GPC of Poly(n-isopropylacrylamide) Smart Material with Universal Calibration using the Agilent 390-MDS Multi Detector Suite

Application Note

Authors

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Introduction

"Smart materials" are capable of varying their physical properties in response to environmental changes or stimuli. Such stimuli include temperature, pH, solvent composition, and electric field strength. In particular, smart hydrogels, which change their shrinking and swelling characteristics in response to external stimuli, have been studied for use in engineering and biomedical applications, such as controlled drug release. Poly(n-isopropylacrylamide) (PNIPAM) gel is an important smart hydrogel that responds to temperature changes. PNIPAM gels exhibit negative thermosensitivity, meaning that they undergo a significant level of shrinkage with increasing temperature. Precise control over a hydrogel's shrinking and swelling characteristics is desirable since this may lead to control over its drug release/uptake properties.

Among other important properties that affect the thermosensitivity of PNIPAM, such as particle structure and size, a key characteristic is the molecular weight distribution. The molecular weight distributions of two PNIPAM polymers were accurately measured by means of GPC with online viscometry, allowing application of the universal calibration technique. This method permits an accurate calibration of the GPC system based upon molecular size in solution (using the relationship between the viscosity of the eluting polymer and its molecular weight). This in turn allows accurate molecular weights to be calculated even though the polymer standards used are not chemically identical to the polymer under investigation, as the column is separating on size not molecular weight. As a result, the molecular weight data usually obtained via this technique are very accurate, in contrast to conventional GPC employing a concentration detector only (eg UV, RI), which provides molecular weight data relative to the polymer calibration standards used.

The 390-MDS can be used to provide accurate molecular weights for polymers of unusual structure by employing differential refractive index and viscometry detectors in combination.

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Methods and Materials

Conditions

Columns:	2 x Agilent PLgel 5 µm MIXED-C, 300 x 7.5 mm (p/n PL1110-6500)
Eluent:	THF + 5% triethylamine
Flow Rate:	1.0 mL/min
Detector Train:	390-MDS incorporating Viscometer and DRI
Detector Temp:	All detectors set at 40 °C

Results and Discussion

A typical dual-detector chromatogram of PNIPAM is shown in Figure 1. Figure 2 describes a typical molecular weight distribution obtained from universal calibration. Average molecular weights obtained from universal calibration are given in Table 1.

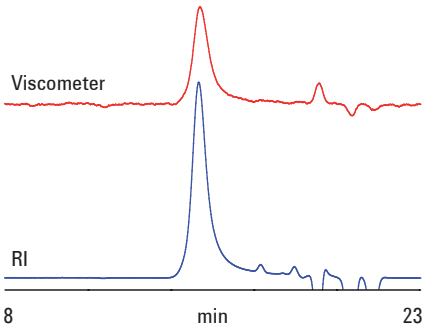

Figure 1. Typical PNIPAM dual-detector chromatography

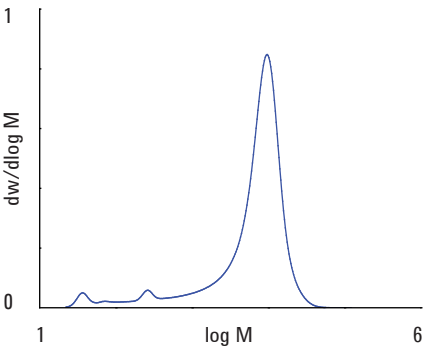

Figure 2. Molecular weight distribution from universal calibration

Table 1. Molecular weight data calculated by both conventional GPC and via the Universal Calibration

Sample	Mw (g/mol)
A (universal)	8,333
A (conventional)	5,010
B (universal)	9,406
B (conventional)	5,448

For comparison, molecular weight averages obtained from conventional calibration are shown above. The results indicate that significantly different molecular weight distributions are obtained using both universal and conventional calibration techniques, suggesting a substantial difference in molecular size between the sample and the standard polymer for a given molecular weight. The results obtained for a universal calibration were in good agreement with those predicated from theory.

Conclusion

PLgel columns and multi-detection provided by the 390-MDS revealed substantial differences in molecular weight distributions of PNIPAM samples, depending on whether or not universal or conventional calibration was used. Whereas conventional GPC with a concentration detector gives only relative results, GPC viscometry employing a viscometer and a differential refractive index detector within the 390-MDS provides an accurate representation of the molecular weights of the samples regardless of the calibrants used.

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