HIGH TEMPERATURE GPC ANALYSIS WITH HSPGEL™ HT COLUMN

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INTRODUCTION

Gel Permeation Chromatography (GPC) of polyolefins uses 1,2,4-trichlorobenzene (TCB) as the mobile phase at elevated temperatures (~140°C). This solvent is toxic and is on the Priority Chemicals List in the EPA National Waste Minimization Program. Replacing traditional GPC columns with columns that enable lab personnel to run experiments in less time and to generate less toxic waste (mobile phase) would benefit any lab analyzing polyolefins.

The application of Waters® HSPgel™ series columns can reduce both run time and solvent consumption. With a single HSPgel (6.0x150 mm) column a sample run may finish within 7 minutes at a flow rate of 0.6 ml/min. The run time is ~5 X less and the solvent use per run is ~9 X less compared with a traditional analysis on a bank of three columns (7.8x300 mm). Using a cumulative matching calibration technique, the GPC results from the HSPgel columns are reproducible and accurate.[1]

A key feature to evaluate when considering column change is that the resulting data are equivalent within acceptable limits. The molecular weight results obtained from a single HSPgel HT MB-M (5µm,6.0x150 mm) column were compared with the molecular weights from a traditional Styragel® HT (10 µm, 7.8x300 mm) three column bank. The GPC system used laser light scattering and viscometer detectors. The data shown here illustrate the usefulness of HSPgel HT series columns for polyolefin samples

EXPERIMENTAL

Conditions

Chromatography system:	Waters Alliance® GPC/V2000 with Precision Detectors PDI2040
Laser wavelength:	690 nm
Scattering angles detected:	15 degree and 90 degree.
Control software:	Alliance GPC2000 (version 2.0)
Temperature:	140°C (sample carousel, injector, and column compartments)
Columns:	HSPgel HT MB-M (5µm, 6.0x150mm); Styragel® HT column bank (2x HT6E and 1x HT2,10 µm, 7.8x300mm)
Mobile phase:	1,2,4-trichlorobenzene (filtered, degassed)
Flow rates:	0.6 ml/min for HSPgel HT column; 1.0 ml/min for Styragel HT columns
Sampling rate:	1Hz
Injection volumes:	52.5 µl for HSPgel HT MB-M column; 319.5 µl for Styragel HT column bank

Materials:

1,2,4-trichlorobenzene (TCB) is from Fisher Scientific (Pittsburgh, PA). Polystyrene narrow standards are from Toyo Soda (Japan). Broad polystyrene sample Dow1683 is from Dow Chemical. Polyethylene standards 1475a, 2886, and 2887 are from National Institute of Standard and Technology (NIST,Gaithersburg, MD). Santonox R antioxidant (CAS number 96-69-5) (Monsanto) was used.

Preparation of standards and samples

Polymer solutions were prepared using TCB solvent with 250mg/L Santonox R antioxidant. The TCB was filtered using PTFE membrane (47mm diameter, 0.45µm pore size, Waters). Solutions were made by directly weighing samples and solvent into 60ml small neck glass bottles using an electrobalance (Sartorius Analytic, Model A120S, Sartorius, Goettingen, Germany). Concentrations were calculated from densities and masses of solvent and samples. Aluminum crimp caps with PETF/Aluminum/Silicone septa (Waters) were used to seal the bottles. A general-purpose laboratory convection oven (VWR model 1330FM) set at 140°C was used to dissolve the polymer solutions. 2 hours heating with gentle swirling (about 1 minute every 30 minutes) was enough to dissolve polyethylene samples. After dissolution, polymer solutions were dispensed into 10 ml vials for GPC experiments.

Data processing

Software:	Empower™ (Build 1154)
Options:	GPC, GPCV, and LS
Light scattering calibrants:	PS narrow standards (Mw: 9,100 and 107,000)
dn/dc:	PS, 0.053 ml/g; PE, 0.109 ml/g
Refractive index:	1.520 (TCB)
Density:	1.31 g/ml (TCB at 140°C)

RESULTS

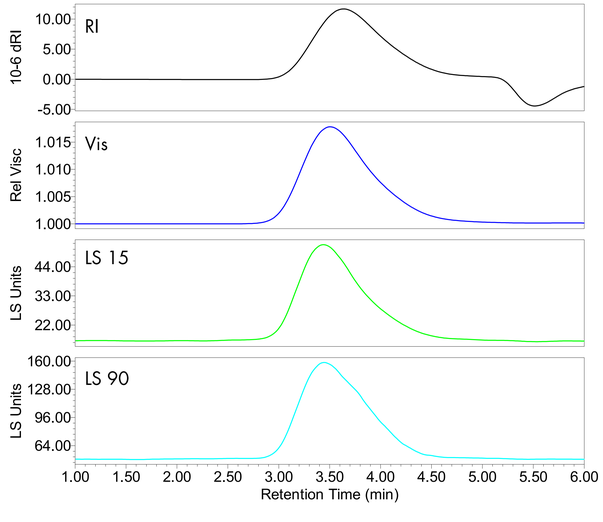

Figure 1. Chromatograms of a PS broad sample on an HSPgel HT MB-M column.

Table 1. Comparison of calculated molecular weight values with the vendor values for narrow polystyrene standards.

Vendor M_w	M_w	RD%
1,010,000	1,010,000	0
706,000	719,000	1.8
422,000	417,000	-1.2
186,000	198,000	6.5
107,000	107,000	0
65,900	64,800	-1.7

Table 2. Comparison of PE & PS Results: HSPgel and traditional column set

Sample	Label Value			3 Conventional Columns[a]			1 HSPgel HT MB-M column[d]		
	Mn (1x10³)	Mw (1x10³)	[η][b] (dL/g)	Mn (1x10³)	Mw (1x10³)	[η][c] (dL/g)	Mn (1x10³)	Mw (1x10³)	[η][c] (dL/g)
Dow1683	100	250	N/A	96	257	0.757	150	232	0.752
NIST1475a	18.3 ±0.4	53.1 ±0.6	1.010 ±0.009	17.6 ±1.6	54.0 ±1.0	1.023 ±0.008	18.4	51.2	0.979
NIST2886	N/A	87 ±6	1.58 ±0.02	77.6	81.1	1.54	77.6	80	1.517
NIST2887	N/A	196 ±14	2.77±0.03	166	190	2.71	162	179	2.765

a: Results of conventional columns are the average of 2 injections for each sample except NIST 1475a, which is the average of 5 injections.
b: The labeled intrinsic viscosity were measured at 130°C in TCB.
c:140°C in TCB
d: Results of HSPgel columns are the average of 3 injections for each sample.

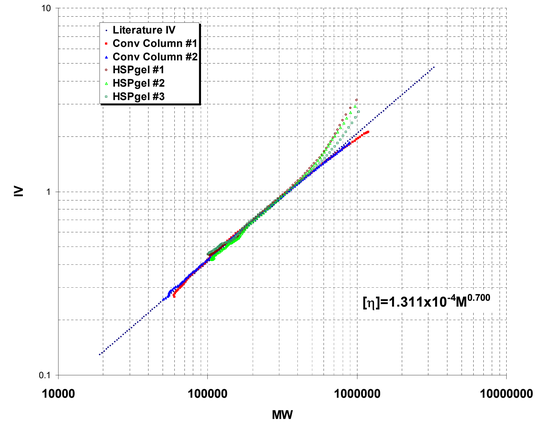

Figure 2. Mark-Houwink plots for Dow 1683 (PS) obtained from both HSPgel column and conventional Styragel HT columns and comparison with literature results[2].

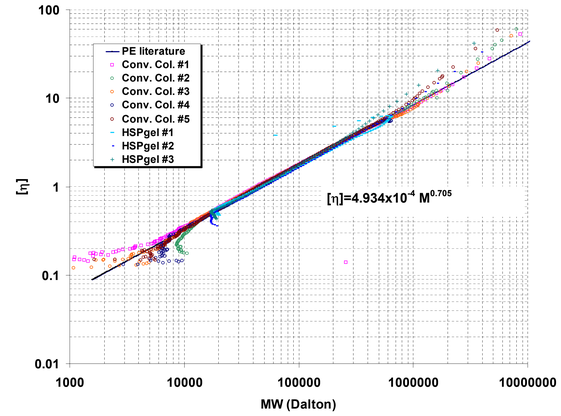

Figure 3. Mark-Houwink plots for NIST 1475a (PE) from HSPgel column and conventional Styragel HT columns and comparison with literature values[2].

CONCLUSIONS

- HSPgel HT series columns are useful for high temperature GPC analyses with RI, viscometry and LS detectors.
- Molecular weights and intrinsic viscosities are within acceptable limits of the values obtained with a traditional 3-column bank
- Shorter run times result in less consumption of toxic solvents
- Run time here < 4.5 X compared with a traditional 3- column bank
- Solvent waste here < 7.5 X compared with a traditional 3- column bank

REFERENCE

1) Jinchuan Yang, Rick Nielson, Peter Alden, Waters Chemistry Operation WW Meeting 2002, WA20727
2) Sun, T., Chance, R. R., Graessley, W. W., Lohse, D. J.; *Macromolecules* 2004, 37, 4304-4312

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