Polystyrene and Polyethylene Calibrants in Gel Permeation Chromatography with TCB

Technical Overview

Introduction

Analysis of polymer molecular weight distributions by conventional gel permeation chromatography (GPC) requires a retention time and molecular weight calibration curve to be generated from a set of standards.

Polystyrene or polyolefin standards in trichlorobenzene (TCB) can be used for high-temperature conventional GPC of polyolefins in TCB. The polystyrene narrow standards are used with appropriate Mark-Houwink parameters to generate polyolefin equivalent molecular weights.

This example compares the calibration curves generated from polystyrene and polyethylene standards in TCB at 160 °C, typical conditions used for polyolefin analysis.

Figure 1 shows overlaid calibration curves generated with polystyrene and polyethylene standards fitted to a third order polynominal. The polystyrene narrow standards have Mp values up to 7 million daltons and the calibration is linear over the whole calibration range.

Conditions

Samples	Agilent polystyrene and polyethylene calibrants
Columns	3 × Agilent PLgel 10 μm MIXED-B, 7.5 × 300 mm (p/n PL1110-6100)
Eluent	TCB + 0.0125% BHT
Flow rate	1.0 mL/min
Inj vol	200 μL
Temp	160 °C
Detector	RI, Agilent PL-BV400HT Viscometer
System	Agilent PL-GPC 220

The polyethylene narrow standards have Mp values up to 120,000 daltons. However, the calibration is not linear. The slope of the curve decreases significantly at low molecular weight.
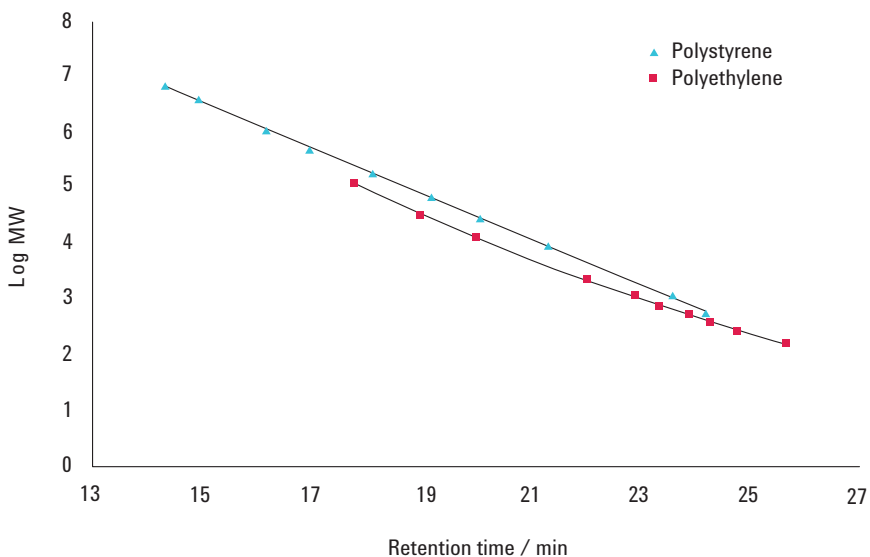
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Figure 1.   Comparison of polystyrene and polyethylene narrow standard calibration curves in TCB at 160 °C on an Agilent PLgel 10 µm MIXED-B three-column set.

GPC separates polymers as a function of size in solution or hydrodynamic volume defined as the sum of intrinsic viscosity $[\eta]$ and molecular weight. By plotting log $(M^*[\eta])$ as a function of retention time, a Universal Calibration can be generated based on size in solution; the results are valid for any polymer. A Universal Calibration is derived for polystyrene and polyethylene standards using an online viscometer. In the absence of a viscometer, the Mark-Houwink relationship may be used if K and α are known. For polyethylene, K and α parameters:

$[\eta\text{-}] = KM^{\alpha}$

recommended by IUPAC are:

Polystyrene in TCB - K = 12.1 × 10^{-5} dL/g
and α = 0.707

Polyethylene in TCB - K = 40.6 × 10^{-5} dL/g
and α = 0.725

Figure 2 shows the resulting Universal Calibration plot for the two sets of narrow standards. The polystyrene and higher molecular weight polyethylene standards fall on a linear calibration curve indicating that they obey the Universal Calibration. However, the low molecular weight polyethylene standards do not obey the Universal Calibration in TCB and the separation is not purely through size exclusion. This explains the differences observed in the conventional calibration curves generated from the polystyrene and polyethylene standards in TCB.
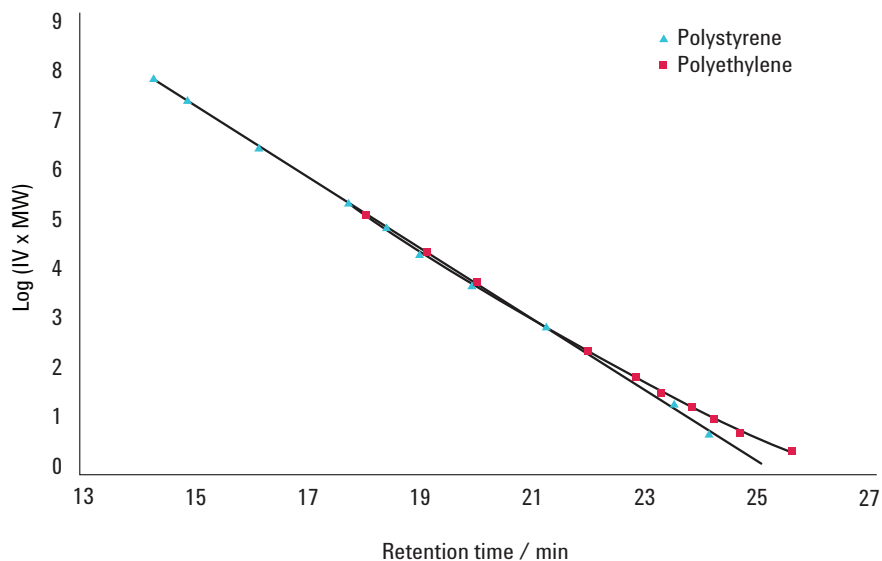
Figure 2.   Universal Calibration curves for polystyrene and polyethylene narrow standards.

GPC/SEC Columns and Calibrants from Agilent

Agilent offers a comprehensive portfolio of GPC/SEC columns and calibrants for high-performance separations based on molecular size in solution. Agilent delivers leading solutions for characterizing and separating polymers by GPC/SEC, and manufactures all components for accurate polymer analysis.

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