

Gel Permeation Chromatography

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Gel permeation chromatography (GPC) has become the most widely used technique for determination of molecular weight distributions. Gel permeation chromatography separates polymers on the basis of molecular size. The smaller polymers spend more time traveling through the pores of the gel and are eluted later than the larger polymers which spend less time in the pores. Thus *elution volume (or elution time) is proportional to molecular size*. It can be shown that hydrodynamic volume is proportional to the product $[\eta]M$ where $[\eta]$ is the intrinsic viscosity and M is the molecular weight (see Painter and Coleman, *Fundamentals of Polymer Science*, pp 353-370). **A plot of $\log [\eta]M$ versus elution volume (or elution time) for a particular solvent, column, and instrument provides a universal calibration curve which can be used for any polymer in that solvent so long as the Mark-Houwink constants are known for the polymer-solvent pair.** Such a calibration curve is obtained by determining the retention volumes (or times) of monodisperse polymer standards. Once the calibration is obtained, the gel permeation chromatogram of any other polymer can be obtained in the same solvent and the molecular weights (usually M_n and M_w) and the complete molecular weight distribution for the polymer can be determined. If the polymer to be analyzed is the *same* polymer as that used in obtaining the calibration, a plot of $\log M$ versus elution volume (or time) can be used since the Mark-Houwink constants for the sample are the same as those for the standards.

Calibration

Below are given data of elution volumes (V) obtained in a GPC for monodisperse polystyrene standards in tetrahydrofuran (THF). The intrinsic viscosities for the solutions were obtained using the Mark-Houwink equation:

$$[\eta] = KM^a$$

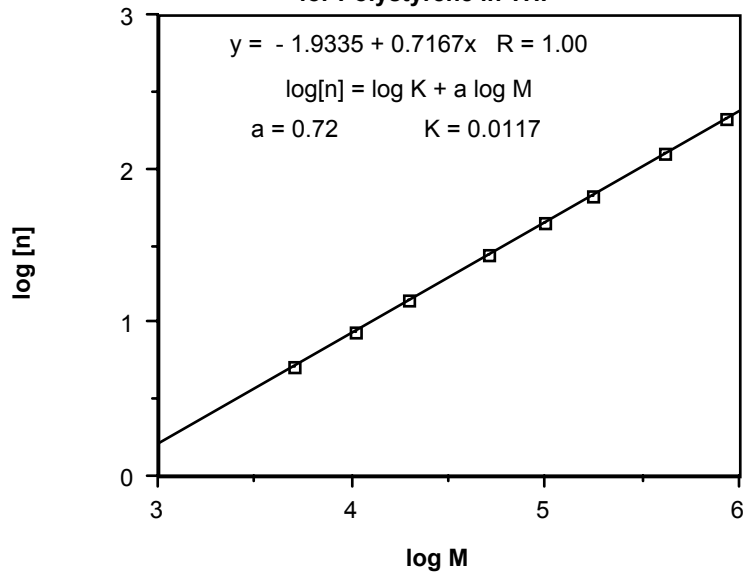
where K and a are the Mark-Houwink constants.

(Note: An example is also given showing a plot used to *determine* the Mark-Houwink constants for the polystyrene - THF system. Monodisperse polystyrene samples were used -- measurement of viscosity elution times of several dilutions of each solution enabled $[\eta]$ values to be obtained. The slope and intercept of the $\log[\eta]$ vs. $\log M$ plot yield the values of ' $\log K$ ' and ' a ', respectively.)

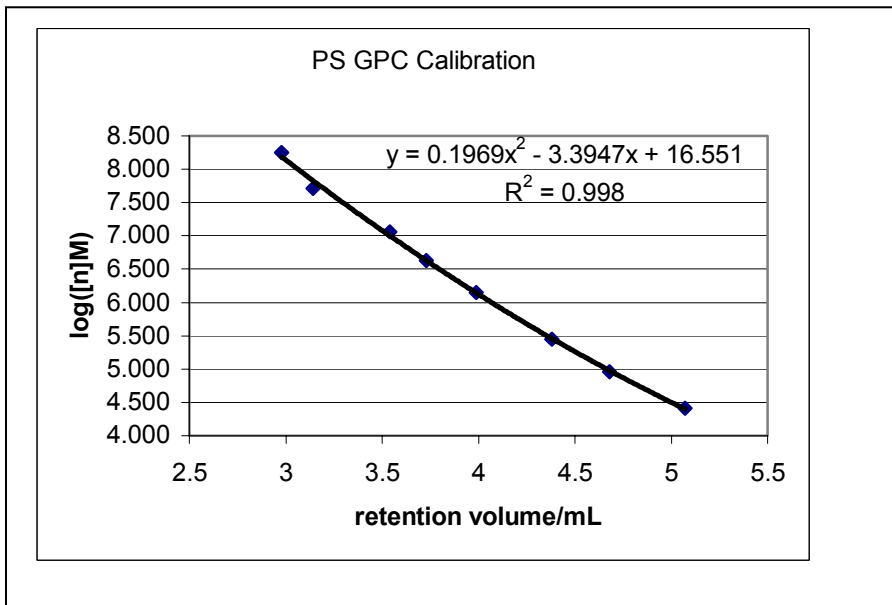
GPC Data for Monodisperse Polystyrene Standards

M/(g/mol)	V/mL	$[\eta]$	$[\eta]M$	$\log([\eta]M)$
867000	2.98	206.7	1.79E+08	8.253
411000	3.14	125	5.14E+07	7.711
173000	3.54	67	1.16E+07	7.064
98200	3.73	43.6	4.28E+06	6.632
51000	3.99	27.6	1.41E+06	6.148
19900	4.38	14	2.79E+05	5.445
10300	4.68	8.8	9.06E+04	4.957
5000	5.07	5.2	2.60E+04	4.415

Mark-Howink Constant Determination for Polystyrene in THF



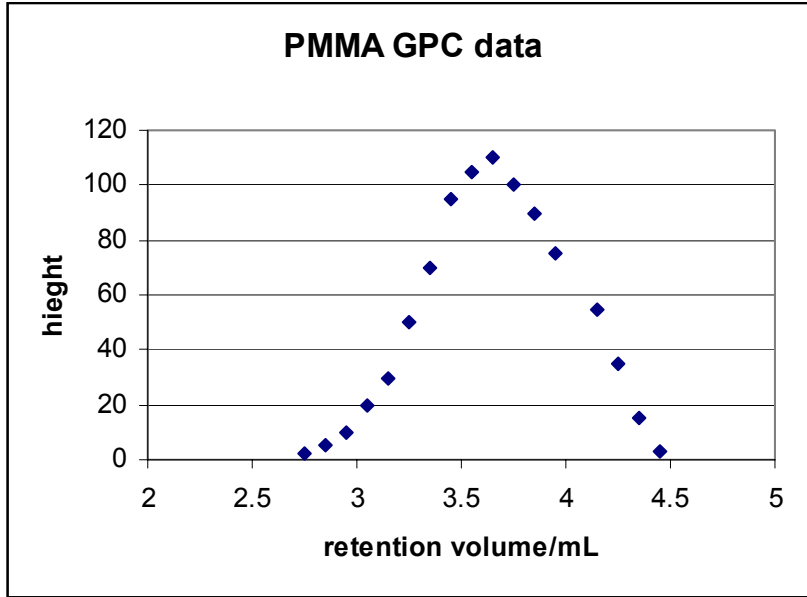
The universal calibration curve ($\log([\eta]M)$ vs. elution volume) based on these data is given below:



Sample Unknown Analysis

A poly(methyl methacrylate) sample was analyzed using this same GPC. The chromatogram obtained is given below:

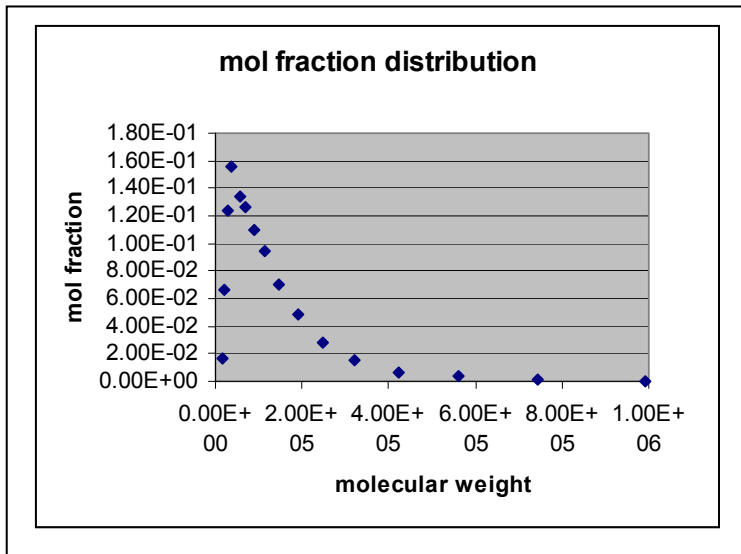
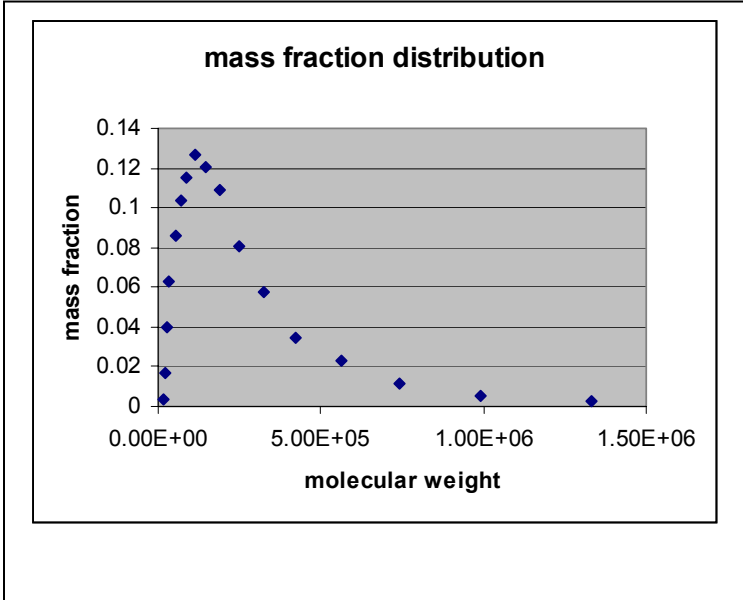
Values of height at various times were taken from this chromatogram (points shown on chromatogram) and the data are given below. The values of K and a for this system are $4.8E-3$ and 0.80 . **The height is assumed to be proportional to (actually equal to) the mass of polymer.**



V/mL	height	log([n]M)	[n]M	M	height/M	height*M	mass fr.	mol fr.
2.75	2	8.70463125	5.07E+08	1.33E+06	1.50E-06	2.66E+06	0.002299	1.47E-04
2.85	5	8.47542525	2.99E+08	9.93E+05	5.04E-06	4.96E+06	0.005747	4.94E-04
2.95	10	8.25015725	1.78E+08	7.44E+05	1.34E-05	7.44E+06	0.011494	1.32E-03
3.05	20	8.02882725	1.07E+08	5.61E+05	3.57E-05	1.12E+07	0.022989	3.50E-03
3.15	30	7.81143525	6.48E+07	4.25E+05	7.07E-05	1.27E+07	0.034483	6.93E-03
3.25	50	7.59798125	3.96E+07	3.23E+05	1.55E-04	1.62E+07	0.057471	1.52E-02
3.35	70	7.38846525	2.45E+07	2.47E+05	2.83E-04	1.73E+07	0.08046	2.78E-02
3.45	95	7.18288725	1.52E+07	1.90E+05	5.00E-04	1.80E+07	0.109195	4.90E-02
3.55	105	6.98124725	9.58E+06	1.47E+05	7.15E-04	1.54E+07	0.12069	7.01E-02
3.65	110	6.78354525	6.07E+06	1.14E+05	9.65E-04	1.25E+07	0.126437	9.46E-02
3.75	100	6.58978125	3.89E+06	8.90E+04	1.12E-03	8.90E+06	0.114943	1.10E-01
3.85	90	6.39995525	2.51E+06	6.98E+04	1.29E-03	6.28E+06	0.103448	1.26E-01
3.95	75	6.21406725	1.64E+06	5.50E+04	1.36E-03	4.13E+06	0.086207	1.34E-01
4.15	55	5.85410525	7.15E+05	3.47E+04	1.58E-03	1.91E+06	0.063218	1.55E-01
4.25	35	5.68003125	4.79E+05	2.78E+04	1.26E-03	9.72E+05	0.04023	1.23E-01
4.35	15	5.50989525	3.24E+05	2.23E+04	6.71E-04	3.35E+05	0.017241	6.58E-02
4.45	3	5.34369725	2.21E+05	1.81E+04	1.66E-04	5.42E+04	0.003448	1.63E-02
Sum	870				1.02E-02	1.41E+08		
Mn = Sum(heights)/sum(height/M) =				8.53E+04	g/mol			
Mw = Sum (height*M)/sum(heights) =				1.62E+05	g/mol			
Mw/Mn=		1.90						

The $\log([\eta]M)$ values are determined using the universal calibration equation. The value of M for each volume is determined using the Mark-Houwink constants.

Values of height/M and $\text{height} \cdot M$ are determined and sums of the heights, height/M and $\text{height} \cdot M$ are obtained. The values of M_n and M_w are obtained from ratios of these sums. The polydispersity index (M_w/M_n) is also obtained. Distribution curves of mass fraction and mol fraction versus M obtained from these data are given below. These are the true molecular weight distribution curves. The experimental values obtained are $M_w = 1.6 \times 10^5$ g/mol and $M_n = 8.5 \times 10^4$ g/mol.



Experimental

A universal calibration curve must be determined for the GPC instrument. Solutions of monodisperse polymer (polystyrene) in THF are prepared at approximately 1% polystyrene by weight in new, degassed THF (check with instructor on polymer and exact concentrations to be used -- 0.02 g polymer per 2.0 ml solvent works well). You will be instructed on operation of the GPC instrument. Flow rates, pressures, and sample injection volumes must be determined carefully and kept constant throughout the procedure. Measure the retention times for the monodisperse polystyrene standards. The intrinsic viscosities of these solutions can be calculated using the Mark-Houwink equation. For polystyrene in THF, Mark-Houwink parameters are $K = 0.015 \text{ ml/g}$ and $a = 0.70$. Plot the universal calibration and polystyrene calibration curves using your data. Fit each curve with a second order polynomial to obtain the calibration equations.

Obtain the gel permeation chromatogram for your polymer (in THF) using the same instrument settings. Make up a solution of appropriate concentration. Use the appropriate calibration curve and your chromatogram to obtain M_n , M_w , the polydispersity, and the two molecular weight distribution curves (mass fraction and mol fraction vs. molecular weight) for your polymer. Include copies of all relevant work and results in your notebook.