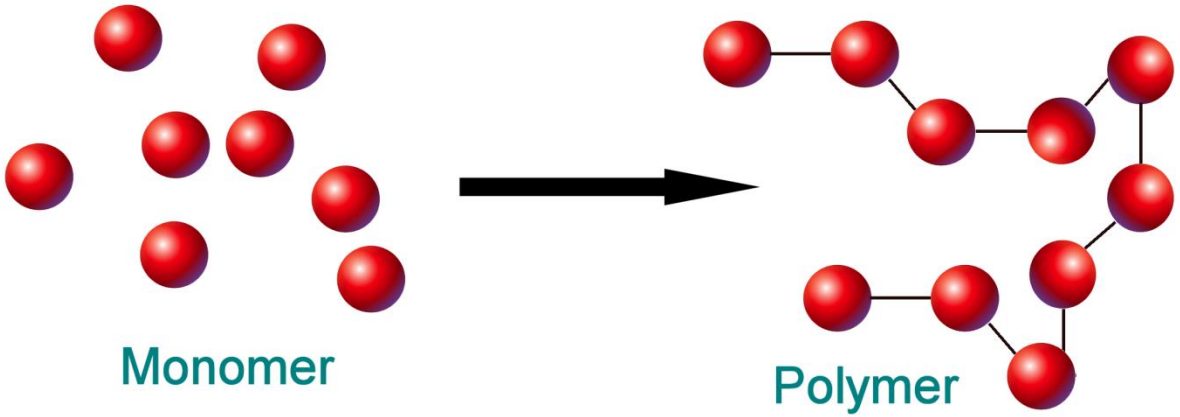
Introduction to GPC Separations

Agilent Technologies

What Are Polymers?

- Polymers are long chain molecules produced by linking small repeat units (monomers) together
- There are many ways to link different types of monomer to form polymers
- Polymers exhibit very different physical properties compared to the monomers, dependent on the length of the polymer chains
- The presence of small amounts of very long or very short chains can have drastic effects on properties of the material



The Primary Goal of GPC is to Discover the Mw Distribution

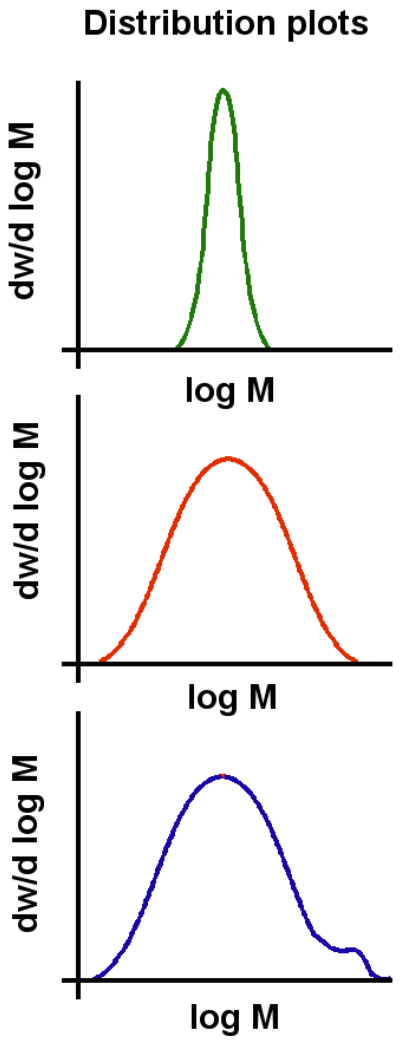
- Samples of synthetic polymers *always* contain polymer chains with a range of chain lengths
- One way to describe the length of the polymer chains is in terms of an average molecular weight, i.e the average of all the chain lengths in the sample

HOWEVER….

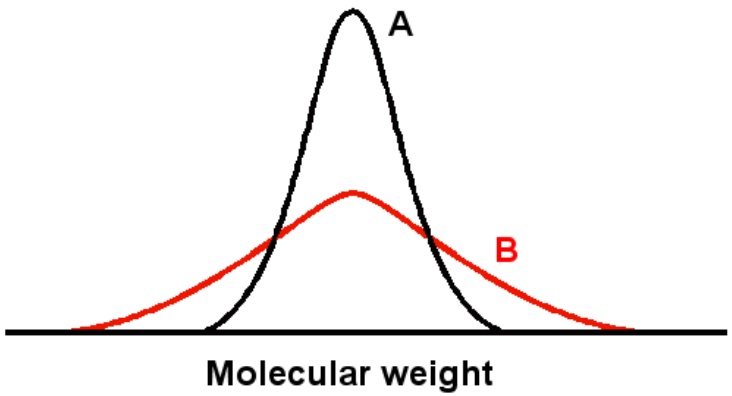
- Different samples of the same polymer can have the same average chain length but very different distributions of chain lengths depending on the method of production
- In polymer science it is the molecular weight *distribution* that is important

Shapes of Distributions

- Even for the same type of polymer, each of these distributions will describe a polymer that behaves differently
- The red and green plots are for low and high polydisperity materials
- The blue plot shows a high polydispersity material with a additional high molecular weight component
- Describing these distributions is not easily, especially if they are complex



Effect of Polydispersity on a Polymer

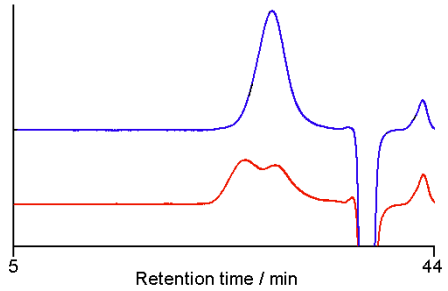


- As the broadness of the the distribution decreases the strength and toughness of the polymer increases
- However as the broadness of the the distribution decreases the polymer becomes more difficult to process
- GPC provides key information to predict the processability and material properties of a polymer

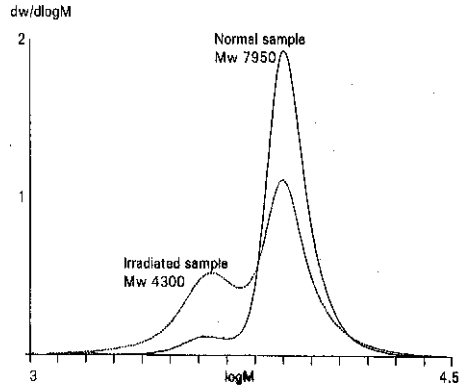
	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+

Incoming QC of Materials & Stability Testing

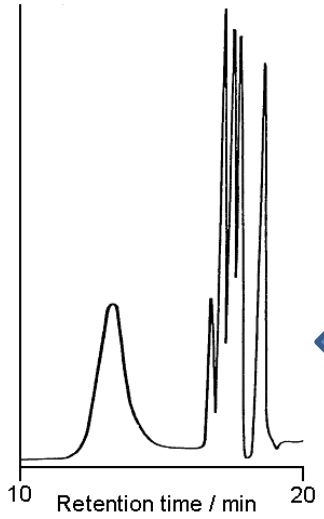
If you buy your polymers in how do you verify that you are starting with the same base material?(Iv Example)



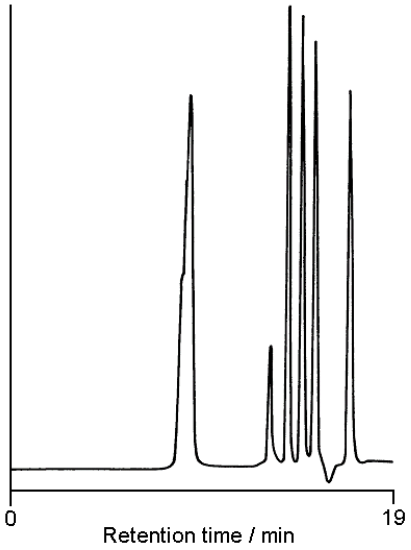
How do you know the polymer has not changed over time?

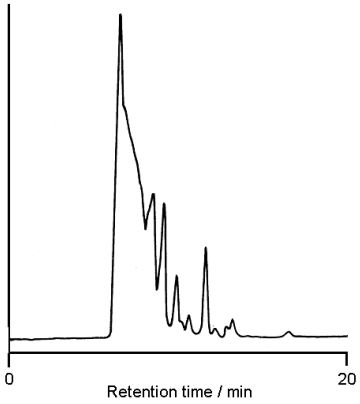


Use of Exclusion/Sample Clean up



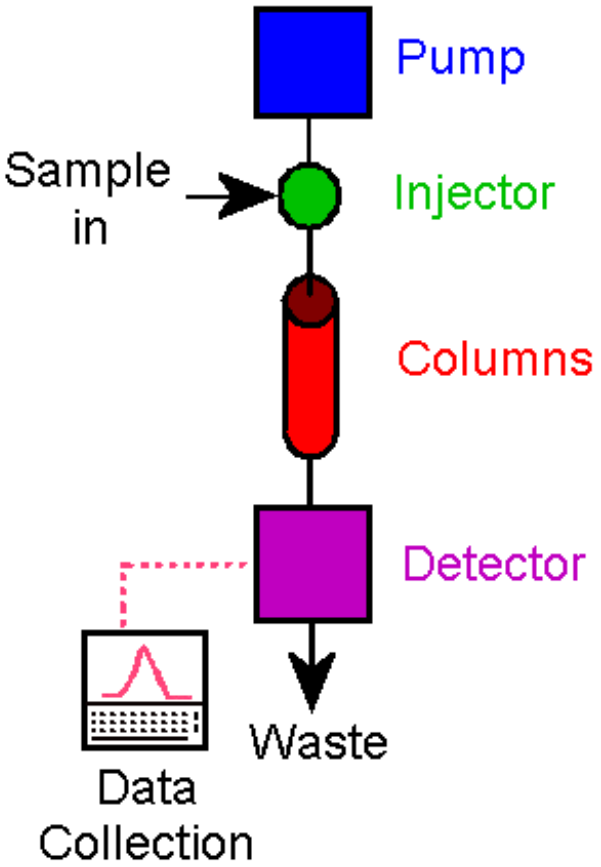
Phtalates





IsoCynates

What Equipment is Needed to do GPC



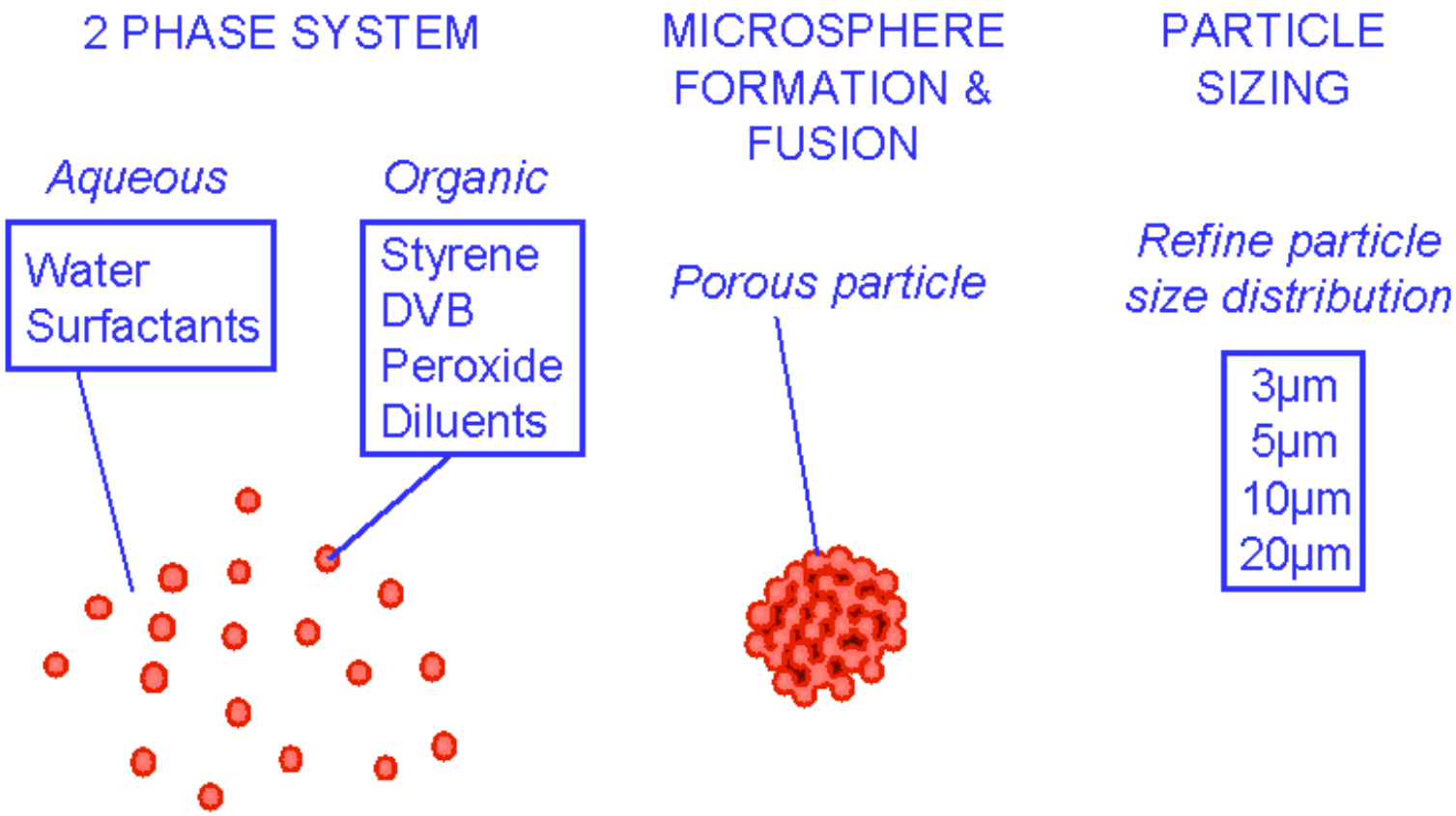
1. Reciprocating piston ***pump*** delivers eluent from reservoir at a constant volumetric flow rate. GPC is always an isocratic separation

2. Two position ***injection valve*** permits introduction of sample solution without interrupting solvent flow. GPC tends to use larger injection volumes than HPLC (typically up to 200ul)

3. ***GPC columns*** perform a separation based on the molecular size of polymer molecules in solution. Resolution and/or resolving range is increased by use of multiple column systems

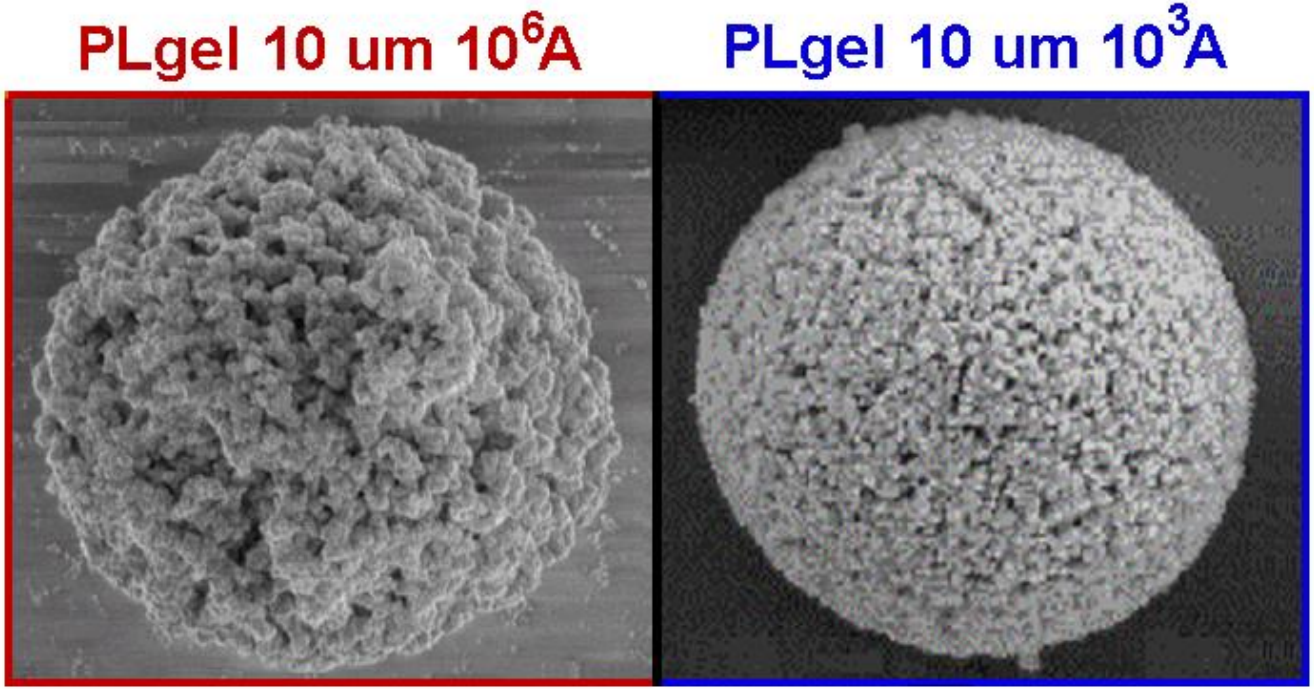
4. ***Detector*** responds to concentration of polymer molecules eluting from the GPC columns

Porous Particles Produced by Suspension Polymerization



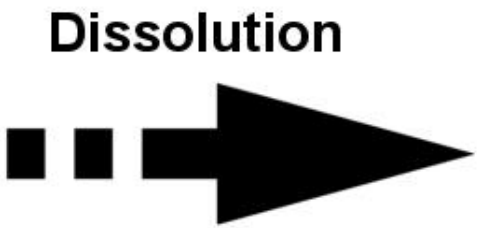
GPC Column Packings

- GPC columns are packing with cross-linked, insoluble beads. These beads have a rigid pore structure that remains intact in the presence of solvent

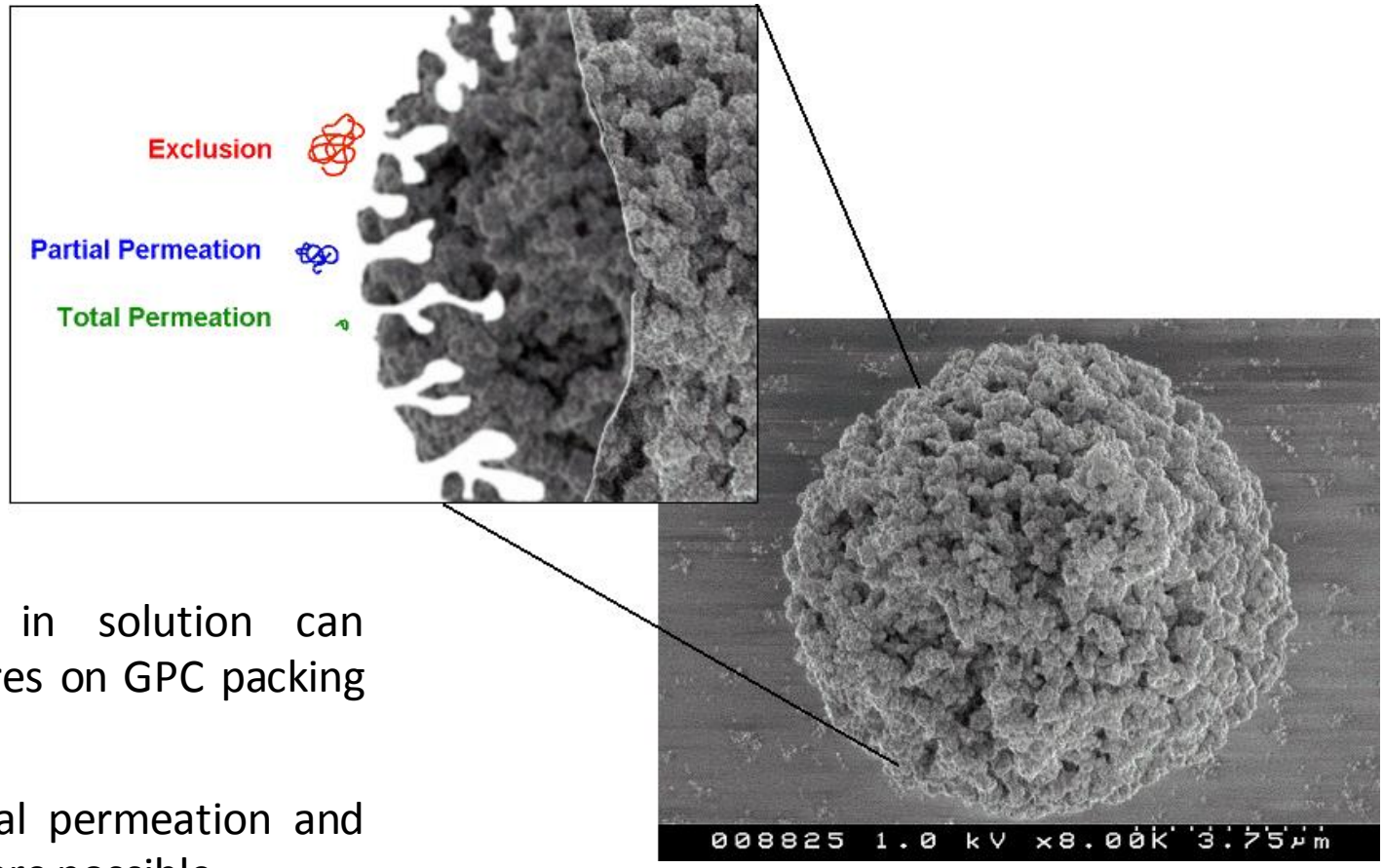


Polymer Behavior in Solution

- GPC is based on the behaviour of polymer molecules in solution
- In the solid state polymers can be considered like spaghetti – a confusing mass of intertwined chains
- In solution, polymer molecules are discrete entities
- Due to entropic effects all but the most rigid of polymer chains curls up in solution to form a ball like shape



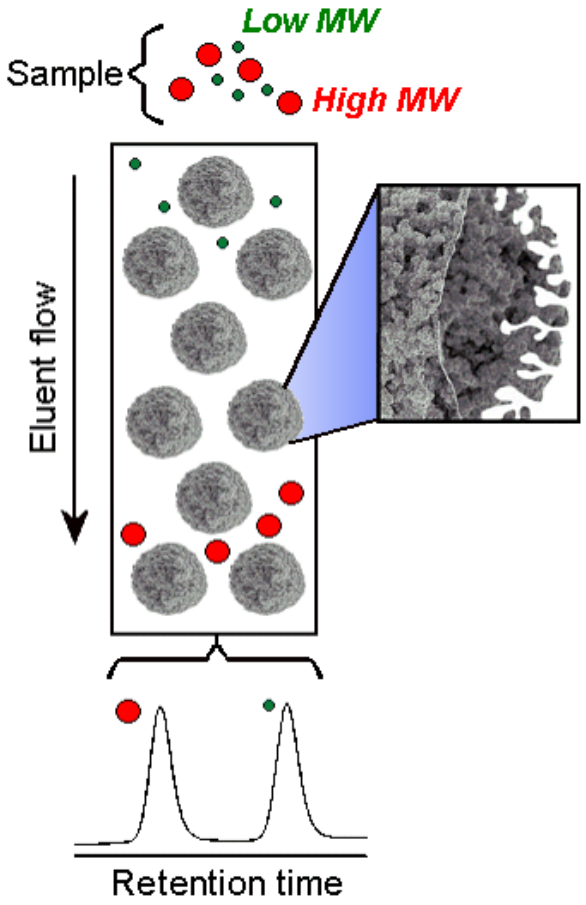
Permeation of Polymer Molecules



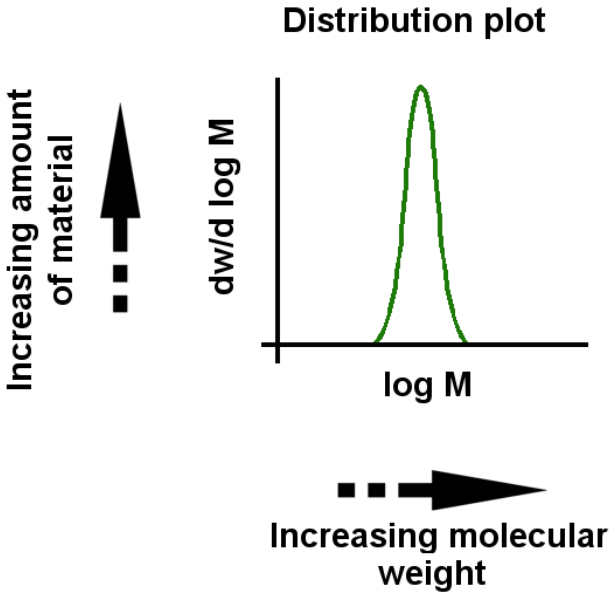
- Polymer coils in solution can permeate the pores on GPC packing materials
- Exclusion, partial permeation and total permeation are possible

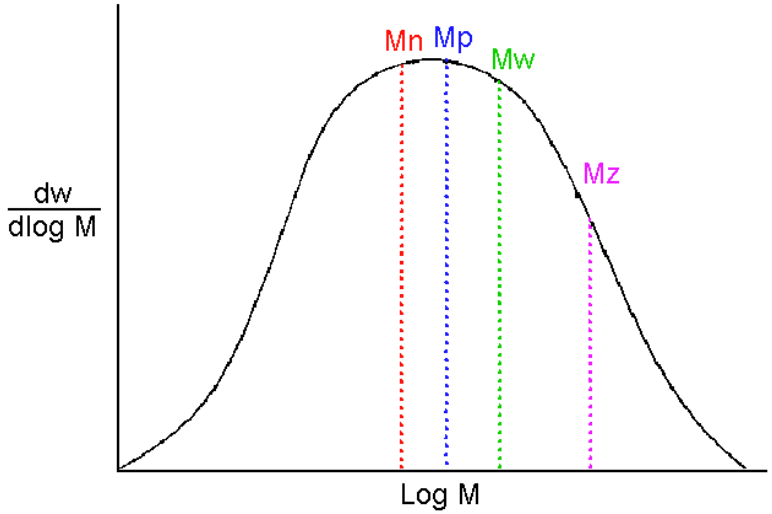
GPC Separation Mechanism

- A GPC column contains these porous polymer particles
- A polymer sample is prepared and injected into the system
- Large molecules cannot permeate the pores and have a shorter residence time in the column
- Small molecules have a long residence time in the column
- Polymer molecules are separated according to molecular size
- Largest elute first, smallest last



Defining the Molecular Weight Distribution

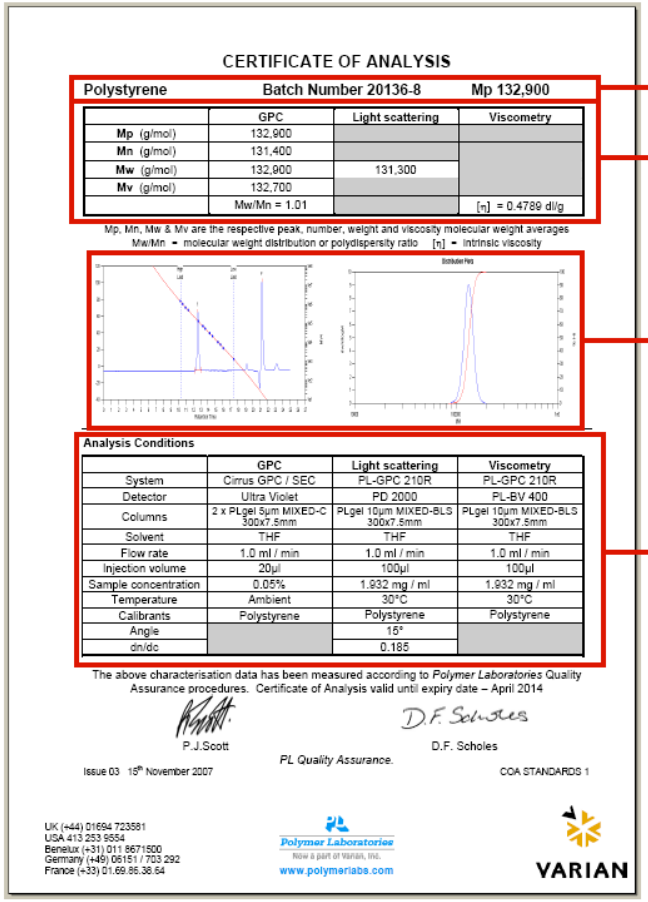




- A molecular weight distribution can be defined by a series of average values
- Except Mp, these are various moments of the average of the molecular weights of the distribution
- Mp is the molecular weight of the peak maxima
- For any polydisperse peak:

Mn<Mw<Mz<Mz+1

Example Certificates of Analysis



CERTIFICATE OF ANALYSIS

Polystyrene | Batch Number 20136-8 | Mp 132,900

	GPC	Light scattering	Viscometry
Mp (g/mol)	132,900		
Mn (g/mol)	131,400		
Mw (g/mol)	132,900	131,300	
Mv (g/mol)	132,700		
	Mw/Mn = 1.01		[η] = 0.4789 dl/g

Mp, Mn, Mw & Mv are the respective peak, number, weight and viscosity molecular weight averages
Mw/Mn = molecular weight distribution or polydispersity ratio [η] = intrinsic viscosity

Analysis Conditions

	GPC	Light scattering	Viscometry
System	Cirrus GPC / SEC	PL-GPC 210R	PL-GPC 210R
Detector	Ultra Violet	PD 2000	PL-BV 400
Columns	2 x PLgel 5µm MIXED-C 300x7.5mm	PLgel 10µm MIXED-BLS 300x7.5mm	PLgel 10µm MIXED-BLS 300x7.5mm
Solvent	THF	THF	THF
Flow rate	1.0 ml / min	1.0 ml / min	1.0 ml / min
Injection volume	20µl	100µl	100µl
Sample concentration	0.05%	1.932 mg / ml	1.932 mg / ml
Temperature	Ambient	30°C	30°C
Calibrants	Polystyrene	Polystyrene	Polystyrene
Angle		15°	
dn/dc		0.185	

The above characterisation data has been measured according to *Polymer Laboratories* Quality Assurance procedures. Certificate of Analysis valid until expiry date – April 2014

P.J.Scott — D.F. Scholes

PL Quality Assurance.

Issue 03 15th November 2007 — COA STANDARDS 1

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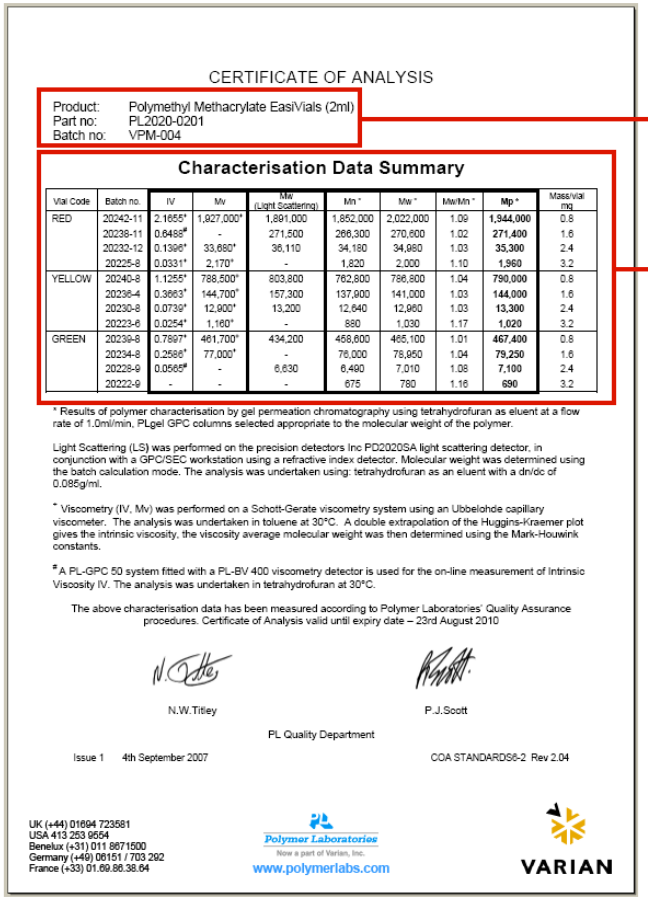
VARIAN

Batch details

Results

GPC data

Analysis details



CERTIFICATE OF ANALYSIS

Product: Polymethyl Methacrylate EasiVials (2ml)
Part no: PL2020-0201
Batch no: VPM-004

Characterisation Data Summary

Vial Code	Batch no.	IV	Mv	Mw (Light Scattering)	Mn *	Mw *	Mw/Mn *	Mp *	Mass/vial mg
RED	20242-11	2.1655*	1,927,000*	1,891,000	1,852,000	2,022,000	1.09	**1,944,000**	0.8
	20238-11	0.6488#	-	271,500	266,300	270,600	1.02	**271,400**	1.6
	20232-12	0.1396*	33,660*	36,110	34,180	34,980	1.03	**35,300**	2.4
	20225-8	0.0331*	2,170*	-	1,820	2,000	1.10	**1,960**	3.2
YELLOW	20240-8	1.1255*	788,500*	803,800	762,800	786,800	1.04	**790,000**	0.8
	20236-4	0.3663*	144,700*	157,300	137,900	141,000	1.03	**144,000**	1.6
	20230-8	0.0739*	12,900*	13,200	12,640	12,960	1.03	**13,300**	2.4
	20223-6	0.0254*	1,160*	-	880	1,030	1.17	**1,020**	3.2
GREEN	20239-8	0.7897*	461,700*	434,200	458,600	465,100	1.01	**467,400**	0.8
	20234-8	0.2586*	77,000*	-	76,000	78,950	1.04	**79,250**	1.6
	20228-9	0.0565#	-	6,630	6,490	7,010	1.08	**7,100**	2.4
	20222-9	-	-	-	675	780	1.16	**690**	3.2

* Results of polymer characterisation by gel permeation chromatography using tetrahydrofuran as eluent at a flow rate of 1.0ml/min, PLgel GPC columns selected appropriate to the molecular weight of the polymer.

Light Scattering (LS) was performed on the precision detectors Inc PD2020SA light scattering detector, in conjunction with a GPC/SEC workstation using a refractive index detector. Molecular weight was determined using the batch calculation mode. The analysis was undertaken using: tetrahydrofuran as an eluent with a dn/dc of 0.085g/ml.

* Viscometry (IV, Mv) was performed on a Schott-Gerate viscometry system using an Ubbelohde capillary viscometer. The analysis was undertaken in toluene at 30°C. A double extrapolation of the Huggins-Kraemer plot gives the intrinsic viscosity, the viscosity average molecular weight was then determined using the Mark-Houwink constants.

A PL-GPC 50 system fitted with a PL-BV 400 viscometry detector is used for the on-line measurement of Intrinsic Viscosity IV. The analysis was undertaken in tetrahydrofuran at 30°C.

The above characterisation data has been measured according to Polymer Laboratories' Quality Assurance procedures. Certificate of Analysis valid until expiry date – 23rd August 2010

N.W.Titley — P.J.Scott

PL Quality Department

Issue 1 4th September 2007 — COA STANDARDS6-2 Rev 2.04

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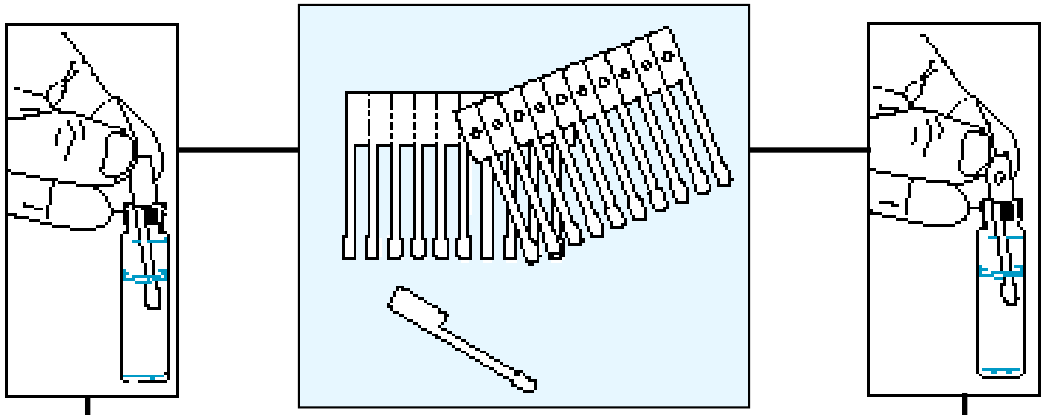
Batch details

Analysis details

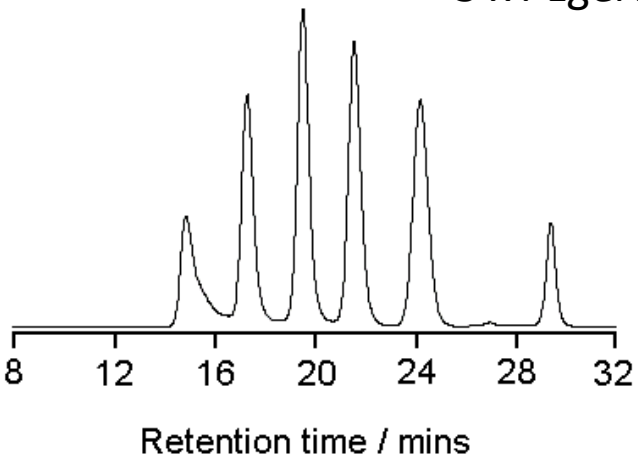
EasiCal Pre-prepared Calibrants

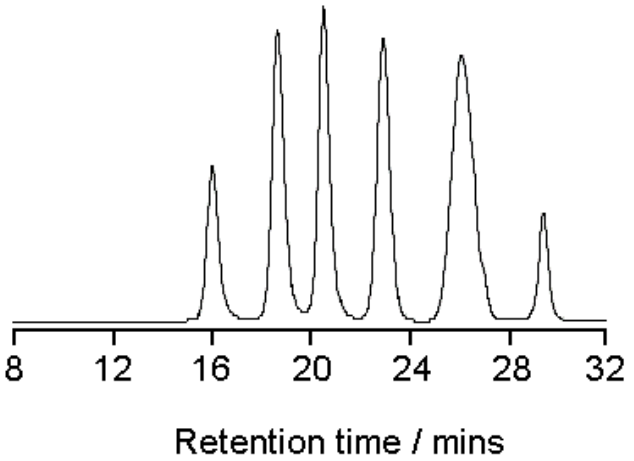
Spatula A



Spatula B

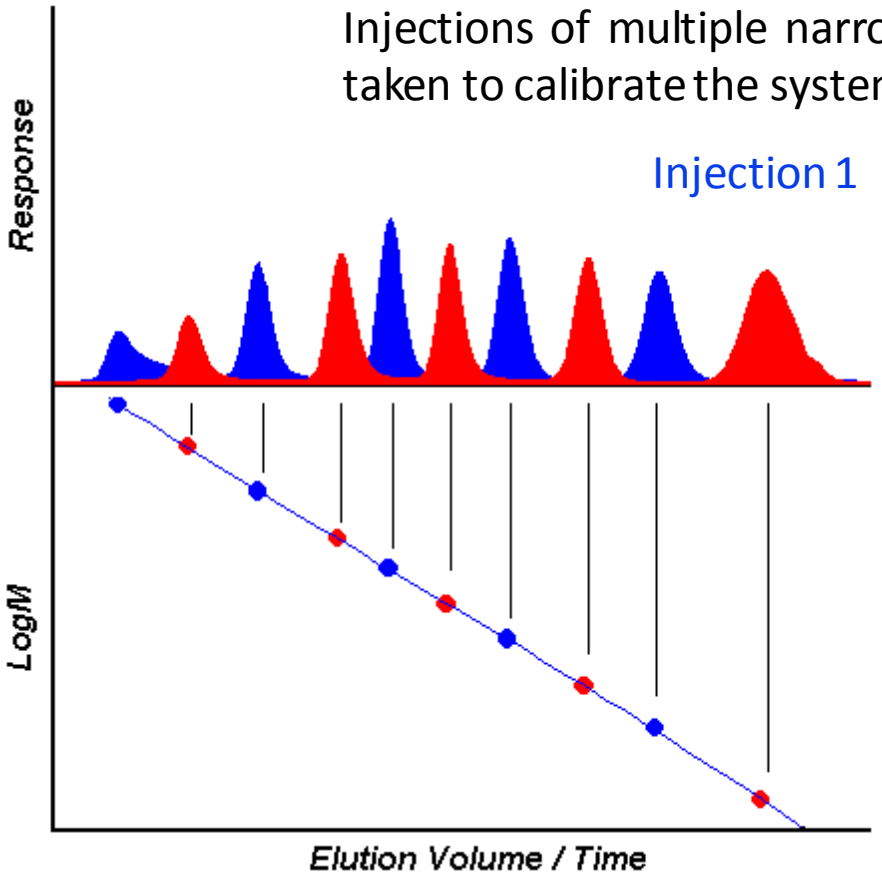
EasiCal PS-1 separation on
3 x PLgel 10µm MIXED-B





Performing Narrow Standard GPC Calibration

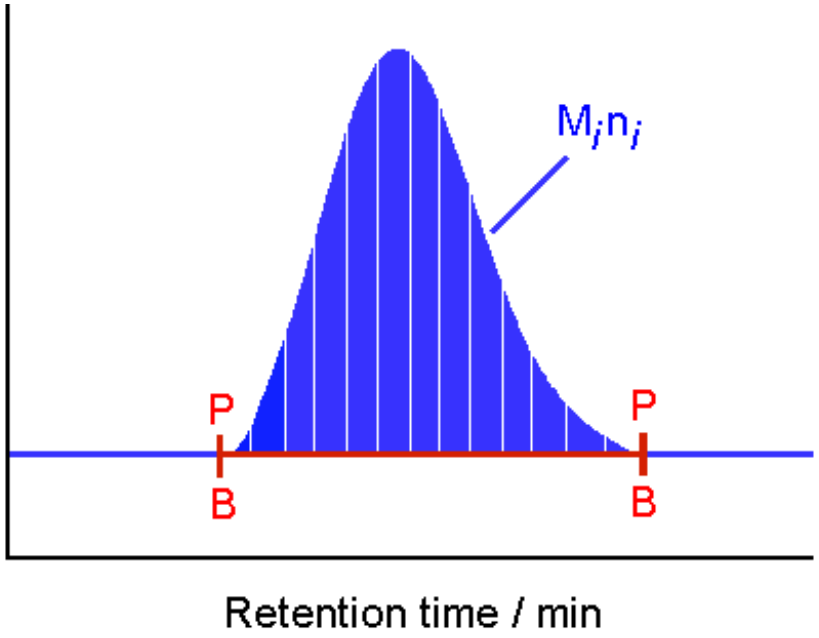
Injections of multiple narrow standards reduces the time taken to calibrate the system



Standards peaks in each chromatogram must be fully resolved to obtain repeatable retention times

Peak Integration in GPC

The sample peak when integrated can be assumed to be a histogram consisting of a number of individual “slices”



For each slice, i, the molecular weight (Mi) can be derived from the RT and the number of molecules (Ni) from the detector response

How is the Mw Distribution Calculated

Number average $Mn = \frac{\Sigma Ni\,Mi}{\Sigma Ni}$

Mn can be correlative with polymer colligative properties, e.g. freezing point depression

Weight average $Mw = \frac{\Sigma Ni\,Mi^2}{\Sigma Ni\,Mi}$

Mw may be correlated with properties such as melt viscosity

Z average $Mz = \frac{\Sigma Ni\,Mi^3}{\Sigma Ni\,Mi^2}$

Mz may be correlated with properties such as toughness

Polydispersity, $d = \frac{Mw}{Mn}$

Polydispersity characterises the shape of the distribution

What are considered “good” results

Molecular Weight Results

Mw = RSD 2-3%

Mn = RSD 3-5%

Polydispersity = <10%

Calibration Results

R^2 = > 0.998

% Deviation = < 10%

<u>Stay Tuned, To Learn Just How Relevant Your Mw Measurement Actually Is!</u>