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Retention mechanisms in liquid chromatography of synthetic polymers

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At present, methods of liquid chromatography (LC) provide the most important information on both average values and distributions of molecular characteristics like molar mass, chemical structure (composition) and physical architecture (topology) of synthetic macromolecules. Gel permeation (size exclusion) chromatography, GPC/SEC, is commonly employed for determination of molar mass of macromolecules. Its basic retention mechanism is steric exclusion based on the changes of conformational entropy of coiled macromolecules entering the pores of the column packing. However, GPC/SEC cannot give information about polymer molar mass in presence of the changing second or even third molecular characteristic. To simultaneously determine two molecular characteristics of complex polymer such as copolymers or polymer blends, the entropy controlled retention mechanism is combined, coupled with the interaction retention mechanisms. The most common interaction retention mechanism employed in coupled LC methods is adsorption i.e. the distribution of solute between a solid surface and a volume of its solution in a mobile phase. Adsorption usually results from the polar interactions among active sites on macromolecules and on the column packing surface, which are controlled by eluent polarity and less often by temperature. The appropriate stationary phase is bare silica gel. Another LC retention mechanism is absorption, (enthalpic partition), the distribution of a solute between the volumes of mobile and stationary phases. The practically applicable volume of LC stationary phase is produced by the chemical attachment, bonding of appropriate groups usually C18 alkyl groups onto a carrier, mainly silica gel. In practice, both adsorption and enthalpic partition retention mechanisms are applied either isocratically or applying mobile phase with the gradually changing composition. All enthalpy based processes in the LC columns are accompanied with the large changes of conformational entropy of macromolecules so that all coupled polymer LC procedures present a combination of enthalpy and entropy based processes.

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