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### Introduction

Polyphenylene Sulfide (PPS) has attracted a considerable amount of interest in the polymer industry due to its high tensile strength, dimensional stability, flame resistance, and excellent stability in organic liquids.<sup>1</sup> PPS is an engineered polymer with a rigid backbone of aromatic rings linked by sulfur atoms. The molecular structure of PPS makes the material useful for a number of applications, including filter fabrics, felts for paper making, ball valves, electrical sockets, and optical fiber cables. One of the main characteristics of PPS is its high resistance to chemical and thermal attacks, thus making PPS a useful structural material.

The same characteristics that make PPS an ideal polymer for various applications also hinder the ability to characterize the polymer, as it has very limited solubility. PPS is virtually insoluble in most organic solvents at ambient temperatures and thus can only be characterized in the solid state or by using elevated temperatures. The limited solubility of PPS makes it very difficult to determine properties such as molar mass averages and molar mass distributions. Traditionally, PPS has been characterized by infrared spectrometry and thermal analysis methods.<sup>2</sup> One method which can also be used to characterize PPS is high temperature gel permeation chromatography (GPC) as PPS is soluble in 1-chloronaphthalene (1-CN) at extremely elevated temperatures (> 200 °C).

The ability to characterize the molar mass averages and distributions of PPS is essential as these properties play a vital role in the determination of mechanical, bulk and solution properties of the processing and end-use properties of a given material. For polymers which are used in textiles, such as PPS, the molar mass averages and distributions determined by high temperature GPC are a good tool for failure analysis investigations. Analysis of PPS using high temperature GPC is traditionally difficult as the analysis must be performed in 1-CN at 220 °C. 1-CN is a difficult solvent to use for analytical experiments as the solvent degrades over time and can cause havoc for detection methods such as refractive index. Here we have used the EcoSEC High Temperature GPC System encompassing a dual flow refractive index detector (RI) to determine the molar mass averages and molar mass distribution of two PPS samples that were exposed to different environments.

### Experimental Conditions

Sample analysis was performed on a system consisting of an EcoSEC High Temperature GPC System (HLC-8321 GPC/HT) equipped with a RI detector. Separation of unfiltered 300 µL injections occurred over a column bank consisting of two 7.8 mm ID × 30 cm, 13 µm particle size TSKgel® GMH<sub>HR</sub>-H(S) HT2 columns (exclusion limit  $4 \times 10^8$  g/mol) (PN 22889) (Tosoh Bioscience LLC) followed by the corresponding guard. The mobile phase and solvent were 1-CN (Fisher) at a flow rate of 1.0 mL/min. Solvent reservoir and pump oven were maintained at 40 °C. Detector, auto injector and column oven were maintained at 220 °C. Two polyphenylene sulfide (PPS) felt samples were provided by Inovatia Laboratories (Fayette, MO). The polymer samples were dissolved in 1-CN at 220 °C and shaken for two hours using the Tosoh Bioscience sample prep system (PN 23801). The final sample concentrations were approximately 2.0 g/L. Data was processed with the EcoSEC GPC Workstation software.

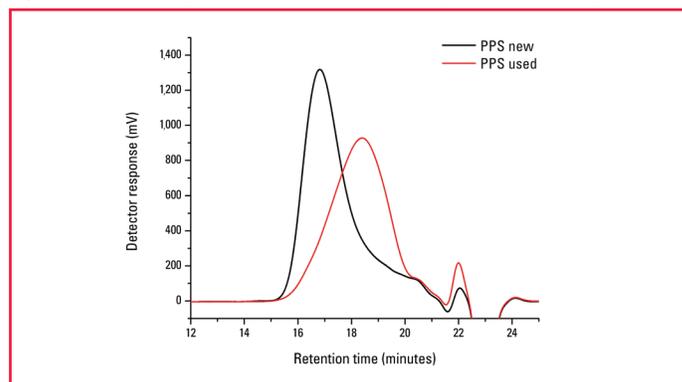
Molar mass averages were determined for each polymer sample using a calibration curve. A calibration curve for each column set was created for the RI detector at 220 °C using Tosoh polystyrene standards, ranging in molar mass from 1,050 to  $2.11 \times 10^6$  g/mol (Tosoh Bioscience LLC). Calibration curve data for polystyrene standards in 1-CN at 220 °C at a flow rate of 1.0 mL/min was fitted with a cubic function and error values were less than 5%.

### Results and Discussion

As mentioned in the "Introduction and Experimental" sections, an EcoSEC High Temperature GPC System encompassing a dual flow refractive index detector was used for a material failure investigation. The molar mass averages and molar mass distributions of two PPS samples, one new and one used, were determined via GPC/RI. The new and used PPS materials were shown to have significant differences when analyzed by GPC/RI. The polystyrene relative molar mass averages, molar mass distributions, and GPC elution profiles of the new and used materials were compared to determine if usage of the PPS sample played a role in the failure of the product.

The GPC chromatograms of the new and used PPS samples as monitored by RI are shown in *Figure 1*. The new PPS sample elutes prior to the used PPS sample. The shorter retention time of the new PPS sample indicates that the new PPS sample is larger in polymeric size than the used PPS sample; as the elution order in GPC is that of an "inverse-sieving" technique, larger analytes sample a smaller pore volume than smaller analytes resulting in the larger analytes eluting from the GPC column prior the smaller analytes. The GPC chromatogram for the used PPS sample is shifted considerably towards the longer retention time, smaller polymeric size, compared to that of the new PPS sample. Thus, the GPC chromatograms alone provide sufficient evidence that the use of the PPS sample has resulted in a decrease in polymeric size within the sample; possibly causing the failure of the product when in use for a predetermined amount of time.

**Figure 1.** GPC elution profile of new and used PPS samples as monitored by RI



The new and used PPS samples can also be compared for failure investigation through their polystyrene relative molar mass averages. As seen in [Table 1](#), the new PPS sample was determined to have a higher number-, weight-, and z-average molar mass than the used PPS sample. Differences observed in the molar mass averages is important in any product failure investigation as the molar mass averages dictate the end-use properties of a products, such as tensile strength, elongation, brittleness, hardness, toughness, etc. The approximately 20 to 50% decrease in the molar mass averages observed between the new PPS and the used PPS is potentially enough evidence to determine that after a predetermined amount of time the end-use product(s) made with this PPS sample will begin to fail or will no longer be able to perform to standards.

**Table 1.** Molar mass averages and polydispersity index of new and used PPS samples via GPC/RI

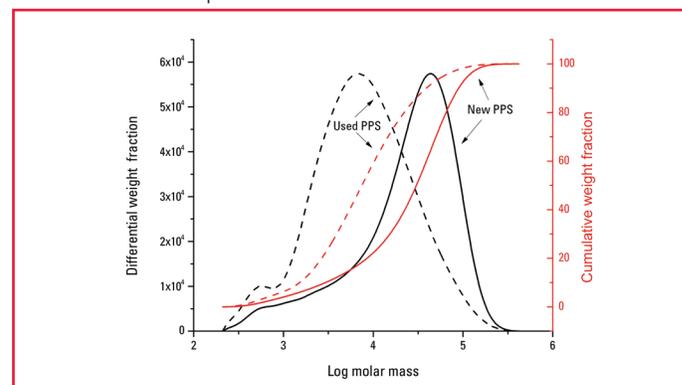
| Sample   | $M_n$ (g/mol) | $M_w$ (g/mol)      | $M_z$ (g/mol)      | $PDI$ |
|----------|---------------|--------------------|--------------------|-------|
| PPS new  | 5,790         | $3.91 \times 10^4$ | $7.19 \times 10^4$ | 6.746 |
| PPS used | 3,176         | $1.62 \times 10^4$ | $5.54 \times 10^4$ | 5.106 |

<sup>a</sup>  $PDI = M_w/M_n$

The differences in the molar mass averages observed between the new and the used PPS samples can also be observed through the molar mass distributions, *MMD*. The *MMDs* of both the new and used PPS samples, as determined using polystyrene relative calibration curves from GPC/RI, are shown in [Figure 2](#). The new PPS sample *MMD* extends significantly further in the high and low molar mass directions than the used PPS sample. The used PPS sample has a considerably higher quantity of low molar mass species than the new PPS sample. The decreased breadth of the molar mass distribution of the used PPS sample compared to the new PPS sample can also be seen through the polydispersity index values, *PDI*, given in [Table 1](#). The *PDI* of the new PPS sample is 25% greater than that of the used PPS, an indication that usage of the PPS results in a significant change in the molar mass distribution of the product.

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**Figure 2.** Overlay of cumulative and differential molar mass distribution of new and used PPS samples



## Conclusions

The EcoSEC High Temperature GPC System with a dual flow refractive index detector was used to perform failure analysis on two PPS samples, one new and one used. GPC/RI analysis was successfully performed using 1-CN at 220 °C using the EcoSEC High Temperature GPC System. The new and used PPS samples were compared via GPC chromatograms and polystyrene relative molar mass averages and distributions. The new PPS sample was determined to have a higher molar mass, broader molar mass distribution and a larger polymeric size than the used PPS sample. Using the PPS sample for a predetermined amount of time appears to decrease the molar mass averages and polymeric size of the polymer. The use of GPC/RI for the failure investigation of PPS allowed for immediate differentiation between the new and used PPS samples based on the GPC/RI elution profile, which was then confirmed through differences in the polystyrene relative molar mass averages and molar mass distributions. The dual flow refractive index design of the EcoSEC High Temperature GPC System permitted the analysis of PPS in a traditionally difficult solvent system for GPC analysis, 1-CN at 220 °C.

## References

- <sup>1</sup>Park, L.S.; Oh, H.S.; Lee, T. H.; Kim, S.H.; Hwang, J.S. *J. Ind. Eng. Chem.*, **2000**, 6, 331-337.
- <sup>2</sup>Zhang, L.; Zhang, C.; Shi, T. *Adv. Mater. Res.* **2010**, 139, 661-665.



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