

Broadening Mechanisms in Size-Based Separations for Polymer Characterization using Superficially Porous Particles

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Size exclusion chromatography (SEC) is one of the most critical tools required for the characterization of polymers, so a better understanding of the fundamental separation mechanisms that occur during SEC can provide information on how the technique may potentially be improved in the future. In this project, band broadening related to longitudinal diffusion is being investigated as a key contributor to performance loss in SEC. Specifically, the effects of longitudinal diffusion on SEC separations of lower molecular weight polymers (under 50 kDa) using new superficially porous particles that consist of a solid particle core and a porous outer shell are being determined. Because of this unique particle morphology, the effective peak broadening that is observed is decreased to fully porous particles, partially because of reductions in longitudinal diffusion. These particle types have been widely used for other chemical separations because of these advantages in chromatographic efficiency, but they have not yet found extensive use in size-based separation mechanisms for polymer compounds.

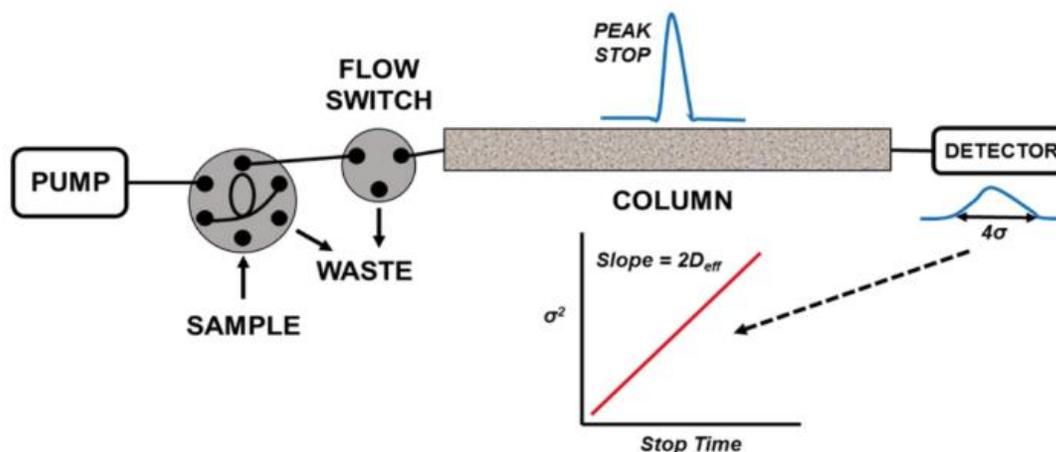


Figure 1. A visualization of the set-up for the stop flow experiments and the general workflow needed to determine the effective diffusion coefficient for a given molecular weight.

To effectively determine the diffusion coefficients of low molecular weight polymer compounds, a stop-flow SEC system was developed (**Figure 1**). For a given polymer size, a sample is injected and width of the polymer peak is calculated after eluting from the column. After this initial width is measured, additional replicate injections are made in a similar fashion, but the flow is stopped for a set time period and then reinitiated to elute the sample off of the column. The stop times used in this study were 0.5 hr, 1 hr, 4 hr, and 8 hr, with the peaks becoming broader as the stop time increases (**Figure 2**). In these experiments, tetrahydrofuran (THF) is used as the mobile phase because it reduces potential interactions between the polymer molecules and particle surface that affect the measurement of band broadening due solely to diffusion. Additionally, the use of THF allows for the calculation of the radius of gyration of the polystyrene standards that are being used, which provides additional information on how a given molecular weight polymer should potentially fit into a given pore size.

Once the various peak widths (and subsequently calculated peak variances) have been determined, the values can be plotted against the various stop times to determine the effective diffusion coefficient of the sample in a given SEC column format, which relates to the magnitude of longitudinal broadening a given polymer will demonstrate (**Figure 3**). Thus far, studies have focused on the use of a column packed with $2.7 \mu\text{m}$ superficially porous particles containing 90 \AA pores, which should be effective for SEC separations of polymers with molecular weights up to 50 kDa. As the project moves forward, comparisons are currently being made to a similar column that contains particles with 160 \AA pores, which extends this molecular weight range up to approximately 100 kDa. In both column formats, the key factor that is being determined is the “obstruction factor”, which is a scalar factor that describes how diffusion

of these molecules is affected by the presence of the chromatographic packing materials in the column. Specifically, for this molecular weight range of polymers, the effect of the pore size on the obstruction factor is being determined.

Thus far, the project has been led by two undergraduate students. One of the two students was partially supported by an additional "Summer Undergraduate Research Fellowship" provided through Rowan University, a highly competitive award for research students at the University that he received through his participation in this project. The preliminary results of this work are scheduled to be presented in a poster by these students at the Eastern Analytical Symposium in November 2019, with further work continuing on through the 2019-2020 academic year. Both students involved with this project are currently planning on pursuing doctoral studies in chemistry based on their experience with research obtained through this project.

This work has also had an impact of the greater research progress of the PI. Related projects on measuring band broadening of other large molecules (typically biomolecules such as proteins) have expanded based on the research capabilities that were increased through this project. Additionally, other modes of chemical separations that have potential use for polymers such as supercritical fluid chromatography (SFC) have become more widely used based on improvements to research infrastructure.

These infrastructure improvements also enabled the successful pursuit of funding through the National Science Foundation focused on SFC.

In the second year of this PRF project, the data set for a 160 Å pore size column will be completed and the use of a hybrid pore size column will be explored, with results of these comparisons developed into a manuscript. Additionally, modifications to the instrument depicted in **Figure 1** will be made to enable the measurement of broadening effects due to polymer dispersity, another effect that can potentially limit the efficiency of size-based characterization of polymer materials.

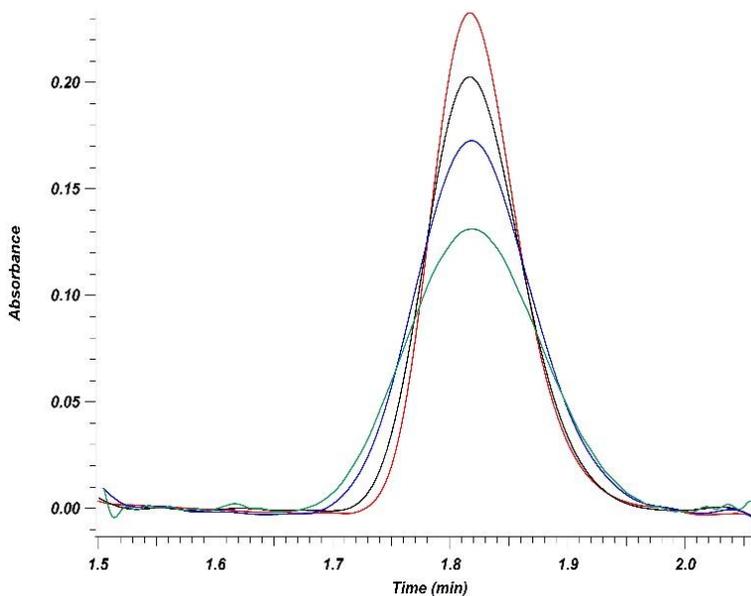


Figure 2. A collection of peaks of the 4.9 kDa polystyrene sample at different stop times including 0 min (red), 60 min (black), 240 min (blue), and 480 min (green).

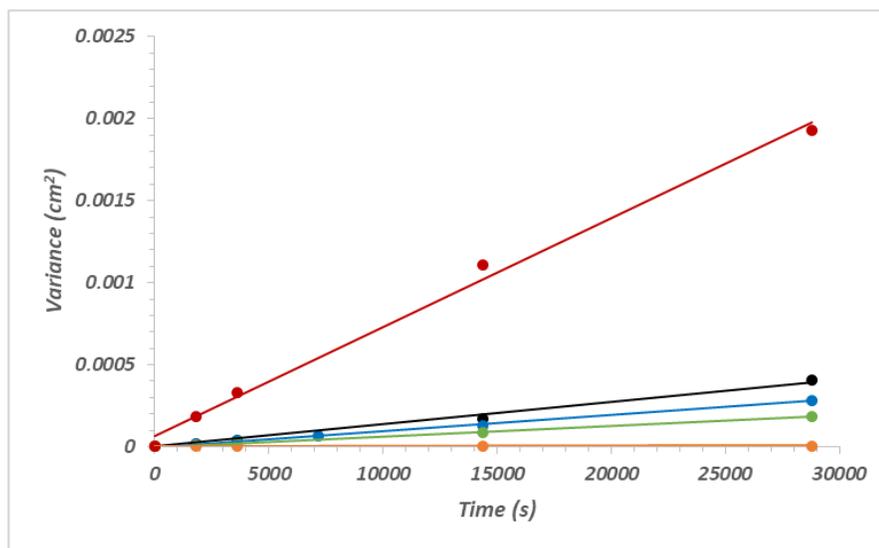


Figure 3. A collection of calibration curves of variance against stop times of varying molecular weights on the 90 Å column, including toluene (red), 1.9 kDa (black), 4.9 kDa (blue), 13 kDa (green) and 27 kDa (orange).