

Characterization of a Conducting Polymer using the EcoSEC® High Temperature GPC System

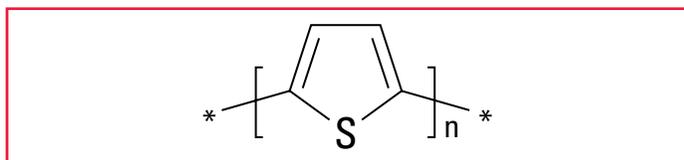
EcoSEC High Temperature GPC System APPLICATION NOTE

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Introduction

Conducting polymers, such as polythiophenes (Figure 1), have been widely investigated over the past several decades due to their potential industrial applications based on their conductivity and organic light-emitting capability. Polythiophenes and their derivatives have recently become of growing interest as they have shown promise in electronic and optical applications, such as organic transistors and solar cells. Polythiophenes are polymerized thiophenes, i.e. the polymer backbone contains sulfur heterocycle that become conductive when electrons are added or removed through doping. To date polythiophenes have been used in the development of electronics, energy storage batteries, photochromic devices, and nonlinear optical devices. Due to the electron-rich character of the thiophene ring, polythiophenes can be easily and reversibly oxidized by chemical and electrochemical means to form highly conducting materials.^{1,2}

Figure 1. Example of monomer repeat unit of polythiophene



The heavy focus on synthesis of conducting polymers facilitates the need for characterization methods. Among the methods employed for the characterization of the intermediates and final conducting polymers are FT-IR, NMR, gel permeation chromatography (GPC), and microscopy. Some conducting polymers have limited solubility, thus require the use of a method such as high temperature GPC for determination of the molar mass averages and molar mass distributions. Similar to other polymers, the molar mass averages and molar mass distributions of conducting polymers play a role in determining the end-use properties of the polymer's applications. 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 conjugated polymers similar to polythiophenes.

Experimental

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 μ L injections occurred over a column bank consisting of two 7.8 mm ID \times 30 cm, 13 μ m particle size TSKgel GMH_{HR}-H(S) HT2 columns (exclusion limit 4 \times 10⁸ g/mol) (PN 22889) (Tosoh Bioscience LLC) followed by the corresponding guard. The mobile phase and solvent were 1,2,3-trichlorobenzene (TCB) (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 145 °C. Two conducting polymers similar to polythiophene were dissolved in TCB at 145 °C and shaken for one hour using the Tosoh Bioscience sample prep system (PN 21914). 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 was created for the RI detector at 145 °C using Tosoh polystyrene standards, ranging in molar mass from 1,010 to 5.48 \times 10⁶ g/mol (Tosoh Bioscience LLC). Calibration curve data for polystyrene standards in TCB at 145 °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 the characterization of two conducting polymers similar to polythiophene. Macromolecular properties such as molar mass and relative polymer size are important as conducting polymers such as polythiophenes are finding use in solar cell and electrical based applications. The polystyrene relative molar mass averages and molar mass distributions of two conducting polymers similar to polythiophene were determined via GPC/RI and can be compared to determine if there is a difference between macromolecular properties, and thus end-use properties, of the two different polythiophene-like conducting polymers synthesized through different mechanisms.

The polystyrene relative number-, weight-, and z-average molar mass values, M_n , M_w , and M_z , respectively, are given in Table 1. All three molar mass averages were determined to be greater for Polymer A than Polymer B. The variation between the molar mass averages of the two conducting polymers may be enough to change the conductivity of the polymers, thus their end-use applications. Differences observed in molar mass averages, as well as distribution, are important as they affect the applicable uses of a conductive polymer.

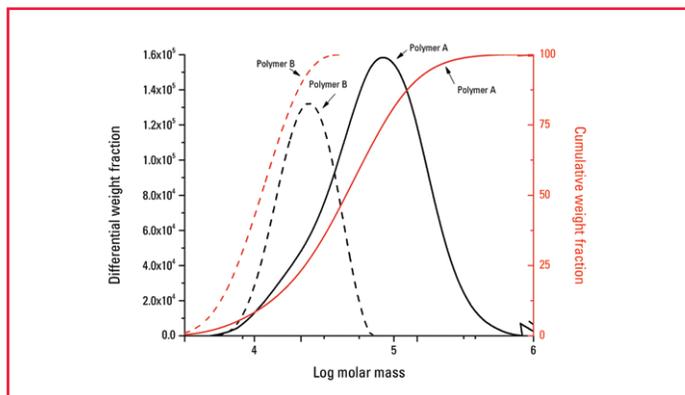
Table 1. Molar mass averages and polydispersity index of two conducting polymer samples via RI

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)
Polymer A	2.58×10^4 $\pm 0.01 \times 10^4$	6.51×10^4 $\pm 0.02 \times 10^4$	1.34×10^5 $\pm 0.03 \times 10^5$
Polymer B	9.39×10^3 $\pm 0.01^a \times 10^3$	1.26×10^4 $\pm 0.04 \times 10^4$	1.60×10^4 $\pm 0.01 \times 10^4$

^a Standard deviation from two injections

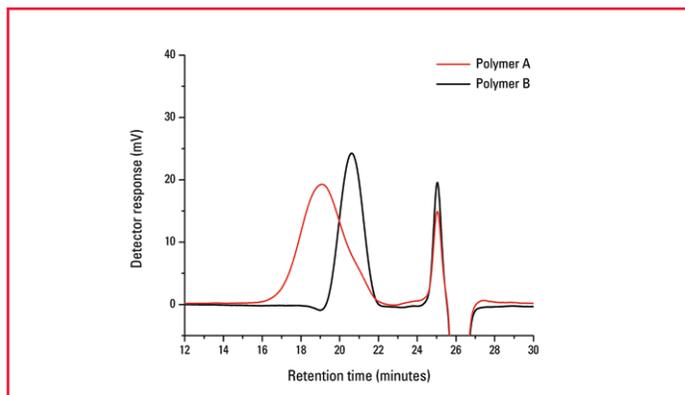
In addition to the molar mass averages, the molar mass distribution, *MMD*, can also influence various properties of conducting polymers. The molar mass distributions of the two conducting polymers, as determined using polystyrene relative calibration curves from GPC/RI, are compared in Figure 2. The molar mass distribution of Polymer A is significantly larger than that of Polymer B, as the *MMD* for Polymer A extends further in the high molar mass region compared to that of Polymer B. Additionally, the difference in the molar mass distributions between the two conducting polymers can be seen through the polydispersity index value for Polymer A and Polymer B and were determined to be 2.58 and 1.33, respectively.

Figure 2. Overlay of cumulative and differential molar mass distribution of two conducting polymer samples



Information regarding the difference between the two conducting polymers can be seen by comparing their GPC elution profiles, **Figure 3**. The shift in GPC retention time amongst the two conducting polymers indicates a variation in polymeric size between the two conducting polymers, as elution order in GPC is that of an “inverse-sieving” technique, large analytes sample a smaller pore volume than smaller analytes resulting in larger analytes eluting from the GPC column prior to the smaller analytes. The GPC chromatogram of Polymer A is shifted considerably towards a longer retention time, thus smaller polymer size, compared to that of Polymer B. Thus, based on the GPC elution profile Polymer A is significantly larger in polymeric size than Polymer B.

Figure 3. GPC elution profile of two conducting polymer samples as monitored by RI



Conclusions

The EcoSEC High Temperature GPC System with dual flow refractive index detector was used to characterize two conducting polymers similar to polythiophene. GPC/RI was successfully performed to determine the polystyrene relative molar mass averages and molar mass distributions of the two conducting polymers. Polymer A was determined to have significantly higher molar mass averages as well as a larger molar mass distribution than Polymer B. The GPC/RI chromatogram also provided evidence that the polymeric size of Polymer A is greater than that of Polymer B. The use of GPC/RI for the comparison of two conducting polymers similar to polythiophene allows for an immediate differentiation between the two samples based on the GPC/RI elution profiles as well as the polystyrene molar mass averages and molar mass distributions. The EcoSEC High Temperature GPC System encompassing a dual flow refractive index detector provides an efficient and reliable method for determining several macromolecular properties which influence the end-use applications of conducting polymers.

References

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