

## PHASE EQUILIBRIA EFFECT ON CATALYTIC OLEFIN POLYMERIZATION

Lenka Krajáková, University of Chemistry and Technology Prague, Department of Chemical Engineering, Czech Republic; Dutch Polymer Institute (DPI), The Netherlands  
lenka.krajakova@vscht.cz

Martina Podivinská, University of Chemistry and Technology Prague, Department of Chemical Engineering, Czech Republic

Juraj Kosek, University of Chemistry and Technology Prague, Department of Chemical Engineering, Czech Republic

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There are many reasons why phase equilibria during the catalytic polymerization are important and why many researches are interested in exploring them. In any type of catalytic polymerization (solution, slurry, gas-dispersion) the proportional relation of the monomer concentration at the active catalyst site to the polymerization rate is essential. Phase equilibria between a solvent, polymer, monomer(s) and co-monomer(s) and related transport processes are important not only for the polymerization kinetics itself, but also the polymer structure formation or subsequent product degassing are closely related to them. Nowadays many experimental techniques are available (e.g. DSC with pressure cell, low-field NMR, (co-)sorption balances), thus the thermodynamics of polyolefins is persistently studied and a lot of new quantitative knowledge about polyolefin thermodynamics was accumulated. But still there is a need for new data required by new or existing production processes and new grades of polyolefins.

In this contribution we present data relevant for gas-phase and slurry polymerization, i.e. sorption equilibria of polymer/solvent(g) and polymer/diluent(l) systems respectively. Sorption of gaseous penetrants in polymer particles was measured by gravimetric method and the results go hand in hand with swelling data measured in video-microscopic apparatus. Thus we gradually developed a huge database of experimental results including sorption of commonly used hydrocarbon penetrants (C2-C7) in various polyethylene and polypropylene samples (covering the full spectrum of commercially produced grades) at different temperatures (relevant to polymerization conditions). Moreover, by using a pressure-decay apparatus we are able to determine also kinetic parameter – diffusion coefficient of gases in polyolefin particles.

Sorption of liquid penetrants in polyolefins was measured using new methodology developed in our laboratory and we present results for the system polymer (PE or PP) and liquid hydrocarbon (C6-C8). Solubilities are measured at different temperatures. Next we present swelling equilibria of polyolefin particles in various liquid diluents and preliminary results of co-swelling experiments for the system PE-hexane-ethylene are discussed.

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