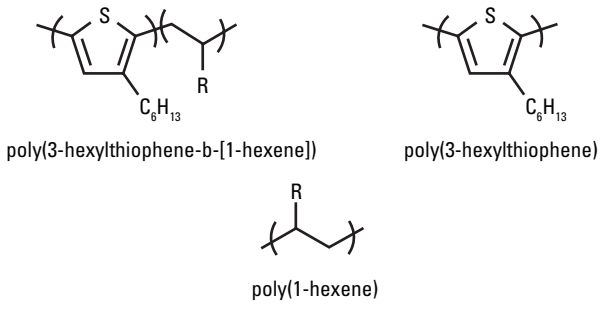
Analysis of gradient copolymers using the EcoSEC® GPC System

EcoSEC GPC System
APPLICATION NOTE

Introduction

Gradient sequence copolymers are novel materials which have provoked interest due to their unique properties compared to their random, alternating and block equivalents. Unlike block copolymers which have an abrupt change in sequence, gradient sequence copolymers exhibit a gradual change in co-monomer composition from one type of monomer to another. An example of a gradient copolymer is poly(3-hexylthiophene-b-[1-hexane]), *Figure 1*, which is composed of poly(3-hexylthiophene) and poly(1-hexene).

Figure 1.



Applications of these materials include making phase-separated polymer blends more compatible, impact dampeners and reinforcements[1]. π-conjugated gradient copolymers can affect the phase separation in polymer/polymer and polymer/fullerene blends. Therefore, the gradient copolymers must be characterized carefully and a need for a method to determine molar mass averages and molar mass distributions of these polymers is crucial. A common way to characterize gradient copolymers is gel permeation chromatography (GPC). Here, we report the use of an all-inclusive GPC system, the EcoSEC GPC system for the analysis and differentiation of the molar mass averages and distributions of a gradient sequence π-conjugated block copolymer and its monomers.

Experimental

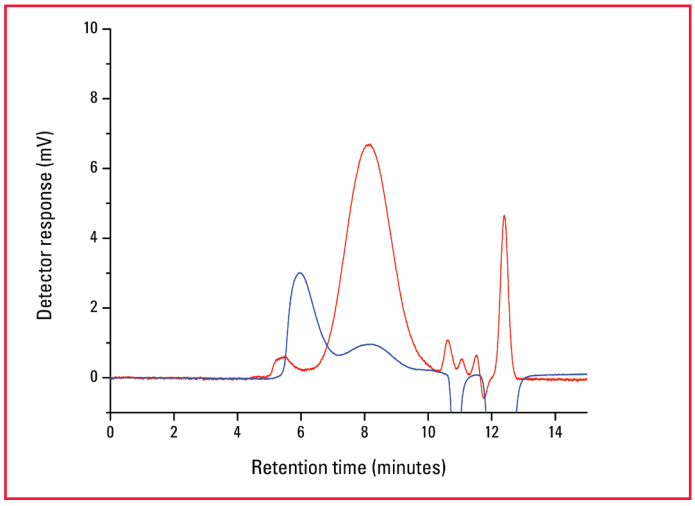
Sample analysis was performed on a system consisting of an EcoSEC GPC System (HLC-8320) equipped with a dual flow RI detector and UV detector. The UV absorbance was monitored at 254 nm and 350 nm. Separation of unfiltered 10 µL injections occurred over a column bank consisting of two TSKgel semi-micro SuperMultipore GPC columns and two TSKgel® semi-micro mixed bead GPC columns. The mobile phase and solvent was THF (BDH) at a flow rate of 0.350 mL/min. Detector, pump oven, and column oven were maintained at 40 °C. For all chromatographic determinations, results are averages of three injections. Data was processed with the EcoSEC GPC Workstation Software, version 1.08.

The molar mass and molar mass distributions of poly(3-hexylthiophene-b-[1-hexane]), poly(3-hexylthiophene) and poly(1-hexene) were determined based on a polystyrene calibration curve. The calibration was created for the RI and UV (254 nm) at 40 °C using PS standards (Tosoh Bioscience) with a molar mass ranging from 500 to 7.0×10^5 g/mol. Calibration curve data at 0.35 mL/min was fitted with a cubic function for the SuperMultipore column set and a linear function for the mixed-bed columns. All error values were less than 5%.

Results and Discussion

The ability to characterize the molar mass averages and distributions of a π-conjugated gradient copolymer is critical for designing polymer blends as molar mass averages and distributions affect the phase separation of polymer blends. An EcoSEC GPC System housing a dual flow refractive index detector was used to perform gel permeation chromatography analysis on poly(3-hexylthiophene-b-[1-hexane]), poly(3-hexylthiophene) and poly(1-hexene). The GPC chromatograms of the copolymer, poly(3-hexylthiophene-b-[1-hexane]), and the two monomers, poly(3-hexylthiophene) and poly(1-hexene), as monitored by the dual flow RI detector and the UV detector, are shown in *Figures 2-4*, respectively. The copolymer, poly(3-hexylthiophene-b-[1-hexane]), displays a distinctive bimodal distribution while the two monomers have a mono-modal distribution. As seen in *Figures 2-4*, by comparing the retention times of the RI detector response for the three samples the later eluting species seen in *Figure 2* has the same retention time as the monomer, poly(3-hexylthiophene), in *Figure 3*. The early eluting species seen in *Figure 2* elutes later than that of the other monomer, poly(1-hexene) *(Figure 4)*, an indication that the later elution species in *Figure 2* is that of the copolymer. The copolymer elutes prior to the monomers is an indication that the copolymer is larger in polymeric size than the monomers; 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 to the smaller analytes.

Figure 2. GPC elution profile of the copolymer, poly(3-hexylthiophene-b-[1-hexane], as monitored by the RI (blue) and UV (red).



The number, weight, and *z*-average molar masses, M_n, M_w, and M_z, as determined using both RI and UV via a polystyrene calibration curve are shown in *Tables 1 and 2*, respectively. The identity of the two components of the bimodal distribution of the GPC elution profile of the copolymer, poly(3-hexylthiophene-b-[1-hexane]), is also supported in the comparison of the molar mass averages of copolymer to that of the two monomers. The molar mass of the later eluting species of the copolymer has molar mass averages similar to that of the monomer, poly(3-hexylthiophene). The early eluting species of the copolymer has molar mass averages and a molar mass distribution greater than that of either of the monomers; an indication that through the synthesis a copolymer was made with a greater molar mass than that of the two monomers.

Figure 3. GPC elution profile of monomer, poly(3-hexylthiophene), as monitored by the RI (blue) and UV (red).

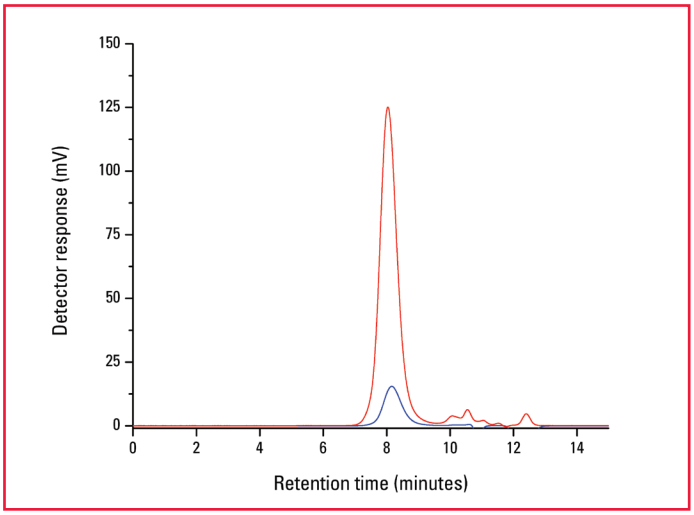


Figure 4. GPC elution profile of monomer, poly(1-hexene), as monitored by the RI (blue).

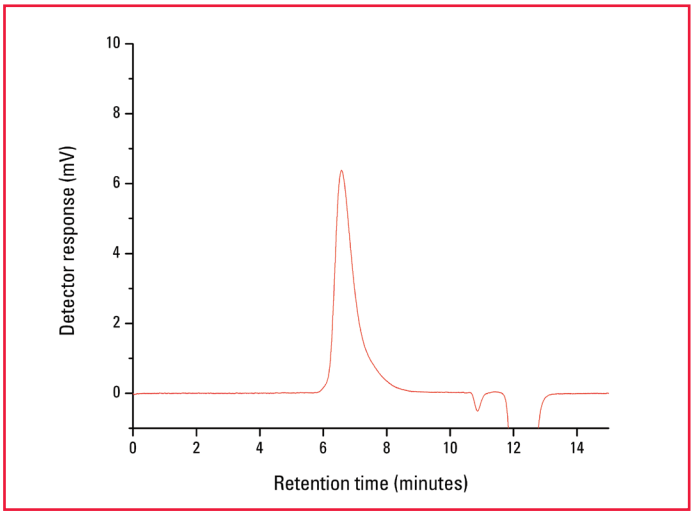


Table 1. Molar mass averages and polydispersity index of copolymer and monomer as determined based on RI calibration.

Sample	M_n	M_w	M_z	PDI[a]
poly(3-hexylthiophene-b-[1-hexane]	3.46×10^5 6.43×10^3	5.12×10^5 2.58×10^4	6.81×10^5 4.75×10^4	1.48 3.88
poly(3-hexylthiophene)	1.65×10^4	2.03×10^4	2.42×10^4	1.26
poly(1-hexene)	1.24×10^5	1.79×10^5	2.21×10^5	1.45

Table 2. Molar mass averages and polydispersity index of copolymer and monomer as determined based on UV calibration.

Sample	M_n	M_w	M_z	PDI[a]
poly(3-hexylthiophene-b-[1-hexane]	8.26×10^5 8.76×10^3	1.08×10^6 2.69×10^4	1.35×10^6 6.48×10^4	1.31 3.08
poly(3-hexylthiophene)	1.70×10^4	2.06×10^4	2.44×10^4	1.21

Conclusions

A copolymer intended to be used in polymer/polymer and polymer/fullerene blends was characterized based on the polystyrene relative molar mass averages and distributions as obtained by gel permeation chromatography using the EcoSEC GPC System with both an RI and UV detector and semi-micro TSKgel GPC columns. Through the comparison of the GPC elution profiles and the molar mass averages of the copolymer, poly(3-hexylthiophene-b-[1-hexane]), and the two monomers, poly(3-hexylthiophene) and poly(1-hexene) it can be concluded that the copolymer sample, poly(3-hexylthiophene-b-[1-hexane]), contains copolymer and excess amounts of one of the monomers, poly(3-hexylthiophene). The GPC elution profiles and molar mass averages of the copolymer and monomer were obtained in less than fifteen minutes with the use of the EcoSEC GPC System and TSKgel semi-micro GPC columns, thus providing a fast and reliable method for the analysis of copolymers.

References

[1]Palermo, E. F., McNeil, A. J. in Lutz, J. F., Meyer, T. Y., Ouchi, M., Sawamoto, M., Eds.; ACS Symposium Series 1170; American Chemical Society: Washington, DC, 2014; pp 287-299

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