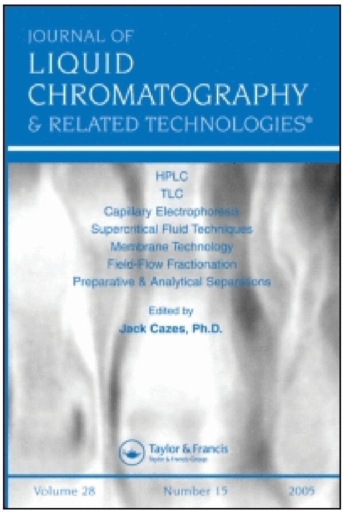

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Characterization of Copolymers and Polymer Mixtures by Gel Permeation Chromatography

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Characterization of Copolymers and Polymer Mixtures by Gel Permeation Chromatography

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ABSTRACT

Estimation of molecular weights from GPC data is complicated when the polymer sample consists of a mixture of homopolymers or of statistical copolymers with nonuniform compositions. This is because sizes of solvated polymer coils depend on solvent interaction with both the homo- and hetero-units of the copolymers and because the extent of solvation of different homopolymers can differ. The overall degree of solvation may change effectively with composition and use of a single "average" set of Mark-Houwink constants in calibration procedures will then produce false molecular weight data from the GPC data. A new molecular weight average, $\bar{M}_x$, is defined to overcome this problem. This average can be determined from the GPC chromatogram and intrinsic viscosity of the sample in the GPC solvent. Mark-Houwink coefficients are not needed. $\bar{M}_x$ lies between $\bar{M}_w$ and $\bar{M}_z$.

Hydrodynamic volumes of solvated polymers are fundamental in determining the gel permeation chromatographic (GPC) elution volumes of the species in a mixture (1-3). All species with the same hydrodynamic volume appear with the same elution volume. For homopolymers in a given GPC solvent, hydrodynamic volumes can be related directly to molecular weights, with allowance where necessary for concentration effects (4-6). When the sample consists of a mixture of homopolymers or statistical copolymers with non-uniform compositions the estimation of molecular weight information from GPC data is much more complicated.

The major difficulty in analyzing the GPC chromatogram of a compositionally heterogeneous polymer sample involves conversion of hydrodynamic volume (Vh_i) of species i to molecular weight (M_i). This is because the size of the solvated polymer coil (and hence the Mark-Houwink constants (7)) depends on the solvent interaction with both the homo- and hetero-units in the case of copolymers (8-10). In some cases, as when the copolymer structure tends toward alternation, the influence of hetero segments may predominate. As a consequence, the values of the Mark-Houwink constants would be relatively insensitive to composition within certain limits. However, in instances where the copolymer composition tends to be more random, or when the sample is a blend of copolymers or homopolymers, the overall degree of solvation will change effectively with blend composition at a given molecular weight, and the use of a single "average" set of Mark-Houwink constants will produce false molecular weight parameters from GPC data. The alternative is to assign a set of effective Mark-Houwink constants at each elution volume, but this is an intractable experimental problem.

We, therefore, propose the use of a new molecular weight average, $\bar{M}_x$, to characterize polymer samples of heterogeneous composition by GPC in cases where a single set of Mark-Houwink constants is unsatisfactory. $\bar{M}_x$, the hydrodynamic volume average, is defined according to:

$$\bar{M}_x = \frac{\Sigma w_i [\eta]_i M_i}{\Sigma w_i [\eta]_i} = \frac{\Sigma w_i [\eta]_i M_i}{[\eta]} \qquad (1)$$

where w_i and $[\eta]_i$ are the weight fraction and intrinsic viscosity, respectively, of all species which exit the GPC columns with elution volume Ve_i. The denominator in equation (1) is equal to the intrinsic viscosity, $[\eta]$, of the whole sample in the GPC solvent. This parameter is measured separately. The values in the numerator are available from the GPC chromatogram. At infinite dilution of the species in the sample (5,11), the product $[\eta]_i M_i$ can be read directly from the universal calibration curve and w_i is equated to the ratio of the area of the GPC detector response at elution volume Ve_i to the total area under the chromatogram. This molecular weight average is particularly useful for mixtures of homopolymers or for copolymers in which composition may vary with molecular weight. The latter materials are produced in free radical batch copolymerizations that exhibit a significant composition drift with conversion and an autoacceleration-induced increase in molecular weights at higher conversions.

The value of $\bar{M}_x$ will fall between $\bar{M}_w$ and $\bar{M}_z$ of the sample. The Mark-Houwink relation for a monodisperse species is:

$$[\eta] = KM^a \qquad (2)$$

where K and a are the M-H constants. Substitution of equation (2) into equation (1) gives:

$$\bar{M}_x = \frac{\Sigma w_i K M_i^{a+1}}{\Sigma w_i K M_i^{a}} = \frac{\Sigma w_i M_i^{a+1}}{\Sigma w_i M_i^{a}} \qquad (3)$$

When a = 1

$$\bar{M}_x = \frac{\Sigma w_i M_i^{2}}{\Sigma w_i M_i} = \bar{M}_z \qquad (a = 1) \qquad (4)$$

and when a = 0

$$\bar{M}_x = \frac{\Sigma w_i M_i}{\Sigma w_i} = \bar{M}_w \qquad (a = 0) \qquad (5)$$

For most random coil polymers in the relatively nonpolar solvents which are commonly used 0.5 $\leq a \leq 0.8$ (7) and $\bar{M}_w < \bar{M}_x < \bar{M}_z$. Because of its dependence on the Mark-Houwink exponent a, $\bar{M}_x$ of a homopolymer will be somewhat solvent dependent. The more familiar $\bar{M}_v$ also exhibits some solvent dependence, for similar reasons.

When the composition of a polymer sample varies along with the molecular weights of the component species characterization of the molecular weight distribution is as formidable experimental problem. Some of the difficulties can be circumvented by use of the $\bar{M}_x$ average which can be estimated from the GPC chromatogram and the intrinsic viscosity of the polymer without a calibration for the components of the sample. Although a single average must convey less information than knowledge of the whole distribution, $\bar{M}_x$ may be expected to correlate with some mechanical and rheological properties of mixtures since its magnitude lies between $\bar{M}_w$ and $\bar{M}_z$. It is recommended that when $\bar{M}_x$ is used to characterize a copolymer or polymer blend, both the parameters $\bar{J}_w$, which is proportional to the weight average hydrodynamic volume of the sample, and the standard deviation σ_J should also be reported:

$$\bar{J}_w = \Sigma w_i [\eta]_i M_i \qquad (6)$$

$$\sigma_J = (\Sigma w_i (J_i - \bar{J}_w)^2)^{1/2} \qquad (7)$$

where $J_i = [\eta]_i M_i$. This procedure provides a molecular weight average to characterize the sample and a measure of the mean and breadth of the distribution of hydrodynamic volumes in the sample.

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