Characterization of long-chain branching in poly(vinylacetate): a comparison of two methods

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A commercial sample of poly(vinylacetate) was fractionated by preparative gel permeation chromatography. Molar masses and branching parameters measured by supplementing analytical gel permeation chromatography with viscometry and with ultracentrifugation were in good agreement. No serious errors were introduced by neglecting the difference between the expansions of branched and linear molecules in a good solvent.

INTRODUCTION

Synthetic polymer molecules with long-chain branching have smaller average sizes, in the melt and in solution, than their linear isomers. That difference is size is responsible for the technological importance of branching in polymer rheology and also is the basis of the common means of estimating long-chain branching. Gel permeation chromatography (g.p.c.) is the method generally favoured for the routine molecular characterization of synthetic polymers and much effort has been devoted to its application to branched samples. The chromatogram then reflects the distributions of molar mass and of branching, and cannot be interpreted in terms of molecular parameters without further information. Methods have been described that combine g.p.c. with viscometry and with ultracentrifugation to derive molar masses and branching parameters.

There is much evidence that elution volume in g.p.c. correlates with hydrodynamic volume, which at infinite dilution is proportional to the product $[\eta] M_r$, where $[\eta]$ is the limiting viscosity number under the conditions of g.p.c. and M_r the relative molecular mass. This principle of universal calibration is applicable to moderately branched samples of polyethylene[1], polystyrene[2] and poly(vinylacetate)[3]; exceptions[4,5] have been reported in the case of highly branched samples, however. The elution volume scale in g.p.c. can be calibrated in terms of hydrodynamic volume by molar mass measurement, chromatography and viscometry of linear fractions. If universal calibration holds, chromatography and viscometry can be used to characterize branched fractions in terms of molar mass. Extension of the method to branched whole polymer requires further assumptions concerning the dependence of branching frequency upon molar mass, and of viscometry upon branching.

In g.p.c. a branched molecule behaves like a linear molecule of smaller molar mass. In sedimentation velocity experiments a branched molecule behaves like a linear molecule of larger molar mass. Use of a calibration established with linear molecules in g.p.c. and in sedimentation velocity respectively under-estimates and over-estimates the molar mass of a branched sample. Tung[6] showed that the true molar mass of a branched sample was the geometric mean of those estimates, provided that a theta-solvent for linear molecules was used for ultracentrifugation, and that branched and linear molecules with identical hydrodynamic volumes under the conditions of g.p.c. have identical hydrodynamic volumes in a theta-solvent for linear molecules.

The estimation of branching by means of g.p.c./viscometry on the one hand and g.p.c./ultracentrifugation on the other relies upon relating the results to model calculations of the effect of branching of various sorts upon the unperturbed radius of gyration and hydrodynamic radius. Difficulties immediately arise concerning the relation of these theoretical quantities to experiments in the good solvents used for g.p.c., and are resolved by assumptions of doubtful validity.

In recent years the g.p.c./viscometry method has been applied extensively[7–10] to the analysis of low-density polyethylene and a few other polymers[11–13]. Molar masses found for branched molecules usually agree with the results of classical measurement; estimates of the branching frequency are often implausible[14], however. The g.p.c./ultracentrifugation method[6] has been littled used, doubtless because ultracentrifugation is a particularly demanding technique at the temperatures necessary for work with low-density polyethylene, the polymer in which branching has the greatest commercial significance. In this communication we compare the methods for the first time, in their application to poly(vinylacetate), with the aim of evaluating the various assumptions made. The work makes use of fractions of linear poly(vinylacetate) available as NPL Certified Reference Materials.

EXPERIMENTAL

Preparation of the linear fractions has been described[15]. Branched samples were produced by a similar fractionation by preparative g.p.c. of a commercial whole polymer (Aldrich: Catalogue No. 18 250-8; lot no. 04). Tetrahydrofuran (Koch–Light) was distilled from lithium aluminium hydride, and contained 0.05% by mass Santonox R (Monsanto) when used as g.p.c. solvent. Methanol (Burrough AR grade) was used as received. Heptan-3-one (Aldrich) was purified by distillation.

Characterization of the linear fractions by membrane

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Table 1 Sedimentation coefficients of linear fractions and molar masses from g.p.c. and ultracentrifugation (u.c.)

S_0	number-average molar mass kg/mol		mass-average molar mass kg/mol	
10^{-13}s	g.p.c.	u.c.	g.p.c.	u.c.
6.03	84.3	86.3	111	102
6.03	101	100	134	121
7.95	146	162	187	187
7.51	159	169	216	193
10.3	272	303	374	362
12.8	445	464	608	556
17.9	733	798	971	899
20.7	1075	1175	1360	1260

osmometry and light-scattering photometry has been described[15]. The analytical gel permeation chromatograph was a Waters Associates 200, with five columns (1.2 m x 1 cm) packed with Styragel (Waters Associates) of nominal exclusion limits: 35, 5 x 10^2, 5 x 10^3, 7 x 10^4 and 5 x 10^5 nm. The temperature was 35°C and the flow rate 0.5 cm^3/min. The injected solutions (2 cm^3) were of concentration 2.5 x 10^{-3} g/cm^3. Limiting viscosity numbers were derived by linear least-squares analysis of data gathered using a FICA viscometer at 35°C with tetrahydrofuran and at 29°C with heptan-3-one as solvent.

Sedimentation velocity data were collected from experiments in methanol at 6°C. A Beckman Model E ultracentrifuge was used at 5312 rad/s and with double-sector cells in a titanium rotor. Schlieren optics were used and concentration profiles within the cells were read from enlarged tracings of the photographic records. Sedimentation coefficients were measured at concentrations of *ca.* 3 x 10^{-3}, 2 x 10^{-3} and 1 x 10^{-3} g/cm^3.

RESULTS AND DISCUSSION

Measurements with linear fractions

The samples of linear molecular structure used were NPL Certified Reference Materials produced by preparative g.p.c. from whole polymers prepared at low temperature (−24°C) and to low conversion (<7%). There is agreement[16,17] that long-chain branching is negligible in material prepared in that way. Details of their characterization are given in an earlier publication[15], in which the product $[\eta]\tilde{M}_r$ was shown to correlate with the elution behaviour of the poly(vinylacetate) fractions and samples of anionic polystyrene. $\tilde{M}_r$ represents the relative molecular mass corresponding to the peak of the chromatograms, identified from a g.p.c. calibration based upon the classical molar mass measurements. The limiting viscosity numbers $[\eta]$ were measured in tetrahydrofuran at 35°C, the conditions used for g.p.c.

Ultracentrifugation was conducted in methanol at 6°C; phase-separation experiments have shown[18] those to be theta-conditions for poly(vinylacetate) prepared to moderate conversions and then saponified and reacetylated.

Sedimentation coefficients were found from the rate of movement of the maximum concentration gradient, neglecting the small error[19] introduced by the difference between the maximum and the root of the second moment. Allowance for the effect of hydrostatic pressure was made by an established method[19]. A concentration dependence was observed, consistent with observations[20,21] under theta-conditions with other polymers, for which the sedimentation coefficient S_c measured at concentration c was related to the value S_0 at infinite dilution by

$$S_0 = S_c(1 + kc) \tag{1}$$

Sedimentation coefficients at infinite dilution were found using equation (1) by extrapolation and by calculation from the value measured at *ca.* 3x 10^{-3} g/cm^3, assuming the Pyun–Fixman[22] relation between frictional coefficient and concentration in the form[21]

$$k = K_s S_0 \tag{2}$$

where K_s is a constant for a given polymer–solvent system. For two samples we found $K_s/10^{-13}$ sec g/cm^3 = 4.24 and 4.33; the mean value was used in the calculation of S_0 for the remainder. The standard errors of fit in determining S_c were about ±5% and the total uncertainty in the S_0 (*Table 1*) values is estimated not to exceed ±10%.

The relation between S_0 and the relative molecular mass was found by an iterative procedure. As a first approximation S_0 was related (linear least-squares on a logarithmic scale) to the relative molecular mass corresponding to the peak of the g.p.c. curve; with that relation the distribution of sedimentation coefficients of each linear fraction was transformed into a distribution of relative molecular mass, and the number-average and mass-average were found by summation. The sedimentation coefficients corresponding to those calculated average relative molecular masses were then related to the corresponding averages found by g.p.c. with a calibration based upon absolute measurements (*Table 1*). The cycle was repeated with this improved relation until no further significant change occurred. The final relation was

$$S_0(s) = (1.60 \pm 0.11) \times 10^{-13} M_r^{(0.509 \pm 0.012)} \tag{3}$$

where the ± terms are standard deviations of fit. Average molar masses calculated by means of equation (3) are compared with those found by g.p.c. in *Table 1*. Agreement is good throughout the range. Although within the likely experimental uncertainty, estimates of the number-average by g.p.c. are slightly smaller and of the mass-average slightly larger; this systematic error is consistent with residual contributions of dispersion in g.p.c. and of diffusion in ultracentrifugation, for which no correction was made.

Theory predicts an exponent in equation (3) of 0.5 for linear molecules at the theta-temperature, since at infinite dilution the relation between sedimentation coefficient, molar mass and hydrodynamic radius R is

$$S_0 = \frac{(1 - \bar{V}\rho)M}{6\pi\eta N_0 R} \tag{4}$$

where $\bar{V}$ is the partial specific volume of the solute and ρ and η are the density and viscosity of the solvent. In the random-flight statistics of linear molecules M is proportional to the mean-square radius of gyration, which is in turn proportional to R^2, so that at the theta-temperature

$$M = K_r R^2 \tag{5}$$

Table 2 Apparent molar masses calculated for branched fractions using calibrations established for linear samples in g.p.c. and ultracentrifugation (u.c.)

Sample descriptor	number-average molar mass kg/mol		mass-average molar mass kg/mol	
	g.p.c.	u.c.	g.p.c.	u.c.
1	171	282	214	337
2	255	420	336	502
3	282	656	410	766
4	398	676	530	779

and hence

$$S_0 = \frac{(1 - \bar{V}\rho)K_r^{1/2}M^{1/2}}{6\eta N_0} \tag{6}$$

Measurements with branched fractions

The branched samples were produced by fractionation by preparative g.p.c. of a commercial whole polymer. Branching was evident in the discrepancy between the number-average and mass-average molar masses of the whole polymer measured classically (47.7 and 435 kg/mol respectively) and those found by g.p.c. using the calibration established for linear polymer (57.1 and 201 kg/mol). Sedimentation velocity, viscosity and g.p.c. measurements with the branched fractions were made under the same conditions as those used for the linear fractions. Additionally, limiting viscosity numbers were measured in heptan-3-one at 29°C, a theta-temperature[23] for linear polymer. Distributions of sedimentation coefficient were corrected analytically[24] for concentration effects, using the parameter found empirically for the linear samples. Systematic error is introduced by this procedure, but since in one case the peak sedimentation coefficient of the distribution found [$(15.34 \pm 0.19) \times 10^{-13}$s] by direct extrapolation of the linear relation between the reciprocal of the sedimentation coefficient and concentration agreed with that found (15.16×10^{-13} s) by analytic correction of the distribution measured at 3×10^{-3} g/cm^3, the error was assumed small.

No correction was made for diffusion since the radial distribution in the ultracentrifuge cell was measured late in each experiment and sedimentation was rapid[25].

Table 2 shows the results of using equation (3) and the calibration established for linear polymer in deriving from ultracentrifugation and g.p.c. respectively average molar masses for the branched fractions. The discrepancy between the results is in the direction expected from the effects of branching in the two methods.

Characterization of branched fractions by g.p.c./viscometry

Relative molecular masses of the branched fractions were calculated from g.p.c. and viscometry by an iterative method[10]. The validity was assumed of universal calibration in terms of hydrodynamic volume, which was taken to be proportional to the product of $[\eta]$ and mass-average relative molecular mass. Support for the assumption comes from the work with linear fractions[15], and Benoit's demonstration[3] that the consequent predictions of mass-average relative molecular mass agreed with classical measurements for branched poly(vinylacetate). Successive approximations[10] were made to a calibration curve in g.p.c. that gave mass-average relative molecular masses for the branched fractions consistent with the measured limiting viscosity numbers in tetrahydrofuran and with the universal calibration curve established with the linear fractions. That derived calibration was then used to calculate the average molar masses collected in *Table 3*. To ensure that the calculated values were not artefacts of the average relative molecular mass chosen[26] for the product $[\eta]M_r$, the iteration was repeated using the number-average. The final relative molecular masses differed by less than 2% from those listed. The calculated mass-average relative molecular masses for the branched fraction were substituted into the Mark–Houwink relation established for linear fractions to find $[\eta]_l$, the limiting viscosity numbers of the respective linear isomers. The ratio

$$g' = ([\eta]_{br}/[\eta]_l)_{M_{br}} \tag{7}$$

of the limiting viscosity numbers of branched and linear isomers (*Table 4*) is the experimental quantity from which information concerning branching is derived.

The random uncertainty of the measured limiting viscosity numbers of the branched fractions is small (<1%); that of the ratio g' is dominated by the replication error of chromatograms (±3%), and the standard errors of prediction of the Mark–Houwink relation (±3% in the relevant region) and the calibration for branched molecules (±5%). The total uncertainty in g' is therefore at least ±6.5%, and hence there is no significant difference between the calculated values; the mean is 0.640.

Quantitative characterization of branching by the g.p.c./viscometry method depends upon inferring from g' an estimate of g_0, the ratio of the unperturbed radii of gyration of branched and linear isomers, which can be related theoretically to branching frequency and topography. Relations between g' and g_0 are semi-empirical and approximate[14]. It is assumed that g' is independent of solvent, and that branched molecules are unperturbed under theta-conditions for linear molecules. Neither assumption is well founded[14], and there is the further difficulty of relating statistical dimensions to effective hydrodynamic size. Consideration of the degree of branching in the fractions studied is deferred until results are compared below with those derived from g.p.c./ultracentrifugation.

Characterization of branched fractions by g.p.c./ultracentrifugation

There is no report of the application of Tung's suggested method[6] of supplementing g.p.c. with data from sedimentation velocity. Since the method is little known, and in order to make its assumptions clear, a résumé of its derivation is given.

Table 3 Molar masses of branched fractions by g.p.c./viscometry and g.p.c./ultracentrifugation

Sample descriptor	number-average molar mass kg/mol		mass-average molar mass kg/mol	
	g.p c./ $[\eta]$	g.p.c./ S_0	g.p.c./ $[\eta]$	g.p.c./ S_0
1	228	218	282	269
2	344	327	437	411
3	401	430	582	560
4	519	519	679	642

Table 4 Limiting viscosity numbers of branched and linear isomers in a good solvent and a poor solvent

	Tetrahydrofutan at 35° C			Heptan-3-one at 29° C		
Sample descriptor	$[\eta]_{br}$ / cm^3/g	$[\eta]_l$* / cm^3/g	g'	$[\eta]_{br}$ / cm^3/g	$[\eta]_l$* / cm^3/g	g'_θ
1	68.53 ± 0.34	112.7	0.608	30.74 ± 0.33	50.71	0.603
2	101.3 ± 0.7	153.7	0.659	40.10 ± 0.24	63.13	0.634
3	127.4 ± 0.3	188.2	0.677	44.98 ± 0.05	72.85	0.618
4	129.1 ± 0.3	209.9	0.615	48.11 ± 0.28	78.69	0.611

* From mass-average molar mass and relevant Mark—Houwink relation[15,23]

For linear molecules at a theta-temperature the sedimentation coefficient at infinite dilution is proportional to the square root of molar mass [equation (6)]. With a branched molecule that relation will yield an apparent molar mass M_s.

$$M_s = \frac{36\pi^2\eta^2N_0^2S_0^2}{(1-\bar{V}\rho)^2K_r} \tag{8}$$

In g.p.c. use of a calibration established for linear molecules in the analysis of a branched sample will yield a second apparent molar mass, namely that of the linear molecule isodiametric in the g.p.c. solvent, provided that universal calibration is valid. Tung[6] assumed that branched and linear molecules isodiametric in the g.p.c. solvent were also isodiametric in a theta-solvent for linear molecules, so that the apparent molar mass found in that way is

$$M_t = K_rR_{br}^2 \tag{9}$$

where R_{br} is the hydrodynamic radius of the branched molecule in a theta-solvent for linear molecules.

From equations (4), (8) and (9) it follows that the true molar mass of a branched sample is given by

$$M = (M_sM_t)^{1/2} \tag{10}$$

and from equations (5), (9) and (10) it follows that

$$h = (M_t/M_s)^{1/4} \tag{11}$$

where h is the ratio of the hydrodynamic radii of branched and linear isomers.

$$h = (R_{br}/R_l)_{M_{br}} \tag{12}$$

For a polydispersed sample the Tung method yields two distributions of apparent molar mass, one based upon hydrodynamic radius and one based upon sedimentation coefficient. The mass-fraction scales of the distribution will be equivalent, on condition that there are no components 1 and 2 present for which $R_1 > R_2$ when $S_1 < S_2$. We assume here that the branching/molar mass relation is such that there are no such components present in the branched fractions studied; the force of the condition and its implications for the general application of the method are discussed below. If the mass-fraction scales are equivalent then the true number- and mass-average molar masses follow from equation (10). Results are compared in *Table 3* with those from g.p.c./viscometry; the agreement is remarkably good.

In contrast to branching analysis by g.p.c./viscometry, the Tung method yields estimates of the parameter h throughout the distribution of molar mass. In practice the experimental uncertainties at the extremes of the distributions preclude a complete determination. For the branched poly(vinylacetate) fractions the parameter h was calculated [equation (11)] from the apparent number-average and mass-average molar masses (*Table 2*). Significant differences were evident neither between the fractions nor within each fraction. The values ranged between 0.83 and 0.91, with a mean of 0.88 and an estimated uncertainty of ±8%.

The methods compared

In view of the approximations of the two methods, the agreement between the estimates of molar mass is surprising. The molar mass estimation by g.p.c./viscometry appeals only to universal calibration; that by g.p.c./ultracentrifugation depends additionally upon assumptions concerning the effect of solvent type upon molecular size. Such assumptions enter the g.p.c./viscometry method in the form used here only in the estimation of branching, and are recognised[14] as a source of disagreement between analyses by that method. The respective assumptions can be related theoretically. Tung's method requires that a branched and a linear molecule isodiametric in a good (g.p.c.) solvent are also isodiametric in a theta-solvent for linear molecules. If $[\eta]M$ is accepted as a measure of hydrodynamic volume, then equal size in a good solvent implies.

$$[\eta]_{br}M_{br} = [\eta]_lM_l \tag{13}$$

where $M_{or} > M_l$, or using equation (7) and the Mark—Houwink relation

$$[\eta]_l = KM^\alpha \tag{14}$$

where $\alpha > 0.5$, it follows that

$$g' = (M_l/M_{br})^{1+\alpha} \tag{15}$$

Similarly, equal size in a theta-solvent for linear molecules implies

$$g'_\theta = (M_l/M_{br})^{1.5} \tag{16}$$

since in a theta-solvent $\alpha = 0.5$, and hence

$$g'/g'_\theta = (M_l/M_{br})^{\alpha-0.5} \tag{17}$$

The g.p.c./viscometry method requires that $g' = g'_\theta$ which is not a consequence of equation (17) unless α is exactly 0.5. Substitution of typical values of M_l/M_{br} and α shows that the discrepancy is unlikely to exceed 10% for moderate branching, however.

Published accounts of the dependence of g' upon solvent for poly(vinylacetate) are contradictory. Graessley and Mittelhauser[27] found that g' was insensitive to solvent type for randomly branched whole polymers. Berry, Hobbs and Long[28] showed that g' was greater in a good solvent for fractions with normal (comb) and random branching; the demonstration was less convincing for the randomly branched fractions, however, since there were acknowledged[28] inadequacies of characterization.

Limiting viscosity numbers of the branched fractions used here were measured (*Table 4*) in tetrahydrofuran at 35°C and in heptan-3-one, reportedly[23] a theta-solvent for linear poly(vinylacetate) at 29°C. The respective Mark–Houwink relations[15,23] and the mass-average molar masses found by universal calibration yielded the limiting viscosity numbers of the linear isomers (*Table 4*). For these randomly branched fractions g' varied little with solvent (*Table 4*), as was found by Graessley and Mittelhauser[27]. No serious error is introduced by assuming g' to be independent of solvent type.

The branching estimates by the two methods can be compared if the ratio of hydrodynamic radii derived from the Stokes equation holds also for viscosity. In that case

$$g' = h^3 \qquad (18)$$

and the mean value of g' found by the g.p.c./ultracentrifugation method (0.681) is within experimental error of that (0.640) found by g.p.c./ viscometry. Further characterization of long-chain branching depends upon relating the experimental ratio g' to the ratio g_0 of the radii of gyration of branched and linear isomers calculated by random flight statistics. Relations of the type

$$g' \sim g_0^{\gamma} \qquad (19)$$

are used commonly[14,29], where theoretical estimates of the exponent γ range from 0.5 to 1.5; empirically[30] $\gamma \sim 0.8$ for randomly branched polymers in a good solvent. With that value, theory[31] for monodispersed samples in a solvent in which branched and linear molecules are unperturbed yields estimates of 7–9 branch points per molecule of the fractions studied here. Long chain branches are formed[32] in the polymerization of vinyl acetate principally by chain transfer to polymer, so that branching was assumed trifunctional and random. Since the quantitative estimation of branching in this way involves approximations of doubtful validity[14], and since the polymerization process was unknown, no attempt was made to relate the results to the mechanism of polymerization and to other empirical determinations of branching frequency in poly(vinylacetate).

The molar mass and branching estimates by g.p.c./ ultracentrifugation depend not only upon universal calibration and the assumptions concerning molecular size, but also upon the equivalence of the mass fraction scales of the two distributions of apparent molar mass M_s and M_t. The assumption concerning hydrodynamic volume has been shown to introduce little error. Since the molar mass estimates by the two methods agree well, the mass fraction scales of the distributions of M_s and M_t must be equivalent. That equivalence implies that there are negligible quantities of components 1 and 2 present for which $R_1 > R_2$ when $S_1 < S_2$. The presence of branched and linear isomers, for which $R_l > R_{br}$ when $S_l < S_{br}$, and a polymerization mechanism that led to branching decreasing with increasing molar mass would invalidate the method. Its success with the poly(vinylacetate) fractions is consistent with the accepted[17,32] mechanism for vinyl acetate polymerization, in which branching increases with molar mass.

The agreement between the two methods of analysis is encouraging and lends confidence to their application to fractions of randomly branched polymer when branching frequency increases with molar mass.

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