

Coil-stretch transition of high molar mass polymers

Hydrodynamic chromatography (HDC) is a size-separation technique for the analysis of high molar mass polymers. Abnormal elution behavior of high molar mass polymers, such as flow rate dependence of relative peak retention time, coelution of different molar mass polymers, and the appearance of double peaks at high flow rates, have been reported.

By coupling HDC with a DAWN EOS detector, such abnormal elution behavior is explained in terms of a chromatographic mode transition from HDC to slalom chromatography (SC). This crossover is induced by coil-stretch transitions of high molar mass polymers in elongational flow.

Figure 1 shows the UV chromatograms for a polystyrene sample with a molar mass of 10M (PS10M) obtained by two columns packed with 3 μm crosslinked polystyrene-divinylbenzene non-porous particles (Polymer Laboratories Ltd.) at different flow rates. The chromatograms shift to *higher* elution volumes with *increasing* flow rate, and a second peak develops at flow rates *higher* than 0.2 mL/min. This peak also shifts to higher elution volume with increasing flow rate.

M_w and $R_{g,z}$ of the sample obtained from MALS indicate *no* obvious degradation at high flow rates. The R_g values as a function of V_e for PS10M obtained at different flow rates are shown in Figure 2. A transition from HDC at low flow rates to SC at high flow rates is demonstrated by the flow rate dependence of the elution order of species with different sizes.

In conclusion, MALS is a powerful detector for determining the absolute molecular size of polymer fractions eluting from packed columns. Moreover, it is capable of investigating the *abnormal* elution behavior of high molar mass polymers—whenever they elute. For high molar mass polymer samples, HDC must be performed at flow rates sufficiently low such that the elongational rate in the column is *less* than the critical strain rate for coil-stretch transitions to occur for all species in the sample.

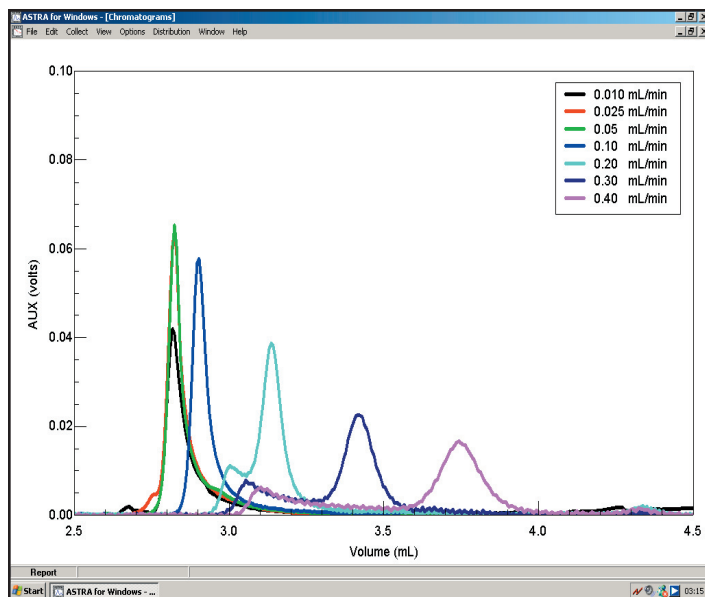


Figure 1. UV chromatograms of PS10M obtained at flow rates of 0.010, 0.025, 0.05, 0.10, 0.20, 0.30, and 0.40 mL/min, respectively.

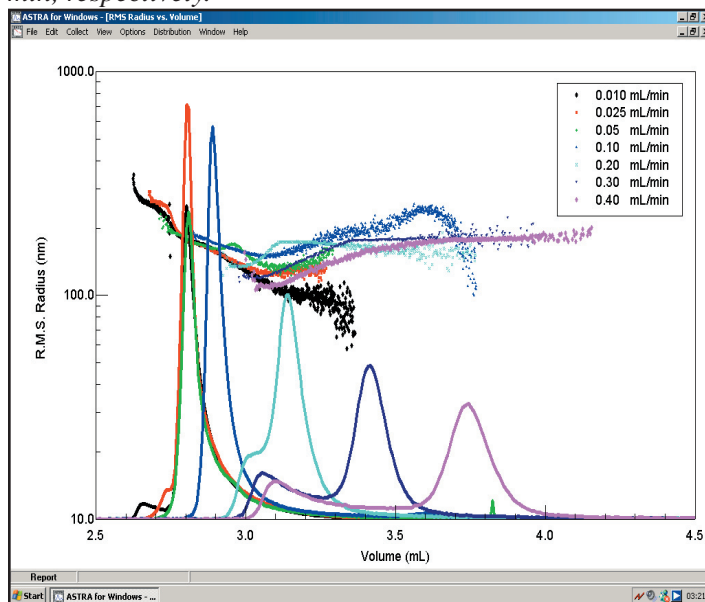
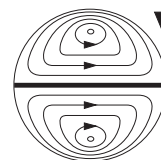


Figure 2. R_g values as a function of V_e for PS10M obtained at flow rates of 0.010, 0.025, 0.05, 0.10, 0.20, 0.30, and 0.40 mL/min, respectively. The lines are the Rayleigh ratios of polymer at scattering angle of 90° at each V_e .

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