Application Brief

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Characterization of Poly(L-lactide)

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Abstract

Polylactide (PLA) is an amorphous to semicrystalline bio-based polymer, which is used in areas such as in packaging and medical applications due to its biodegradability. Samples of relatively high crystallinity require fluorinated solvents such as hexafluoroisopropanol (HFIP) to enable solubilization. The application brief describes the GPC/SEC characterization of PLA with Agilent PFG columns in HFIP as the mobile phase.

Introduction

PLA (also known as polylactic acid or polylactide) is a bio-based and biodegradable, thermoplastic, semicrystalline aliphatic polyester derived from renewable resources, such as corn starch or sugarcane. Although PLA has been known for more than a century, it has only been of commercial interest in recent years due to its biodegradability.

The repeating unit of PLA, lactic acid, exists in two enantiomeric forms: L- and R-lactic acid. Poly(L-lactide) (PLLA) and poly(R-lactide) are composed of only one of both enantiomers. The stereochemical composition of PLA influences the crystallinity of PLA, which in turn affects the solubility in different solvents. Pure PLLA has a crystallinity of approximately 37%, a glass transition temperature between 50 and 80 °C, and a melting temperature between 173 and 178 °C. PLLA can be processed, like most thermoplastics, into fibers and films.[1]

PLA is sensitive to hydrolytic degradation as well as to degradation during processing. As molar mass affects the properties of a material, particularly in medical applications, effective methods for molar mass control are of utmost importance.

The detection with refractive index detectors (RI) and multi-angle light scattering detectors (MALLS) is based on the refractive index increment (dn/dc), which is also influenced by which solvent is used. Trichloromethane (TCM) is typically a good solvent for most polylactide samples. However, dn/dc in TCM is relatively low, and so higher concentrations are required to achieve a reasonable signal-to-noise ratio (S/N) when using RI or MALLS detection, especially when analyzing samples of lower molecular mass by GPC/SEC-MALLS. In tetrahydrofuran (THF), the dn/dc is higher, and reasonable S/Ns can be more easily achieved. However, depending on the stereochemical composition, not all PLA samples dissolve in THF. For this reason, there is great interest in a GPC/SEC method that provides a high RI and solubility irrespective of crystallinity.

Fluorinated solvents such as HFIP or tetrafluoroethanol (TFE) typically dissolve every (noncrosslinked) polylactide sample and provide reasonable dn/dc for PLAs, allowing for GPC/SEC-MALLS analysis. Fluorinated solvents are costly, although the use of microbore columns with a smaller inner diameter (4.6 mm) leads to less solvent consumption.

Experimental

Table 1. Instrument and sample conditions.

	Conditions
Pump	Isocratic pump Flow rate: 1 mL/min Mobile phase: hexafluoroisopropanol, 0.05 M potassium trifluoroacetate
Injection system	Autosampler Injection volume: 50 µL
Columns	PFG 7 µm precolumn, 8 × 50 mm (p/n PFA080507) PFG 7 µm linear XL, 8 × 300 mm (p/n PFA083007LXL) PFG 7 µm linear XL, 8 × 300 mm (p/n PFA083007LXL)
Temperature	23 °C
Sample Concentration	1 mg/mL
Calibration	Agilent Calibration kit Poly(L-lactide) high (p/n PSS-PLAKITH)
Detectors	Refractive index (RI) detector
Software	Agilent WinGPC

Results and discussion

Various narrowly distributed poly(L-lactide) samples were analyzed in HFIP on two PFG 7 µm linear XL columns connected in series. PFG columns are based on modified silica particles, which are more robust in fluorinated solvents compared to polymer-based particles and exhibit a notable pressure stability.

Figure 1 shows an overlay of the RI detector traces. Despite a concentration of 1 mg/mL and an injection volume of 20 µL, good S/Ns were achieved for all samples.

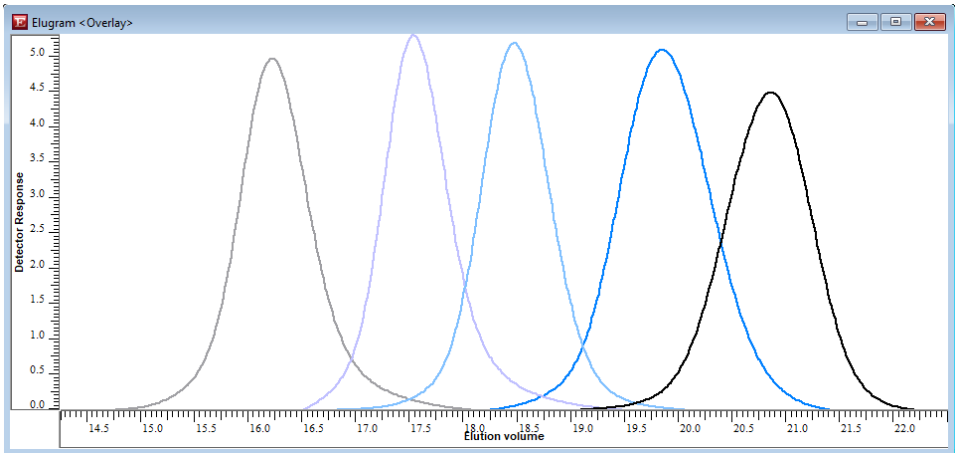

Figure 1. Overlay of RI traces for five different poly(L-lactide) samples.

The corresponding molecular weight distributions (MWD) are overlaid in Figure 2. Conventional calibration with narrow distributed poly(L-lactide) reference materials (p/n PSS-PLAKITH) was used. The analytical setup can be used for the analysis of polylactide samples over a wide molar mass range.

Conclusion

Polylactides can be successfully characterized in fluorinated solvents such as HFIP using PFG columns. The use of fluorinated solvents for PLAs has the advantage of providing a high dn/dc value resulting in reasonable signal-to-noise ratios, when RI and MALLS detection is applied. In addition, typically all polylactide samples can be dissolved.

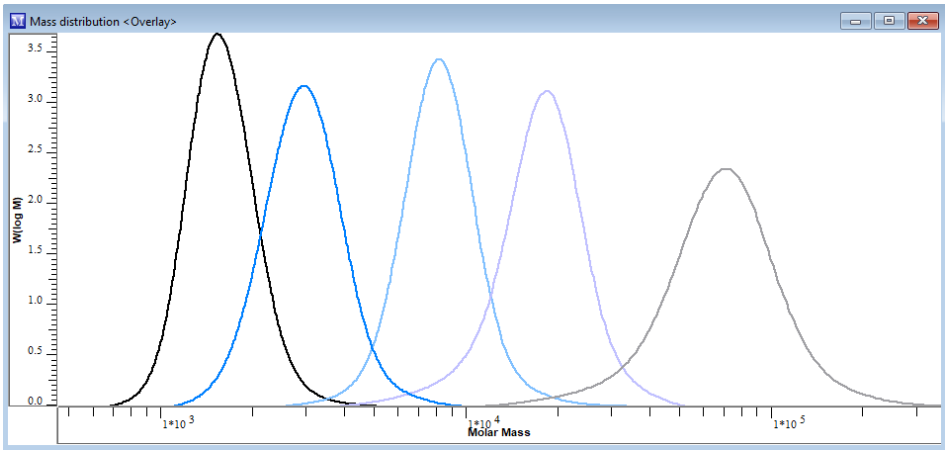

Figure 2. Comparison of the molecular weight distributions (based on calibration with poly(L-lactide) high MW calibration kit, p/n PSS-PLAKITH).

Reference

1. Polymer Data Handbook; Oxford University Press, Inc., **1999**.

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