mass-transfer in polymerizing particles has been widely discussed in scientific literature. Various particle models such as the often used multigrain model[3] have been developed, a review can be found e.g. in.[4] In technical reaction conditions, with usually inerts being present, mass-transfer in polymerizing particles is believed to mainly occur via diffusion.[4] Hence important parameters for characterization of mass-transfer are both the effective diffusion coefficient and the effective length of diffusion. Often the particle radius simply has been assumed to be the effective length of diffusion, which needs to be discussed critically.

Sliepcevich et al.[5] measured solubility and diffusivity of ethylene and propylene in two different polypropylene samples by using the polymer as column material in gas chromatography. Partition coefficients determined were slightly higher compared to estimations based on Stern equation. Effective Diffusion coefficients in the range of $3 \cdot 10^{-11}$ to $2 \cdot 10^{-10}$ m^2/s were determined assuming the particle radius being the effective length of diffusion. With increasing particle size, increasing effective diffusion coefficients were observed.

Novak et al.[6] reported gravimetric sorption experiments of ethylene in polypropylene at different temperatures. In[7] they report gravimetric sorption/desorption studies with two different polypropylene samples with different morphology. Effective diffusion lengths in the range of 150 μm resp. 330 μm, the later one being the particle radius, were identified.

Bartke et al.[8] compared mass-transfer of ethylene and propylene in different polypropylene powders by gravimetric sorption experiments assuming the particle radius being the effective length scale of diffusion. The determined diffusion coefficients were in the range of $1 \cdot 10^{-10}$ to $3 \cdot 10^{-10}$ m^2/s and did not differ significantly with porosity or nature of the penetrant (ethylene or propylene).

Patzlaff et al.[9,10] measured sorption of propylene in polypropylene homopolymer powder assuming the particle radius being the effective length scale of diffusion. They observed increasing effective diffusion coefficients with increasing particle size and attributed this to decreasing effective diffusion lengths with increasing particle size, due to morphological effects. Effective diffusion lengths were not quantified.

Gonzales et al.[11] measured diffusivity of ethylene and propylene in different atactic and isotactic polypropylenes, both in different size fraction of powder and in films samples. While effective diffusion coefficients determined from powder samples were dependent on the particle size and polymer sample, effective diffusion coefficient determined from film measurements were in the same magnitude for all polymers. The authors concluded that the particle radius is not the effective length scale of diffusion.

Scope of This Study

Scope of this study is to investigate and quantify solubility and mass-transfer of ethylene and propylene in heterophasic polypropylene copolymers by sorption experiments.

Experimental Setup and Measurement Procedure

The sorption experiments were carried out in a high-pressure sorption balance at Technical University of Berlin. The setup is described elsewhere[12] in more detail. The polymer sample (usually between three and five grams) is placed in a sample holder within the measurement chamber. The load of the sample holder is transferred via a magnetic suspension coupling (Rubotherm GmbH, Bochum) to a laboratory scale with 10 μg of sensitivity (Mettler Toledo) situated above the measurement chamber. The measurement chamber is equipped with a pressure transducer and temperature control system and connected to a suitable gas manifold. The measured weight is registered by data acquisition software. The data acquisition software corrects the measured weight for the buoyancy force acting on the sample and the sample holder. Buoyancy force has to be considered, because it depends on the surrounding gas density, which is changing in the beginning of a sorption experiment. In principle, swelling of the polymer can affect the buoyancy force acting on the polymer sample. Patzlaff et al.[9] reported that in videomicroscopic studies performed by Abboud et al.[13], no measurable swelling effect could be observed during absorption of propylene in polypropylene particles. Due to the much lower solubility of ethylene in polypropylene, also for ethylene-absorption no significant swelling of the polypropylene samples is expected. Hence swelling is not considered in the buoyancy correction.

After loading the polymer sample was degassed via evacuation of the measurement chamber and the desired measurement temperature was adjusted. The sorption experiment starts with inflow of monomer. Due to absorption of monomer, the measured weight increases. Constant pressure and therefore reliable results are usually reached after approx. one minute of measurement time.

A typical sorption curve can be seen in Figure 1:

From the weight of the polymer sample and the sorbed mass in steady state, solubility of the penetrant in the polymer can be

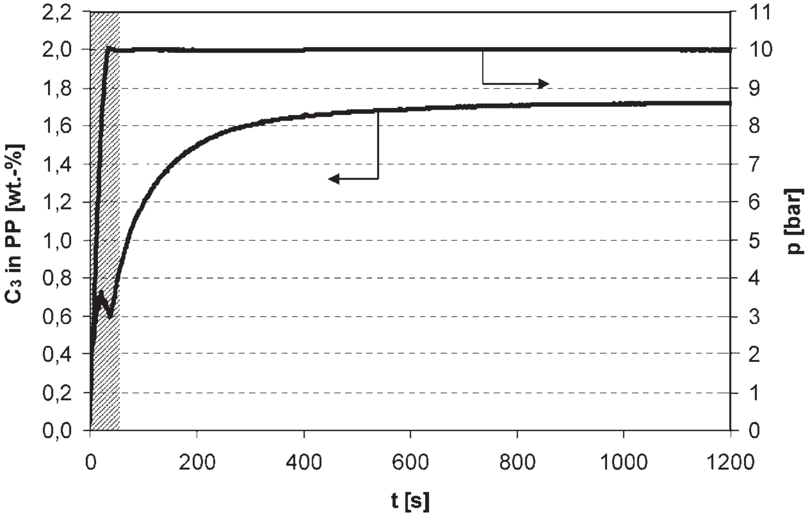

Figure 1.

Typical sorption curve, here unsieved sample B, sorption of propylene at $p_{C3} = 10$ bars and T = 70 °C. Shaded area: oscillations due to start up, white area: suitable data for analysis.

Table 1.
Polymer samples used in this study.

Sample code	Polymer type	Rubber content [wt.%]	Sauter-radius r_{32} [μm]
A	homo-PP	0	297
B	homo-PP	0	268
C	Heco-PP, low RC	24,5	297
D	Heco-PP, low RC	26,6	273
E	Heco-PP, high RC	40,9	229
F	Heco-PP, high RC	42,7	273

calculated. From the slope of the sorption curve, information about kinetics of mass transfer can be gained.

Polymer Samples

The following polymer samples (Table 1), provided by SABIC Europe B.V., have been investigated in this study:

Polypropylene homopolymer is abbreviated as homo-PP, heco-PP is the abbreviation for heterophasic polypropylene copolymers. RC stands for rubber content (in wt.-%), Sauter radii r_{32} have been calculated back from particle size distribution data.

Crystallinity α (weight fraction of crystalline material in the polymer) of the samples has been analyzed by Differential Scanning Calorimetry (crystallinity analyzed from second melting peak).

Taking into account that the rubber phase is completely amorphous, crystallinity can be directly correlated with rubber content in a straight forward correlation, which is in good agreement with experimental data, see Figure 2:

Equilibrium Solubilities

Sorption experiments with both ethylene and propylene have been carried out at 70 °C and 10 bars monomer partial pressure.

From the weight of the polymer sample and the sorbed mass in steady state, solubility of the penetrant in the polymer can be calculated. Gross solubilities in the range of 1,8 to 3 wt.-% propylene in polypropylene and 0,35 to 0,5 wt.-% ethylene in polypropylene have been measured. Measured ethylene and propylene

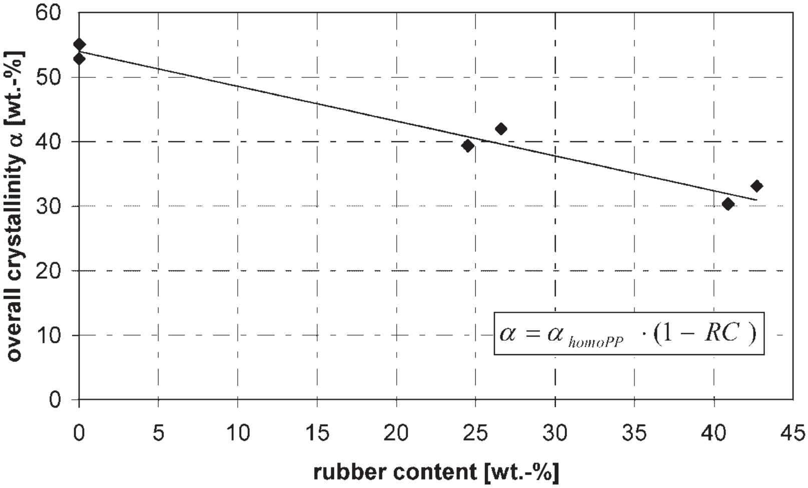

Figure 2.
Crystallinity vs. rubber content.

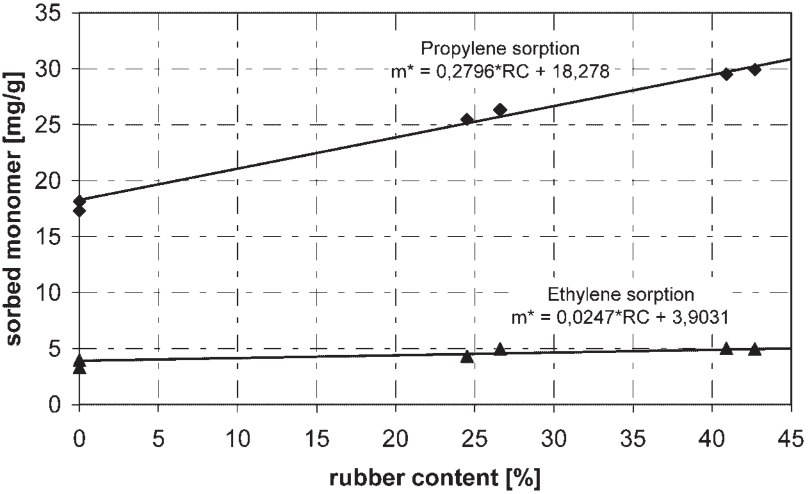

Figure 3.
Equilibrium solubilities of ethylene and propylene in polypropylene as function of rubber content.

solubilities can be depicted as function of the rubber content, see Figure 3.

As expected, gross solubilities of both monomers are increasing with increasing rubber content, since with increasing rubber content also the amorphous fraction of polymer is increasing.

Surprising in Figure 3 is the different slope of solubility as function of rubber content for ethylene and propylene. Extrapolating Figure 2 to 100% rubber content gives an estimate for monomer solubility in the (amorphous) rubber phase, which can be compared with the solubility in the amorphous fraction of the homopolymer (equal to 0% rubber content).

As a result in Table 2 the equilibrium solubilities at T = 70 °C and p = 10 bars partial pressure for both ethylene and propylene in the rubber phase and the amorphous fraction of the homopolymer are given together with estimations based on Stern-equation.[1]

The experimental determined equilibrium solubilities are in the magnitude of the predictions by Stern equation. Propylene solubility in the rubber phase is slightly higher compared to the solubility in the amorphous fraction of homopolymer, where as the solubility of ethylene is slightly lower in the rubber phase compared to the solubility in the amorphous fraction of homopolymer. Consequently, the equilibrium propylene/ethylene ratio at T = 70 °C and p = 10 bars is in the rubber phase with a value of about 4,8 $\text{mol}_{C3}/\text{mol}_{C2}$ significantly higher compared to the equilibrium ratio at the same conditions in the amorphous fraction of the homopolymer with about 3,1 $\text{mol}_{C3}/\text{mol}_{C2}$. This finding is of importance,

Table 2.
equilibrium solubilities of ethylene and propylene at T = 70 °C and p = 10 bars in amorphous fraction of homo PP and in the rubber phase compared to predictions according to Stern equation.

	Homo PP	Rubber phase	Prediction[1]
Solubility of propylene	18,28 mg/g		
– in amorphous fraction	39,73 mg/g 0,95 mmol/g	46,24 mg/g 1,10 mmol/g	0,76 mmol/g
Solubility of ethylene	3,90 mg/g		
– in amorphous fraction	8,48 mg/g 0,30 mmol/g	6,37 mg/g 0,23 mmol/g	0,25 mmol/g
Propylene/ethylene ratio	**3,1** mol/mol	**4,8** mol/mol	**3,0** mol/mol

since for copolymerizations the changed propylene/ethylene equilibrium ratio can lead to reduced ethylene incorporation in the rubber phase.

However, it has to been noticed that the equilibrium ratios given have been calculated back from single component solubility data, co-sorption effects have not been considered.

Differences in solubility between homo PP and rubber have been reported also by Tsuboi et al.[2]

Mass-Transfer

Analyzing the slope of the sorption curves, conclusions on kinetics of mass-transfer sorption experiments can be drawn.

Unsieved Powder Samples

As first approach for analysis of the powder samples, transient diffusion in a spherical particle with the particle Sauter radius being the effective length scale of diffusion is assumed. For this case, an analytical solution of the transient diffusion equation has been derived by Crank:[14]

$$\frac{\mathrm{m}_{\mathrm{sorbed}}(t)}{\mathrm{m}_{\mathrm{sorbed,\ eq.}}} = 1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{\exp[-\mathrm{D}_{\mathrm{eff}} \cdot n^2 \cdot \pi^2 \cdot t/\mathrm{r}_{\mathrm{diff}}^2]}{n^2} \tag{1}$$

$\mathrm{m}_{\mathrm{sorbed}}(\mathrm{t})$ is the sorbed mass at time t, $\mathrm{m}_{\mathrm{sorbed,\ eq}}$ is the sorbed mass in equilibrium, $\mathrm{D}_{\mathrm{eff}}$ is the effective Diffusion coefficient and $\mathrm{r}_{\mathrm{diff}}$ is the effective diffusion radius.

It has to be noticed that this is a quasi-homogeneous approach treating the polymer particle as one single phase, the effective Diffusion coefficient is not a molecular diffusion coefficient, but a gross mass-transfer parameter, possibly also dependent on particle morphology.

Effective Diffusion coefficients were determined via fitting Equation 1 to experimental sorption curves assuming the Sauter radius r_{32} being the effective length scale of diffusion.

The obtained effective diffusion coefficients, see Table 3, are all in the range of 6.5 to 11 times 10^{-11} m^2/s, which is a typical range for effective diffusion coefficients.

There is no significant difference in effective diffusion coefficients for ethylene compared to propylene. From the obtained data, a weak tendency to slightly increased diffusion coefficients with increasing rubber content can be seen.

Influence of Particle Size

In literature[5,9–11] strong influence of the particle size on effective diffusion coefficients has been reported. This is important information, because it enables to validate mass transfer models and to determine the effective length scale for diffusion.

In order to evaluate the influence of particle size on effective diffusion coefficients for the heterophasic copolymers studied here, selected polymer samples were sieved into six different size fractions. With these size fractions, sorption experiments

Table 3.
Effective diffusion coefficients obtained from sorption experiments with unsieved polymer samples assuming the sauter radius being the effective length scale for diffusion.

Sample code	Rubber content	Sauter-radius	$\mathrm{D}_{\mathrm{eff}}$ for C2	$\mathrm{D}_{\mathrm{eff}}$ for C3
	[wt.%]	r_{32} [μm]	[10^{-11} m^2/s]	[10^{-11} m^2/s]
A	0	297	8	7,5
B	0	268	7	6,5
C	24,5	297	10	9,5
D	26,6	273	9,5	9
E	40,9	229	8	8
F	42,7	273	11	10

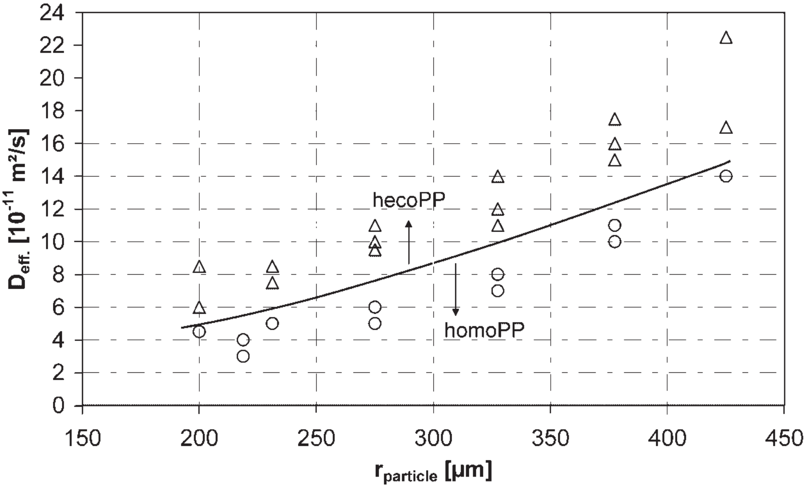

Figure 4.
Dependency of effective diffusion coefficients on particle size.

were carried out and analyzed as already described. As effective diffusion length, the mean radius of the particular size fraction was assumed.

The results are depicted in Figure 4. As can be seen, there is a significant size dependency of the effective diffusion coefficients. For the biggest particle size fraction, the effective diffusion coefficients are roughly three times higher compared to the smallest particle size fraction.

This clearly indicates that the mass-transfer model assumed on the first hand, diffusion in particles with the particle radius being the effective length scale of diffusion, is not valid in the studied system.

The earlier observed increase of effective diffusion coefficients in case of heterophasic copolymers compared to polypropylene homopolymers can be confirmed, also within one sieved fraction effective diffusion coefficients are in case of heterophasic copolymers roughly 50 to 100% higher compared to the corresponding homopolymers.

Sorption in Compressed Films

As mentioned already earlier, the effective diffusion coefficients determined from powder sample measurements are gross mass-transfer parameters, possibly also dependent on particle morphology. In order to separate morphological influences such as porosity from molecular diffusion properties, additional sorption experiments with pore-free compressed films of defined geometry, prepared out of selected polymer samples, have been carried out.

Films of the dimension 34 × 30 × 1 mm were prepared by melting at 180 °C under compression at 20 bars pressure for five minutes, followed by additional five minutes compression at 200 bars and subsequent cooling down of the polymer films.

Sorption experiments were carried out according to the procedure described already at 70 °C and 10 bars partial pressure ethylene resp. propylene.

For analysis of the sorption experiments, the analytical solution for the transient diffusion equation in an infinite plate derived by Crank[14] was used:

$$\frac{\mathrm{m}_{\text{sorbed}}(t)}{\mathrm{m}_{\text{sorbed, eq.}}} = 1 - \frac{8}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{\exp[-\mathrm{D}_{\text{membrane}} \cdot (2 \cdot n + 1)^2 \cdot \pi^2 \cdot t / \mathrm{l}^2_{\text{diffusion}}]}{(2 \cdot n + 1)^2} \tag{2}$$

$\mathrm{l}_{\text{diffusion}}$ is the effective diffusion length. Here half of the thickness of the membrane, i.e. 500 μm, was assumed as effective

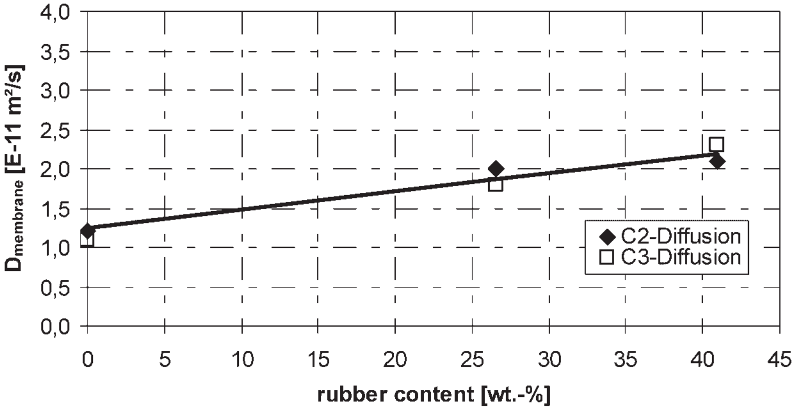

Figure 5.
Membrane diffusion coefficients determined from polymer film samples as function of rubber content.

diffusion length. Membrane diffusion coefficients were determined by fitting Equation 2 to the experimental sorption curves.

The determined membrane Diffusion coefficients are in the range of 1.1 to 2.3 times 10^{-11} m^2/s (see Figure 5), so considerably lower than the effective diffusion coefficients determined from powder samples.

Also membrane diffusion coefficients increase slightly with increasing rubber content. This can be explained by decreasing crystallinity with increasing rubber content. Crystalline regions in the polymer might act as diffusion barriers or obstacles and hence slow down diffusion for polypropylenes with low rubber content, or formulated the other way round, the amorphous rubber regions might act as 'highways' for monomer transport in the semi-crystalline matrix material.

Effective Length Scale for Diffusion in Polymer Particles

In order to obtain values for the effective diffusion length in polymer particles, the membrane diffusion coefficient determined by sorption in compact films was used in the transient diffusion equation for spherical particles (Equation 1). The diffusion length r_{diff} was adjusted in order to fit the experimental results of sorption measurements with the corresponding powder sample. This procedure was carried out for more than 40 different sorption measurements, the result can be seen in Figure 6.

Surprisingly, nearly all experiments, independent of sorbent (ethylene or propylene), independent of rubber content and independent of particle size, can be described by a constant diffusion length of approx. 120 to 130 μm.

This indicates that the relevant length scale for diffusion in polymer particles is in between macroparticle and microparticle scale considered in the classical particle models such as the multigrain-model.[3,4]

All polymer samples analyzed in this study have first been polymerized in similar homopolymerization conditions. The scale of the effective diffusion length, significantly bigger than a catalyst particle, but also clearly smaller than the final polymer particle, suggests that the effective diffusion length must develop during polymerization, until it approaches a more or less final value and doesn't change with further particle growth.

Development of the effective diffusion length in early stages of the polymerization and dependency of the effective diffusion length on polymerization conditions remain interesting questions to be addressed in future.

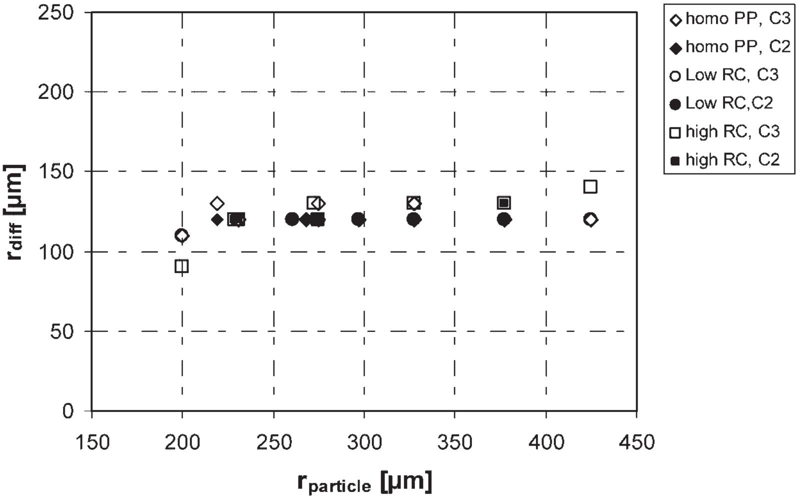

Figure 6.
Effective diffusion length for diffusion in polypropylene particles.

Conclusion

Sorption experiments of ethylene and propylene in different polypropylene samples, both homopolymer and heterophasic copolymers with different rubber content have been carried out in a high-pressure magnetic suspension balance at 10 bars pressure and 70 °C.

The gross solubilities measured can be well correlated with the rubber content of the polymer samples. Solubility of ethylene and propylene in the rubber phase differ from solubility in the amorphous fraction of the homopolymer, especially the concentration *ratio* of propylene to ethylene differs significantly between rubber phase and amorphous fraction of the homopolymer, which is important for copolymerization kinetics.

From the slope of monomer uptake, information on kinetics of mass-transfer can be gained. No significant differences were observed in terms of mass-transfer for ethylene and propylene. With increasing rubber content, effective diffusion coefficients increase slightly, which is likely to be connected to reduced crystallinity. Sorption studies with both powder samples and compressed films allow obtaining information about both effective diffusion coefficients and the effective length scale of diffusion. It could be shown that the particle radius is not the characteristic length of diffusion in the studied powder samples. Mass transfer of nearly all samples could be described by a constant diffusion length of 120 to 130 µm, independently on particle size.

This finding indicates that the relevant length scale for diffusion in polymer particles is in between macroparticle and microparticle scale considered in classical particle modeling. Particle size dependency of mass-transfer is much less pronounced as predicted by classical mass-transfer models, which can be important also for calculation of particle size distributions.

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