A Theoretical Study of the Separation Principle in Size Exclusion Chromatography

The principle of polymer separation in size exclusion chromatography (SEC) is studied based on a classical equilibrium partitioning theory. The task is to examine the correlation between the mean span dimension of polymer chains and their equilibrium partition coefficients with confining pores. Using an extended formulation of the recently developed confinement analysis from bulk structures (CABS) method, we calculate the partition coefficients for both linear and branched polymer chains with cylindrical pores—a model pore geometry that is considered to be more realistic for voids in SEC columns than the commonly considered slit model. The partition coefficients plotted as a function of the mean span dimension relative to the pore diameter are truly universal for wide pores and nearly so for flexible polymer chains with different architectures (linear, star, two-branch-point, and comb) in the range of the partition coefficient relevant to SEC separation. We also examine the correlation between the mean span dimension and the SEC retention volume using the experimental data by Sun et al. [Macromolecules 2004, 37, 4304−4312]. It is found that when the mean span dimension is plotted as a function of the retention volume, results for both linear and branched polyethylene molecules lie nearly on the master curve determined by linear polystyrene standards. Our findings support the equilibrium thermodynamic separation principle in SEC. Since the mean span dimension is a purely geometric size parameter applicable to any chain architecture, its use in the interpretation of SEC data is appealing.