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RETENTION MECHANISMS IN LIQUID CHROMATOGRAPHY OF SYNTHETIC POLYMERS

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Liquid chromatography (LC), provides information on both average values and distributions of molecular characteristics of synthetic polymers, their molar mass, chemical structure and physical architecture. Gel permeation (size exclusion) chromatography, GPC/SEC, is commonly employed for determination of polymer molar mass. Its basic retention mechanism is steric exclusion, controlled by the changes of conformational entropy of coiled macromolecules entering the pores of the column packing. However, GPC/SEC cannot give actual information about polymer when two molecular characteristics are changed simultaneously - as in copolymers or in polymer blends. In this case, the entropic retention mechanism is to be coupled with the enthalpic retention mechanisms. The ambition is to suppress molar mass effects so that separation depends only on other molecular characteristic. Yet, it should be remembered that all enthalpy-based processes in a LC column are accompanied with large changes of conformational entropy of macromolecules. The most common enthalpic retention mechanism employed in coupled LC methods is adsorption, the distribution of a solute between volume of its solution and a surface of column packing. It is as a rule controlled by eluent polarity. 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 phase. The practically applicable volume of LC stationary phase is created by the chemically attached appropriate groups, usually C18 alkyl groups on a carrier, mainly silica gel. Both adsorption and enthalpic partition retention mechanisms are performed either isocratically or with a mobile phase gradient. Direct practical employment of the third enthalpic retention mechanism, polymer phase separation is rather difficult. Sample is precipitated on the column inlet and then gradually dissolved and eluted. However, solubility of polymers strongly depends on their molar mass so that the molar mass effect is difficult to suppress.

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