

Application compendium

ANALYSIS OF POLYMERS BY GPC/SEC ENERGY & CHEMICAL APPLICATIONS

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Introduction

Crude oil, or petroleum, is the main source of organic polymeric chemicals for industry. The major chemicals are derived from two constituents of oil, namely olefins such as ethylene and propylene, and aromatics such as benzene, toluene, and xylene.

These raw materials are then broken down into more basic polymers, for example polyethylene, polypropylene, elastomers, asphalts, and liquid hydrocarbons. Millions of tons of these compounds are produced and used worldwide every year.

Analysis of polymers by the liquid chromatography technique of gel permeation chromatography/size exclusion chromatography (GPC/SEC) reveals information that influences many of their key physical parameters, including strength, brittleness, melt flow, and how easily the material is processed. As such, GPC/SEC is a very important technique for companies synthesizing polymers and is essential for assessing their molecular weight distribution, a characteristic that influences many of their physical properties. Generally, increasing molecular weight leads to higher performance characteristics, while an increase in the width of the distribution (the polydispersity) leads to a loss of performance but an increase in the ease of processing.

Industrial intermediate or prepolymers are analyzed by GPC using a range of solvents and temperatures. Some simple polymers such as phenol-formaldehyde resins can be characterized at near-ambient temperatures on a straightforward GPC system with no sample pretreatment. Others, such as engineering polymers, are particularly difficult to analyze, because they are generally tough and hard to dissolve and therefore require aggressive solvents, extensive sample prep, and elevated temperatures. For these applications a high-performance, integrated GPC system is essential.

Agilent offers a full range of GPC systems, columns, and standards for every polymer that requires a GPC solution. This compendium illustrates some of these solutions for the analysis and characterization of key polymers of interest to chemical and energy companies.





Polyolefins

Polyolefin is a general term describing polymers created from simple olefins or alkenes. Many different types of olefin exist, from the most simple, ethylene, to alpha-olefins of increasing complexity. Polyolefins are of great interest as two of them, polyethylene (polythene) and polypropylene, are among the highest tonnage polymers produced in the world.

Interest in the analysis of polyolefins comes from the desire to create new materials with custom properties, from the development of new catalysts and from the need to perform quality control on polymer production.

Many polyolefins, typically those containing over 10% ethylene and polypropylene monomers, are of limited solubility in a number of solvents. This is because the characteristic high strength and toughness of these materials results from their high crystallinity. Increased crystallinity requires break up of any inter-chain bonds in order to dissolve the material. Several solvents can be used, but in general the most effective is trichlorobenzene, a viscous solvent with a distinct odor. Ortho-dichlorobenzene is also used in some laboratories, but solubility in this solvent is less effective.



High molecular weight polyolefins

Polyolefins range from low molecular weight hydrocarbon waxes to ultra-high molecular weight rigid plastics. The molecular weight distributions of polyolefins is directly related to physical properties such as toughness, melt viscosity and crystallinity. High molecular weight polyolefins tend to exhibit very broad molecular weight distribution (MWD). For such samples, small particles with small pore sizes are not desirable since shear degradation may occur, and so the high-pore-size particles of PLgel Olexis are recommended.

Conditions (Figures 1 and 2)

Samples: Polyethylenes
Columns: 3 x PLgel Olexis, 7.5 x 300 mm (p/n PL1110-6400)
Eluent: TCB + 0.015% BHT
Injection volume: 200 μ L
Flow rate: 1.0 mL/min
Temperature: 160 $^{\circ}$ C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

Artifacts known as dislocations can arise in blended columns, resulting from a mismatch of the pore volume of components in the blend. Dislocations lead to false modalities and polydispersities. Avoiding dislocations was an integral part of the design brief for PLgel Olexis columns. Accurate blending of these components produces a column that gives a smooth molecular weight distribution, providing a true reflection of the shape of the MWD. PLgel Olexis is perfect for studies that require accurate polydispersity index and modality information.

Figure 1 shows a range of polyolefin samples analyzed on a PLgel Olexis column, covering the spread of molecular weights. There are no dislocations and the peak shape of the very broad samples shows true sample modality.

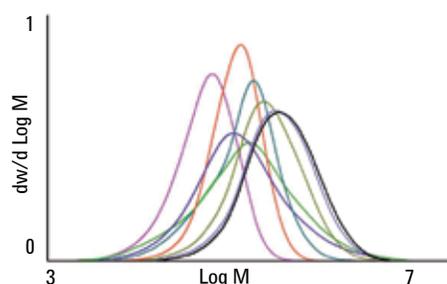


Figure 1. Agilent PLgel Olexis reveals true modalities across the range of polyolefins

Given the accurate resolving power of PLgel Olexis you can be sure that unusual peak shapes are real and not artifacts; unusual peak shapes of some samples will be true reflections of their modality. This is important for studies into reaction mechanisms and catalyst behavior (Figure 2).

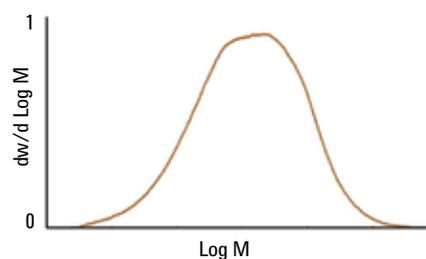


Figure 2. A true change in peak shape revealed by Agilent PLgel Olexis of a multi-modal material manufactured from a multi-site catalyst

Lower molecular weight polyolefins

The diversity of petroleum products demands a variety of GPC column types for optimized analysis. Low molecular weight liquid hydrocarbons require high resolution of individual components. This is illustrated in Figure 3, where three linear hydrocarbons are resolved easily to base line in a reasonably short analysis time.

Conditions

Samples: Linear hydrocarbons
Columns: 2 x PLgel 5 μ m 100Å, 7.5 x 300 mm (p/n PL1110-6520)
Eluent: TCB
Flow rate: 1.0 mL/min
Temperature: 145 °C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

Peak Identification

1. C₃₆ H₆₄
2. C₂₂ H₄₆
3. C₁₄ H₃₀

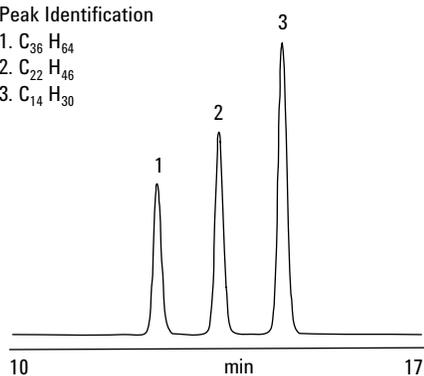


Figure 3. Linear hydrocarbons separated to base-line on an Agilent PLgel two-column set

Figure 4 shows the separation of a selection of low molecular weight linear hydrocarbons.

Conditions

Samples: Linear hydrocarbons
Columns: 2 x PLgel 3 μ m 100Å, 7.5 x 300 mm (p/n PL1110-6320)
Eluent: TCB
Flow rate: 0.8 mL/min
Injection volume: 20 μ L
Temperature: 145 °C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

Peak Identification

1. C₃₆
2. C₂₄
3. C₂₀
4. C₁₆
5. C₁₂

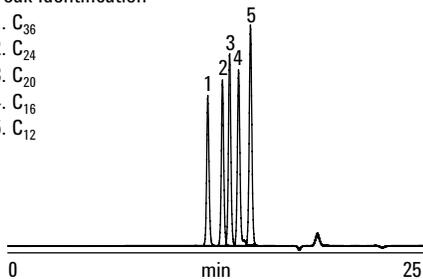


Figure 4. Separation of low-molecular-weight hydrocarbons

The PLgel 100Å columns have a GPC exclusion limit of 4,000 molecular weight (polystyrene equivalent). Intermediate products can be analyzed using the PLgel MIXED-D column that has a linear molecular weight resolving range up to an exclusion limit of around 400,000 molecular weight. The 5 μ m particle size maintains high column efficiency and thus fewer columns are required and analysis time is relatively short.

Figure 5 shows a chromatogram of a relatively low molecular weight hydrocarbon wax obtained on PLgel 5 μ m MIXED-D columns.

Conditions

Samples: Hydrocarbon wax
Columns: 2 x PLgel 5 μ m MIXED-D, 7.5 x 300 mm (p/n PL1110-6504)
Eluent: TCB
Flow rate: 1.0 mL/min
Injection volume: 200 μ L
Temperature: 160 °C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

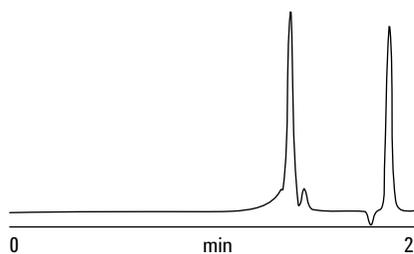


Figure 5. A low molecular weight wax

Asphalt

Figure 6 shows the analysis of asphalt used in road surfacing. Subsequently derived information regarding the molecular weight distribution of such materials is invaluable in determining their processibility and final properties.

Conditions

Columns: 2 x PLgel 5 μ m MIXED-D, 7.5 x 300 mm (p/n PL1110-6504)
 Eluent: THF
 Flow rate: 1.0 mL/min
 Temperature: 40 $^{\circ}$ C
 Detector: Agilent 1260 Infinity GPC/SEC System

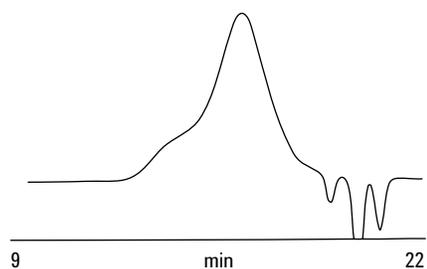


Figure 6. Fast analysis of asphalt on Agilent PLgel 5 μ m MIXED-D columns

High-density polyethylene – repeatability study

A commercial sample of high-density polyethylene (HDPE) was prepared at 2 mg/mL using the PL-SP 260VS Sample Preparation System, with a dissolution temperature of 160 $^{\circ}$ C and a dissolution time of two hours. Eight aliquots of the master batch solution were dispensed into PL-GPC 220 autosampler vials and placed in the autosampler carousel of the PL-GPC 220 High Temperature GPC/SEC System where the hot zone temperature was 160 $^{\circ}$ C and the warm zone 80 $^{\circ}$ C to avoid sample degradation (Figure 7).

Conditions

Columns: 3 x PLgel 10 μ m MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
 Eluent: TCB + 0.0125% BHT
 Flow rate: 1.0 mL/min
 Injection volume: 200 μ L
 Temperature: 160 $^{\circ}$ C
 Instrument: PL-GPC 220 High Temperature GPC/SEC System

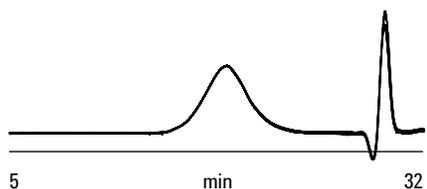


Figure 7. Overlay of the raw data chromatograms obtained for eight consecutive injections of HDPE



The data were analyzed against a polystyrene standards calibration using the following Mark-Houwink parameters to obtain the polypropylene equivalent molecular weight averages that are shown in Table 1.

Polystyrene in TCB¹ $K = 12.1 \times 10^{-5}$ $\alpha = 0.707$

Polyethylene in TCB² $K = 40.6 \times 10^{-5}$ $\alpha = 0.725$

Table 1. Summary of results from eight injections of HDPE

Injection number	Mn	Mp	Mw
1	17,289	76,818	333,851
2	16,988	77,434	335,496
3	17,428	77,514	332,616
4	17,521	77,052	335,635
5	17,348	76,520	334,212
6	17,487	77,728	333,511
7	16,898	77,578	335,642
8	17,457	77,288	334,923
Mean	17,302	77,241	334,485
Std Dev	220	387	1,048
% Variation	1.3	0.5	0.3

Figure 8 shows an overlay of the molecular weight distribution calculated for the eight consecutive injections of the HDPE sample, and illustrates the excellent repeatability obtained with the PL-GPC 220 High Temperature GPC/SEC System using PLgel 10 μ m MIXED-B columns.

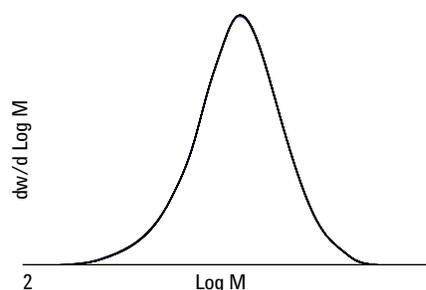


Figure 8. Molecular weight overlay of eight consecutive injections of HDPE

Reference

1. H. Coll, D. K. Giddings. *J. Polym. Sci.* **8**, 89 (1970).
2. T. G. Scholte, N. L. J. Meijerink, H. M. Schoffeleers, A. M. G. Brands. *J. Appl. Polym. Sci.* **29**, 3763 (1984).



Guar gums

Industrial grade guar gum powder and derivatives are used in oil well fracturing, oil well stimulation, and mud drilling. In the oil field industry, guar gum is employed as a surfactant, synthetic polymer and deformer that is suited for all rheological requirements of water-based and brine-based drilling fluids.

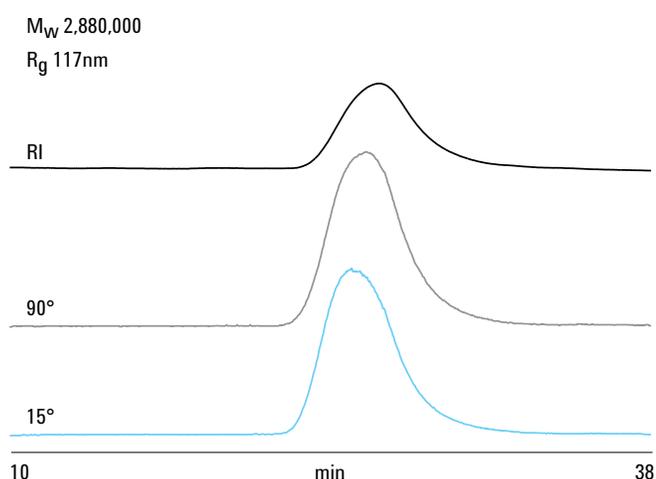


Figure 9. Light scattering and refractive index detection chromatograms for a guar gum on the Agilent 1260 Infinity Multi-Detector GPC/SEC System with an Agilent PL aquagel-OH two-column set.

High viscosity guar gums are used as drilling aids in oil well drilling, geological drilling and water drilling.

In this application, using a light-scattering detector is essential since the MWs based on column calibrations are significantly underestimated when using conventional RI detection. Light scattering is most beneficial since conventional GPC calibrants are not available at these high MWs.

Conditions

Columns: PL aquagel-OH 60 15 μ m, 7.5 x 300 mm (p/n PL1149-6260),
 PL aquagel-OH 40 15 μ m, 7.5 x 300 mm (p/n PL1149-6240)
 Eluent: 0.2 M NaNO₃, 0.01 M NaH₂PO₄, pH 7
 Flow rate: 0.5 mL/min
 Instrument: Agilent 1260 Infinity Multi-Detector GPC/SEC System

Monitoring MW degradation is key because it is related to the performance of the thickener.



Engineering polymers

Engineering polymers are particularly difficult to analyze – they are generally tough and difficult to dissolve, often requiring aggressive solvents and elevated temperatures. They have only limited solubility in a small number of solvents. This is because high strength and toughness are usually a result of high molecular weight and/or high crystallinity.



Increasing molecular weight requires untangling the molecular chains to dissolve the material, whereas increased crystallinity requires break-up of any inter-chain bonds that may be present. For these applications at high temperature, a high performance integrated GPC system, such as the PL-GPC 220 High Temperature GPC/SEC System, is a necessity.

Table 2. Effects of molecular weight distribution on the properties of engineering polymers

	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+

Polyether ethyl ketone (PEEK) - tubing

Polyether ether ketone (PEEK) was developed in 1977 by ICI and was one of the first of the new generation of engineering thermoplastics developed for chemical resistance, high mechanical strength and high thermal stability – the useful properties of the material are retained up to temperatures as high as 315 °C. A crystalline material with repeat units of two ethers and a ketone group in the polymer backbone, PEEK is a high cost material. For many applications, such as the manufacture of piston components in engines, the insulation of cables and the production of high performance aircraft parts, this cost is justified as there are no other plastics that can offer the same performance properties. The industrial performance of PEEK makes analysis of this material by GPC difficult. PEEK has excellent chemical resistance and is unaffected by many organic and inorganic chemicals, dissolving only in strong or concentrated anhydrous oxidizing agents. Previous methods for analyzing PEEK have involved mixtures of trichlorobenzene and phenol running at high temperatures.

For this analysis, the PEEK sample was dissolved in a small volume of dichloroacetic acid at 120 °C for two hours. After dissolution, the sample was diluted to the required concentration of 0.2% (w/v) with chloroform and injected into a system running at temperature after filtration to remove undissolved material.

The PEEK sample eluted as a broad polymer peak with an MW of 70,000 g/mol and a polydispersity of 2.2. The large system peak observed at the end of the run was due to the excess dichloroacetic acid used in the preparation of the sample.

Conditions

Sample: Polyether ether ketone (PEEK)
Columns: 2 x PLgel 10 µm MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
Eluent: 80% Chloroform
20% Dichloroacetic acid
Flow rate: 1.0 mL/min
Injection volume: 200 µL
Instrument: PL-GPC 220 High Temperature GPC/SEC System

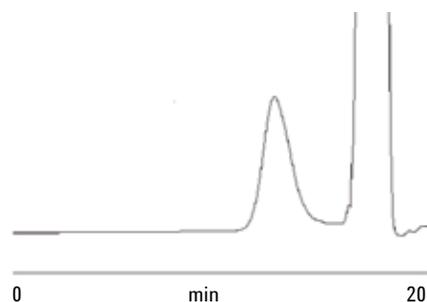


Figure 10. Chromatogram of a PEEK sample

Polybutylene terephthalate (PBT) in HFIP – machined parts, bottles

Polybutylene terephthalate (PBT) resins are used in a wide variety of applications in which toughness and resistance to damage are highly advantageous. However, mechanical and thermal stress during the production of molded parts can cause degradation, giving a reduction in desirable physical properties.

The molecular weight distribution of the resin is a key measure of the onset of degradation and therefore of estimating the mechanical strength of the final product. PBT is soluble in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), a polar organic solvent, which is excellent for dissolving polar polymers such as polyamides and polyesters. The analysis was carried out in HFIP modified by the addition of 20 mM sodium trifluoroacetate to prevent aggregation. Two Agilent PL HFIPgel columns, designed specifically for HFIP applications, were employed for the analysis at a temperature of 40 °C. The PL-GPC 220 High Temperature GPC/SEC System was used with differential refractive index and viscometry detection. GPC coupled with a molecular weight sensitive viscometer allowed calculation of molecular weights based on hydrodynamic volume using the Universal Calibration approach, leading to molecular weights independent of the standards used to generate the column calibration. Agilent polymethylmethacrylate (PMMA) standards were employed to generate the Universal Calibration.

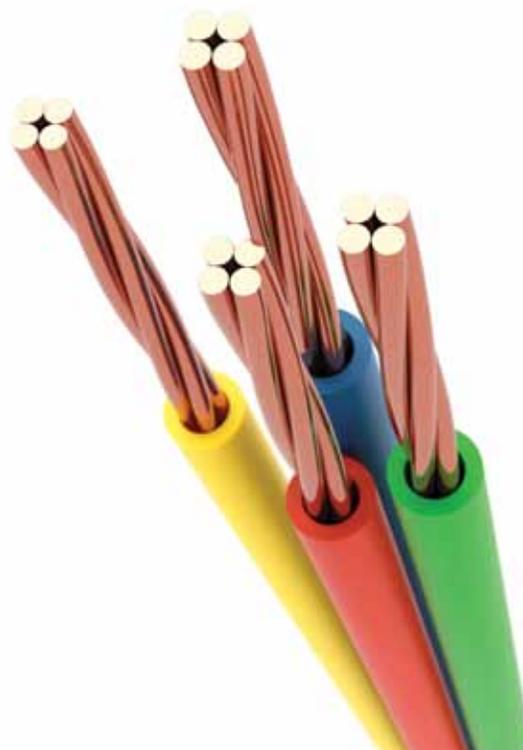


Table 3 shows the molecular weight averages and intrinsic viscosity for the sample before and after molding, as determined by GPC/viscometry. Clearly, the molecular weight distribution indicates that after molding, the material has suffered from degradation and is less robust than the virgin material.

Conditions

Samples: PBT resin
 Columns: 2 x PL HFIPgel, 7.5 x 300 mm (p/n PL1114-6900HFIP)
 Eluent: HFIP + 20 mM NaTFA
 Flow rate: 1.0 mL/min
 Injection volume: 200 µL
 Temperature: 40 °C
 Instrument: PL-GPC 220 High Temperature GPC/SEC System, viscometer

Table 3. Molecular weight averages and intrinsic viscosity for the PBT resin sample

	Mn/g mol ⁻¹	Mw/g mol ⁻¹	Intrinsic viscosity/g ⁻¹
Virgin resin	24,400	48,600	0.535
Molded part	11,200	24,000	0.306

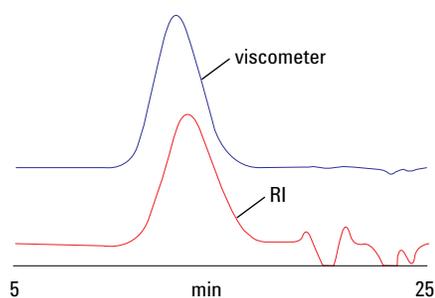


Figure 11. Example overlay of a dual-detector chromatogram of the virgin PBT resin before molding

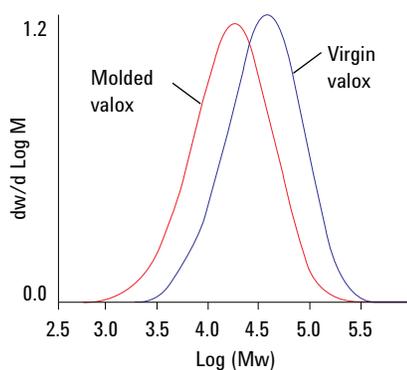


Figure 12. Molecular weight distributions of the two samples

Polyethylene terephthalate in o-chlorophenol as an alternative solvent

As an alternative to the use of HFIP, PET can be analyzed in o-chlorophenol. This viscous solvent requires elevated temperatures and is a hazardous substance. The samples were dissolved by heating to 110 °C for 30 minutes. The polymer remains in solution at room temperature but the high viscosity of the eluent means that high temperature GPC is necessary. Three grades of PET, with different intrinsic viscosities, were analyzed and compared, showing minor differences between the materials.

Conditions

Sample: PET resin
 Columns: 2 x PLgel 10 µm MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
 Eluent: o-Chlorophenol
 Flow rate: 1.0 mL/min
 Temperature: 100 °C
 Instrument: PL-GPC 220 High Temperature GPC/SEC System

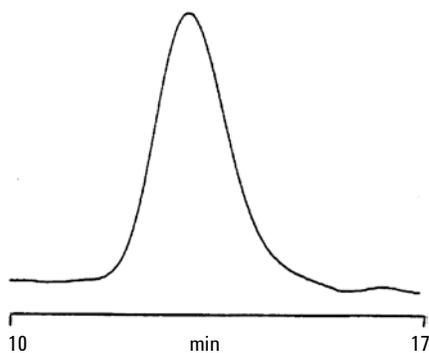


Figure 13. Chromatogram of a PET sample

Peak Identification

- 1. IV=0.72
- 2. IV=0.75
- 3. IV=0.84

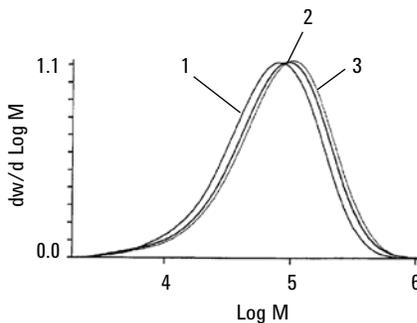


Figure 14. Molecular weight distributions of the PET samples

Branching analysis of polyethylenes with Agilent GPC/SEC Software - plastic bags and containers

The presence of long chain branching (over six carbons in length) in polyolefins strongly influences physical properties such as melt viscosity and mechanical strength. The distribution chain branches in polyolefins are determined by the polymerization mechanism and there is significant interest in the production of materials with well-defined and characterized molecular weight and branching distributions for specific applications.

Here we describe the analysis of three samples of polyethylene with the PL-GPC 220 High Temperature GPC/SEC System by GPC/viscometry. Two of the samples had been synthesized by a mechanism to promote branching while the third was a standard linear reference material NBS 1475.

Refractive index and viscometry detectors were employed and the data was analyzed with Agilent GPC/SEC Software using the Universal Calibration approach. Polystyrene standards were used to generate the Universal Calibration and the unbranched sample was used as a linear model in the determination of branching.

Figure 15 shows the molecular weight distributions for the three samples. The black plot is for the unbranched sample. Although there was some overlap, the samples clearly had significantly different molecular weights.

Figure 16 shows the Mark-Houwink plots for the three samples. The uppermost sample is the unbranched material. The other two samples have lower intrinsic viscosities at any given molecular weight, with the unbranched polymer indicating the presence of branching. This can be expressed in terms of g , the branching ratio, defined as follows, where g is a constant:

$$g = \left[\frac{\text{Intrinsic viscosity (branched)}}{\text{Intrinsic viscosity (linear)}} \right]^{1/\epsilon}$$

Conditions

Sample: Polyethylenes
 Columns: 3 x PLgel Olexis, 7.5 x 300 mm (p/n PL1110-6400)
 Eluent: TCB + 0.015% BHT
 Flow rate: 1.0 mL/min
 Injection volume: 200 μ L
 Temperature: 160 $^{\circ}$ C
 Instrument: PL-GPC 220 High Temperature GPC/SEC System

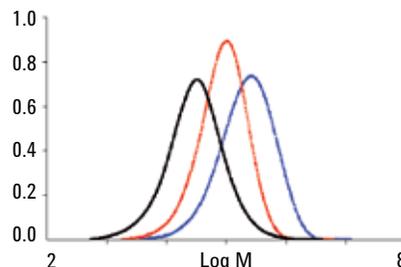


Figure 15. Molecular weight distribution plots for the three polyethylene samples – the black plot is for the unbranched sample

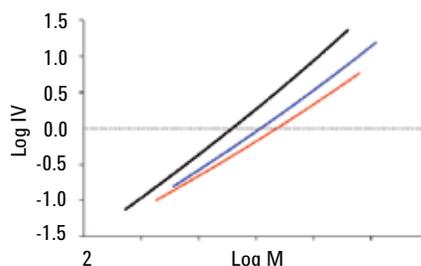


Figure 16. Mark-Houwink plots for three samples of polyethylene

The unbranched sample was used as the linear model and so gives a g value of unity (except at high molecular weight due to scatter in the data). The other two samples both exhibit a decrease in g as a function of molecular weight, indicating that as molecular weight increases, the number of branches increases. Based on these calculated g values, a branching number, or number of branches per 1,000 carbon atoms, can be generated. This is achieved by fitting the data into a model.

The Agilent GPC/SEC Software offers a selection of branching models that can be employed in this approach. In this case a model was used that calculates a number-average branching number, assuming a random distribution of branches on the polymer. Figures 17 and 18 show the g plots and branching-number plots obtained for the samples.

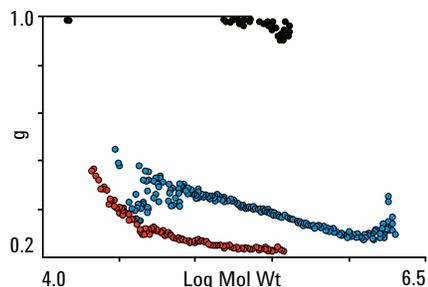


Figure 17. Branching ratio *g* plots for the three polyethylene samples – the black plot is the unbranched sample

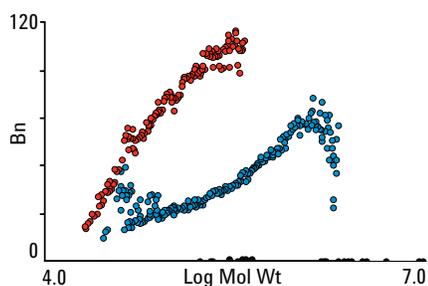


Figure 18. Calculated branching numbers as a function of molecular weight for three samples of polyethylene – the black plot is the unbranched sample

The results show that of the two branched samples, the trend in molecular weight distribution does not follow the trend in branching distribution. The sample showing the most branching at any given molecular weight has a lower molecular weight than the second sample. Clearly, understanding both the molecular weight and branching distributions will give an insight into the processibility and end use of the two materials.

Polyphenylene sulfide analysis - high performance membranes, felts and insulators

Polyphenylene sulfide (PPS) is an engineering polymer with a rigid backbone of alternating aromatic rings linked by sulfur atoms. It is useful as a structural material due to its high resistance to both chemical and thermal attack, and the material is very stiff, even at high temperatures. PPS is used in a number of applications, including as a filter fabric for coal boilers, in felts used in paper making, in electrical insulation applications and in the manufacture of specialty membranes. PPS is naturally insulating, although the addition of a dopant can be used to make the material semi-conducting.

PPS is particularly difficult to analyze by GPC. The high chemical and thermal resistance of the material means that it is only soluble in specialist solvents such as ortho-chloronaphthalene at elevated temperatures of around 200 °C. PL-GPC 220 High Temperature GPC/SEC System is capable of operation at these temperatures, and the PLgel column material can perform the analysis of PPS.

Conditions

Columns:	3 x PLgel 10 µm MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
Eluent:	o-Chloronaphthalene
Flow rate:	1.0 mL/min
Temperature:	210 °C
Detector:	RI
Instrument:	PL-GPC 220 High Temperature GPC/SEC System

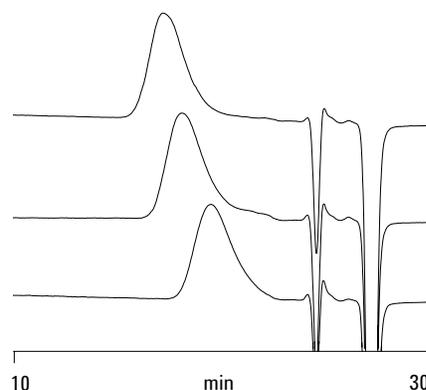
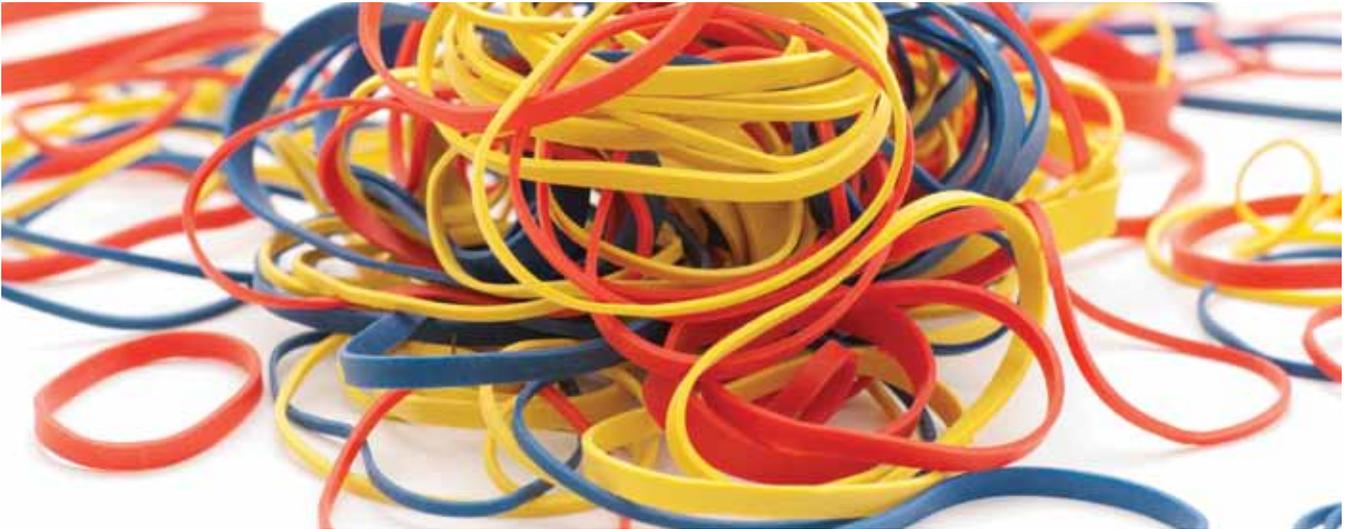


Figure 19. Overlaid chromatograms of three samples of polyphenylene sulfide



Elastomers

Elastomer is a general term used to describe rubbers – polymers that exhibit elasticity. Elasticity is the ability to deform under external stress but return to the original form after removal of the stress.

Elastomers may be thermosets that require curing, or thermoplastics that contain both plastic and elastomeric species, and may be natural or synthetic in origin. Thermosetting elastomers are composed of polymeric chains joined by crosslinks, formed by curing reactions such as the vulcanization of natural rubber, creating a loose lattice structure. This allows chains to move relative to one another during deformation but return to their original positions when relaxed, allowing the material to reversibly extend. Without the cross-linkages the applied stress results in a permanent deformation. Thermoplastic elastomers contain plastic and elastomeric regions within the structure, with weaker non-covalent interactions between chains providing the anchor points, allowing the material to return to its original form after removal of the external force.



Synthetic rubbers

Polybutadiene was one of the first types of synthetic elastomer to be invented and has largely replaced natural rubber in a wide variety of industrial applications.

Two PLgel 5 μm MIXED-C columns were used for this analysis with the results shown in Figures 20 and 21. The polybutadiene sample was prepared accurately at a nominal concentration of 2 mg/mL in tetrahydrofuran and injected into the system without further treatment. For the purpose of light scattering calculations, an average dn/dc was used for the sample.

Mark-Houwink (log intrinsic viscosity versus log M) plots (Figure 22) were generated from the viscometry and light scattering data. The curvature in the Mark-Houwink plot may be a result of structural changes in the polymer as a function of molecular weight.

Conditions

Sample: Polybutadiene
Columns: 2 x PLgel 5 μm MIXED-C, 7.5 x 300 mm (p/n PL1110-6500)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 100 μL
Instrument: Agilent 1260 Multi-Detector GPC/SEC System

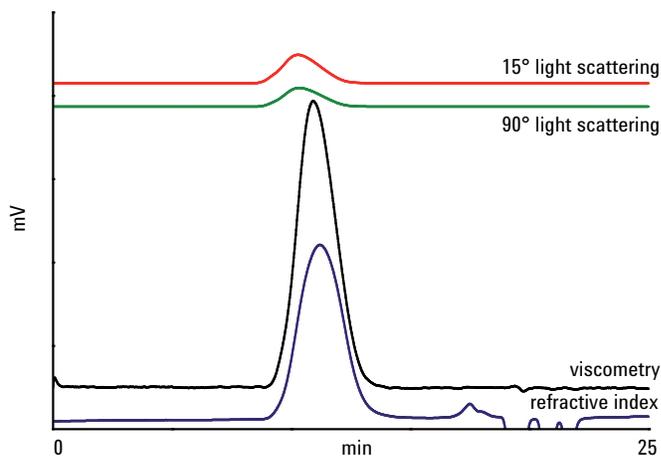


Figure 20. Triple detection of a polybutadiene showing typical data for this type of sample

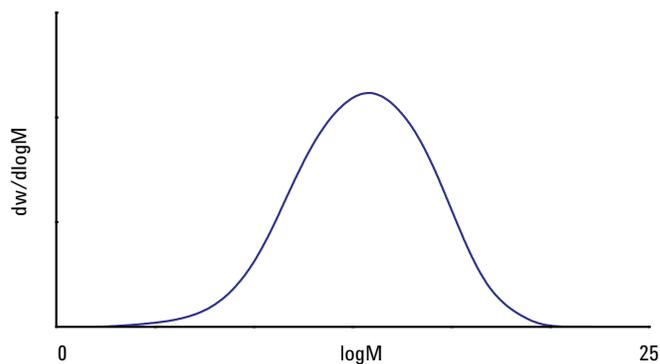


Figure 21. Molecular weight distribution of a polybutadiene with a broad Gaussian peak shape

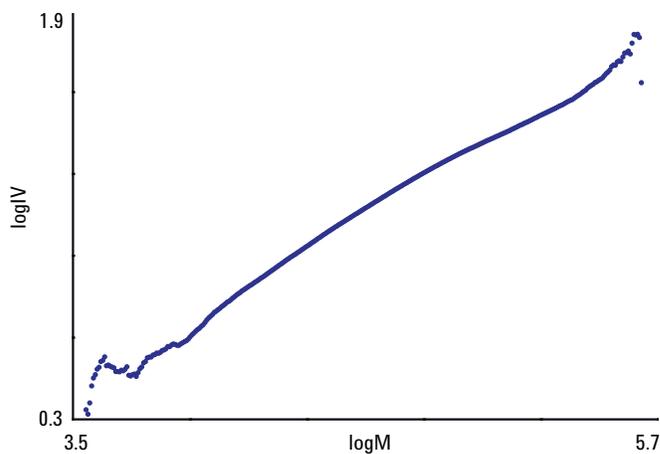


Figure 22. Mark-Houwink plot of a polybutadiene with curvature that may be attributed to structural changes as a function of molecular weight

General synthetic elastomer analysis

Polyisoprene can be produced synthetically. Together with polybutadiene and styrene butadiene, it is a common elastomeric material. Polybutadiene is a synthetic rubber manufactured from the monomer 1,3-butadiene. With high wear resistance, it is used in tire manufacture, and to coat electronic assemblies due to its extremely high electrical resistivity. Polybutadiene exhibits 80% recovery after stress, one of the highest stress-recovery values of a synthetic material.

Styrene butadiene rubber (SBR) is a synthetic rubber copolymer of styrene and butadiene. With good abrasion resistance it is widely used in car tires, after blending with natural rubber.

The extended operating range of the PLgel 10 μ m MIXED-B column (up to 10,000,000 MW) makes it ideally suited to the analysis of a wide range of high molecular weight elastomers (Figure 23). Sample solutions are routinely filtered prior to injection to remove insoluble "gel fractions", common to most elastomers.

Conditions

Columns: 3 x PLgel 10 μ m MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
Eluent: THF
Flow rate: 1.0 mL/min
Loading: 0.2% w/v, 100 μ L
Injection volume: 200 μ L
Temperature: 40 $^{\circ}$ C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

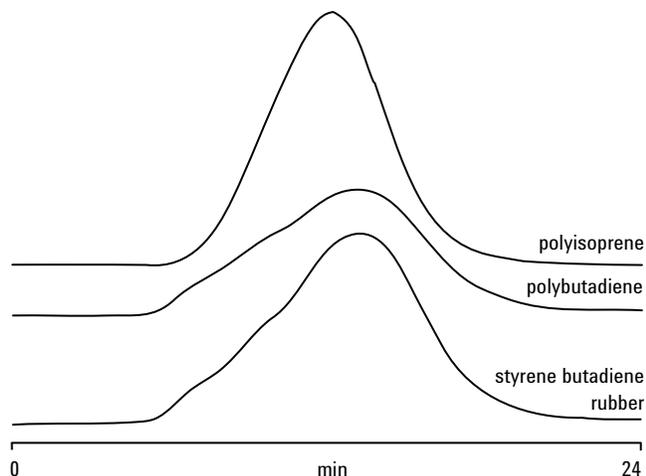


Figure 23. Chromatograms of three types of synthetic rubber with multimodal peak shapes



Hexane is a good solvent for butyl rubber although it can be chromatographed using other solvents, such as THF. The polarity of hexane is very low compared with more traditional solvents for GPC such as THF. However, it can be used successfully with PLgel columns (Figure 24).

Conditions

Columns: 3 x PLgel 10 μ m MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
Eluent: Hexane
Flow rate: 1.0 mL/min
Instrument: PL-GPC 50 Integrated GPC/SEC System

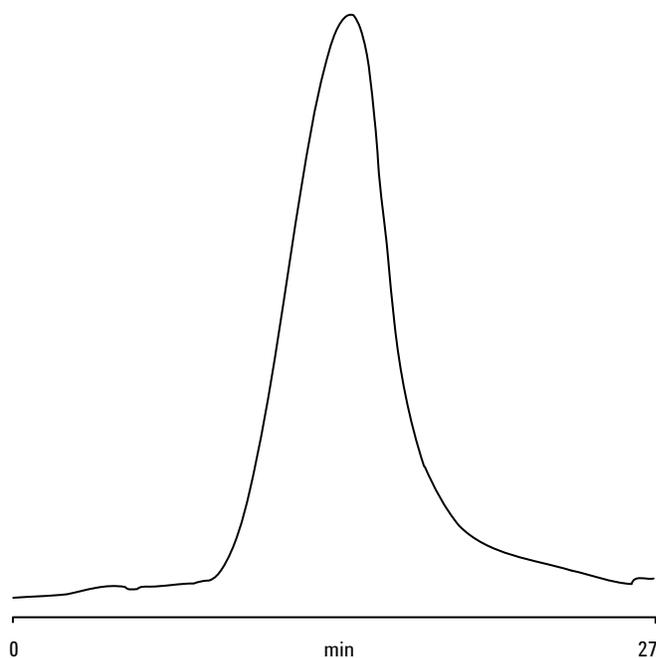


Figure 24. Butyl rubber chromatogram in hexane showing that a good peak shape can be obtained

Commercial grades of styrene butadiene rubber can contain very high molecular weight fractions and so, for successful GPC separations, the sample concentration must be minimized in order to avoid viscous streaming effects. Some grades of SBR can also contain low molecular weight mineral oil as a modifier (known as oil-extended grades) that can be resolved from the polymer peak, thus permitting quantification using Agilent ELSD (Figure 25).

Conditions

Columns: 2 x PLgel 20 μ m MiniMIX-A, 4.6 x 250 mm (p/n PL1510-5200)
Eluent: THF
Flow rate: 0.3 mL/min
Loading: 1 mg/mL, 100 μ L
Detector: Evaporative light scattering
(neb=45 °C, evap=90 °C,
gas=0.7 SLM)

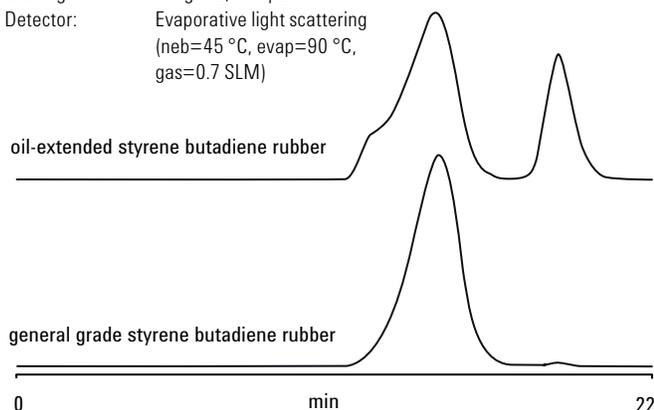


Figure 25. Chromatograms of two styrene butadiene rubbers, one oil-extended, showing the presence of the low molecular weight additive

The sample of oil-containing SBR, shown in Figure 26, was analyzed using refractive index detection. To ensure dissolution, the sample was warmed to 50 °C and gently stirred for three hours. Filtering using 0.5 μ m filters is recommended to remove any gel fractions. The PLgel MIXED-B packing permits resolution of both polymer and oil peaks.

Conditions

Columns: 2 x PLgel 10 μ m MIXED-B, 7.5 x 300 mm
(p/n PL1110-6100)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 100 μ L
Instrument: PL-GPC 50 Integrated GPC/SEC System

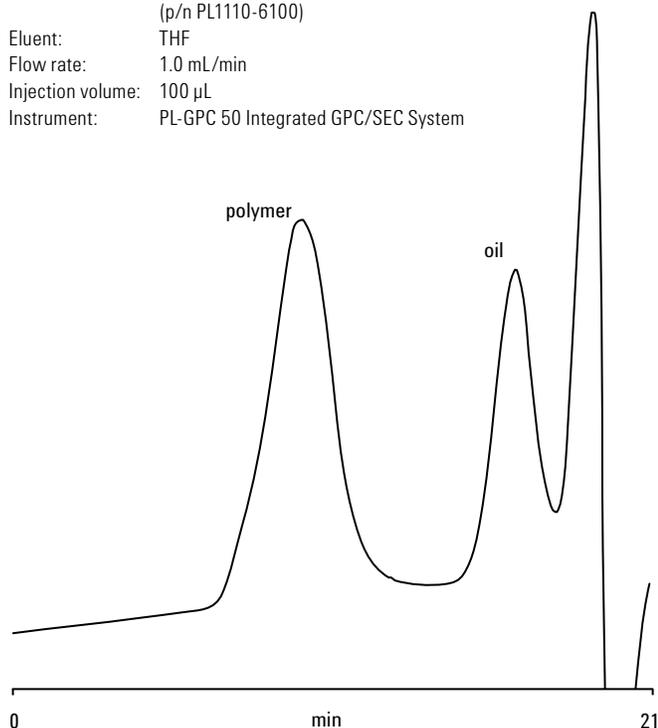


Figure 26. Chromatogram of an oil-extended styrene butadiene rubber showing the presence of a low molecular weight oil additive

Polydimethyl siloxane

Polydimethyl siloxane (PDMS) is a non-toxic, non-flammable silicon-based polymeric material noted for its unusual rheological behavior. Composed of polymer chains of formula $(\text{CH}_3)_3\text{SiO}[\text{SiO}(\text{CH}_3)_2]_n\text{Si}(\text{CH}_3)_3$, PDMS is a viscoelastic material which, with long flow times or at high temperatures behaves like a liquid, and with short flow times or at low temperatures behaves like a rubber. PDMS is produced in a range of grades from liquids through to rubbery semi-solids depending on the molecular weight of the constituent chains. It is a widely used material and can be found in applications such as silicone caulks, lubricants, damping fluids and heat transfer fluids.

PDMS was analyzed by GPC using the PL-GPC 50 Integrated GPC/SEC System. Due to the importance of the viscometric properties of the material in many final applications, a PL-GPC 50 viscometer was included as well as the standard refractive index detector. Results are shown in Figures 27 and 28. This combination of detectors also allows analysis of the material by the Universal Calibration method, giving accurate molecular weights that are not reliant on the chemistry of the standards used for calibration (in this case, polystyrene standards). Although PDMS is soluble in tetrahydrofuran, it is also isorefractive with this solvent and, therefore, THF is not suitable for the analysis and toluene is a more suitable solvent.

Conditions

Columns: 2 x PolyPore, 7.5 x 300 mm (p/n PL1113-6500)
Eluent: Toluene
Flow rate: 1.0 mL/min
Injection volume: 100 μ L
Instrument: PL-GPC 50 Integrated GPC/SEC System, viscometer

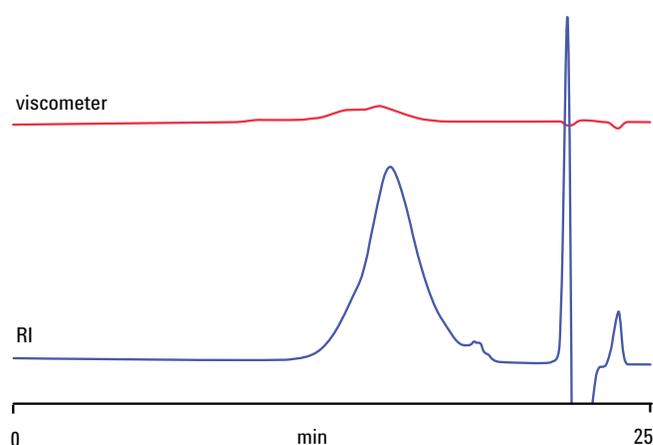


Figure 27. Example overlaid refractive index and viscometer chromatograms for a sample of polydimethyl siloxane showing typical peak shapes

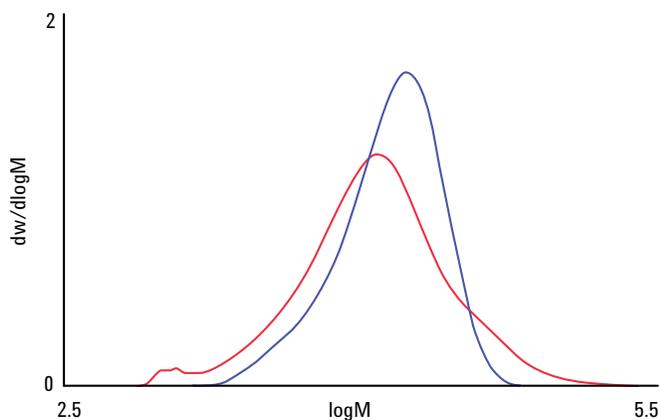


Figure 28. Overlaid molecular weight distributions for two different grades of polydimethyl siloxane with different performance characteristics

Although quite different in molecular weight, the Mark-Houwink plot (Figure 29) shows that the two materials are structurally very similar, indicating that their viscoelastic behavior as a function of molecular weight would be comparable.

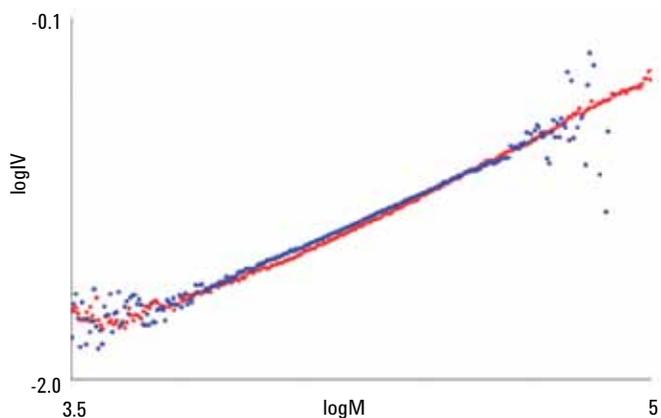


Figure 29. Mark-Houwink plots calculated for two samples of polydimethyl siloxane show that the materials are structurally very similar

Poly(styrene/butadiene) copolymers

A poly(styrene/butadiene) block copolymer mimics many of the properties of natural rubber and has applications in a wide variety of industrial areas. Its characteristics are provided by the hard polystyrene chains being surrounded by a network of rubbery polybutadiene, which provides strength and flexibility over a large temperature range. The copolymer is a thermoplastic elastomer and therefore can be easily used in manufacturing by injection molding, or blended into an existing product to increase elasticity or impart toughness. The molecular weight distribution is critical, as any homopolymer will significantly affect the resultant end properties.

In the analysis described here distinct differences were observed arising from the presence of homopolymers along with the intended copolymer (Figures 30 and 31).

Conditions

Columns: 2 x PLgel 5 μ m MIXED-C, 7.5 x 300 mm (ρ /n PL1110-6500)
 Calibration standards: Polystyrene EasiVial
 Eluent: THF (250 μ L/L BHT)
 Temperature: 40 $^{\circ}$ C
 Injection volume: 100 μ L
 Instrument: Agilent 1260 Mult-Detector GPC/SEC System

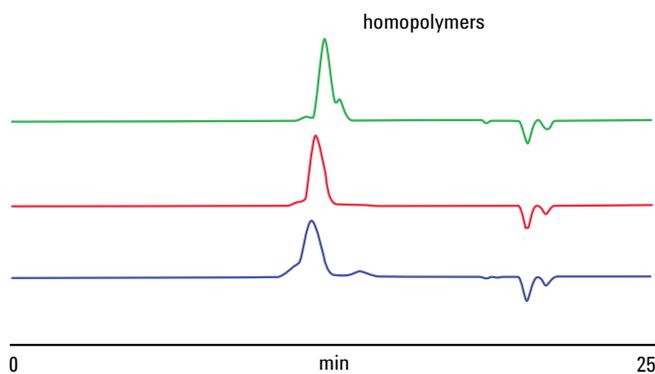


Figure 30. Chromatograms for styrene butadiene rubbers showing the presence of homo- and copolymers

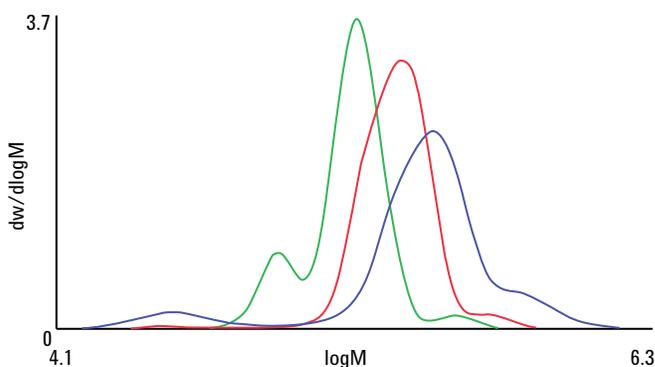


Figure 31. Overlaid molecular weight distributions for the styrene butadiene rubber samples showing a clear change in molecular weight distribution between samples



Low molecular weight resins

The term resin is used to describe materials manufactured by the addition polymerization of reactive monomers, often accompanied by the elimination of a small molecule. These synthetic methodologies result in materials with a relatively low molecular weight and a wide polydispersity, often containing oligomers and considerable monomer content. A feature of these polymers is the presence of reactive groups at the end of the polymer and oligomer chains, and many such materials are used as prepolymers that can be further reacted to form new products.

Characterizing and understanding the molecular weight distribution of resin materials is key to their performance. However, the polymers produced by condensation polymerizations tend to be highly functional and contain reactive groups, and many classes of material grouped by their reactive functionality, for example polyurethanes, have widely differing chemical structures. As a result, analysis of these materials by GPC/SEC can be challenging due to the possibility of interactions occurring between the packing material contained in the GPC/SEC column and structural elements of the material.

Low polarity resins

Low polarity resins may be analyzed on polystyrene/divinylbenzene columns in typical GPC solvents, such as THF.

The PlusPore series of columns has been specifically designed for high resolution GPC. These packing materials are based on the industry-standard, highly crosslinked polystyrene/divinylbenzene (PS/DVB) packing material, for the widest applicability and solvent compatibility. Each is made using a novel polymerization process to produce particles which exhibit a specific, controlled pore structure for optimum GPC performance.

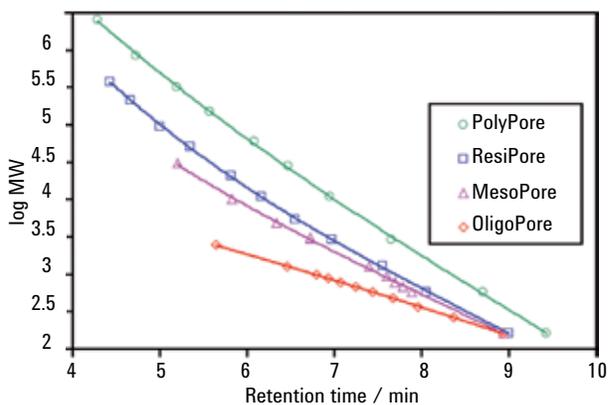


Figure 32. PlusPore calibration curves showing the resolving ranges and near linear calibrations of the columns

The ideal choice for polymer analysis

The composition of oligomers in resins is of great commercial importance, as is the determination of residual monomer in the quality control of polymers. Ideally, separation of discrete components is required to identify and quantify specific components of interest. To achieve this, small particle size packings are used to produce high resolution separations. The MesoPore column, with an exclusion limit of 25,000 molecular weight, has a guaranteed minimum efficiency of 80,000 plates/meter. Typical application chromatograms are shown in Figures 33 to 37.

Conditions

Sample: Isocyanate
Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
Eluent: THF (stabilized)
Flow rate: 1.0 mL/min
Detector: RI

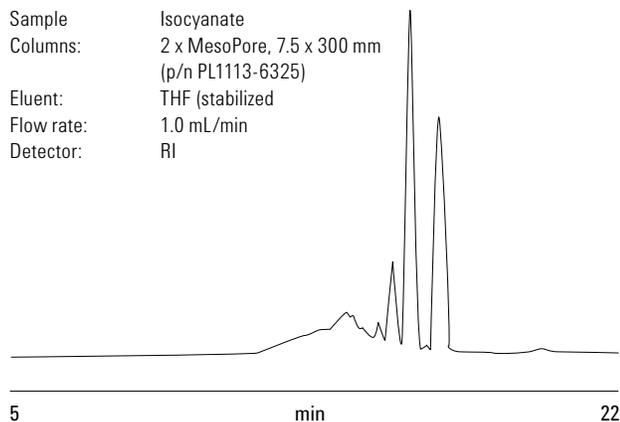


Figure 33. Chromatogram of an isocyanate sample showing polymer and oligomeric detail

Conditions

Sample: Polyol
Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
Eluent: THF (stabilized)
Flow rate: 1.0 mL/min
Detector: UV, 240 nm

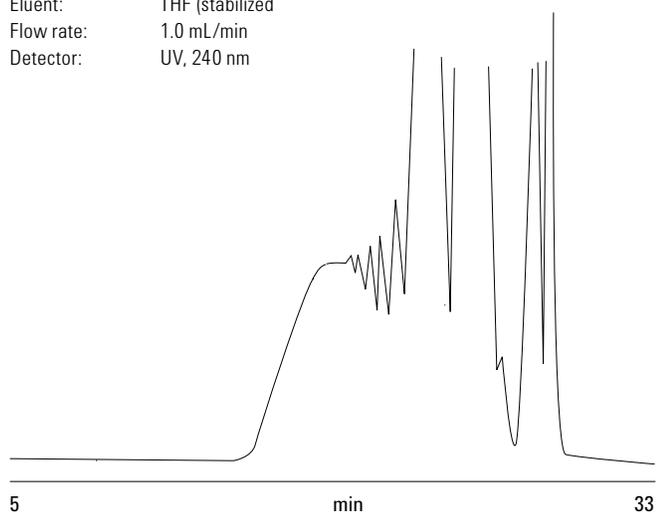


Figure 34. Chromatogram of a polyol sample showing the presence of large amounts of oligomers

Conditions

Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 20 μ L
Detector: RI

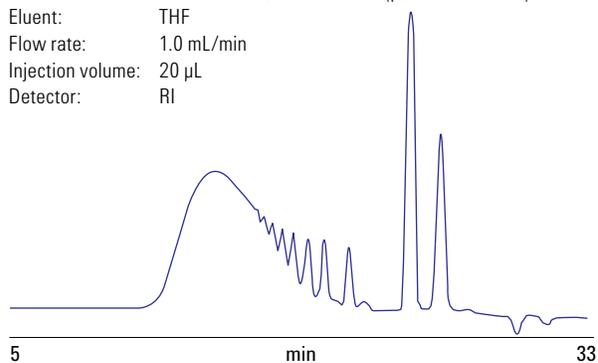


Figure 35. Chromatogram of a polyurethane sample with oligomers and residual monomers

Conditions

Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 20 μ L
Detector: RI

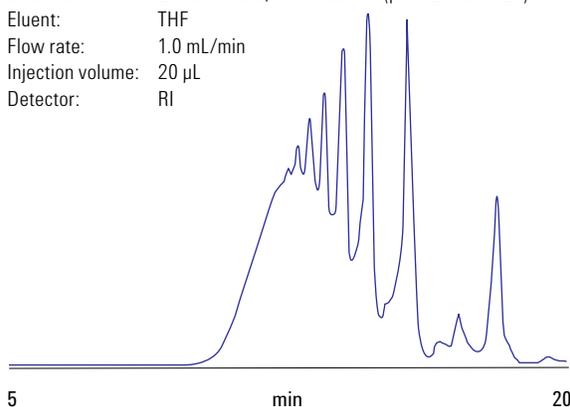


Figure 36. Chromatogram of an epoxy resin sample showing oligomers dominating the distribution

Conditions

Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 20 μ L
Detector: RI

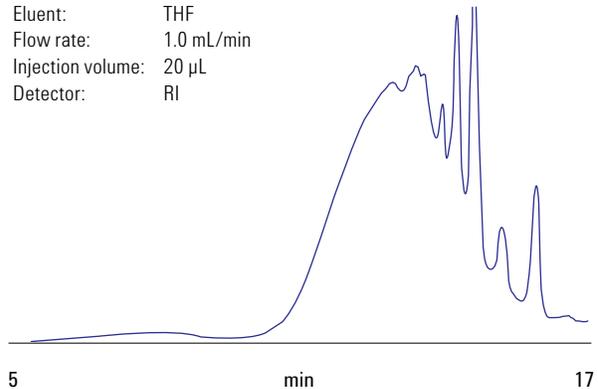


Figure 37. Chromatogram of a polyesterimide sample with a complex distribution of polymer and oligomer content

For higher molecular weight resins, the determination of molecular weight distribution is a primary objective in GPC analysis and columns with a broader resolving range are required. The ResiPore column has been specifically designed for such applications where material above 400,000 molecular weight is unlikely to be present. Figures 38 to 41 illustrate typical application chromatogram.

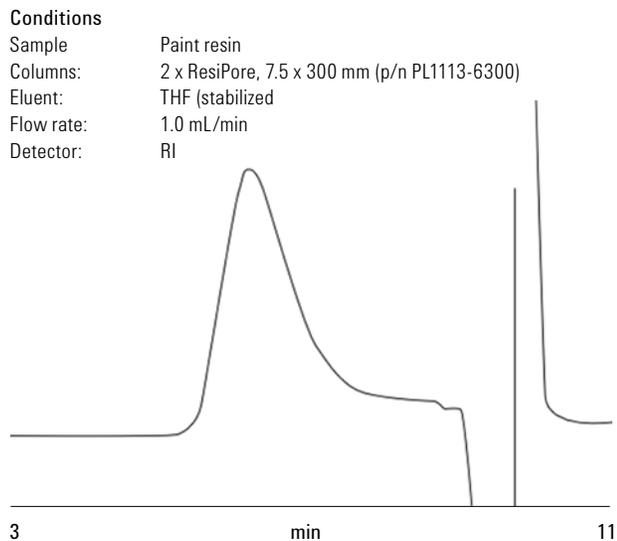


Figure 38. Chromatogram of a paint resin sample showing low molecular weight content with the polymer

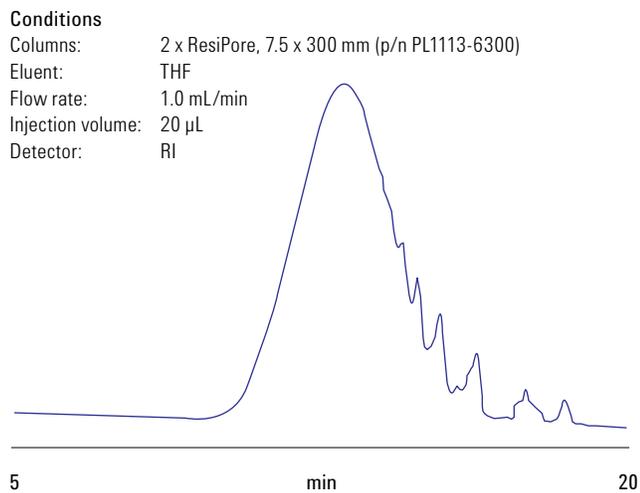


Figure 39. Chromatogram of higher molecular weight epoxy resin sample with some oligomer content

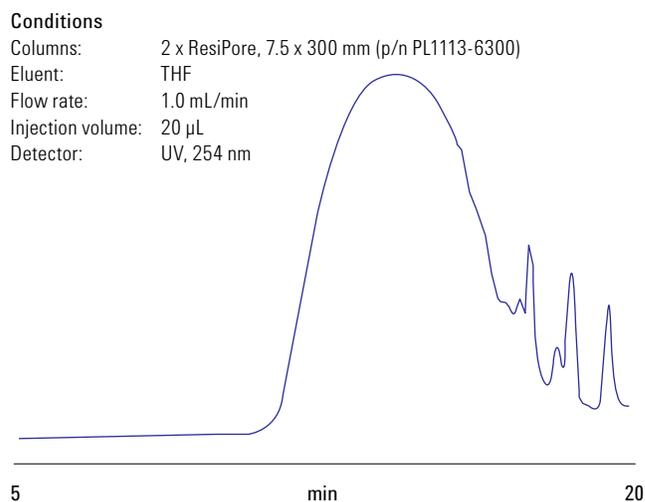


Figure 40. Chromatogram of an alkyd resin sample with a broad molecular weight distribution

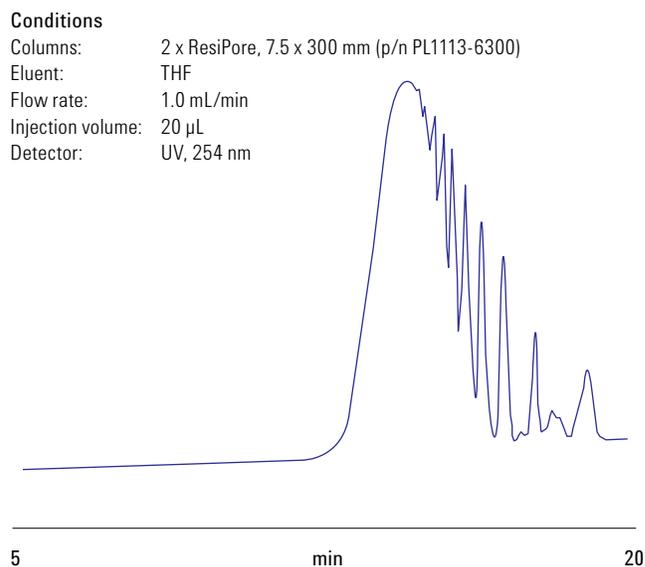


Figure 41. Chromatogram of a polyester sample showing oligomeric detail

Polyester polyol

This separation demonstrates the resolution of the oligomeric species in a polyol sample prepared from adipic acid and butandiol using MesoPore columns.

Conditions
 Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
 Eluent: THF
 Flow rate: 1.0 mL/min
 Detector: UV, 254 nm

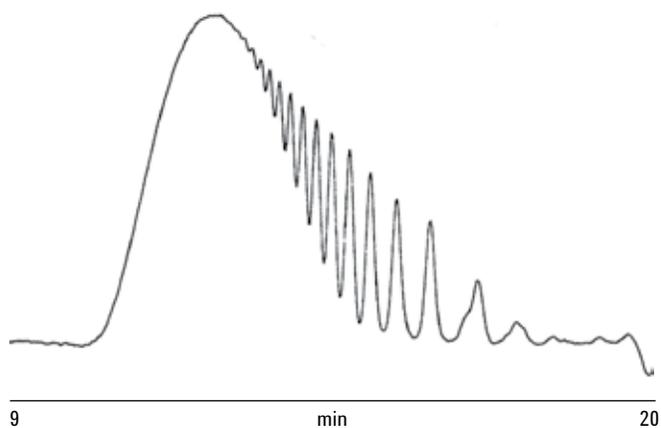


Figure 42. Chromatogram of a polyester polyol sample, a complex material with a UV chromophore

Phenolic resins

Phenol-formaldehyde reactions produce two main products:

- (a) Novolacs - under acidic conditions
- (b) Resols - under basic conditions (excess aldehyde).

Chromatograms showing excellent oligomeric detail were produced for each product, when using high efficiency MesoPore columns.

Conditions

Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
 Eluent: THF
 Flow rate: 1.0 mL/min
 Detector: UV

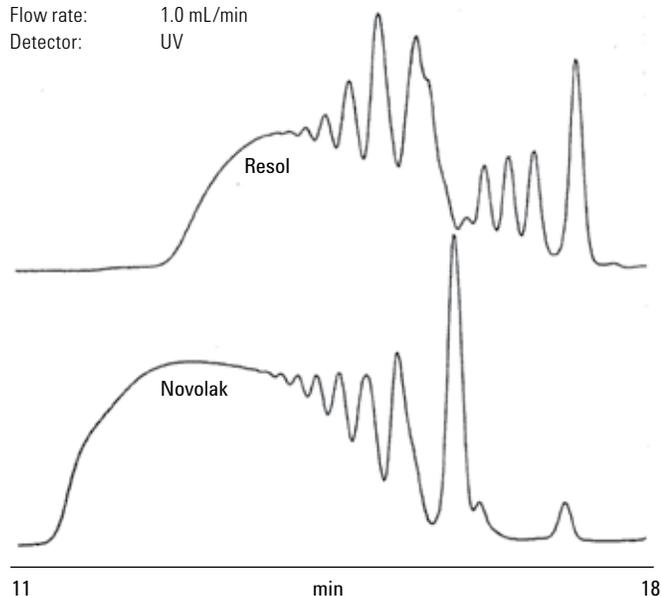


Figure 43. Overlaid chromatograms of two phenolic resin samples showing differences as a result of synthesis conditions

Adipate polyesters

Polyesters are produced from the condensation of a diacid with a dialcohol, eliminating water in the process. Depending on the acid and alcohol used, polyester can have a wide range of properties, including flexibility or hardness, stability to hydrolytic degradation and solvent, abrasion and shock resistance, properties which are useful for a wide range of applications. Adipate esters are produced by the condensation of a dialcohol with adipic acid. Saturated adipate polyesters are used as cast elastomers; depending on the dialcohol used in the synthesis, linear or branched polyesters may be obtained. These polyesters are reacted with isocyanates to produce prepolymers with residual isocyanate groups that are precursors to mixed polyurethanes, a very important commercial class of material.

Figure 44 shows two adipate polyester materials. The high resolution GPC columns are able to resolve the polymers into individual oligomers giving a characteristic peak shape that can be used to identify and 'fingerprint' different batches of polymers.

Conditions

Samples: Adipate polyesters
 Columns: 2 x MesoPore, 7.5 x 300 mm (p/n PL1113-6325)
 Eluent: THF (stabilized)
 Flow rate: 1.0 mL/min
 Injection volume: 20 µL
 Detector: RI

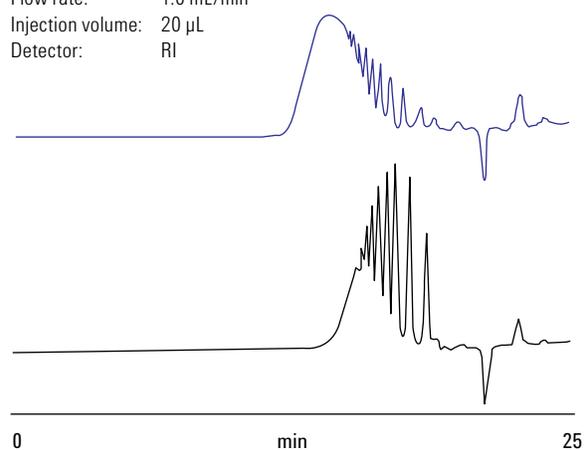


Figure 44. Overlaid chromatograms of adipate polyester samples showing clear differences between two batches



Higher molecular weight phenolic resins

The term “phenolic resin” is used to describe a group of thermosetting resins produced through the reaction of phenol with an aldehyde. Phenolic resins were the earliest synthetic polymers to be developed, Bakelite in 1907, and possess useful mechanical and physical properties. Applications of phenolic resins include electrical insulation, molding, lamination and adhesives. Due to the relatively low cost and favorable properties of phenolic resins, they are produced in the greatest volume of all thermosetting polymers. Key characteristics of phenolic resins are their molecular weight distribution and oligomeric “fingerprint”, as these both have significant effect on the end use properties of the resin.

In this case, the use of high resolution GPC columns is advantageous, since these allow an optimized oligomeric separation and provide detailed information regarding the oligomeric sample composition. These phenolic resins are non-polar and so they can be analyzed in THF using PS/DVB columns. Four distinct grades of phenolic resin were analyzed using a ResiPore column set. Resulting from the small particle size (3 μm) and optimized pore size distribution of this column packing material, good resolution was obtained in the molecular weight range of interest.

The chromatography obtained from each phenolic resin sample is shown in Figure 45. Differential molecular weight distributions are in Figure 46. This plot clearly shows significant differences in molecular weight distribution and the relative amounts of oligomeric material.

Conditions

Columns: 2 x ResiPore, 7.5 x 300 mm (p/n PL1113-6300)
 (conditioned with 10 injections of a typical sample solution at 10 mg/mL)
 Eluent: THF (stabilized with 250 μL/L BHT)
 Flow rate: 1.0 mL/min
 Injection volume: 20 μm
 Detector: RI

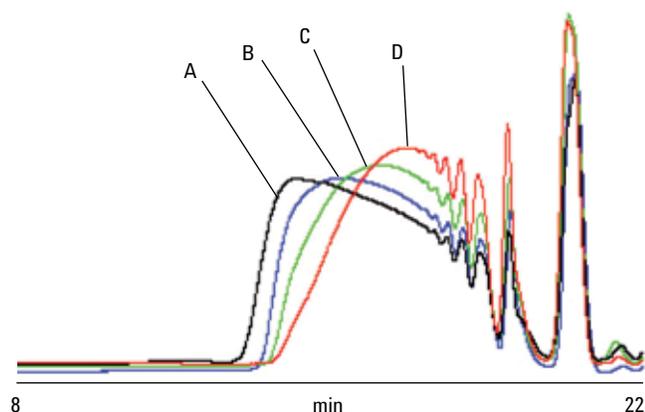


Figure 45. Overlaid GPC chromatograms obtained from four samples of phenolic resin showing differences in elution behavior

Conditions

Columns: 2 x ResiPore, 7.5 x 300 mm (p/n PL1113-6300)
 (conditioned with 10 injections of a typical sample solution at 10 mg/mL)
 Eluent: THF (stabilized with 250 μL/L BHT)
 Flow rate: 1.0 mL/min
 Injection volume: 20 μm
 Detector: RI

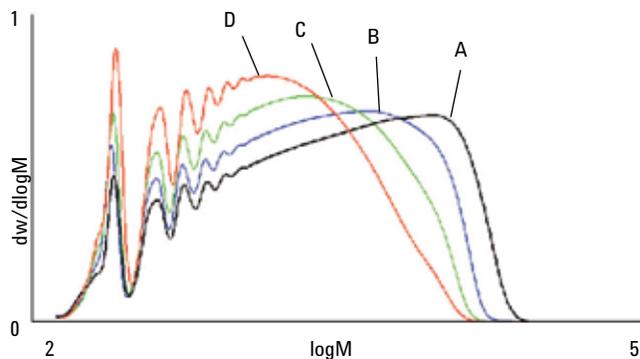


Figure 46. Overlaid molecular weight distributions from the GPC of four samples of phenolic resin - the same oligomers are present, but the overall molecular weights are very different



Preparative GPC of epoxy resin oligomers

Preparative GPC can be used to separate and isolate individual components of a sample based on size exclusion. By scaling up analytical separations, preparative GPC can be used to isolate practical quantities of individual components which can be used in further analysis. Agilent has developed the OligoPore preparative GPC column, which is ideally suited to the separation and isolation of individual oligomers from oligomer distributions and complex mixtures. This application illustrates the use of OligoPore preparative columns in the fractionation of epoxy oligomers. Figure 47 shows the general structure of an epoxy oligomer. A commercial epoxy resin, Epikote 828, is composed of two main epoxy oligomers where $n=0$ and $n=1$ and small amounts of the mono and di-epoxy water adducts.

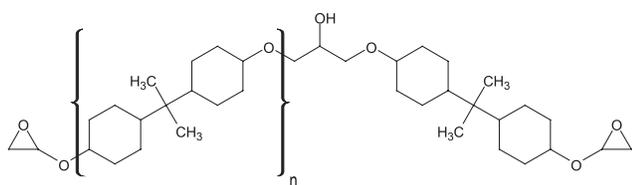


Figure 47. General structure of Epikote 828 epoxy resin oligomers

Analytical scale

Initially, the optimum loading of Epikote 828 on the OligoPore columns was analyzed on an analytical scale. Figure 48 shows analytical chromatograms at concentrations of 0.5% to 2.0% (w/v). The chromatograms show that Epikote 828 could be analyzed at a concentration of 2.0% (w/v) without serious loss of resolution.

Conditions

Samples: Epikote 828, 0.5-2.0% (w/v)
Columns: 2 x OligoPore, 7.5 x 300 mm (p/n PL1113-6520)
Eluent: THF
Flow rate: 1.0 mL/min
Injection volume: 100 μ L
Detector: UV

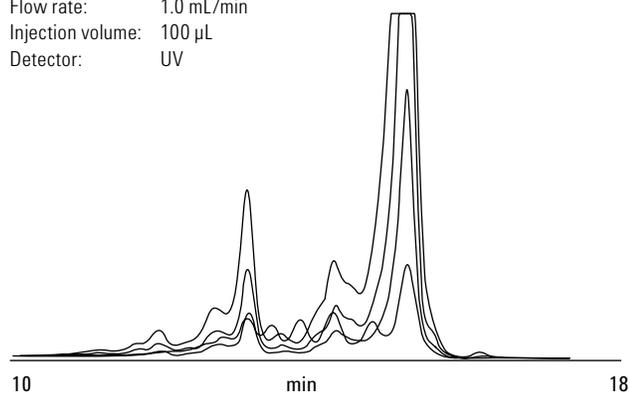


Figure 48. Overlaid chromatograms of epikote epoxy resin samples at different loadings

Preparative scale

OligoPore preparative columns were used to fractionate and purify the two oligomers from the resin. A preparative GPC system was set up with a 2 mL injection loop, two OligoPore 25 x 300 mm columns and a flow rate of 10.0 mL/min, an appropriate ten-fold scale-up over the analytical separation. The flow rate from the columns was split into two lines, about 0.5 mL/min went to a UV detector, the remainder of the flow to a waste/fraction collector. The epoxy resin sample was injected at a concentration of 1.0% (w/v). Figure 49 shows a chromatogram of Epikote 828 obtained on the preparative columns indicating the resolution obtained. The sample was re-run and the two oligomers $n=0$ and $n=1$ were collected. The fractions were then analyzed on two OligoPore analytical columns.

Figure 50 shows the original analytical chromatogram of Epikote 828 run at a concentration of 2.0% (w/v) and an overlay of analytical chromatograms of the $n=0$ and $n=1$ oligomers collected from the OligoPore preparative GPC columns.

Conditions

Samples: Epikote 828, 1.0% (w/v)
Columns: 2 x OligoPore, 7.5 x 300 mm (p/n PL1113-6520)
Eluent: THF
Flow rate: 10.0 mL/min, ca 9.5 mL/min collected
0.5 mL/m into the detector
Injection volume: 2 mL
Detector: UV

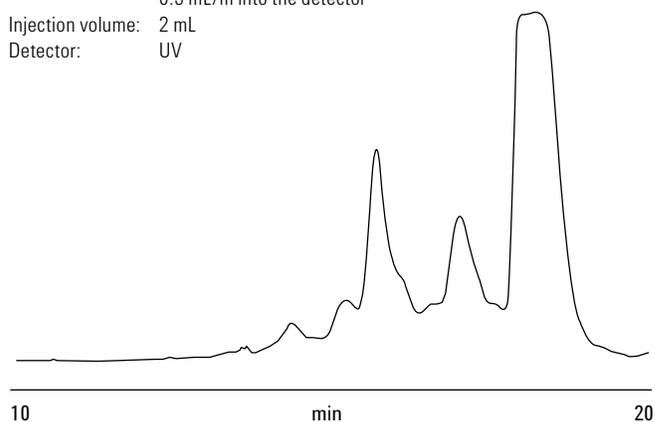


Figure 49. Chromatogram of an epikote 828 sample on a preparative scale column showing which oligomers could be isolated

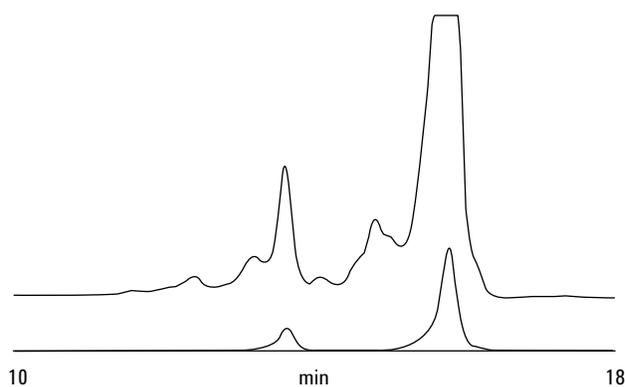


Figure 50. Overlaid chromatograms of an epikote 828 sample (top) and two separated fraction samples (bottom) showing the isolation of components through preparative GPC

High polarity resins

Increasingly, the choice of solvent for use as a GPC eluent is becoming more diverse since the polymers to be analyzed are more demanding in terms of solubility. Polar organic solvents are often the most suitable choice (see Table 4). However, such solvents usually exhibit relatively high viscosity, and demand the application of elevated temperature in order to improve the separation and reduce the column operating pressure.

The compatibility of GPC packing materials with this range of solvents assumes increasing importance in high performance separations of modern polymer systems. Column performance should be unaffected by solvent transfer, which demands a high degree of chemical and physical stability in the column bed.

Table 4. Solubility and eluent choices for different polymer types

Polymer Type	Solvent
ABS	DMF
Cellulose	DMSO/DMAC
Poly(acrylates)	DMF/DMAC
Poly(acrylonitrile)	DMF
Poly(ethylene oxide)	DMF
Poly(urethane)	DMF/DMAC
Poly(vinyl pyrrolidone)	DMF/DMAC

Intermediate polarity packing

PolarGel columns contain macroporous copolymer beads with a surface of balanced polarity, comprising hydrophobic and hydrophilic components. As the polarity of the bead surface is intermediate between the nonpolar PLgel and the highly polar PL aquagel-OH materials, PolarGel is ideal for the analysis of high polarity polymers that are insoluble in water yet show interaction effects with styrene/divinyl benzene columns due to their high polarity.

PolarGel columns perform well in many applications that do not work well on typical organic GPC columns. The low swell of the PolarGel material in a range of solvents explains the stability of the packing, see Figure 51.

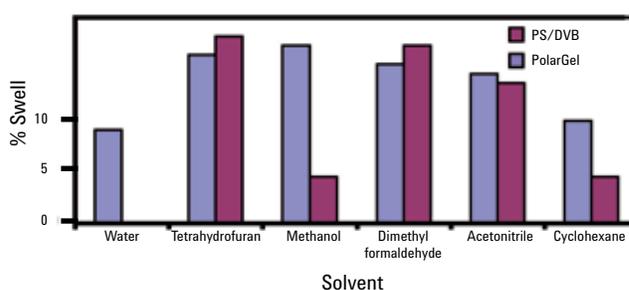


Figure 51. Swell data for PolarGel and a PS/DVB material showing the low swell of Agilent PolarGel



Broad solvent compatibility

As PolarGel columns combine intermediate surface polarity with low swell and high mechanical stability, they are used in a wide range of highly polar solvents, such as water, dimethyl formamide (DMF) and dimethyl acetamide (DMAc), and relatively low polarity solvents, such as tetrahydrofuran (THF), see Figure 52. PolarGel-L columns are MIXED bed columns containing a number of constituents carefully blended to give a wide operating range focused at low molecular weight, making them suitable for a variety of applications up to ca. 30,000 g/mol (polyethylene glycol/oxide in water).

Conditions

Samples: EasiVial PEG/PEO and PMMA Standards (4 mL vials)
Columns: 2 x PolarGel-L, 7.5 x 300 mm (p/n PL1117-6830)
Eluent: Water, acetone, DMF, DMAc, THF
Flow rate: 1.0 mL/min
Injection volume: 100 μ L
Detector: PL-GPC 50 Integrated GPC/SEC System, RI

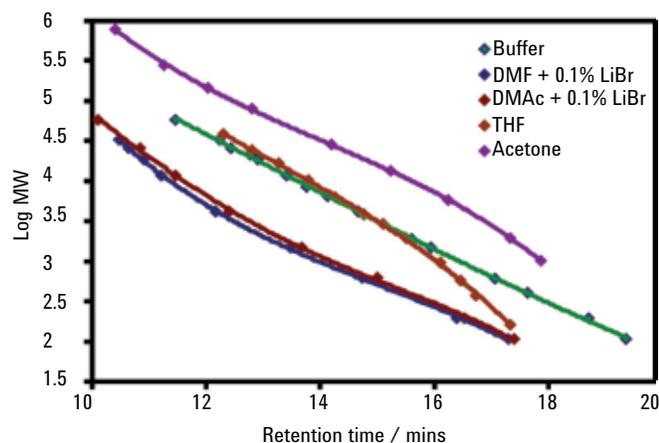


Figure 52. Calibration curves of Agilent PolarGel-L in different solvents showing the near linear calibrations obtained in a solvent with a wide range of polarities

Phenol-formaldehyde resins

Phenol-formaldehyde (P-F) resins are thermoplastic materials made with an excess of phenol in an acid catalyzed reaction with formaldehyde. P-F resins are commonly used as precursors to varnishes and other surface finish products.

Two types of phenol-formaldehyde resin were analyzed to obtain an indication of differences in molecular weight, if any. The samples were made up in 0.2% (w/v) DMF, with 0.1% LiBr added to reduce sample aggregation, and injected without further treatment. The results of the analyses are shown in the overlaid chromatograms and molecular weight distributions.

Conditions

Columns: 2 x PolarGel-M, 7.5 x 300 mm (p/n PL1117-6800)
Eluent: DMF + 0.1% LiBr
Flow rate: 1.0 mL/min
Injection volume: 100 μ L
Temperature: 50 $^{\circ}$ C
Instrument: PL-GPC 50 Integrated GPC/SEC System, RI

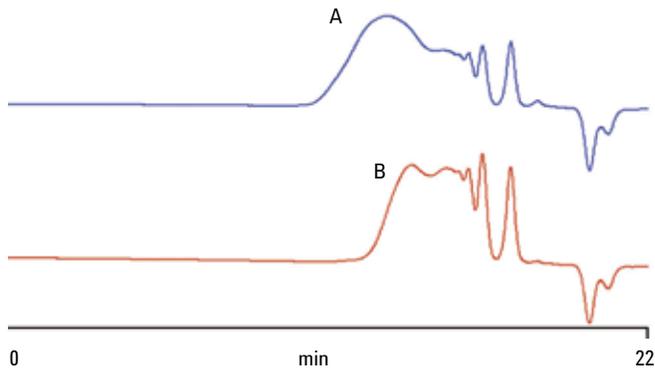


Figure 53. Agilent PolarGel-M reveals the composition of two phenol-formaldehyde resins, with clear differences between the materials

Conditions

Columns: 2 x PolarGel-M, 7.5 x 300 mm (p/n PL1117-6800)
Eluent: DMF + 0.1% LiBr
Flow rate: 1.0 mL/min
Injection volume: 100 µL
Temperature: 50 °C
Instrument: PL-GPC 50 Integrated GPC/SEC System, RI

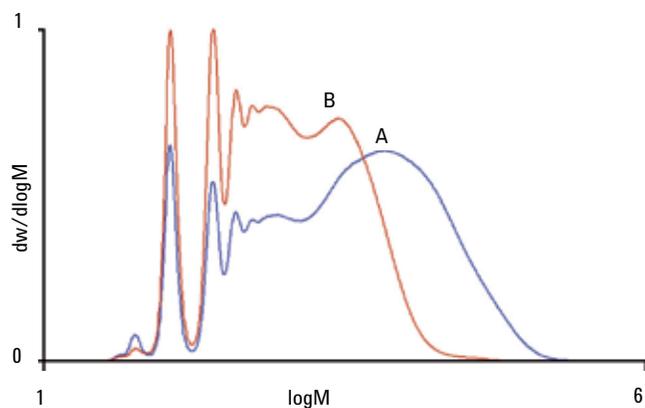


Figure 54. Overlaid molecular weight distributions of two phenol-formaldehyde resins show the same oligomers are present

Melamine resins

Melamine resins are durable thermosetting plastics formed by the condensation polymerization of melamine with formaldehyde. They are commonplace in the home as they are employed to laminate chipboard, creating inexpensive furniture, as well as being used in the manufacturing of kitchen tableware and food packaging. The molecular weight distribution of melamine resins determines many of the final properties of the polymer and therefore their application. Subtle differences in the molecular weight distribution of melamine resin samples, is essential.

The molecular weight distributions of two different samples of melamine were investigated by conventional gel permeation chromatography using a set of two PolarGel-L (7.5 x 300 mm) columns and the PL-GPC 50 Integrated GPC/SEC System. The samples were analyzed in the polar organic solvent dimethylacetamide (DMAc) which contained 0.1% LiBr.

Conditions

Sample: Two samples of melamine resin
Columns: 2 x PolarGel-L, 7.5 x 300 mm (p/n PL1117-6830)
Eluent: DMSO + 0.1% LiBr
Flow rate: 1.0 mL/min
Temperature: 50 °C
Instrument: PL-GPC 50 Integrated GPC/SEC System, RI

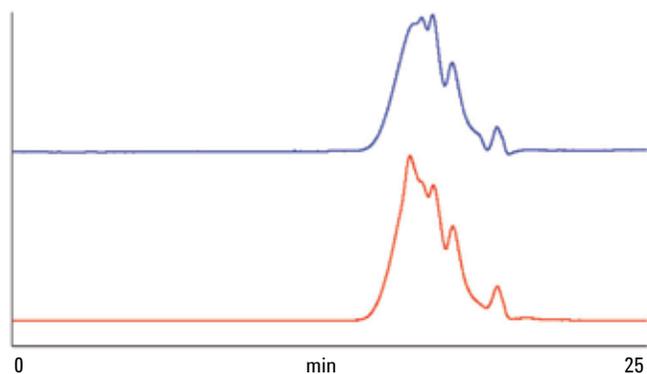


Figure 55. Chromatograms for two melamine samples showing obvious differences

Conditions

Sample: Two samples of melamine resin
Columns: 2 x PolarGel-L, 7.5 x 300 mm (p/n PL1117-6830)
Eluent: DMSO + 0.1% LiBr
Flow rate: 1.0 mL/min
Temperature: 50 °C
Instrument: PL-GPC 50 Integrated GPC/SEC System, RI

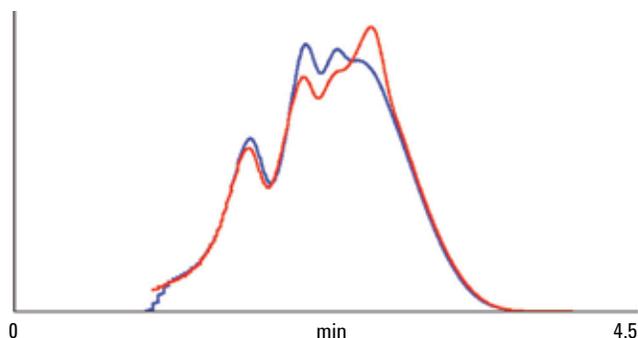
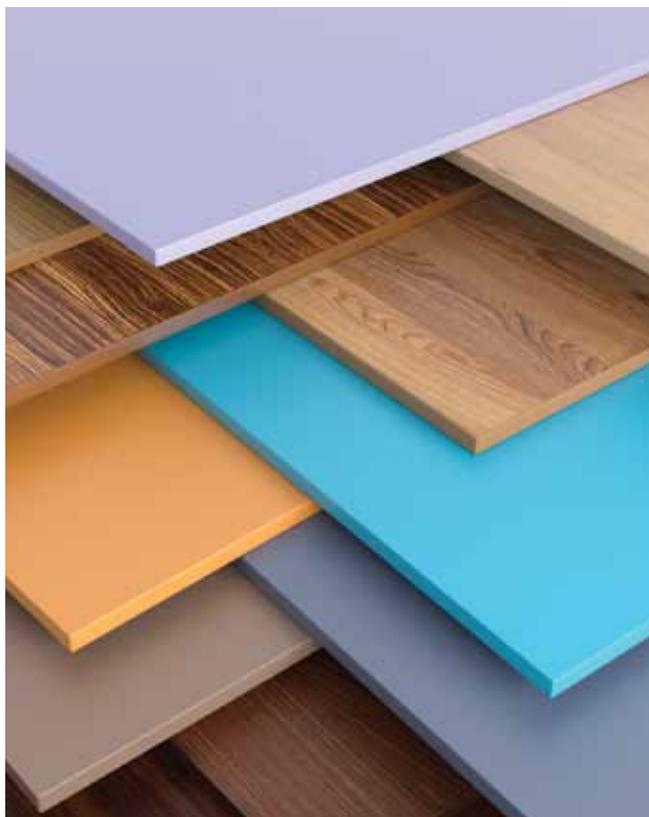


Figure 56. Overlaid molecular weight distributions for two melamine resin samples highlighting changes in the distributions

The two samples of melamine resins analyzed by conventional gel permeation chromatography on the PL-GPC 50 Integrated GPC/SEC System clearly had quite different molecular weight distributions, with differing ratios of the various oligomers present.



Nylon

For many polymer systems, the choice of solvent for the analysis is complex. Many polymers are soluble in only a small number of solvents, and the choice of solvent dictates the running conditions of the analysis. Many of the solvents required are exotic by HPLC standards and often are relatively unpleasant to handle and use from a health and safety perspective.

An example of such an analysis is that of nylon, a common polyamide that has a range of uses, most commonly in clothing. Despite the ubiquitous nature of nylon, the polyamide is only soluble in a few solvents that are suitable for use in GPC/SEC molecular weight distribution determinations. Two such solvents are 1,1,1,3,3,3-hexafluoro-2-isopropanol (HFIP) and meta-cresol. Both can be used to solubilize polyamides and have advantages and drawbacks when used as solvents in GPC/SEC.

HFIP

HFIP is a viscous, colorless liquid with a pungent odor. It is an excellent solvent for polyamides and esters and can be used to analyze nylon. Typically, a small amount of sodium trifluoroacetate is added to the eluent to reduce sample aggregation. HFIP is viscous but has a low boiling point and so the analysis is often performed at 40 °C to reduce the back pressure in the column. HFIP is also highly polar and can cause calibrations to become non-linear for MIXED-bed columns. Therefore, Agilent produced a special PL HFIPgel column for use in this solvent, with a multipore structure that is unaffected by the solvent. This work shows the analysis of two samples of nylon in HFIP.

The system was calibrated using polymethylmethacrylate standards and, therefore, all molecular weight values quoted are relative to these standards (Figure 57). Both samples were prepared as 0.1% w/v solutions and found to be fully soluble in the eluent, HFIP + 0.02 M NaTFAc.

Conditions

Columns: 2 x PL HFIPgel, 4.6 x 250 mm, 9 µm (p/n PL1515-5900HFIP)
 Calibrants: Agilent polymethylmethacrylate narrow standards
 Eluent: HFIP + 0.02 M NaTFAc
 Sample concentration: 0.1% w/v
 Injection volume: 100 µL
 Flow rate: 0.3 mL/min
 Temperature: 40 °C
 Pressure: 30 bar
 Detector: DRI

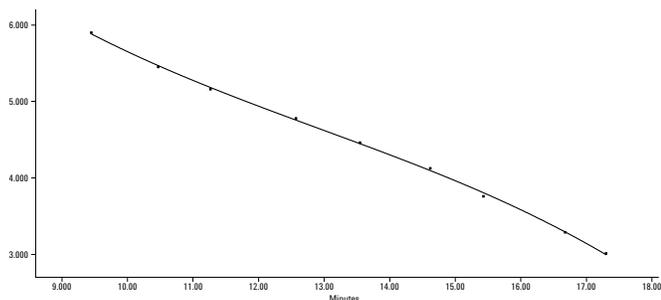


Figure 57. Calibrating an Agilent PL HFIPgel column using polymethylmethacrylate narrow standards

Figure 58 shows both samples eluting within the operating range of the PL HFIPgel column packing (2,000,000 to 500). Sample 2 displays the highest molecular weight. An example of the molecular weight averages that can be calculated for one of the samples is shown in Table 5.

Table 5. Molecular weight characteristics of nylon with HFIP as solvent

Mz+1	106,545
Mz	71,804
Mw	44,081
Mp	37,402
Mn	19,962
Mv	40,638
Polydispersity	2.208
Peak area	317,647

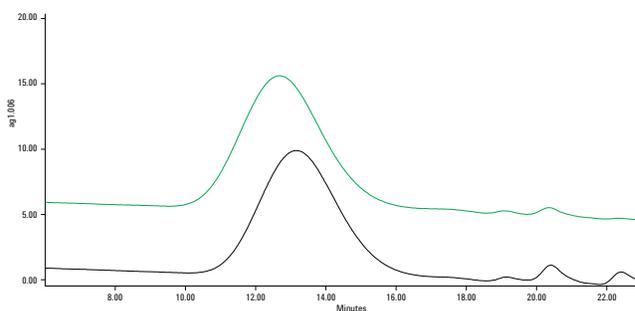


Figure 58. Raw data chromatogram of two nylon samples on a two-column set of Agilent PL HFIPgel 9 µm columns with HFIP solvent

Any differences or similarities that exist between samples are further highlighted in the combined molecular weight distribution plots in Figure 59.

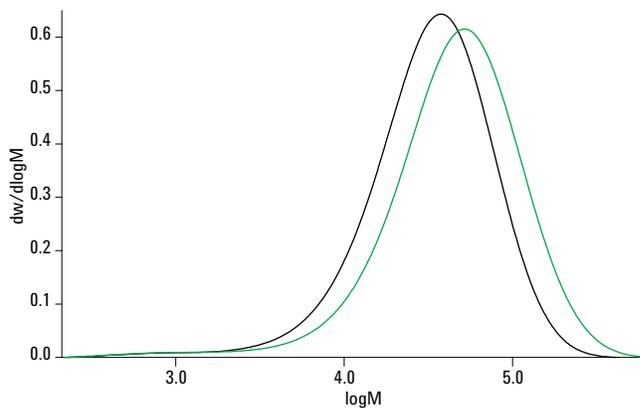


Figure 59. Overlaid molecular weight distributions of two nylon samples on two Agilent PL HFIPgel 9 µm columns

Meta-cresol

Meta-cresol is a methyl phenol compound that is excellent at solubilizing many polymers, including polyamides such as nylon. It has a pungent 'moth-ball' aroma but is relatively safe to handle compared to HFIP. However, it is extremely viscous and requires running at an elevated temperature to reduce the backpressure in the columns.

The system was calibrated using polystyrene standards and, therefore, all molecular weight values quoted are relative to these standards. Agilent EasiCal calibrants were used to obtain a 10 point calibration from only 2 injections (Figure 60). The sample was prepared as a 0.2% w/v solution and found to be fully soluble in m-cresol.

Overnight sample preparation was used as part of the dissolution process, with gentle warming of the sample solution prior to injection to ensure full solubility.

Conditions

Columns: 2 x PLgel 10 μ m MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
 Calibrants: Agilent EasiCal PS-1 (polystyrene) (p/n PL2010-0501)
 Eluent: m-Cresol
 Injection volume: 200 μ L
 Flow rate: 1.0 mL/min
 Temperature: 100 $^{\circ}$ C
 Pressure: 55 bar
 Detector: DRI

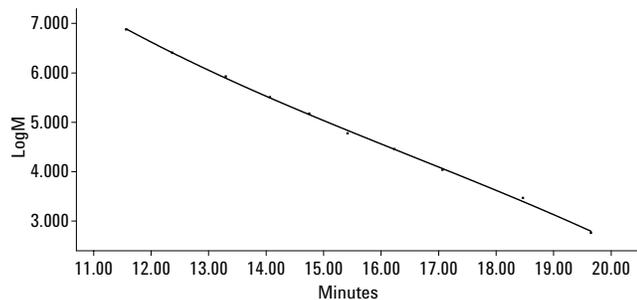


Figure 60. Calibrating the Agilent PLgel 10 μ m MIXED-B column using Agilent EasiCal PS-1 standards

Figure 61 shows repeat injections for a sample of nylon. A shoulder of high molecular weight material is clearly evident in the leading portion of the distribution. Table 6 and Figure 62 show the calculated molecular weight averages for each injection, and Figure 62 demonstrates the good repeatability by comparison of the overlaid molecular weight distribution plots.

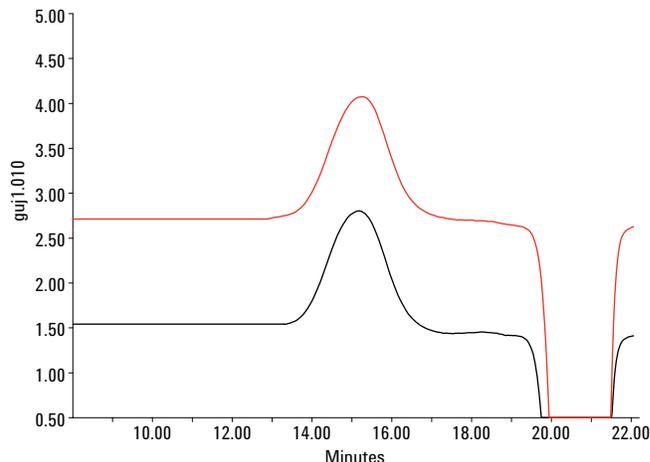


Figure 61. Raw data chromatogram of a sample of nylon on a two-column set of Agilent PLgel 10 μ m MIXED-B columns with m-cresol as solvent

Table 6. Molecular weight characteristics of an injection of nylon with m-cresol as solvent

Mz+1	1,509,517
Mz	506,837
Mw	151,806
Mp	91,715
Mn	75,874
Mv	131,838
Polydispersity	2.001
Peak area	28,822

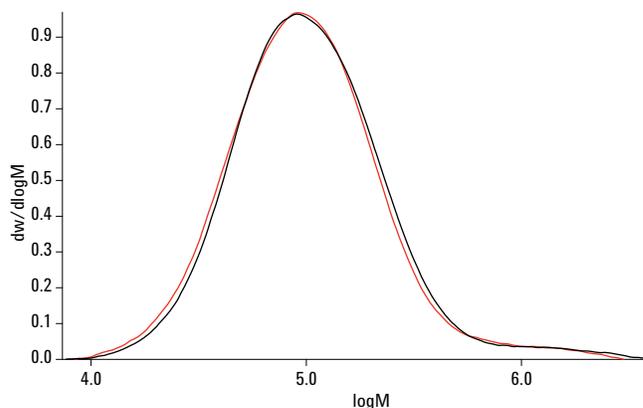


Figure 62. Overlaid molecular weight distributions of nylon samples on two Agilent PLgel 10 μ m MIXED-B columns with m-cresol as solvent.

GPC/SEC system configurations

The following Tables (7 to 15) will assist you in selecting the right system for your application. They show which components are required, and which are optional.

Agilent 1260 Infinity GPC/SEC System

Table 7. Sample delivery module requirements by application, for the Agilent 1260 Infinity GPC/SEC system



		Sample Delivery Modules			
		G1310B	G1322A	G1316A	G1329B
		1260 Infinity Isocratic Pump	1260 Infinity Standard Degasser	1260 Infinity Thermostatted Column Compartment	1260 Infinity Standard Autosampler or
					G1328C
					1260 Infinity Manual Injector
		GPC/SEC only requires isocratic flow	Solvent degassing recommended for GPC	Up to 80 °C TCC accomodates three 7.5 x 300 mm GPC columns	Typical injection volumes in GPC/SEC are 20, 50, and 100 µL
Application					
Natural and synthetic rubbers	e.g. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone, butyl rubber, PDMS	✓	✓	✓	✓
Polyesters and polyamides	e.g. Polyethylene terephthalate, polylactic acid, polyamide, nylon, adipate polyesters	✓	✓	✓	✓
Resins	e.g. Epoxies, polyurethane, acrylate polymers, phenolics, P-F, novolac, melamine	✓	✓	✓	✓
Vinyl polymers	e.g. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓	✓
Waxes	e.g. Carnauba, paraffin wax	✓	✓	✓	✓
UV-absorbing polymers	e.g. Polystyrene, poly(styreneacrylonitrile), polymethylmethacrylate, polybutadienes, polycarbonates, polyacrylic acids	✓	✓	✓	✓

Key

✓ Required

✓ Optional

Table 8. Detector and software requirements by application, for the Agilent 1260 Infinity GPC/SEC system



Application		Detectors		Control, Collection and Analysis Software	
		G1362A	G1314F	G7850AA	G7854AA
		1260 Infinity Refractive Index Detector	1260 Infinity Variable Wavelength Detector or G1365D 1260 Infinity Multiple Wavelength Detector	Agilent GPC/SEC Software	Agilent GPC/SEC Instrument Drivers
		Includes 8 µL flow cell and LAN interface	For single or multi-wavelength analysis	Standalone software dedicated to GPC calculations	Provides instrument control and data collection
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓		✓	✓
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓		✓	✓
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics	✓		✓	✓
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓		✓	✓
Waxes	eg. Beeswax, carnauba, paraffin wax	✓		✓	✓
UV-absorbing polymers	eg. Polystyrene, poly(styreneacrylonitrile), polymethylmethacrylate, polybutadienes, polycarbonates, polyacrylic acids	✓*	✓*	✓	✓

* At least one of the detectors (the 1260 Infinity Refractive Detector, the 1260 Infinity Variable Wavelength Detector, or the 1260 Infinity Multiple Wavelength Detector) is required, but it is optional which you choose.

Key

✓ Required

✓* Optional

Agilent 1260 Infinity Multi-Detector GPC/SEC System

Table 9. Sample delivery module requirements by application, for the Agilent 1260 Infinity Multi-Detector GPC/SEC System



Application		Sample Delivery Modules			
		G1310B	G1322A	G1316A	G1329B
		1260 Infinity Isocratic Pump	1260 Infinity Standard Degasser*	1260 Infinity Thermostatted Column Compartment*	1260 Infinity Standard Autosampler or
					G1328C
					1260 Infinity Manual Injector
		GPC/SEC only requires isocratic flow	Solvent degassing recommended for GPC	Up to 80 °C TCC accommodates three 7.5 x 300 mm GPC columns	Typical injection volumes in GPC/SEC are 20, 50 and 100 µL
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓	✓	✓	✓
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓	✓	✓	✓
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics	✓	✓	✓	✓
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓	✓
Waxes	eg. Beeswax, carnauba, paraffin wax	✓	✓	✓	✓
UV-absorbing polymers	eg. Polystyrene, poly(styreneacrylonitrile), polymethylmethacrylate, polybutadienes, polycarbonates, polyacrylic acids	✓	✓	✓	✓

* Highly recommended

Key

✓ Required

✓ Optional

Table 10. Detector requirements by application, for the Agilent 1260 Infinity Multi-Detector GPC/SEC System



		Detectors				
		G7800A	G7801A	G7802A	G7803A	G1314F
		1260 Infinity Multi-Detector Suite	1260 Infinity MDS Refractive Index Detector	1260 Infinity MDS Viscometer	1260 Infinity MDS Dual Angle Light Scattering Detector	1260 Infinity Variable Wavelength Detector or G1365D 1260 Infinity Multiple Wavelength Detector
		Includes integrated control module for data collection and manual control	Refractive index detector, most common detector for GPC	Viscometer, for conformational information	Dual angle light scattering detector, 15° and 90°, for absolute Mw	For single or multi-wavelength analysis, only one channel collected
Application						
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓	✓	✓	✓	
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓	✓	✓	✓	
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics	✓	✓			
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓	✓	
Waxes	eg. Beeswax, carnauba, paraffin wax	✓	✓	✓		
UV-absorbing polymers	eg. Polystyrene, poly(styreneacrylonitrile), polymethylmethacrylate, polybutadienes, polycarbonates, polyacrylic acids	✓	✓*	✓*	✓	✓***

* At least one of the detectors (the 1260 Infinity MDS Refractive Index Detector, or the 1260 Infinity MDS Viscometer) is required, but it is optional which you choose.

Key

✓ Required

✓ Optional

** Only required in the absence of the 1260 Infinity MDS Refractive Index Detector

Table 11. Software requirements by application, for the Agilent 1260 Infinity Multi-Detector GPC/SEC System



		Control, Collection and Analysis Software		
		G7850AA	G7852AA	G7854AA
		Agilent GPC/SEC Software	Agilent GPC/SEC Multi-Detector upgrade*	Agilent GPC/SEC Instrument Drivers
		Standalone software dedicated to GPC calculations	Upgrade to Agilent GPC/SEC software dedicated to multi-detector GPC calculations	Provides instrument control and data collection
Application				
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓	✓	✓
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓	✓	✓
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics	✓		✓
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓
Waxes	eg. Beeswax, carnauba, paraffin wax	✓		✓
UV-absorbing polymers	eg. Polystyrene, poly(styreneacrylonitrile), polymethylmethacrylate, polybutadienes, polycarbonates, polyacrylic acids	✓		✓

* Required if 1260 Infinity MDS Viscometer and/or 1260 Infinity MDS Dual Angle Light Scattering Detector selected

Key
 ✓ Required
 ✓ Optional

Agilent PL-GPC 220 High Temperature GPC/SEC System

Table 12. Sample delivery modules, software, sample preparation and detector requirements by application, for the Agilent PL-GPC 220 High Temperature System

Application		Sample Delivery Modules		Additional Detectors	
		G7820A	PL-GPC 220 Integrated High Temperature GPC/SEC System	G7821A	G7822A
		Complete basic system includes degasser, pump, autosampler, oven and RI detector		Viscometer, used to generate the Universal Calibration. Housed inside oven	Dual angle light scattering detector, 15° and 90°, for absolute Mw. Housed inside oven
Polyamides	eg. Polyamide, nylon	✓		✓	✓
Polyolefins	eg. Polyethylene, polypropylene, poly(ethylene-co-norbornene)	✓		✓	✓
Waxes	eg. Polyethylene wax	✓		✓	✓
EVA copolymers	eg. Vinyl acetate ethylene copolymer	✓		✓	✓
PBT/ PET	Polybutylene terephthalate, polyethylene terephthalate	✓		✓	✓
PPS	Polyphenylene sulfide	✓		✓	✓
Linear hydrocarbons	C _n H _{2n+2}	✓			
PEEK	Polyether ether ketone	✓		✓	✓

Key

✓ Required

✓ Optional

Agilent PL-GPC 220 High Temperature GPC/SEC System

Table 13. Sample delivery modules, software, sample preparation and detector requirements by application, for the Agilent PL-GPC 220 High Temperature System



Application		Control, Collection and Analysis Software			Sample Preparation
		G7850AA	G7852AA	G7825A	G7825A
		Agilent GPC/SEC Software	Agilent GPC/SEC Multi-Detector upgrade*	PL DataStream	PL-SP 260VS Sample Prep System
		Standalone software dedicated to GPC calculations	Upgrade to Agilent GPC/SEC software dedicated to multi-detector GPC calculations	Required for data collection of up to four channels of data (A/D converter)	Sample prep and filtration system, with agitation and heating to 250 °C
Polyamides	eg. Polyamide, nylon	✓	✓	✓	✓
Polyolefins	eg. Polyethylene, polypropylene, poly(ethylene -co - norbornene)	✓	✓	✓	✓
Waxes	eg. Polyethylene wax	✓	✓	✓	✓
EVA copolymers	eg. Vinyl acetate ethylene copolymer	✓	✓	✓	✓
PBT/ PET	Polybutylene terephthalate, polyethylene terephthalate	✓	✓	✓	✓
PPS	Polyphenylene sulfide	✓	✓	✓	✓
Linear hydrocarbons	C _n H _{2n+2}	✓		✓	✓
PEEK	Polyether ether ketone	✓	✓	✓	✓

* Required if PL-GPC 220 Viscometer and/or PL-GPC 220 Dual Angle Light Scattering Detector selected

Key

✓ Required

✓ Optional

Agilent PL-GPC 50 Integrated GPC/SEC System

Table 14. Sample delivery module requirements by application, for the Agilent PL-GPC 50 Integrated GPC/SEC System



		Sample Delivery Modules		
		G7810A	G7810A#011	G7813A
		PL-GPC 50 Integrated GPC/SEC System	PL-GPC 50 with degasser*	PL-GPC 50 Autosampler
		Complete basic system, including pump, injection valve, oven and RI detector	With added internal degasser. Cannot be retro-fitted	56 vial positions. Available as 2 mL and 4 mL split tray
Application				
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓	✓	✓
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓	✓	✓
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics	✓	✓	✓
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓
Waxes	eg. Beeswax, carnauba, paraffin wax	✓	✓	✓

* Highly recommended

Key

✓ Required

✓ Optional

Table 15. Detector and software requirements by application, for the Agilent PL-GPC 50 Integrated GPC/SEC System



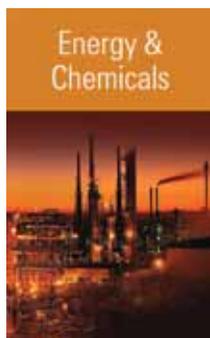
		Additional Detectors		Control, Collection and Analysis Software		
		G7811A	G7812A	G7850AA	G7852AA	G7854AA
		PL-GPC 50 Viscometer	PL-GPC 50 Dual Angle Light Scattering Detector	Agilent GPC/SEC Software	Agilent GPC/SEC Multi-Detector upgrade*	Agilent GPC/SEC Instrument Drivers
		Viscometer, used to generate the Universal Calibration. Housed within PL-GPC 50 unit	Dual angle light scattering detector, 15° and 90°, for absolute Mw. Housed within PL-GPC 50 unit	Standalone software dedicated to GPC calculations	Upgrade to Agilent GPC/SEC software dedicated to multi-detector GPC calculations	Provides instrument control and data collection
Application						
Natural and synthetic rubbers	eg. Gum arabic, polybutadiene, polysiloxane, polybutadiene, polyisoprene, SBR, silicone	✓	✓	✓	✓	✓
Polyesters and polyamides	eg. Polyethylene terephthalate, polylactic acid, polyamide, nylon	✓	✓	✓	✓	✓
Resins	eg. Epoxies, polyurethane, acrylate polymers, phenolics			✓		✓
Vinyl polymers	eg. Polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polyacrylonitrile	✓	✓	✓	✓	✓
Waxes	eg. Beeswax, carnauba, paraffin wax			✓		✓

* Required if PL-GPC 50 Viscometer and/or PL-GPC 50 Dual Angle Light Scattering Detector selected

Key

✓ Required

✓ Optional



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