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PROGRESS IN LIQUID CHROMATOGRAPHY OF SYNTHETIC MACROMOLECULES

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High performance liquid chromatographic (HPLC) methods represent the most important tool for molecular characterization of synthetic polymers. Mean molar mass (MM) and molar mass distribution (MMD) of linear and branched homo-polymers can be readily determined by gel permeation (size exclusion) chromatography (GPC/SEC). GPC/SEC also provides several other useful data such as limiting viscosity numbers, constants of viscosity law, and sizes of macromolecules in solution and even extent of preferential solvation of polymers in mixed solvents. Recent progress in GPC/SEC comprises improved instrumental hardware and data processing procedures. High sample throughput of the ultra-fast GPC/SEC enables acceleration of analyses, which is especially important in combinatorial material chemistry and in production control. Still, further improvements of the SEC method are needed, which include its hardware, especially columns and detectors, as well as standardization of sample preparation, measurement, and data processing. GPC/SEC exhibits excellent intra-laboratory repeatability, which evokes a notion of its high reliability. However, recent series of the round robin tests revealed surprisingly poor inter-laboratory reproducibility of results. Evidently, accuracy of many GPC/SEC results may be rather limited. GPC/SEC hardly enables precise molecular characterization of complex polymer systems, which possess more than one distribution in their molecular characteristics. Typically, polymer mixtures, copolymers and functional polymers exhibit besides MMD also distribution in their chemical structure. To assess above distributions, new HPLC procedures are developed. These are based on the controlled combinations of entropic (exclusion) and enthalpic (interaction) retention mechanisms within one column or in a series of independent separation systems. Enthalpic retention mechanisms in HPLC of synthetic polymers include adsorption, partition, phase separation. The resulting approaches are denoted coupled polymer HPLC and two- or multi-dimensional polymer HPLC. We shall review recent progress and problems in GPC/SEC, as well as in coupled and two-dimensional polymer HPLC procedures and outline anticipated future development.

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