

Characterization of Long-Chain Branching in Poly(vinyl Acetate) by Sedimentation Velocity and Exclusion Chromatography

The work¹ leading to the production of reference samples of linear poly(vinyl acetate) has been extended to the analysis of long-chain branching in that polymer. A method has been developed that leads to estimates of the ratio of the hydrodynamic radii of branched and linear isomers throughout the distribution of the branched sample, without the need for molar mass measurements. The method employs ultracentrifugation and exclusion chromatography and is a variant of one proposed some years ago by Tung.² In that work, however, explicit appeal was made to measurements of molar mass, and the utility of the approach in the qualitative recognition of branching was not brought out.

The relative molecular mass M_r of a polymer of linear structure is related empirically to elution volume v in exclusion chromatography (EC) by an expression of the form

$$\ln M_r = \Phi(v) \quad (1)$$

where Φ is a polynomial function, and to the sedimentation coefficient in ultracentrifugation by

$$S = KM_r^\alpha \quad (2)$$

where K and α are empirical constants; sedimentation coefficients are assumed throughout to refer to infinite dilution in a poor solvent. It follows that for linear molecules

$$\ln S = \ln K + \alpha\Phi(v) \quad (3)$$

A branched molecule has a larger elution volume and a larger sedimentation coefficient than its linear isomer, so that branching gives rise to positive deviations from eq. (3). Those deviations can be used qualitatively to recognize long-chain branching and for quantitative estimation, without the need for measurements of molar mass. In this communication a procedure for that estimation is presented, and the results are compared with the conventional^{3,4} exclusion chromatography/viscometry method for some fractions of branched poly(vinyl acetate). An empirical relation like eq. (3) holds between elution volume and limiting viscosity number $[\eta]$ for linear molecules. But since a branched molecule has a *smaller* limiting viscosity number than its linear isomer, branching does not entail deviation from that relation; estimation of branching by methods based upon exclusion chromatography and viscometry requires molar mass measurements.

Consider first the case of a monodispersed branched sample. Measurements by ultracentrifugation will yield a sedimentation coefficient S_{br} . Measurements by exclusion chromatography will yield, from eq. (3), the sedimentation coefficient S_1 of the linear molecule of identical elution volume. There is much evidence that elution volume in exclusion chromatography is determined by hydrodynamic volume under the experimental conditions, so that the sedimentation coefficient derived from eq. (3) corresponds to the linear molecule isodiametric in the good solvent used for exclusion chromatography. There is no reason to assume in general that the volumes of branched and linear molecules increase similarly on moving from a poor solvent to a good one. Published data^{2,5,6} for randomly branched fractions of poly(vinyl acetate) and polyethylene are consistent with that assumption, however, and its use here allows S_1 to be ascribed to the linear molecule isodiametric with the branched molecule in a θ solvent for the former. The degree of branching can be derived from S_1 and S_{br} in the following way.

The relation between sedimentation coefficient, molar mass, and hydrodynamic radius R is

$$S = \frac{(1 - \bar{v}\rho)M}{6\pi\eta N_0 R} \quad (4)$$

where \bar{v} is the partial specific volume of the solute and ρ and η are the density and viscosity of the solvent. Hence, for isodiametric linear and branched molecules

$$(S_1/S_{br})_{R_{br}} = (M_1/M_{br})_{R_{br}} \quad (5)$$

Branching is often characterized by the parameter

$$h = (R_{br}/R_1)_{M_{br}} \quad (6)$$

or, using eq. (4),

$$h = (S_1/S_{br})_{M_{br}} \quad (7)$$

Now, from eq. (2),

$$(S_1)_{M_{br}} = KM_{br}^\alpha \quad (8)$$

and substitution from eq. (5) yields

$$(S_1)_{M_{br}} = K \left(\frac{M_1 S_{br}}{S_1} \right)_{R_{br}}^\alpha \quad (9)$$

Or, using eq. (2),

$$(S_1)_{M_{br}} = (S_1)_{R_{br}} (S_{br}/S_1)_{R_{br}}^\alpha \quad (10)$$

Substitution into eq. (7) then yields

$$h = (S_{br}/S_1)^{\alpha-1} \quad (11)$$

the central equation for the proposed treatment. It allows the estimation of branching in a mono-dispersed sample from (1) sedimentation velocity experiments in a θ solvent for linear molecules, when $\alpha = 0.5$; (2) exclusion chromatography; and (3) an empirical relation between sedimentation coefficient and elution volume for linear molecules.

Application of the method to polydispersed samples follows simply. Then sedimentation velocity experiments yield distributions of sedimentation coefficient

$$g(\ln S) = dm_f/d \ln S \quad (12)$$

and exclusion chromatography yields distributions of elution volume

$$h(v) = dm_f/dv \quad (13)$$

where m_f represents mass fraction of polymer present. For linear molecules the distributions are related by

$$g(\ln S) = h(v)dv/d \ln S \quad (14)$$

and the derivative $dv/d \ln S$ follows from eq. (3). Use of eq. (14) will transform the chromatogram of a branched sample into an apparent distribution of sedimentation coefficient $g'(\ln S)$, which, by an extension of the argument above, will represent the linear sample of identical distribution of hydrodynamic radius in a θ solvent for linear molecules.

Stepwise integration of the two distributions $g(\ln S)$ and $g'(\ln S)$, which will differ only for branched samples, yields the integral distributions $G(\ln S)$ and $G'(\ln S)$. The mass-fraction scales of the two distributions will be equivalent if branching increases with sedimentation coefficient. That condition is likely to hold when branching is a result of chain transfer to polymer, as is the case⁷ for low-density polyethylene and poly(vinyl acetate). Comparison of the two distributions then yields directly the sedimentation coefficient of the linear molecule isodiametric with each molecular species present in the branched sample, and hence with eq. (11), a complete estimate of branching.

The proposed method was tested in the analysis of four fractions of branched poly(vinyl acetate) produced by preparative exclusion chromatography of a commercial whole polymer. Details of the fractionation, exclusion chromatography, and ultracentrifugation have been given elsewhere. Since the ultracentrifugation was conducted under θ conditions⁸ (methanol at 6°C) for linear poly(vinyl acetate), the theoretical value of 0.5 was taken for α in eq. (14); empirically⁹ we found $\alpha = 0.509 \pm 0.012$ for this system.

In order to minimize the systematic uncertainties due to diffusion in ultracentrifugation and dispersion in exclusion chromatography, values of h were calculated [eq. (11)] corresponding to a mass fraction in $G(\ln S)$ and $G'(\ln S)$ of 0.5. Results were compared (Table I) with those of conventional exclusion chromatography/viscometry method. For the latter method a molar mass scale is necessary; it was based upon exclusion chromatography of NPL reference samples of linear poly(vinyl acetate), certified as to number-average and mass-average molar mass. With that additional information, the branched fractions were characterized as to molar mass (Table I). It is clear that the branching estimates via $EC/[\eta]$ and EC/S agree well and that the proposed method, based upon

TABLE I
Branching Analyses by the Proposed and Conventional Methods

Molar mass, kg/mol		Sedimentation coefficient, 10^{-13} sec		h	
Number average	Mass average	S_{br}	S_1	$\overline{EC}/[\eta]$	EC/S
228	282	10.16	7.70	0.85	0.87
344	437	12.55	9.52	0.87	0.87
401	582	15.54	11.74	0.88	0.87
519	679	15.39	11.40	0.85	0.86

EC/S , is qualitatively useful for recognizing long-chain branching and quantitatively useful for estimating branching without the need for molar mass characterization, at least for fractions.

Extension of the method to a sample of molar mass distribution broad enough to be associated with a significant change in the parameter h presents a number of additional difficulties. The breadth of distribution of sedimentation coefficient accessible to measurement is limited. Estimation of S_1 and S_{br} in the wings of a broad distribution becomes increasingly subject to uncertainties introduced by the corrections for the effects of pressure and diffusion. The latter correction becomes particularly important at lower molar mass, where variation in h is most likely. In practice the method is likely to be restricted to fractionated material.

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