Synthesis of Polyacrylonitrile-block-Polystyrene Copolymers by Atom Transfer Radical Polymerization

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Block copolymers were also characterized by SEC equipped with a MALS on-line detector. The system consisted of a Waters 150C chromatograph equipped with two Styragel columns (500 and $10^4$ Å nominal porosities, Waters), a MALS Dawn DSP-F photometer (Wyatt), and a Waters 410 differential refractometer as concentration detector. The experimental conditions were the following: DMF + 0.01 M LiBr as mobile phase, 80°C, and 0.8 mL/min flow rate. The specific refractive index increment, dn/dc, of the block copolymers with respect to the DMF solvent was measured by a KMX-16 differential refractometer (LDC Milton Roy).

For the calculation of molecular weights the light scattering detector needs of the dn/dc value of the copolymer with respect to the used solvent. In general the measured dn/dc of the copolymers were in good agreement with the values calculated assuming a linear function of the copolymer chemical composition. The values of molecular weights and their distributions obtained by SEC-MALS were very similar to those obtained by conventional SEC using a RI detector (Table 2), indicating that such PAN-b-PS copolymers have a good compositional and dimensional homogeneity (see figure below for an example of the superimposition of the MALS 90° photodiode and the RI concentration detector traces).
Only in the case of the polymers with the higher content in AN, as well as for the homopolymers, the MALLS detector exhibited signals with pre-peaks or shoulders which did not superimpose with the refractometric detection, indicating the presence of aggregates in the solution.

Figure 1. SEC traces in DMF + 0.01 M LiBr mobile phase, 90° photodiode MALS (dashed line) and RI (solid line), of PAN-\textit{b}-PS of entry 5 in Table 2.