ASYMMETRIC FLOW FIELD FLOW FRACTIONATION IN THE RESEARCH AND DEVELOPMENT OF SYNTHETIC POLYMERS

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Although being known for about three decades, asymmetric flow field flow fractionation (AF4) for many polymer scientists still represents a mysterious and difficult method. However, the current instrumentation makes AF4 comparable with well-known and widely used size exclusion chromatography (SEC) with several advantages given by the absence of stationary phase and thus strongly reduced probability of secondary separation mechanisms and shearing degradation, and the upper separation limit extended by at least two orders of magnitude. In the characterization of synthetic polymers, AF4 is typically coupled with a multi-angle light scattering (MALS) photometer and a refractive index (RI) detector. The set-up can determine not only absolute molar mass (MM) distribution, but also the conformation plot, i.e., the relation between the root mean square (RMS) radius (radius of gyration) and MM, which provides information about the molecular structure.

The systematic comparison of the results acquired by AF4-MALS with those from SEC-MALS draws the following conclusions: (i) both methods give almost identical results for linear polymers with the MM not exceeding several millions; (ii) for polymers containing fractions with MM over $\approx 10^7$ g/mol, AF4-MALS yields higher weight-average and *z*-average MM due to the reduction of shearing degradation; (iii) AF4 allows more efficient separation of branched macromolecules due to the elimination of anchoring of the branched macromolecules in the pores of SEC packing. An example of AF4 separation of polymer corresponding to (ii) and (iii) is given in Figure 1. Notice the efficient separation covering four decades of MM as well as the conformation plot unaffected by abnormal SEC elution of branched macromolecules.



Figure 1 MM versus retention time plot overlaid on signals of RI (dashed) and MALS (solid) detectors (left) and the conformation plot (right) of polybutadiene.