Determining the *∂n/∂c* of a Polymer Using the EcoSEC® GPC System

Introduction

Concentration sensitive detectors, such as differential refractive index (RI) detectors, are by far the most widely used detection method for polymer analysis by gel permeation chromatography (GPC), as they meet the minimum detection requirements for calculation of molar mass averages and distributions using peak position calibration curves. In general, concentration sensitive detectors measure the concentration of analyte at each slice eluting from the GPC column(s). In single detector GPC experiments the molar mass averages and distributions of a polymer sample are obtained using a relative or peak-position calibration curve based on the retention time of the peak apexes of the chromatograms for a series of linear, narrow polydisperse standards of known molar mass and chemistry. In multi-detector GPC experiments, such as those using multi-angle light scattering (MALS) or viscometry detectors, a concentration sensitive detector is also needed as concentration of the analyte at each slice eluting from the GPC column(s) is required for molar mass related calculations.

Multi-detector GPC experimental set-ups that include RI and MALS detectors also require a prior knowledge of a factor known as the specific refractive index increment (*∂n/∂c*) for absolute molar mass calculations. The *∂n/∂c* is the change in refractive index of a solution with respect to changes in the concentration of the solution, for a given analyte at a specified wavelength and solvent-temperature conditions. In other words, the *∂n/∂c* describes how sensitive the refractometer will be at measuring changes in the concentration of a particular analyte, as the RI detector response is proportional to both the concentration of dissolved analyte, *c*, and the *∂n/∂c*:

$$RI \propto c \times \frac{\partial n}{\partial c}$$

Accurate quantification of the *∂n/∂c* is essential for the characterization of polymers as the detector response of both RI and MALS detection are proportional to *∂n/∂c*; $RI \propto c \times \partial n/\partial c$ and, $MALS \propto c \times (\partial n/\partial c)^2$ where *c* is concentration and *M* is molar mass.

The *∂n/∂c* of a sample is typically determined with the RI detector in batch mode (the detector uncoupled from the separation system), by measuring the detector response of a series of accurately known dilute analyte concentrations. In the EcoSEC GPC System a batch mode type experiment is performed by uncoupling only the sample side of the dual flow RI detector from the separation system and then measuring the detector response of a series of accurately known dilute analyte concentrations. The relationship between concentration and RI detector response is linear, thus, the slope of a plot of the differential refractive index (the difference between detector response of the neat solvent and that of each individual concentration) on the ordinate and the concentration of the solutions on the abscissa is equal to the *∂n/∂c*.

∂n/∂c Determination

Experimental Set-up

The *∂n/∂c* was determined for an analyte at a given solvent/temperature condition by using the dual flow RI detector of an EcoSEC GPC System (HLC-8320) (Tosoh Bioscience LLC) in batchmode. The RI detector of an EcoSEC GPC System was uncoupled from the separation system by stopping the sample side pump of the EcoSEC GPC System, discounting the GPC columns and waste lines (which travels across the EcoSEC GPC System), *Figure 1*, and connecting a Razel model A-99EJ syringe pump to the sample side flow path and tubing from the outlet of the RI detector to a waste container, *Figure 2*. The Razel syringe pump was used to inject neat solvent followed by a series of five to nine sample dispersions, ranging in an order of magnitude in concentration, directly into the sample side of the dual flow RI detector, at a flow rate of 0.1 mL/min. The reference side pump of the EcoSEC GPC System remained connected and flowing at a flow rate of 0.1 mL/min. RI data was collected and processed using Wyatt Technology's ASTRA 6.1 software using method 'batch determine dndc'. A DAWN8+ MALS photometer or a ViscoStar Viscometer (both from Wyatt Technology Corporation) was used to collect the RI detector response in the ASTRA 6.1 software. A calibration constant of 2.560×10^{-4} for the EcoSEC GPC System RI detector was used in the ASTRA 6.1 software.

Figure 1. The EcoSEC GPC System tubing to be disconnected for batch mode RI experiments.

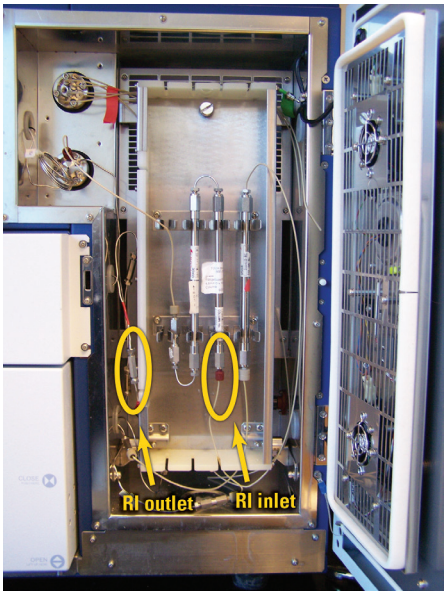

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Figure 2. The EcoSEC GPC System connected for batch mode RI experiments.[a]

[a]A Razel model A-99EJ syringe pump is connected to the sample side flow path and tubing is connected to the outlet of the RI detector and sent to a waste container

Measuring the ∂n/∂c

The *∂n/∂c* is determined for each analyte at a given solvent-temperature condition by injecting five to nine dissolutions of gradually increasing concentrations directly into the sample side of the RI detector in the EcoSEC GPC System using an external syringe pump, starting with neat solvent. An example of the EcoSEC GPC System RI detector response as a function of time for a series of dissolutions of increasing concentrations for a PMMA based resin is shown in *Figure 3*. The first and last plateaus correspond to the neat solvent and are used to determine the baseline, while the ladder-like plateaus correspond to the increase in sample concentration between dissolutions. A *∂n/∂c* plot is then constructed by plotting the differential refractive index (the difference between detector response of the neat solvent and that of each individual dissolution) on the ordinate and the concentration of the dissolution on the abscissa. The slope of this plot is the *∂n/∂c* of the solution. An example of a *∂n/∂c* plot for a PMMA based resin using the EcoSEC GPC System is shown in *Figure 4*.

Figure 3. RI detector response (V), for eight concentrations, ranging from 0.25 to 1.75 g/L, of a PMMA resin in THF at 35 °C and a flow rate of 0.1 mL/min.

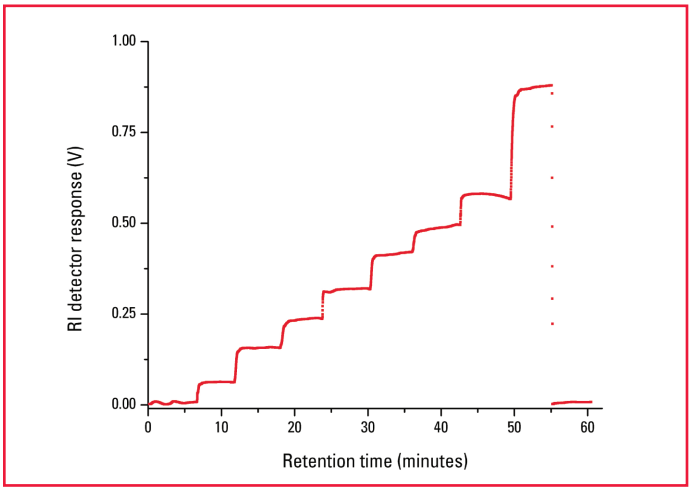
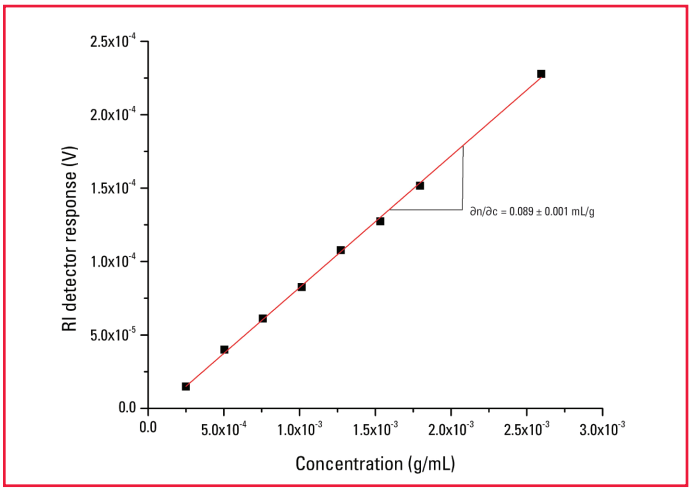


Figure 4. Baseline subtracted RI detector response (V), as a function of concentration for a PMMA resin in THF. The slope of the red line is 0.089 mL/g, the *∂n/∂c* of the sample at the solvent-temperature conditions of the experiment.



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