Determination of Polymer Structure by Gel Permeation Chromatography

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Introduction
Gel permeation chromatography (GPC) is an established method of determining the molecular mass of polymers. Compared with other methods of analysis, such as osmometry and static light scattering, it has the advantage that it determines not merely average values but the complete distribution of molecular weights. However, in its conventional form, (i.e., using a single concentration detector), GPC only gives relative molecular masses. To overcome this limitation and meet the growing demand for the characterization of increasingly complex polymers, detectors sensitive to molecular weight, such as light scattering and viscosity, can be used in GPC. In this way, true molecular weight distributions can be obtained, as well as size distributions and further structural information, such as the degree of polymer branching.

Conventional GPC
In GPC molecules are separated according to their hydrodynamic volume. Their molecular weights (MW) and molecular weight distribution can be determined from the measured retention volume (RV) by means of a calibration curve (log MW against RV), which must be set up with the aid of a number of standards of known molecular weight. But, as the relationship between molecular weight and size depends on the type of polymer, the calibration curve depends on the polymer used, with the result that true molecular masses can only be obtained if the calibration standards and the sample are of the same type. In all other instances, the results are only relative. Large deviations from the true molecular weight occur in the instance of branched samples, in particular, because the molecular density of these is substantially higher than in linear chains (1, 2).

The detectors used are either refractive index (RI) or ultraviolet (UV) detectors. Their signals depend solely on concentration, not on molecular weight or polymer size. For RI detectors the following applies:

\[
\text{RI signal} = K_{RI} \cdot \text{dn/dc} \cdot c \quad [1]
\]

where \(K_{RI}\) is an apparatus-specific sensitivity constant, \(\text{dn/dc}\) the refractive index increment and \(c\) the concentration.

Molecular Mass–Sensitive Detectors — Determining Molecular Weights
Today, viscosity and/or light-scattering detectors are very often used to overcome the limitations of conventional GPC. The signal of light-scattering detectors is directly proportional to the molecular weights of the polymers:

\[
\text{LS signal} = K_{LS} \cdot (\text{dn/dc})^2 \cdot \text{MW} \cdot c \quad [2]
\]

This equation shows that the concentration and \(\text{dn/dc}\) value must be known to determine the molecular mass. The refractive index increment, \(\text{dn/dc}\), appears squared in the equation with the result that any inaccuracy in this value leads to very large deviations in molecular weight. Whether or not light-scattering detectors can be used depends decisively on the refractive index increment of the polymer solvent combination.

Where values are high, as in the situation of polystyrene in tetrahydrofuran (THF) \((\text{dn/dc} = 0.185)\), for instance, useable signals are obtained down to molecular masses of approximately 1000 g/mol. In the situation of other polymers, such as polylactide in THF \((\text{dn/dc} \approx 0.049)\), the size of the signal is only about 7% of the polystyrene-in-THF signal at the same concentration and molecular weight, making reliable evaluation at low MW impracticable.

The advantage of light scattering in GPC is that, once the \(K_{RI}\) and \(K_{LS}\) have been ascertained using suitable substances, molecular weight can be directly determined without a calibration curve, provided that the signal-to-noise ratio is adequate for this.

With regard to viscosity detectors, the following equation applies:

\[
\text{Visc. signal} = K_{Visc} \cdot IV \cdot c \quad [3]
\]

The viscometer provides the intrinsic viscosity \((IV = [\eta])\) of the polymer directly. For low molecular weights, the sensitivity of the viscosity detector exceeds that of light scattering, even at high \(\text{dn/dc}\) (see Figure 1). This means that true molecular weights can be obtained, by means of universal calibration (see later), even for samples where the signal-to-noise ratio of light scattering is inadequate. This is especially useful when polymers possess a low-molecular weight fraction, which is difficult to assess by means of light scattering.

Intrinsic viscosity is inversely proportional to the molecular density of the polymer

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**Figure 1:** Extract from a triple chromatogram of polystyrene (MW ≈ 2000 g/mol) in chloroform: \(c \approx 4.5 \text{ mg/mL}, \text{dn/dc} \approx 0.160\). The viscosity signal-to-noise ratio is already markedly better than light scattering at a molecular weight of approximately 2000 g/mol. \((-) = R_I, (-) = \text{Visc}, (-) = \text{LS}.\)
coil. The product of molecular mass and intrinsic viscosity, therefore, gives the hydrodynamic volume:

\[ \text{MW} \cdot \text{IV} = \frac{5}{2} \cdot N_A \cdot V_h \]  

where \(N_A\) is the Avogadro constant (3). A universal calibration curve can be created on the basis of this relationship, using a viscosity detector. If the log(\(\text{MW} \cdot \text{IV}\)) versus retention volume is used instead of the conventional calibration curve, true molecular weights are obtained regardless of whether the chains are linear or branched, or the type of calibration standards, the chemical composition or the structure (4).

**“Viscosity and/or light-scattering detectors are very often used to overcome the limitations of conventional GPC.”**

**Determining Polymer Structures**

The so-called radius of gyration (\(R_g\)) can be obtained by light-scattering detection at several angles \(\theta\). This is done by determining the initial slope of the plot of the inverse light-scattering intensity against \(\sin^2(\theta/2)\). However, angular dependence occurs only with polymers whose coil diameter is greater than about \(1/20\) of the wavelength of the light. This corresponds to an \(R_g\) of approximately 15 nm and, in the case of polystyrene, to an MW of approximately 150 000 g/mol. Below this limit, the light cannot resolve any structure, and determination of the \(R_g\) is not possible. In the instance of branched polymers, the limit is located at markedly higher molecular masses, because these possess a substantially higher molecular density. In addition to this limitation at low molecular size there is a further problem at the upper end. Large

Figure 2: Comparison of (a) conformation and (b) Mark-Houwink plots of a dextran sample. The Mark-Houwink plot makes it possible to differentiate clearly between areas with short-chain branching and those with long-chain branching.
polymers often display a non-linear angular dependence of the inverse light-scattering intensity, so that the initial slope (and hence the $R_g$) cannot be reliably determined by multi-angle light scattering (5).

As already stated above, the intrinsic viscosity, $[\eta]$, of polymer samples is measured by means of GPC viscosity detectors. As the reciprocal density of the polymer coil in solution, $[\eta]$ represents a direct, sensitive structural parameter and, therefore, a traditional parameter in the polymer industry. The well-known Mark-Houwink plot $[\eta] = K \cdot MW^\alpha$ can be obtained by means of the double-logarithmic plot of intrinsic viscosity against MW. The Mark-Houwink plot is the central plot of polymer structure analysis. It reflects structural changes in the polymer, such as branching and chain rigidity. The slope, described by the Mark-Houwink exponent can vary between 0 for solid spheres and 2 for rod-shaped structures (3). Analogous to the Mark Houwink plot, the so-called conformation plot can be constructed from light-scattering data by plotting log $R_g$ against log MW. Its slope can only vary between 0 and 1. For this reason, structural changes are much more evident from viscosity detection (see Figure 2).

Generally speaking, structural parameters can be determined more directly, in a wider MW range, and are more easily reproducible, by means of viscosity detection than by light scattering.

Combining the advantages of both detectors leads to triple detection (RI/viscosity/LS): molecular masses can be determined by light scattering, and structure information through intrinsic viscosity. In addition, this combination makes it possible to determine and differentiate between aggregates and microgels. To analyse low MW and/or low-$dn/dc$ polymers, universal calibration can be used without the need to convert the GPC system (6).

**Summary**

It is advantageous to use light scattering to determine molecular weights provided the signals are sufficiently intensive (sufficiently high $dn/dc$ and MW). When it comes to determining structure, viscosity detectors are more suitable, because they measure structural differences directly and can be used over a substantially wider range of molecular weights. Triple detection combines these detection capabilities into a single system to give molecular weight and structure without limitations.

**References**


Rainer Walkenhorst obtained his chemistry PhD at the University of Bielefeld, Germany in 1995. After holding a postdoctoral position in the USA he joined Viscotek in 1998 as an applications manager.