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Analysis

Comments on the Measurement of Long Chain Branching by Size Exclusion Chromatography

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Summary

A technique for measuring long chain branching as a function of polymer molecular weight uses SEC with a low angle laser light scattering (LALLS) detector to compare M_w of an eluting species with the molecular weight of the linear counterpart that has the same retention time. This technique is correct only if all species in the SEC detector cells have the same constitution. Evidence is presented that indicates that this condition prevails for low density, high pressure polyethylene and polyvinyl alcohol. Alternative forms of data representations are suggested. A major uncertainty in the data treatment is the value to be assigned to the ratio of radii of gyration of linear and branched polymers with the same molecular weight. A method is suggested to measure this ratio directly, as a function of molecular weight, if the eluting species at any instant are uniform in branching character.

SEC estimates of long chain branching frequency in polymers proceed from the structure parameter g' which compares the intrinsic viscosities of branched and linear polymers with the same composition and molecular weight:

$$g' = \frac{[\eta]_b}{[\eta]_\ell} \tag{1}$$

where $[\eta]_b$ is the intrinsic viscosity of the branched polymer and $[\eta]_\ell$ is the intrinsic viscosity of the linear species, both in the SEC solvent. It is necessary also to consider the ratio, g, of the mean squared radii of gyration, $\langle R_G^2 \rangle$, of the same polymers:

$$g = \frac{\langle R_G^2 \rangle_b}{\langle R_G^2 \rangle_\ell} < 1 \tag{2}$$

The value of g has been calculated for a number of specific branched structures in Theta solvents (1,2). Calculation of g' for use in equation (1) is not clearcut because the degree of draining of macromolecules is not known exactly and because the degree of expansion of linear and branched molecules in a given solvent may be different. Various relations have been proposed of the form:

$$g' = g^k \tag{3}$$

where k has been suggested to have magnitudes between 0.5 and 1.5 (3-6). More is said of k later.

At equal GPC elution volume and infinite dilution the molecular weights of linear and branched species of uniform constitution are related by (7):

$$[\eta]_b M_b = [\eta]^* M^* \tag{4}$$

where the subscript b and superscript * refer to the branched and linear polymers that elute with the same SEC retention time. That is to say, the species M_b and M^* have equal solvodynamic volumes in the SEC solvent. In general, $M_b \geq M^*$ and:

$$[\eta]_b = g'[\eta]_\ell = g'KM_\ell^a = KM_b^a \tag{5}$$

In equation (5) K and a are the Mark-Houwink constants for monodisperse versions of the linear polymer in the SEC solvent:

$$[\eta] = KM^a \tag{6}$$

and M_ℓ and M_b are linear and branched polymers, respectively, with the same molecular weight:

From equations (4) and (6):

$$[\eta]^* M^* = K(M^*)^{a+1} \tag{7}$$

and equation (4) can therefore be expressed as:

$$g'KM_b^{a+1} = K(M^*)^{a+1} \tag{8}$$

so that:

$$g' = \left[\frac{M^*}{M_b}\right]^{a+1} = g^k \tag{9}$$

This is the basis of a technique for measuring the relation between long chain branching and molecular weight using SEC with a low angle laser light scattering (LALLS) detector. At any given elution volume M_b is measured as $\overline{M}_w$ by the LALLS detector, while M^* is calculated from the universal calibration curve for linear species (8, 9).

This application of equation (9) is correct if all the species in the SEC detector cell have the same constitution. Then, if axial dispersion effects are insignificant, $\overline{M}_w = \overline{M}_n = \overline{M}_z =$ etc. for the polymers under examination and a single-valued relation exists between polymer molecular weight and solvodynamic volume.

If the material in the detector cell consists of polymers with different extents of long chain branching, however, then M_b is actually equal to $\overline{M}_n$ (10), whereas the LALLS detector measures $\overline{M}_w$.

Indirect methods have been used to estimate $\overline{M}_n$ as a function of elution volume (11). Unfortunately, there is no way to validate such techniques experimentally because a detector capable of measuring $\overline{M}_n$ on-line is not available. In principle, polymers with long chain branching can be characterized by a series of three detectors including a concentration detector, the LALLS unit and an on-line viscometer detector (12), if one is available.

As a general rule, the application of eq.(9) in SEC-LALLS measurements must be deemed incorrect, for the reasons given. Here we discuss whether this procedure may be practically useful, nevertheless, for particular polymers like polyethylene and poly(vinyl alcohol), where we have some experimental data.

The contents of the detector cell can reasonably be supposed to be of uniform architecture if the degree of long branching does not increase with increasing molecular weight. Since the species under examination at any elution volume presumably all have the same solvodynamic volume the material in the detector may consist of branched polymers along with lower molecular weight, more linear species. Our experience with polyethylene with the SEC-LALLS technique shows however that long chain branching generally decreases with increasing molecular weight (9). The higher molecular weight molecules therefore tend to occupy greater solvodynamic volumes and will not elute at the same retention volume as smaller, more branched species. (This variation of branching with molecular weight is to be expected from consideration of the high pressure process for ethylene polymerization. The reaction is non-isothermal, with higher temperatures favoring both smaller polymers and long chain branching by chain transfer to polymer.)

In the case of reacetylated poly(vinyl alcohol) the measured long chain branching appears to be invariant with molecular weight, at least for the samples studied to date (13,14). This also may be construed as circumstantial evidence for uniformity of structure at a given SEC elution volume, again because molecules with different molecular weight cannot elute together if the concentration of long branches does not increase with molecular weight.

We conclude that the procedure based on equation (9) with $M_b=\overline{M}_w$ is plausible for the two polymer types that have been studied.

To avoid ambiguity, however, it may be appropriate to describe the data generated as "weight average number of long branches per weight average molecule with specified radius of gyration." The reasons for this terminology are as follows.

The particular model that has been used in this work to date is based on the Zimm-Stockmayer (2) formula for weight average number of branches in a randomly branched polymer with trifunctional branch points. The LALLS procedure actually measures $\overline{M}_w$ at given elution volume, V_e. V_e can be readily translated to solvodynamic radius, R_S, by using the universal calibration curve (7, 15, 16). R_S may be related in turn to R_G by (17):

$$R_S = 0.77\ R_G \tag{10}$$

An alternative way to express the data is to compute $\langle R_G \rangle_n$, $\langle R_G \rangle_w$, $\langle R_G \rangle_z$ and so on from the experimental chromatogram along with the universal calibration curve and to estimate $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, etc. from the LALLS detector. Comparisons of corresponding average sizes and molecular weights may be informative, at least in a qualitative manner.

Either data representation can be extended to estimates of long branch frequency if M_b can be assumed to be equal to $\bar{M}_w$ and if the physical model (2) and value of k are considered reasonable. The latter assumptions may, in fact, be even more difficult to justify than the first one.

A major uncertainty in the branching calculations is due to the assumption that k in eq. (3) is a constant for a given polymer, whereas it is more likely to be a function of polymer architecture, like density, length and constitution of the branches. Thus, if the branch density changes through the molecular weight distribution (as is sometimes assumed for commercial low density polyethylenes) then k also changes. There is therefore an understandable desire to avoid the use of k and eq. (3) in calculations of long chain branching. An attempt to accomplish this is described in the following paragraphs.

We note that g is defined by eq. (2) as the ratio of mean square radii of linear and branched polymers having the same molecular weight. At the same time, the hydrodynamic volume, V_H, of species of broad distribution polymers that elute from the SEC apparatus with elution volume V_e is given by (16)

$$V_H = \frac{4\pi[\eta]M}{9.3 \times 10^{24}} \tag{11}$$

and (15,16,18):

$$V_H = \frac{4}{3}\pi R_G^3 \tag{12}$$

The particular SEC column set can be calibrated using standard polymers with known molecular weights and Mark-Houwink coefficients in the SEC solvent. From eqs. (11) and (12), one can determine R_G of the species that elute at given V_e. Finally, knowing the $\bar{M}_w$ of those species that elute at V_e from the LALLS-SEC combination it is a simple matter to calculate the V_H and R_G of the corresponding linear versions of the polymer. The ratio of the radii of gyration obtained from universal calibration and direct LALLS measurements gives g directly, without the necessity of involving eq. (1) or eq. (3).

As before, however, this method will be valid only if the contents of the LALLS detector cell have uniform long branch character.

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