Molar Mass Determination of a Synthetic Rubber Resin via Single-, Dual- and Triple-Detector Gel Permeation Chromatography

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Introduction

Natural and synthetic rubbers are key components to many applications, *e.g.* clothing, vehicles, toys, fire arms, etc. Currently synthetic rubbers constitute 75% of all rubber consumption worldwide. Due to the high consumption of synthetic rubber and synthetic rubber products, it is critical to understand the relationship between molecular structure and physical properties, as these properties directly affect how useful products perform under a variety of demanding end-use conditions. The molecular characteristics of greatest significance for the physical properties of synthetic rubbers are considered to be the nature of the monomer units, molar mass, cross-linking, chain structure, and chain branching.[1] The ability to characterize the molecular properties of rubber compounds present analysts with one of their most difficult challenges, as compounds may contain over 15 different ingredients,[2] some in very low concentrations, and analysis goals can range from quality control to reverse engineering to failure analysis.

The most preeminent technique analysts use for the characterization of physicochemical properties of natural and synthetic rubbers is gel permeation chromatography (GPC). One of the advantages of GPC is that it can be used to provide molar mass averages and molar mass distributions of both the raw polymers used in the rubber product and the final compounded product. Traditionally, single-detector GPC systems encompassing a refractive index detector (RI) has been used to determine polystyrene relative molar mass averages.[2] The developments and advances in dual- (RI and differential viscometry [VISC]) and triple- (RI, VISC, and multi-angle light scattering [MALS]) detector GPC systems over the past twenty years has resulted in the increased use of multi-detector GPC systems for the determination of "absolute" molar mass averages, as a single-detector GPC system can easily be expanded to a dual- or triple-detector GPC system with the addition of external VISC and MALS detectors.

Here we demonstrate the expansion of the EcoSEC GPC System, equipped with a dual flow RI detector for single-detector GPC experiments, to a dual- and triple-detector GPC system encompassing external VISC and MALS detectors for multi-detector GPC experiments. The multiplicity of detector combinations allows for the determination of the molar mass averages and distributions and various other polymer parameters, *e.g.* radius of gyration, viscometric radius, and intrinsic viscosity, of a synthetic rubber via three independent modes: (1) polystyrene relative calibration curve (GPC/RI), (2) universal calibration curve (GPC/RI/VISC), and (3) absolute molar mass (GPC/RI/VISC/MALS).

Experimental Conditions

Single-detector GPC analysis was performed using the EcoSEC GPC System (HLC-8320) equipped with a refractive index detector (RI) (Tosoh Bioscience LLC). Dual- and triple-detector GPC analysis was performed by either coupling in parallel an ETA-2010 Viscosity detector (Polymer Standards Service) or a SLD 7000 Light Scattering Photometer (Polymer Standards Service) and an ETA-2010 Viscosity detector (Polymer Standards Service) to the EcoSEC GPC System mentioned above.

Separation of unfiltered 25 µL injections occurred over a column bank consisting of three 4.6 mm ID × 15 cm, 6 µm particle size TSKgel® SuperMultiporeHZ-H columns (separation range ~1,000 to $1.0 × 10^7$ g/mol, exclusion limit $4.0 × 10^7$ g/mol) (Tosoh Bioscience LLC). The mobile phase and solvent were tetrahydrofuran (THF) (Fisher Chemical) at a flow rate of 0.35 mL/min. Detector, pump oven, and column oven were maintained at 35 °C. The synthetic rubber resin sample was prepared by diluting the sample in THF for a final concentration of ~1.6 to 2.6 g/L and left to sit for 3 hours before analysis was performed. All chromatographic determinations are averages of six injections from two separate sample dissolutions. Data was processed with WinGPC® Unity software version 7.4.0.

Molar mass averages obtained from single-detector GPC experiments were determined based on a polystyrene relative calibration curve created from PStQuick Kit MP-H polystyrene mix standard (Tosoh Bioscience LLC) ranging in molar mass from 1,110 to $5.5 × 10^6$ g/mol under the same experimental conditions as sample analysis. The calibration curve data was fitted with a linear function and error values were less than 6%. Molar mass averages from dual-detector GPC experiments were determined based on an universal calibration curve created using ten polystyrene standards (Tosoh Bioscience LLC) ranging in molar mass from $1.0 × 10^4$ to $6.8 × 10^6$ g/mol under the same experimental conditions as sample analysis, *Figure 1*. The universal calibration curve data was fitted with a linear function and had a R^2 value of 0.999. For triple-detector GPC experiments the normalization of SLD 7000 Light Scattering Photometer and calculation of interdetector delays were performed using a virtually monodisperse polystyrene standard with a molar mass of $9.6 × 10^4$ g/mol (Tosoh Bioscience LLC). All MALS data were fitted using the Debye model for data from seven different angles ranging from 35° to 145°. The specific refractive index increment ($\partial n/\partial c$) value of the synthetic rubber resin sample was determined previously to be 0.118 mL/g.

Figure 1. Universal calibration curve for ten polystyrene standards ranging in molar mass from $1.0 × 10^4$ to $6.8 × 10^6$ g/mol
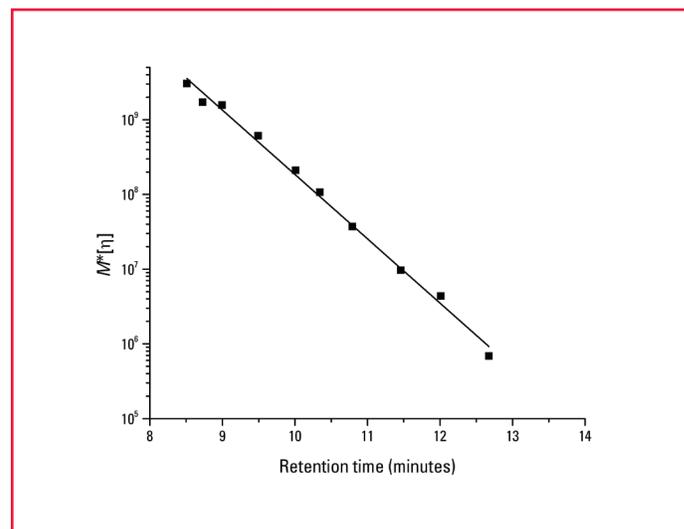
Results and Discussion

The molar mass averages of a synthetic rubber resin sample were determined using three independent methods: (1) polystyrene relative calibration via single-detector GPC, (2) universal calibration via dual-detector GPC and (3) absolute detection via triple-detector GPC. In general, the three methods are expected to provide different values for the molar mass averages and molar mass distributions as each method is dependent on different parameters and involves various assumptions. Molar mass averages obtained via single-detector GPC using calibrant-relative calibration are dependent on the chemistry and architecture of both the standards used to construct the curve and the analyte under analysis. Relative calibration curves are quite precise, but their accuracy is only good when the chemistry and architecture of the analyte are identical to those of the calibration standards.[3] Molar mass averages obtained via universal calibration are considered to be absolute in nature, that is independent of chemistry and architecture, but are dependent on solvent and temperature conditions. Universal calibration curves can be constructed using standards of chemistry and/or architecture different from those of the analyte under analysis, since the calibration is based on the product of the molar mass, M, and the intrinsic viscosity, $[\eta]$, of the polymer sample. Molar mass averages obtained via multi-angle light scattering are absolute in nature, as they are independent of solvent and temperature conditions and calibration curves are not required to obtain quantitative information.

The molar mass averages and polydispersity index as obtained by the three methods mentioned above are given in *Table 1*. As mentioned previously the molar mass averages as determined by the three different methods are not expected to be equal. As seen in *Table 1* the molar mass averages, M_n, M_w, and M_z, using all three methods are in fair agreement with one another. The similarity between the molar mass averages obtained via absolute detection (MALS) and the various calibration methods could be a result of several factors. The chemistry and architecture of the synthetic rubber resin may be fairly similar to that of the standard used for the calibrant-relative calibration (linear polystyrene) making the calibrant-relative calibration data more accurate. Additionally, the solvent and temperature conditions used for sample analysis may be classified as "good" thus increasing the reliability of the universal calibration. The molar mass polydispersity is also in agreement amongst the three methods as $PDI > 1$, an indication that the synthetic rubber resin is polydisperse with respect to molar mass.

Table 1. Molar mass averages and polydispersity index of a synthetic rubber resin obtained via GPC/RI, GPC/RI/VISC and GPC/RI/VISC/MALS.

Detection Method	M_w (g/mol)	M_n (g/mol)	M_z (g/mol)	PDI^a
Single-detector GPC (GPC/RI)	1.185×10^5 $\pm\ 0.006^b \times 10^5$	4.265×10^5 $\pm\ 0.031 \times 10^5$	7.657×10^5 $\pm\ 0.024 \times 10^5$	3.60 $\pm\ 0.04$
Dual-detector GPC (GPC/RI /VISC)	1.082×10^5 $\pm\ 0.341 \times 10^5$	4.285×10^5 $\pm\ 0.337 \times 10^5$	9.094×10^5 $\pm\ 0.521 \times 10^5$	3.96 $\pm\ 0.15$
Triple-detector GPC (GPC/RI/VISC/MALS)	1.327×10^5 $\pm\ 0.329 \times 10^5$	4.800×10^5 $\pm\ 0.609 \times 10^5$	9.387×10^5 $\pm\ 0.441 \times 10^5$	3.62 $\pm\ 0.18$

^{a} $PDI = M_w/M_n$; ^{b} Standard deviations from six injections

The GPC chromatograms of the synthetic rubber resin, as monitored by the individual detectors in the triple-detector GPC experimental set-up, are given in *Figure 2*. It should be noted that the GPC chromatograms as monitored by the RI and VISC in single- and dual-detector GPC experiments are comparable to those of the triple-detector GPC experiments. Unlike the single- and dual-detector GPC experiments the triple-detector GPC experiments also allow for the determination of the radius of gyration and its distribution. The radius of gyration was determined to be 33 ± 1 nm with a $PDI = 1.2$. The molar mass and size polydispersity of synthetic rubber resin can also be observed in *Figure 2*, as both the molar mass and radius of gyration, R_G, decrease with increasing elution volume.

Figure 2. GPC elution profile of a synthetic rubber resin as monitored by RI (red), VISC (black) and MALS (green) and molar mass (red) and radius of gyration (green) distrubtions as determined by MALS.
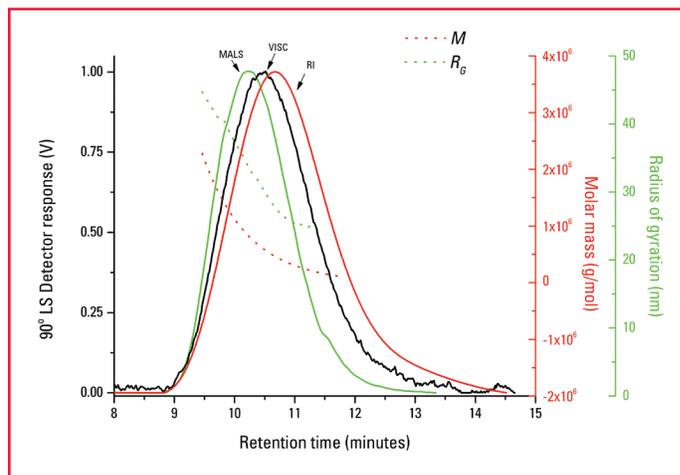
Conclusions

Single-, dual-, and triple-detector GPC experiments were performed using the EcoSEC GPC System encompassing a dual flow refractive index detector coupled either to differential viscometry or differential viscometry and multi-angle light scattering. The molar mass averages of a synthetic rubber resin were determined using three independent methods: (1) polystyrene relative calibration curve (GPC/RI), (2) universal calibration curve (GPC/RI/VISC), and (3) absolute molar mass (GPC/RI/VISC/MALS). A comparison between the three methods showed the molar mass averages and polydispersity of the three methods were in fair agreement with one another. The use of the EcoSEC GPC System in conjunction with VISC and MALS for triple-detector GPC experiments allowed for the characterization of the synthetic rubber resin based on absolute molar mass and polymeric size, providing a more detailed picture of the molecular characteristics and thus the physical properties of the synthetic rubber resin.

References

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