

# **Adsorption and Confinement of Polymers in Nanopores**

by

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The polymer adsorption in nanopore surfaces is relevant to technological applications involving macromolecular separation in high performance liquid chromatography (HPLC), nanoporous support design in polyolefin and hydrogenation catalysis, biosensors, and nanofluidic devices.

This thesis specifically focused on elucidating the adsorption and diffusion of polymers in nanopores. This study is particularly relevant for the development of novel polymer separation techniques, including interaction chromatography (IC) and large scale adsorption/desorption-based fractionation.

In particular, we investigated the adsorption of monodisperse polystyrene (PS) with a wide range of molecular weight (2,000 ~ 3,000,000 g/mol) in nanoporous silica with an average pore diameter ranging from 8 to 100 nm at a various solvent quality condition. We found that the adsorption phenomena of polymers in nanopores were greatly influenced by time, temperature, concentration and solvent quality, while the size interplay between polymer chain and nanopore plays a major role. When a polymer chain is much smaller than a pore, the adsorption behavior follows the trend on a flat surface. However, when a polymer chain is similar or larger than a pore, the surface excess decreased sharply due to limited accessibility of polystyrene at the nanopore entrance as well as in nanopores.

In case of polydisperse PS in cyclohexane, the adsorption in nanopores showed the strong tendency of the exchange adsorption dominated by high molecular weight polymers. However, PS in carbon tetrachloride exhibited the weak exchange adsorption corresponding the optimum molecular weight to win the competition in both the diffusion through pores and the exchange over low molecular weight PS in nanopore surfaces.

The diffusion of high molecular weight polymers confined in small nanopores can be further enhanced by the addition of displacers. The addition of specific displacers (nonpolar and good solvent for PS (e.g. benzene, toluene, and xylene)) after pre-adsorption has significantly increased the surface excess. This suggests that polymers adsorbed in nanopores are kinetically trapped, and thus the addition of displacers will facilitate the diffusion by solubilizing polymer chains in nanopores.