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Gel Permeation Chromatography: A Review

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Gel permeation chromatography (GPC) enables the molecular weight distribution of a polymer sample to be determined in two or three hours. In the few years since its development it has revolutionised polymer characterisation. This review describes the essentials of the technique, its history and its relevance to polymer technology. Apparatus for GPC is also described with greatest emphasis being given to apparatus similar to that commercially available from Waters Associates Inc. The problems associated with chromatogram interpretation, instrumental broadening and calibration are discussed.

1. Introduction

During gel permeation chromatography (GPC)*, a polymer solution is washed down a chromatograph column packed with porous particles. Experimentally it is observed that the volume of solvent required to elute a certain molecular species is a decreasing function of molecular size.

GPC has revolutionised polymer characterisation. Using this technique it is now possible to obtain the molecular weight distribution of a very small sample of polymer in two or three hours. More traditional methods, which involve fractionation followed by characterisation of the resulting fractions, need much more material and may take weeks rather than hours. This being the case, GPC has opened up entirely new fields of research which were previously impractical. With the introduction of a commercially-manufactured gel permeation chromatograph, this useful technique has rapidly become established and is now available to many small laboratories with no previous experience in chromatographic techniques.

2. The Development of GPC

The separation process which defines GPC was first observed in the elution of low molecular weight non-ionic substances with water from a column packed with ion-exchange resin particles [1, 2]. Swollen starch gels [3, 4] and agar gel [5, 6], which are non-ionic natural products, were also used successfully for the separation of polysaccharides and proteins by this process. The technique did not become widespread, however, until a series of chemically-produced hydrophylic gels became available [7].

Application to hydrophobic polymers was initially less encouraging. Gels were produced by the copolymerisation of styrene with divinylbenzene [8, 9]. However, these produced only small separation in the high molecular weight region, despite being very highly swollen. Much more successful results were achieved by copolymerising in the presence of a diluent which was a solvent for the monomers, but not for the polymer [10]. The resulting gels have a rugged internal structure and high permeability which can be controlled by varying the amount and nature of the diluent present at the time of cross-linking. These gels (Styragels†) are the ones most widely used for GPC at the present time.

Much recent work has been directed at producing a porous packing material more stable at the high temperatures necessary for the analysis of many polymers such as polyethylene. Promising results have so far been obtained using porous silica [11] and glass beads [12] and such column packings are now commercially available (Porosil† and Bioglass‡ respectively). The disadvantage of these column packings is that they have polar groups on their surfaces and

*Gel permeation chromatography is sometimes referred to as gel filtration, molecular sieve chromatography, exclusion chromatography or gel chromatography.
†Commercially available from Waters Associates Inc., Framingham, Massachussetts.
‡Commercially available from Bio-Rad Laboratories, Richmond, California.

there is a tendency for the solutes to be adsorbed on the column packings causing a decrease in separation efficiency. Such effects can, however, be eliminated by a surface reaction in which the hydroxyl groups are replaced by methyl or phenyl groups before column packing [13].

Other current research is directed towards the production of gels with greater separation efficiency. Polyvinyl acetate gels have been produced by copolymerisation of vinyl acetate and divinyl esters of dicarboxylic acids [14]. These gave very high resolution and separation of the low molecular weight oligomers of a disperse polymer sample has been achieved. Such gels are now commercially available (Mercksgels manufactured by E. Merck A.G., Darmstadt, W. Germany).

3. The Separation Process

It is generally assumed that the separation process relies on the preferential penetration of smaller molecules into the pores of the column packing material. This may be due to either the inability of large molecules to enter certain regions of the gel due to their size (steric exclusion) or the larger diffusion coefficients of smaller molecules.

Steric exclusion theories [15-18] which assume simple geometrical models for the gel have been presented, but implicit in these theories is the assumption that the time of molecular diffusion into the gel is very small compared to the time the solution zone takes to pass the gel particle, i.e. there is an equilibrium distribution between the mobile and stationary phases. They relate the total available pore volume per molecule to the mean molecular diameter in solution. The predicted dependence of elution volume on molecular weight is in broad agreement with experiment in each case.

Diffusion theories [19, 20] have also been presented and these too, in certain cases, successfully predict the molecular weight dependence of the elution volume. In one theory [19], the equation of Renkin [21] is used to relate the effective pore radius to the Stokes radius of the solute. The other theory [20] uses the solution of Fick's diffusion equation for the simplified model of diffusion along a single coordinate that extends to infinity.

Using the known polymer diffusion coefficients, it has been calculated that, with normal GPC conditions, sufficient time is available for complete diffusion into the gel to set up an equilibrium distribution [22]. Also, at very slow flow rates the elution volume of high molecular weight polymers does not approach that of low molecular weight material [23-25]. Thus the basic separation mechanism cannot be incomplete diffusion. Incomplete diffusion may modify the basic exclusion process however, particularly for high molecular weight material and high flow rates. A more general theory [26] incorporating both finite diffusion rate and steric exclusion shows how the non-equilibrium effects decrease the separation efficiency. In the theory it is assumed that diffusion occurs with radial symmetry into a spherical stationary phase. The theory cannot be compared with experiment as easily as the other theories since, in general, an analytical solution of the equations is not possible.

A theory has been presented [27-29] which suggests that separation can be achieved simply by flow of a polymer solution through fine capillaries or through a column of non-porous beads. The separation is caused by the quadratic velocity profile of fluid in a capillary; the centres of the mass of the larger molecules cannot approach as close to the capillary wall as the smaller molecules and so the larger molecules have larger average velocities. Such a mechanism could explain the separation which was observed when proteins were eluted from a column packed with impermeable glass beads [30]. Up to the present time the relative importance of steric exclusion and flow separation in normal gel permeation chromatography has not been evaluated.

4. Apparatus

Gel permeation chromatography has been carried out for several years using very simple equipment. A single glass column packed with Sephadex gel and fed by a constant head solvent reservoir has proved adequate for many applications, particularly in the biochemistry field [31].

Following the production of gels compatible with organic solvents, a commercial gel permeation chromatograph was developed by Waters Associates Inc. [32]. This liquid chromatography apparatus has enabled laboratories with no previous chromatographic experience to establish polymer characterisation on a routine basis. It is with this type of apparatus that the phenomenal growth of GPC has occurred and with which the majority of this review is concerned. A brief description of this most widely used GPC

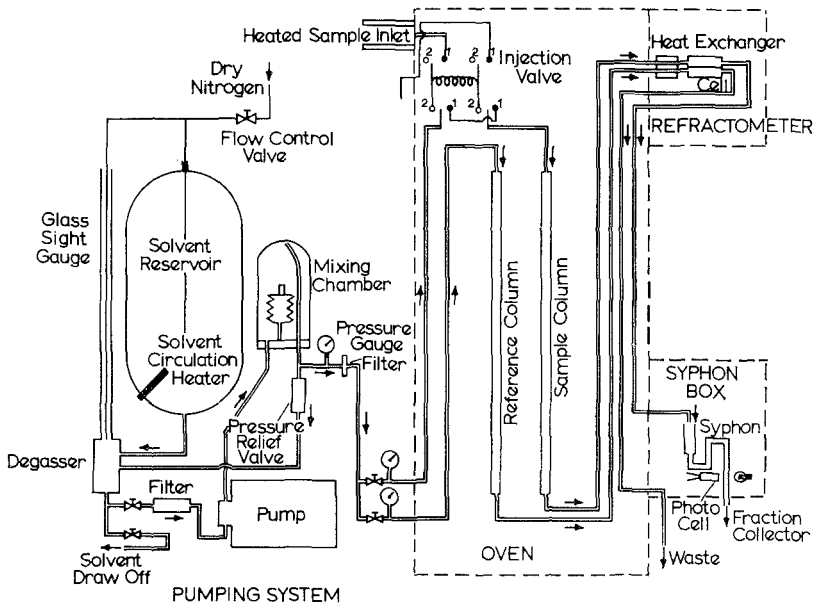

Figure 1 Schematic diagram of the gel permeation chromatograph commercially available from Waters Associates Inc.

system will now be given.

The apparatus consists essentially of a pumping system, a series of sample separation columns with a sample injection system, a series of reference columns, a detector for measuring the weight of polymer in the eluant at a given time, and a system for recording the sample elution volume. Its operation can be readily understood by reference to the schematic diagram (fig. 1).

4.1. Pumping System

In the pumping system, gases are displaced from the solvent at the degasser which should be the hottest point of the instrument. Degassed solvent, as well as flowing to the pump, can be drawn off independently for use in the preparation of sample solutions. Pumps in common use cause pressure oscillations in the output line, but these are damped by a bellows in the mixing chamber. This chamber also ensures that any changes in impurities in the solvent streams occur gradually.

4.2. Columns

Usually each analysis column contains only a small range of pore size, such that it separates over a limited range of molecular size. For separation over a wide range of molecular size, therefore, several columns in series are needed. Typically four columns are used.

The sample solution is introduced into a sample loop, volume 2 cc, by a heated syringe. Normally the flow by-passes the loop, but by operation of a sample injection valve the sample stream can be diverted into the sample loop, pushing the polymer solution into the sample column set.

The reference column set consists of a series of columns similar to those of the sample set. Ideally solvent should take the same time to reach the detector via the reference column set as via the sample set. This nulls out residual pressure and impurity level fluctuations which would otherwise have a detrimental effect on the instrument baseline. The reference column set also provides a suitable pressure drop in the reference line facilitating flow control. Both sets of columns and the sample injection valve and loop are kept in an oven enabling them to be maintained at a temperature sufficiently high to keep the polymer in solution.

4.3. The Detector

After leaving the columns, the two solvent streams are taken to the detector, where the concentration of polymer in the sample column eluant is monitored continuously. In the Waters chromatograph a differential refractometer is used which records the difference in refractive index between the two solvent streams. Since the solvent refractive index is a function of temperature and the refractive index differences measured are very small, extremely good temperature control of the refractometer cell is necessary. To

achieve this, the solvent streams pass through a heat exchanger before entering the cell itself and the temperature of the cell and heat exchanger are controlled by a proportional temperature controller.

Ultra-violet of infra-red detectors can also be used for GPC provided that the polymer has a suitable absorption peak in the wavelength range used [33]. A flame ionisation detector has also been used successfully [34]. Because of the fundamental significance of intrinsic viscosity in calibration (to be discussed later), an automatic rapid analysis time viscometer has recently been developed [35] and this can be used in series with one or more of the above detectors to measure the viscosity of the solution continuously as it elutes from the column. The dependence of the intrinsic viscosity on the elution volume can thus be determined.

4.4. Measurement of Elution Volume

After leaving the detector, the reference stream passes to waste and the sample stream is collected in a syphon. Every time the syphon empties, which is at 5 cc intervals, the liquid passes between a light source and photocell detector. With the change in output of the photocell, a pulse is supplied to the chart recorder. Thus the chart time is calibrated in terms of the volume of solvent eluted from the sample column set.

4.5. Preparation of Fractions

Each 5 cc of sample eluant emptied from the syphon can be collected separately using a fraction collector, thus GPC can be used for the preparation of polymer fractions. With the normal analytical instrument, the quantity of each fraction is very small due to the small sample injected weight, although even these minute quantities can be of considerable use in certain cases (for example morphological studies of solution-grown polyethylene crystals [36]).

For the preparation of much larger fractions, a preparative scale chromatograph, the Anaprep, is now commercially available (manufactured by Waters Associates Inc.). This instrument is similar in principle to the analytical model, but uses columns of much larger diameter with a considerably greater solvent flow rate. It enables fractions to be prepared in sufficient quantities for measurements of mechanical properties. Typical sample injected weights are about 1 g.

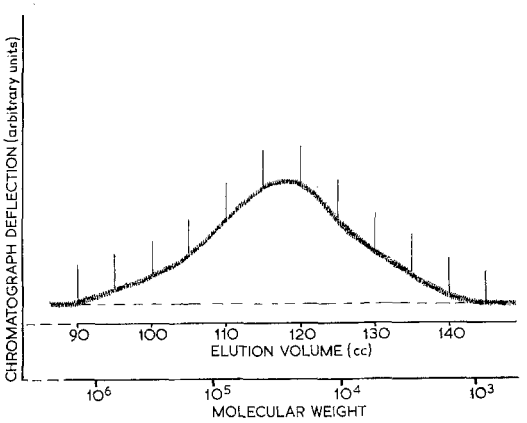

Figure 2 Chromatogram of a typical commercially-available linear polyethylene-Marlex 6009. The elution volume absisca has been related to molecular weight using the GPC calibration curve.

5. The Chromatogram

A typical chromatogram (of a commercial linear polyethylene sample – Marlex 6009) is shown in fig. 2. With the usual differential refractometer detector, the ordinate records the difference between the refractive indices of the polymer solution and the solvent. For the dilute solutions analysed, this is proportional to the weight of polymer in an increment of elution volume.

Although a comparison of the chromatograms of two or more samples is all that is necessary in many applications, for complete utilisation of the data it is often desirable to make the GPC measurements quantitative. This requires correction of the chromatogram for instrumental broadening and calibration of the sample elution volume in terms of molecular weight of the polymer analysed. Both of these problems will be discussed later.

After calibration, the more usual differential molecular weight distribution $Z(M)$ can be determined from the sample chromatogram $y(v)$. $Z(M)$ is defined such that $Z(M)\,\mathrm{d}M$ is the weight of polymer which has molecular weight between M and $M + \mathrm{d}M$. $y(v)$ is the weight of polymer which is eluted from the chromatograph between elution volumes v and $v + \mathrm{d}v$. It can be easily shown [37] that $Z(M)$ and $y(v)$ are related by the equation

$$Z(M) = [K/(-\mathrm{d}M/\mathrm{d}v)]\, y(v) \qquad (1)$$

In other words, after replacement of the elution volume scale by a molecular weight scale using the calibration curve, it is incorrect to simply expand the molecular weight scale to make it

linear. On expansion, it is also necessary to divide the chromatogram deflection by a factor proportional to the slope of the M/v calibration curve (i.e. proportional to the product of M and the slope of the log M/v calibration curve).

Average molecular weights can be calculated from the chromatogram directly. For example using equation 1 and the definition of number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, it is easily shown [37] that

$$\bar{M}_n = \frac{\int_0^\infty y(v)\,dv}{\int_0^\infty [y(v)/M(v)]\,dv} \qquad (2)$$

and

$$\bar{M}_w = \frac{\int_0^\infty M(v)\,y(v)\,dv}{\int_0^\infty y(v)\,dv} \qquad (3)$$

The burden of calculation of average molecular weights and of production of a differential molecular weight distribution from chromatograms can be considerably reduced by use of a computer programme [38].

6. Instrumental Broadening

When a monodisperse substance is analysed by GPC, it is eluted over an appreciable range of elution volume. This instrumental broadening also happens to each component of a sample containing a range in molecular weight. Thus the chromatogram observed for a disperse sample is "smeared out" because of imperfect instrumental resolution and the deflection at each elution volume depends not only on the abundance of the component corresponding to that elution volume, but also on the abundance of its neighbouring components.

The efficiency of a chromatograph column is conventionally indicated by a rather arbitrary parameter, the "height equivalent of one theoretical plate" (HETP). Its value can be determined experimentally from the gaussian chromatogram of a monodisperse substance using the equation

$$\text{HETP} = L(\sigma/v)^2 \qquad (4)$$

where L is the column length, v is the peak elution volume, and σ is the standard deviation of the peak (which is equal to one quarter of the distance between the intercepts on the baseline of lines drawn tangentially to the curve at the points of inflexion). σ gives a quantitative measure of instrumental broadening.

Many factors can contribute to the observed instrumental broadening and each of these is accounted for in a theoretical expression for the HETP value derived from general dynamic theories of chromatography [39]. A deviation from the equilibrium distribution between the gel pores and the mobile phase, because of the finite rate of polymer diffusion, increases instrumental broadening which is, therefore, smaller at lower flow rates, for lower molecular weight samples, and when smaller gel particles are used. Longitudinal diffusion, flow pattern and non-equilibrium effects, all in the mobile phase, also contribute to the broadening. The significant volume of solvent required to introduce a sample on to the column and mixing in the detector cell can also be significant under certain circumstances [40].

6.1. Measurement of Instrumental Broadening

In general, the instrumental broadening, which can be defined by the width of the chromatogram of a monodisperse substance, will be a function of the elution volume, though usually the broadening only increases gradually with decrease in elution volume. At large elution volumes, low molecular weight monodisperse substances can be used to determine the instrumental width. At lower elution volumes, however, less direct methods have to be used.

Narrow molecular weight polymer fractions (such as anionically polymerised polystyrenes [41]) can be used and the contribution to the spread due to the molecular weight dispersion either neglected [42], or estimated from the measured ratio of the weight and number-average molecular weights [43]. Because of the errors in molecular weight measurements, the correction for polydispersity can only be made approximately and this method is only useful for narrow fractions when the width due to the polydispersity is small. Alternatively if the molecular weight distribution is known, assumed values for the instrumental broadening may be used to evaluate the expected chromatogram. The correct value for the broadening is, then, that which gives the best fit between the predicted and experimentally observed chromatogram [23]. Again this method is limited by the accuracy with which the initial molecular weight distribution can be defined.

Another method for the estimation of instrumental broadening uses a flow reversal technique [44]. When a polymer sample is exactly half way through the sample column set, the flow is reversed. The width of the resultant chromatogram then gives twice the spread due to the instrumental broadening in the first half of the column set since the spread due to the polydispersity is reversible. One experimental difficulty with this method is the presence of impurity peaks which normally elute at very low elution volumes following the polymer sample. These interfere with the chromatogram when flow reversal is used [23]. It is usually necessary either to use a detection system such as an I.R. detector, which is sensitive to the polymer but not the impurities, or to use special sample preparation techniques to reduce the impurity level [45].

6.2. Correction for Instrumental Broadening

There are several computational methods available for the correction of instrumental broadening [41, 46-48] and their application has been discussed by Duerksen and Hamielec [23, 45].

As an example, a brief outline of the method of Tung [46] will be given. This method assumes that each molecular species of the polymer sample is instrumentally broadened independent of other components to give a gaussian elution profile. The resultant chromatogram deflection at a given elution volume is the sum of the deflections of each gaussian component at that elution volume. Thus, for a continuous distribution, an integral equation is obtained which relates the actual chromatogram to the molecular weight distribution function. In general, numerical solutions are necessary and these can allow for a gradual variation in instrumental broadening with elution volume. However, for the log-normal distribution, with a logarithmic dependence of molecular weight on elution volume and constant instrumental broadening over the range in sample elution volume, an analytical solution is possible [46]. The result shows that the instrumentally-broadened curve, which is gaussian, can be corrected simply by narrowing it (heightening it by the same factor) by subtracting from the square of its standard deviation the square of the standard deviation of the instrumental broadening. Resolution correction using this formula is standard practice in X-ray crystallography. It has proved to be of considerable use for the correction of the instrumental broadening of peaks which occur in the chromatograms of nitric acid degraded polyethylene [43].

None of the available methods for correction of instrumental broadening is completely satisfactory. They can all give inconsistent oscillations in the calculated molecular weight distributions [23]. Another disadvantage is that in GPC broadening is often asymmetric and causes skewing and tailing of chromatograms. This effect cannot be corrected adequately by any of the methods. Thus none of the available correction procedures should be applied universally without consideration of their limitations.

7. Calibration

Calibration is necessary in order that the elution volume absiscae of chromatograms can be related to polymer molecular weight (as is done in fig. 2). It is performed most simply by using very narrow distribution fractions of the polymer under investigation. In this case, the peak elution volume of the narrow chromatogram is assumed to correspond to the known polymer molecular weight. A calibration curve can be constructed if a number of samples of different molecular weights are available.

Using narrow fractions and low molecular weight monodisperse samples, it has been shown experimentally that, over the useful separation range of a GPC column, the functional relationship between the molecular weight M of a molecular species, and its elution volume v is of the approximate form [10, 49]:

$$\log M = a - b\,v \qquad (5)$$

where a and b are constants.

For many polymers, the fractions available are not always sufficiently narrow. It is then necessary to use samples with appreciable dispersion of molecular weight for which either $\bar{M}_n$ or $\bar{M}_w$, or both, are known. With such samples there are two possible methods for the determination of the calibration curve. The first [50] assumes that the calibration curve has the form of equation 5. A "seek and find" computer programme is used whereby trial values of a and b are selected and for each pair of values the molecular weight averages are calculated from the chromatograms of the samples and assumed calibration curve. The calibration curve is defined as the pair of values which gives the best fit between the calculated and experimental molecular weight averages. The second approach [37] assumes that the calibration curve can be taken to have the form of equation 5 for the range of molecular

weight in each sample. It does, however, allow for the curve to have different values of a and b in different regions. In this procedure a single molecular weight average together with the chromatogram of the sample is used to calculate the envelope curve, formed on the log M/V diagram by all possible calibration lines which are consistent with the chromatogram and average molecular weight. The calibration curve is tangential to this computed curve. Thus, from a series of samples, the best calibration curve (which need not be linear) can be drawn through the series of computed curves.

As an alternative to using molecular weight, it was initially suggested [32] that extended chain length be used in calibration. It was then hoped that, since GPC separation appears to be due to differences in molecular size, such a curve would be independent of polymer type. This has been shown to be incorrect [51, 52].

Several attempts have been made to determine a parameter which will give a common calibration curve for different polymers. It has been shown that many different types of polymer, including branched polymers, all fall on a single curve when a plot of $[\eta]M$ against elution volume is made, where $[\eta]$ is the intrinsic viscosity of the narrow distribution polymer fraction of molecular weight M [53]. Now the radius of the sphere which in suspension would have the same effect on the macroscopically observed viscosity as the polymer molecule, i.e. the hydrodynamic radius R, may be defined from $[\eta]$ using the equation [54].

$$[\eta] = \Phi R^3/M \tag{6}$$

The universal calibration obtained using $[\eta]M$ therefore, suggests that it is the hydrodynamic radius of the polymer in solution which governs GPC separation.

Other results have been presented which suggest that the radius of gyration R_G of the polymer molecule in solution (or the mean square end-to-end distance which is proportional to R_G^2 for flexible polymers), can also be used as a universal calibration parameter [51]. R_G was calculated from $[\eta]$ using the following equations, which are based on quite complex viscosity theories [55]:

$$[\eta] = \phi(\epsilon) R_G^3/M \tag{7}$$

$$\phi(\epsilon) = \phi_0 (1 - 2.63\epsilon + 2.86\epsilon^2) \tag{8}$$

The parameter ϵ is a function of the molecular weight exponent α of the Mark-Houwink equation. The measurements were confined to linear polymers with comparable polymer-solvent interactions (and therefore similar α values) in which case the radius of gyration and hydrodynamic radius are proportional. Thus these results are also consistent with a separation mechanism based on the hydrodynamic volume.

Another separation parameter, the unperturbed polymer dimension (L_0) has also been used successfully to construct a universal calibration curve [56]. L_0 is a measure of the mean radius the polymer molecule would have in the absence of solvent. It can be related to $[\eta]$ using the equation:

$$[\eta] = \phi \left[\frac{L_0^2}{M}\right]^{3/2} M^{1/2} f(\alpha)^3 \tag{9}$$

It can be seen that for linear polymers with comparable polymer-solvent interactions L_0, like R_G, is directly proportional to the hydrodynamic radius. However, in addition to linear polymers with similar polymer-solvent interactions, it has been claimed that a single curve is obtained for polystyrene and cellulose trinitrate which have significantly different α values. Plots of log $[\eta]M$ against elution volume did not give a single curve for these polymers. These data are a subject of controversy, however, because of uncertainties over the magnitudes of the assumed unperturbed dimensions [57]. In addition it is difficult to understand the mechanism of any separation process based upon the unperturbed dimension.

Universal calibration is still, therefore, a subject of much controversy.

The above results are of great practical significance since they enable a calibration curve, applicable to one polymer, to be calculated from the data of a different polymer. Thus narrow distribution polystyrene fractions, which are commercially available, can be used to predict directly the log M/elution volume calibration curve of a different polymer for which characterised fractions may not be available. For example, if the elution volume of a molecular species is determined by the product $[\eta]M$ then, by introducing the dependence of $[\eta]$ on M (i.e. the Mark-Houwink equation $[\eta] = K M^{\alpha}$), the log M/v calibration curves can be directly related by the Mark-Houwink constants, which are often available in the literature [58]. This approach has been successfully applied to the important practical case of polystyrene and polyethylene [52].

8. Factors Influencing the Calibration Curve

The operational variables which influence GPC calibration are solution concentration, injection time, temperature and solvent flow rate. Each of these will now be discussed.

8.1. Solution Concentration and Injection Time

When the weight of sample injected on to the column is increased by increasing the solution concentration or injection time, the sample elution volume increases, the increase being larger for larger molecular weight samples [23, 25, 59-61]. Measurements of the functional dependence of elution volume v on injected weight W are contradictory: the data of some workers show a linear relationship [23, 25] whilst those of others do not [59-61].

The rate of increase of v with W (measured at zero concentration in the case of the data for which dv/dW is not constant) correlates with the intrinsic viscosity for a wide range of polymer types. Since this correlation is largely independent of the elution volume for different polymers, the injected weight effect has been attributed to a viscosity effect which occurs mainly, if not entirely, during flow in the interstices between the gel particles [25]. One hypothesis [22] for the effect is that when the zone of solution first enters the column it creates a zone of higher viscosity. The resulting increase in pressure forces solvent to push through the sample zone at a weak point causing an uneven velocity profile until considerable dilution has occurred. Such an effect would explain the larger elution volume and also the distortion and tailing which occurs for large viscosity solutions.

To eliminate errors due to the injected weight effect, the elution volume of calibration standards and also the sample chromatogram should ideally be obtained at several injected weights and extrapolation to zero injected weight be made. It has been suggested [25] that extrapolation of the sample chromatogram is unnecessary, since for broad distribution samples each molecular species has a considerably smaller concentration than for the narrow fractions which are normally used in calibration. The accuracy of this assumption obviously depends on the molecular weight and molecular weight spread of the sample and the sample injection weight. Use of a sufficiently small injection weight is not always possible since the lowest usable weight is limited by the detector sensitivity and baseline stability.

Variations in sample injection time, in addition to affecting the calibration curve due to the injection weight effect discussed above, also increase the mean sample elution volume since the solution is effectively injected at a later mean elution volume [25]. This is because the reference zero elution volume is always measured from the point at which injection was commenced. After readjusting the zero elution volume point to the mean sample injection point, variations in injection time only affect the appearance elution volume via the injection weight effect.

8.2. Temperature

An increase in column temperature has been shown to decrease the elution volume for polyisobutene with trichlorobenzene solvent [51]. The magnitude of the decrease was exactly that expected by the increase which occurs in the hydrodynamic radius or radius of gyration of the polymer molecule. These results, therefore, show that thermal expansion of the gel, which might be expected to increase the elution volume has a negligible effect.

8.3. Flow Rate

With increase in flow rate in the range 0.1 to 1.0 cc/min using the conventional GPC apparatus, a significant increase in sample elution volume has been observed [24, 25]. For low molecular weight samples this increase has been shown to be almost entirely due to systematic errors which arise when the sample elution volume is measured with a syphon [24]. Elimination of this error still leaves a significant flow rate dependence of the elution volume of high molecular weight samples. This dependence is considerably reduced by use of very low concentrations [24] and can be almost entirely attributed to the "viscosity effect" discussed in section 8.1.

At flow rates larger than 1 cc/min, the appearance volume decreases slightly with increase in flow rate [23, 25]. This effect is probably due to incomplete molecular diffusion into the gel at larger flow rates. This results in an earlier elution of the polymer from the column. Other effects which could cause a flow rate dependence are changes in the velocity profile with flow rate and reduction in gel pore volume due to the increased pressures which accompany higher flow rates.

9. The Importance of GPC

The influence of GPC on polymer science has been discussed in an excellent review by R. F. Boyer [62].

The molecular weight distribution of a polymer directly affects its processability and properties. One example which has been reported [63] is the spinability into fibres of polyacrylonitrile. It was shown that three samples, each of the same weight-average molecular weight, but different molecular weight distribution, had vastly different spinabilities. Another technologically important example is quoted in a US Patent [64]. This suggests that narrow mclecular weight distribution polymers would be more suitable for use as additives for petroleum oil in order to reduce the variation in viscosity with temperature. This is because low molecular weight material contributes little to the viscosity (and is therefore an expensive filler) and very high molecular weight material is degraded in use.

GPC in addition to quantifying many important effects such as those mentioned above also offers the possibility of industrial control because of the rapid analysis time. It is, therefore likely to become increasingly important to polymer technology.

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Letters

Superplastic Behaviour of a Splat Cooled Al-17 wt % Cu Alloy

Al–Cu alloys near the eutectic composition (33 wt % Cu) have shown a superplastic behaviour within a wide temperature range [1–3]. In general, hot working or quenching from high temperatures is used to get a superplastic structure in such alloys. Independent of the fabrication method two main characteristics are required in order to obtain superplasticity: a small equiaxed grain structure and a high structural stability of the alloy at the test temperature. A small grain size can be obtained easily by splat cooling the molten material, resulting in a very high solidification rate since the heat is extracted rapidly by conduction through a cool substrate [4]. Nucleation and growth of the equilibrium phases can be prevented completely. New metastable phases and highly supersaturated solid solutions can be formed. In addition, large morphological modifications are always obtained, resulting in a refined structure. The necessary high structural stability at elevated temperature is an intrinsic property of a two phase mixture of equiaxed grains when the two phases have a large difference in chemical composition [5].

During the investigation of the mechanical properties of binary Al-alloys, prepared by splat cooling, a hypo-eutectic composition Al-17 wt % Cu showed superplastic behaviour in tensile tests. The foils suitable for mechanical tests were obtained from small amounts of the liquid alloy splat cooled between two copper plates. These plates were moved against each other with high speed, solidifying and deforming the drop of liquid alloy between them [6].

The tests were performed with an INSTRON machine at a constant cross head speed of 0.2 cm/min. The specimens were about 50 μm thick, 4 mm wide and had a gauge length of 7.2 mm. The test temperature was 400° C. The specimens were heat-treated at this temperature for about 3 h before applying the load. The total elongation was 600%. This value is impressive if we consider that the tensile specimens cut from the splat cooled foils were not perfectly sound and smooth, but exhibited surface irregularities and central cavities which could act as notches and so affect the ductility. In addition, these large elongations were obtained on tensile specimens with a larger length to thickness ratio than have standard samples for tensile tests. Such samples generally show elongation to fracture values smaller than the standard ones [7]. Experimental evidence of this fact was shown by measuring the total elongation of specimens having the same dimensions as the splat cooled samples which had been cut from rolled and fully annealed strips of