Thermodynamics of Polymer Adsorption onto Nanoporous Silica and its Application in the Large Scale Purification of Poly(styrene)-*block*-Poly(alkyl methacrylate) Diblock Copolymers

by

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ABSTRACT

As a result of unavoidable inconsistencies in their synthesis via controlled radical polymerization techniques, block copolymers inherently have distributions in chemical composition and molecular weight in each block that can have significant impact on their viscoelastic properties as well as their ability to self-assemble into ordered phases. High performance liquid chromatography is routinely utilized for determining the average molecular weight distribution that exist in synthetic polymers and is becoming increasingly popular for the fractionation and purification of chemically diverse complex polymer materials such as diblock copolymers. However, the inability of HPLC fractionation to provide meaningful quantities of purified complex polymers makes this method extremely inefficient and limits the ability to characterize purified fractions further.

Overall, this dissertation work can be digested in two distinct parts. In the first part, high performance liquid chromatography was used as a tool for studying the influential parameters affecting the critical adsorption point of poly(styrene) and poly(alkyl methacrylate) homopolymers. The understanding gained in the first portion was depended on for the development of large scale fractionation procedures. In the second part, a chemically diverse variety of poly(alkyl methacrylate)-*block*-poly(styrene) diblock copolymers synthesized by atom transfer radical polymerization and anionic polymerization were purified by large scale adsorption-based fractionation procedures that included chromatographic filtration and the sequential adsorption/desorption of bulk diblock copolymer materials. The impact of diblock copolymer purification is addressed by comparing the molecular weight distribution, chemical composition distribution, viscoelastic properties, and small-angle X-ray scattering profiles.