

**A Quantitative Study of the Fraction of Polymer Trains Participation in
Polymer Adsorption**

by

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ABSTRACT

This thesis investigates the differences between the changes in enthalpy of adsorption for high ($\Delta\hat{H}_{\text{ads}}^{\text{H}}$) and low ($\Delta\hat{H}_{\text{ads}}^{\text{L}}$) molecular weight (Mw) polymers. It will be shown that as the Mw increases, there is a correlation to the decrease in average change in ΔH_{ads} as each additional monomer is added onto the polymer's backbone. The enthalpy of adsorption relating to polymer retention has been measured by the application of the van't Hoff equation to the temperature dependence of retention behavior in high performance liquid chromatography (HPLC) systems.

Two different weight average Mw ranges of polystyrene were collected and divided into two groups based on their recorded mass. Those measuring under 4,000 g/mol were labeled as a low Mw species ($\text{PS}_{\text{Mw}}^{\text{L}}$), while any sample over 10,000 g/mol was placed in the high Mw category ($\text{PS}_{\text{Mw}}^{\text{H}}$). Each of these samples was then run through an HPLC system fitted with a C18 modified silica column stationary phase with three distinct compositions, 60/40, 57/43, 54/46 (v/v ratio) of methylene chloride to acetonitrile as the eluent. From each run, the retention time of the solvent (t_0) and the peak retention time of the polymer (t_{R}) was then noted so that the retention factor (k) could be determined. That value was then imputed into the van't Hoff equation in order to calculate the ΔH_{ads} for the two different Mw regimes.

The commonly accepted conformation of polymers adsorbed onto a surface, with "trains" that have contact with the surface while their "loops" and "tails" remain mostly in solution was also tackled. This was determined by relating the slope of the $\text{PS}_{\text{Mw}}^{\text{H}}$ chains to their $\text{PS}_{\text{Mw}}^{\text{L}}$ counterparts, which, due to conformational restrictions and lack of repeating units, are forced to lay completely flat along the particle surfaces and cannot form "loops" and "trails". The fraction (ξ), of monomers in contact with the stationary phase surface was found to vary slightly depending on solvent quality but remained around 0.2.