Calibration Procedures for Branched Poly (Vinyl Acetate) in Size Exclusion Chromatography

T. A. Coleman[a]; J. V. Dawkins[a]

[a] Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, England

PLEASE SCROLL DOWN FOR ARTICLE

CALIBRATION PROCEDURES FOR BRANCHED POLY(VINYL ACETATE)˙IN SIZE EXCLUSION CHROMATOGRAPHY

T. A. Coleman and J. V. Dawkins

Department of Chemistry
Loughborough University of Technology
Loughborough, Leicestershire LE11 3TU, England

ABSTRACT

Bulk monomer polymerisations have been performed at low
and high temperatures in order to produce samples of poly(vinyl
acetate) having linear and branched structures. Long-chain
branching attached through the acetate group in poly(vinyl
acetate) was removed by a process of hydrolysis and reacetyla-
tion. Fractions were isolated by fractional precipitation from
linear polymers and from reacetylated whole polymers. A
calibration procedure in size exclusion chromatography (SEC)
involving the off-line experimental measurement of the intrinsic
viscosity of polymers and fractions was examined, from which it
was concluded that long-chain branching in samples of poly(vinyl
acetate) obtained by the high conversion polymerisations at 353 K
is of the hydrolysable type. The SEC calibration method
proposed by Ram and Miltz for branched polymers was investigated
and found to provide acceptable molecular weight data for
branched samples of poly(vinyl acetate).

INTRODUCTION

Polymerisation of vinyl acetate is commonly performed to
high monomer conversion at an elevated temperature. Such conditions

for the radical polymerisation of this monomer inevitably lead to
poly(vinyl acetate) (PVA) having branched structures (1). Branching
arises through chain transfer reactions involving propagating
radicals, and the branching structures which result may be
classified as hydrolysable (i.e. detachable from the main chain
by hydrolysis) and permanent or non-hydrolysable (i.e. not
removed by hydrolysis). The characterisation of these two types
of branching is important not only for PVA but also for poly
(vinyl alcohol) which is generally produced by the hydrolysis
of PVA (2,3). Consequently, characterisation of the structural
changes that may occur in PVA on hydrolysis and subsequent
reacetylation can provide information on the types of branching
in PVA and on the existence of branching in poly(vinyl alcohol).

In the past two decades methods involving size exclusion
chromatography (SEC) have been studied for the characterisa-
tion of molecular weight distribution (MWD) and degree of long-
chain branching (LCB) in branched polymers (4,5). Because SEC
provides a molecular size distribution, these methods character-
ising MWD and LCB require an independent measurement of polymer
size, either on-line or off-line to the chromatograph with a
technique such as viscometry or light scattering. The principles
of methods involving analytical SEC with a concentration detector
and the off-line determination of solution viscosity for the
whole polymer were established by the work of Drott and
Mendelson (6) who showed that determinations of both MWD and
LCB required the application of universal calibration based on
hydrodynamic volume and relations for the dependence of molecular
dimensions on LCB for various branching models. Variants of the
Drott and Mendelson procedure have been used to deduce values of
the branching index λ (defined as the number of branches per
unit molecular weight) for PVA (7,8).

A major aim in our characterisation programme on PVA has
been the determination of accurate molecular weight data. We
have therefore considered the SEC calibration method proposed

by Ram and Miltz (9) for branched polymers (RM method) which
also involves analytical SEC and the off-line measurement of
solution viscosity, since this calibration method requires no
assumptions on branching model and branching index λ. The RM
method does not appear to have been applied widely to PVA,
although it has been reported that this method provides excellent
molecular weight results for polyethylene having long-chain
branching (10). The RM method does require the universal
calibration plot of log hydrodynamic volume against retention
volume V_R to be valid. Hydrodynamic volume, as proposed by
Grubisic and co-workers (11), is defined by [n]M, where [n] is
the intrinsic viscosity (dl g^{-1}) of the polymer in the SEC
eluent and M is the molecular weight of the polymer. At a
given value of V_R, we may write

$$\log [n]_{ps}M_{ps} = \log [n]_e M_e = \log [n]_b M_b \qquad (1)$$

where subscript ps represents polystyrene, subscript e represents
linear PVA, and subscript b represents branched PVA. This
universal calibration procedure assumes that separation in SEC
is by a steric exclusion mechanism and that non-exclusion
secondary mechanisms are not involved (12).

A further aim of our work has been a comparison of as-
polymerised PVA with PVA produced by reacetylation of hydrolysed
PVA. In view of the possible difficulties which may arise in
the chemical modification of polymers (13), it is important to
demonstrate that the PVA resulting from the hydrolysis/re-
acetylation reactions is separating in SEC by a steric exclusion
mechanism. The presence of residual hydroxyl groups or other
groups introduced by side reactions during chemical modification
might result in secondary separation mechanisms in SEC
involving polymer-substrate interactions. The occurrence of
secondary adsorption mechanisms, for example, can lead to the
displacement of the log hydrodynamic volume plot to high V_R (12).

RAM AND MILTZ CALIBRATION METHOD

SEC characterisation of branched polymers requires a
relation between $[\eta]$ and M. For linear polymers, the Mark-
Houwink equation may be used

$$[\eta] = K M^{\alpha} \tag{2}$$

where K and α are assumed to be constants. For branched polymers,
Ram and Miltz (9) extended equation (2) into the polynomial
form

$$\ln [\eta] = \ln K + a \ln M + b \ln^2 M + c \ln^3 M \tag{3}$$

The third and fourth terms on the right hand side in equation (3)
are only considered to be significant when long-chain branching
is present above a minimum molecular weight M_0. For polymers
having $M \leqslant M_0$, equation (2) will then be valid; it follows from
equation (3) that when $M = M_0$

$$b \ln^2 M_0 + c \ln^3 M_0 = 0 \tag{4}$$

and therefore that b and c are related by

$$c = -b/\ln M_0 \tag{5}$$

A value of $[\eta]_{calc}$ of a whole polymer may be calculated from the
summation of the viscosity $[\eta]_i$ of each species i according to
the relation

$$[\eta]_{calc} = \Sigma [\eta]_i \, w_i \tag{6}$$

where w_i is the weight fraction of each species i which is
obtained from the SEC chromatogram. Therefore, combination of
equations (3) and (6) yields

$$[\eta]_{calc} = \Sigma[\eta]_i w_i = \Sigma w_i \ K \ M_i^{(a + b \ \ln M_i + c \ \ln^2 M_i)} \qquad (7)$$

With the independent experimental measurement of $[\eta]$ for the whole polymer, a cyclic iteration procedure involving equation (7) to find the dependence of molecular weight M_i on V_R is then employed on a computer as follows. As a first approximation, the universal calibration relation

$$[\eta]_i \ M_i = K_e \ M_i^{(1 + a_e)} \qquad (8)$$

which follows from combining equations (1) and (2) is used to convert the axis of V_R on a chromatogram to molecular weight. Equation (7) is then iterated to calculate b for a given M_0 by matching $[\eta]_{calc}$ with the experimental $[\eta]$, when the value of c is also known from equation (5). These values of b and c are then used with the universal calibration which is represented by equation (8) for $M_i < M_0$ and by

$$[\eta]_i \ M_i = K_e \ M_i^{(1 + a_e + b \ \ln M_i + c \ \ln^2 M_i)} \qquad (9)$$

for $M_i > M_0$. A second value of b is then calculated by repeating the iteration of equation (7) to match $[\eta]_{calc}$ with the experimental $[\eta]$, and the whole process continued until the M_i calibration curves differ by less than 1%.

EXPERIMENTAL

Polymer Samples

Vinyl acetate monomer (B.D.H.) was purified by distillation through a Vigreux column at 323 K under a reduced pressure of nitrogen. A single distillation collecting the middle fraction was sufficient to remove the quinol stabiliser from the as-received monomer. The purified monomer was polymerised immediately with azobisisobutyronitrile as initiator which had been recrystallised twice from absolute ethanol by cooling a saturated solution, obtained at 273 K, to 253 K.

Low temperature polymerisation of bulk monomer was initiat-
ed by the photolytic decomposition of azobisisobutyronitrile by
ultraviolet irradiation. The photochemical reactor was purged
with nitrogen. Polymerisation temperatures were between 233 and
268 K. Polymerisation was allowed to proceed to about 5%
conversion. Isolation of the polymer first involved removing a
large fraction of the unreacted monomer by distillation at
reduced pressure, followed by adding acetone to the remaining
monomer-polymer solution, and then adding this mixture with
stirring to the precipitant consisting of a large excess of
isopropanol/hexane (1:5). Further purification was effected
by reprecipitation twice from methanol solution into distilled
water, and the polymer was finally dried under vacuum.

High temperature polymerisation of bulk monomer was
initiated by the thermal decomposition of azobisisobutyro-
nitrile at 353 K. Polymerisations were performed in sealed
tubes which were filled and sealed by standard vacuum line
procedures. Polymerisations were performed for about 100 min
in order to achieve at least 80% conversion of monomer.
Isolation of the polymer involved opening the tube and adding
acetone followed by precipitation into isopropanol/hexane (1:5)
as before. Further purification was performed as described for
polymers produced by low temperature polymerisation.

Two commercial PVA products which we designate B160T and
B500T were obtained from B.D.H. Chemicals Ltd. for comparison
with laboratory-prepared samples. The nominal molecular weights
quoted by the supplier of these products were 160,000 and
500,000.

Hydrolysis and Reacetylation

Complete hydrolysis of PVA to poly(vinyl alcohol) was
performed in methanol solution with sodium hydroxide (0.2 molar)
at 313 K. The precipitated product was recovered by filtration,
washed extensively with methanol in a Soxhlet extractor and
dried under vacuum. Acetylation of poly(vinyl alcohol) to PVA
was performed according to the method described by Braun and

co-workers (14). The determination of the degree of reacetyla-
tion required titrimetric analysis of the remaining acetylating
agent.

Fractionation

Fractions of PVA were obtained by fractional precipitation
at 298 K with methanol as solvent and water as non-solvent.
Non-solvent addition was made carefully until a slightly turbid
solution was obtained. Each fraction was then redissolved by
heating the mixture to 303 K. The mixture was then allowed to
cool with stirring to 298 K. Stirring was then stopped and the
fraction allowed to settle out overnight. After isolation from
the supernatant solution, a fraction was redissolved in methanol,
reprecipitated with a large excess of water, and dried under
vacuum. Further fractions were collected by repeating the
procedure.

Solution Viscometry

The solution viscosity of PVA whole polymers and fractions
in tetrahydrofuran (BDH AR, stabilised with 0.1% quinol) was
measured with an Ubbelohde suspended level dilution viscometer
at 298 K. The flow time for tetrahydrofuran (THF) was 157 s,
and kinetic energy corrections were therefore not significant.
The viscometer allowed up to 5 successive dilutions, and the
initial concentration of PVA in the viscometer was adjusted so
that the relative viscosity was below 2 and so that the most
dilute solution had a relative viscosity above 1.2. Solution
viscosity data were extrapolated linearly according to the
Huggins plot to infinite dilution in order to find $[\eta]$ (dl g^{-1}).

Size Exclusion Chromatography

SEC of PVA whole polymers and fractions was performed with
a modified Waters 502 ALC/GPC instrument having refractive
index detection. The solvent was THF at a constant flow rate
of 1 cm^3 min^{-1}. The column (Polymer Laboratories) was a mixed
bed PL gel column (60 cm) containing crosslinked polystyrene
gels and was calibrated with polystyrene standards (Polymer
Laboratories) having molecular weights from 200 to 2 x 10^6.

Solution injection volumes were 200 µL with sample concentra-
tions in the range 0.02-0.05% (w/v). Data analysis was
performed with a "Trivector Systems" microprocessor, and
because the computer output was in terms of retention time,
results for V_R in Tables and Figures are in s units (which
are directly related to volume units by the eluent flow rate).
Calculations of the number average and weight average molecular
weights, $\overline{M}_n$ and $\overline{M}_w$ respectively, and the polydispersity $\overline{M}_w/\overline{M}_n$,
were obtained from a chromatogram with a computer program
employing the molecular weight calibration M_{ps} established with
polystyrene standards.

RESULTS AND DISCUSSION

Hydrolysis and Reacetylation

Polymerisation of vinyl acetate to low conversion at
temperatures below 273 K is assumed to produce linear PVA (1).
Chromatograms for three polymers obtained by low temperature
polymerisation are shown in Figure 1. These samples were then
hydrolysed and reacetylated, and the chromatograms for the re-
acetylated polymers in Figure 1 clearly indicate no significant
change in the shape of the chromatograms before and after
hydrolysis and reacetylation. The difference between $\overline{M}_w$ for the
as-polymerised and reacetylated samples in Figure 1 was
calculated to be <2% and the degree of reacetylation was
estimated to be ≥99.9%. These results suggest therefore that
samples produced in our low temperature polymerisations do not
contain hydrolysable branches and that the reacetylation method
was capable of fully reacetylating the polymers.

PVA whole polymers (B3M and B4M) obtained by high tempera-
ture polymerisation to high monomer conversion were hydrolysed
and reacetylated to remove hydrolysable branches (samples
designated B3R and B4R). Molecular weight distributions in
Figure 2 for as-polymerised PVA from high conversion poly-
merisation at high temperature are much broader than the
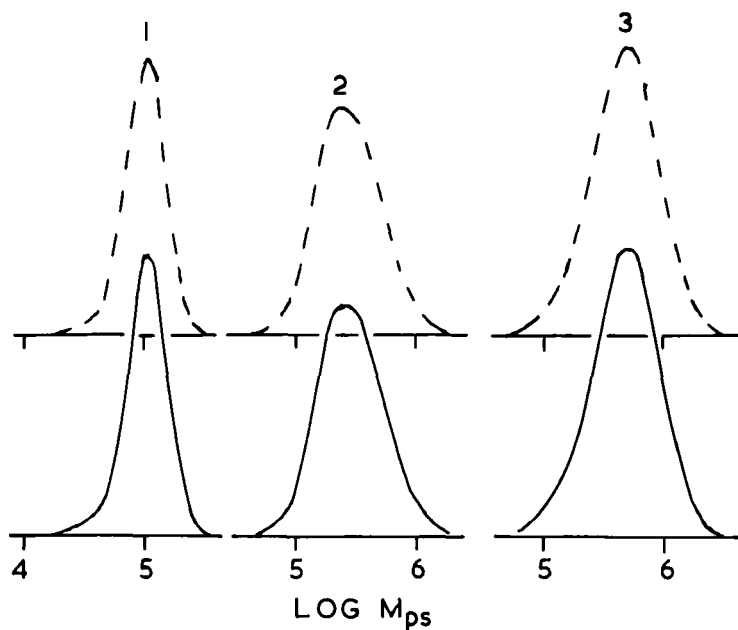distributions given in Figure 1. The wide distributions arise

FIGURE 1

Size exclusion chromatograms of linear PVA samples 1, 2 and 3.
————, as-polymerised; -----, after hydrolysis and reacetylation.

from long-chain branching in large macromolecules. This high
molecular weight tail seen in the chromatograms for the as-poly-
merised samples in Figure 2 is decreased considerably after
the hydrolysis and reacetylation of the samples, so that these
reacetylated samples have narrower distributions and lower
molecular weights than the as-polymerised branched samples.

SEC Calibration with Intrinsic Viscosity

Characterisation data for the fractions are summarised in
Tables 1 and 2. Samples from high temperature polymerisations
were hydrolysed and reacetylated before fractionation.
Consequently, the fractions in Table 2 will not contain
hydrolysable branches but could have non-hydrolysable branching.
In order to compare the fractions in Tables 1 and 2, SEC calibra-

B3R⊣   ⊢B3M

3   4   5   6   7

LOG M$_{ps}$

B4R⊣   ⊢B4M
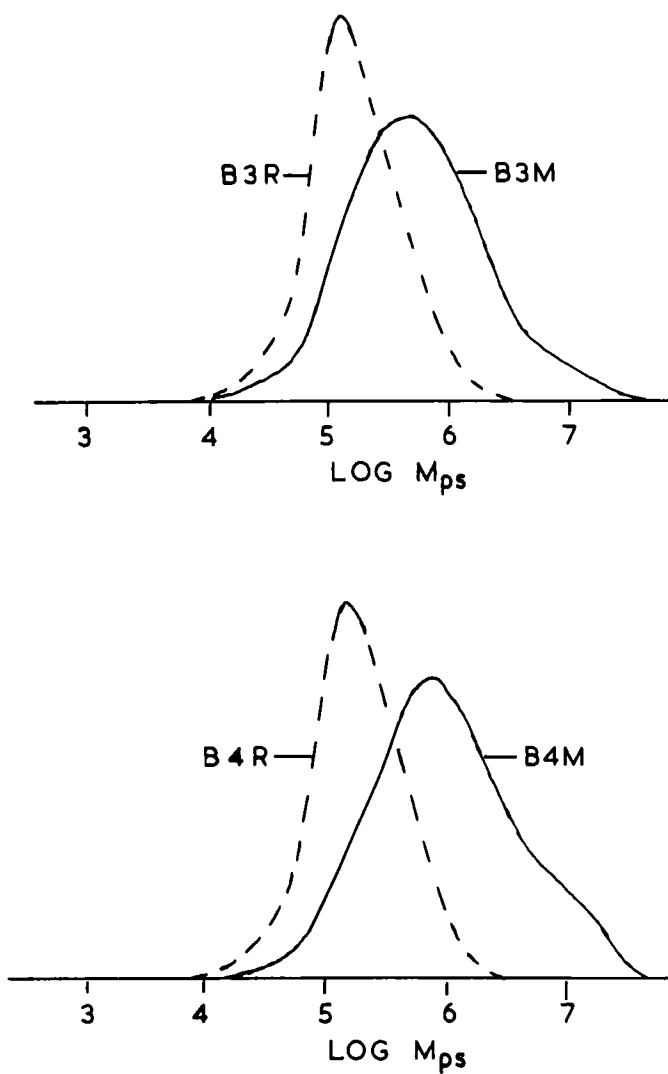
3   4   5   6   7

LOG M$_{ps}$

FIGURE 2

Size exclusion chromatograms of PVA samples B3 and B4 obtained
by high conversion polymerisation at high temperature. ———,
as-polymerised; -----, after hydrolysis and reacetylation.

TABLE 1

Intrinsic Viscosity and Retention Results, and Molecular Weight
Data (Based on Polystyrene Calibration) for Fractions of Linear
PVA (Polymerised at Low Temperature).

Fraction	[η]	$\bar{V}_w$	$\bar{M}_n$(ps)	$\bar{M}_w$(ps)	$\bar{M}_w/\bar{M}_n$
LF6	1.241	667	247400	395000	1.60
LF7	1.220	670	248700	374800	1.51
LF8	1.185	674	251800	337300	1.34
LF9	0.640	712	117100	148600	1.27
LF14	0.408	742	68930	83510	1.21
LF15	0.378	748	63090	75630	1.20

TABLE 2

Intrinsic Viscosity and Retention Results, and Molecular Weight
Data (Based on Polystyrene Calibration) for Fractions of PVA
Sample B4R (Polymerised at High Temperature to High Conversion,
Hydrolysed and Reacetylated).

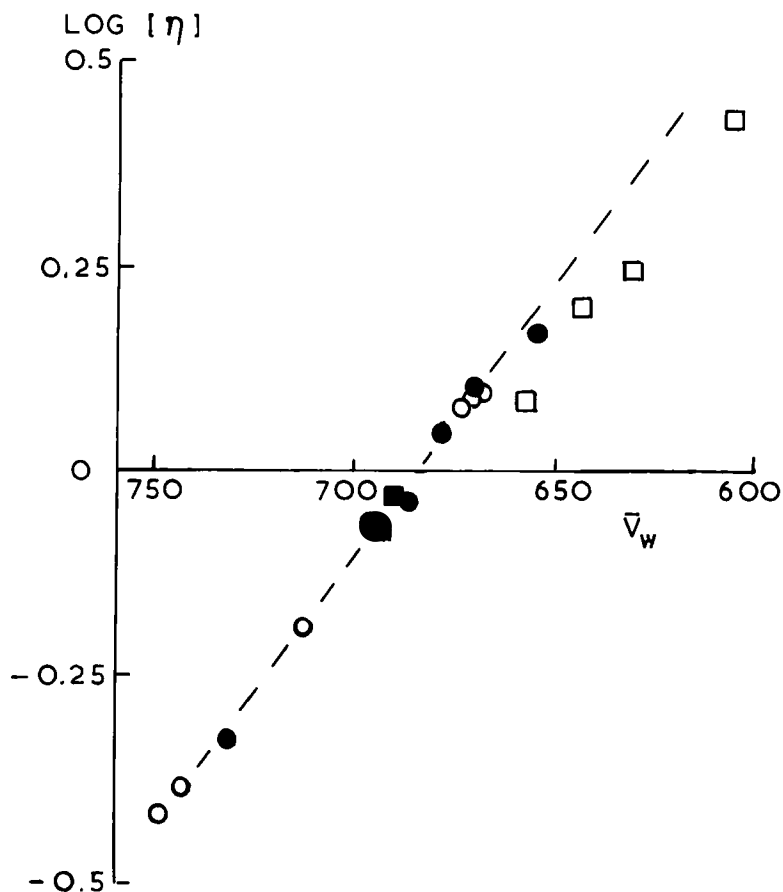| Fraction	[η]	$\bar{V}_w$	$\bar{M}_n$(ps)	$\bar{M}_w$(ps)	$\bar{M}_w/\bar{M}_n$
RF3	1.460	655	340400	536900	1.58
RF5	1.256	670	258800	369700	1.43
RF4	1.105	678	207400	309000	1.49
RF2	0.913	687	192000	251900	1.31
RF7	0.862	696	165000	206900	1.25
RF9	0.468	730	86580	104400	1.21

FIGURE 3

SEC calibration of intrinsic viscosity of PVA against weight
average retention volume (determined with ps calibration). o, PVA
fractions from linear polymers; ●, PVA fractions from whole
polymer B4R (hydrolysed and reacetylated before fractionation);
□, as-polymerised whole polymers B3M, B4M, B160T and B500T; ■,
whole polymers B3R and B4R after hydrolysis and reacetylation.

tion data are presented in Figure 3, where it is evident that
there is little difference between the two types of fractions.
Therefore, the fractions obtained by reacetylation of hydrolysed
PVA and the fractions of linear PVA appear to separate by the
same SEC mechanism. In view of the establishment of the validity
of universal calibration for linear PVA and ps in tetrahydro-
furan (15), it is concluded that SEC separations of the re-
acetylated samples of PVA produced here do not involve non-
exclusion secondary mechanisms. The results for the fractions
in Figure 3 also indicate that in the molecular weight range
examined long-chain branching of the non-hydrolysable type (if
present) is not significant enough to influence intrinsic
viscosity behaviour.

When plotting SEC calibration data, the polydispersity of
the fractions must be considered. Calibration methods for
broad distribution samples have been reviewed elsewhere (16).
The retention volume parameter $\overline{V}_w$ in Figure 3 was assigned as
follows. Values of $\overline{M}_n(ps)$ and $\overline{M}_w(ps)$ for each sample in
Tables 1, 2 and 3 were computed from a chromatogram using a
polystyrene calibration. From this calibration curve a value of
the weight average retention volume $\overline{V}_w$ corresponding to $\overline{M}_w(ps)$ was
identified. One reason for choosing this procedure was that
fractions obtained by fractional precipitation appear to have
chromatograms which are closely represented by an exponential
distribution function (17), when the molecular weight correspond-
ing to the retention volume at the peak position of the
chromatogram is $\overline{M}_w$. The values of $\overline{V}_w$ in Tables 1 and 2 were equal
to or close to peak retention volumes. A second reason for
choosing the $\overline{V}_w$ parameter was to facilitate a comparison with the
whole polymers having broader distributions, because methods
based on peak retention volume must be arbitrary for samples
having a range of polydispersities. Characterisation data for
the whole polymers are summarised in Table 3. The SEC calibra-
tion data in Figure 3 clearly show that the as-polymerised whole

TABLE 3

Intrinsic Viscosity and Retention Results, and Molecular Weight
Data (Based on Polystyrene Calibration) for Whole Polymers of PVA
(B3M and B4M from High Conversion Polymerisation at High Tempera-
ture, B3R and B4R after Hydrolysis and Reacetylation, B160T and
B500T Commercial Samples).

Polymer	$[\eta]$	$\bar{V}_w$	$\bar{M}_n(ps)$	$\bar{M}_w(ps)$	$\bar{M}_w/\bar{M}_n$
B3M	1.744	630	186700	1014100	5.43
B3R	0.852	693	97000	219200	2.26
B4M	2.722	606	304800	2016600	6.62
B4R	0.927	690	103700	238100	2.30
B160T	1.204	657	143200	511300	3.57
B500T	1.403	643	164500	713100	4.34

polymers deviate from the calibration curve, whereas the whole
polymers after hydrolysis and reacetylation correspond to the
calibration curve for the fractions. The observation for as-
polymerised whole polymers is consistent with these samples having
hydrolysable long-chain branching. This follows because the curve
in Figure 3 may be regarded as a double logarithmic plot of $[\eta]$
against M, since the SEC calibration relates log M to $\bar{V}_w$, and so
the deviation at high $\bar{V}_w$ arises from branched molecules at a given
M having a smaller molecular size and therefore lower $[\eta]$ than
linear chains. Consequently, our results indicate that for PVA
prepared here at 353 K branching through the acetate group
resulting in hydrolysable branching is far more important than
branching at the main chain. This conclusion is in agreement
with other observations (1, 18-20).

Ram and Miltz Method for SEC Calibration

        In order to perform the calculations in the RM method, values
of the Mark-Houwink constants K_e and a_e for linear PVA in tetra-

hydrofuran are required in equations (8) and (9). Agreement
between the most recent determinations of these constants (8, 15)
is not good. Values of K_e and a_e consistent with our universal
calibration data were estimated as follows. From equations (1)
and (2), the molecular weight M_e of linear PVA at a given $\overline{V}_w$ is
related to a calibration established with polystyrene standards by

$$\log M_e = \log K_{ps}M_{ps}^{1 + a_{ps}} / [\eta]_e \qquad (10)$$

From the careful studies of solution viscosity of polystyrene in
tetrahydrofuran (15, 21), we employed the constants for ps in the
following Mark-Houwink equation

$$[\eta] = 1.16 \times 10^{-4} M^{0.724} \qquad (11)$$

Since $[\eta]_e$ has been measured for the linear PVA fractions (see
Table 1), values of M_e may be determined with equation (10). A
double logarithmic plot of the values of $[\eta]_e$ in Table 1 against
the derived values of M_e was then made, from which the following
values of K_e and a_e were obtained

$$[\eta] = 0.942 \times 10^{-4} M^{0.737} \qquad (12)$$

It is evident in Table 4 that these constants lie between values
reported by other workers. Clearly, equations (10), (11) and (12)
show that the SEC molecular weight calibrations for linear samples
of ps and PVA will be close together. It should be noted that
since we have SEC chromatograms and the data for $[\eta]_e$ for the
linear PVA fractions, it is possible to determine K_e and a_e by the
procedure first proposed by Weiss and Cohn-Ginsberg (22). Our
results indicated that whilst values of K_e and a_e determined by
the Weiss/Cohn-Ginsberg procedure for fractions were in fair
agreement with equation (12) estimates of the constants when
whole polymers were used in this procedure were much less
satisfactory. It is possible that the breadth of the molecular

TABLE 4

Mark-Houwink Constants for Poly(vinyl acetate) in Tetrahydrofuran.

$K/10^{-4}$	a	Reference
0.51	0.791	8
1.56	0.708	15
0.942	0.737	Equation (12)

weight distribution of the whole polymers may contribute to errors in the procedure.   Several other workers have observed difficulties in obtaining reasonable values for K and a by the Weiss and Cohn-Ginsberg procedure, as reviewed elsewhere (16).

The RM method was applied to all fractions and whole polymers. Calibration curves were obtained for a series of M_0 values. From these M_b calibrations for the branched whole polymers, average molecular weights were computed, as shown in Table 5. Comparison with average molecular weight data based on an M_e calibration clearly shows that $\overline{M}_w$ is much more sensitive to the larger (and hence more highly branched) macromolecules than $\overline{M}_n$. As expected, $\overline{M}_w$ increases in Table 5 when branching is allowed for in the calibration method, i.e. at a given V_R a branched macromolecule has a higher value of M than a linear macromolecule having the same hydrodynamic volume. Consequently, the molecular weight distribution in Table 5 is broader for the branched whole polymers than samples of linear PVA (see for comparison the chromatograms in Figure 2). The bracketed values of average molecular weight in Table 5 are obtained from itera- tions in which although the molecular weights are no longer changing, $[\eta]_{calc}$ from equation (7) does not match the experimental value. The possible cause of this problem is that the selected value of M_0 is too high. As M_0 is increased, the fraction of

TABLE 5

Average Molecular Weights for Whole Polymers of PVA Obtained by
SEC with the Ram and Miltz Calibration Method.

M_o	B160T		B500T	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
linear	149,300	520,250	171,200	727,250
20,000	155,550	600,250	178,400	845,600
50,000	153,700	601,500	176,300	847,500
100,000	152,300	602,900	175,000	848,700
200,000	(151,100)	(605,700)	(173,200)	(850,300)

M_o	B3M		B4M	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
linear	192,700	1,026,900	313,600	2,026,900
20,000	200,740	1,217,600	330,470	2,436,300
50,000	198,300	1,219,800	326,100	2,438,000
100,000	(196,200)	(1,210,100)	322,450	2,439,050
200,000	194,700	1,149,200	(319,100)	(2,439,300)

polymer of a given sample above this value decreases. The values
of $M_i > M_o$ have to be increasingly modified in order to fit $[\eta]_{calc}$
to the experimental value of $[\eta]$. If M_o is too high, no amount of
modification suffices and the iteration routine fails. Therefore,
the behaviour of the computer program provides a possible check
on the choice of value for M_o.

The selection of the correct value for M_o is an important
consideration not only for the RM method but also for the general
problem of the properties of branched PVA in solution. The
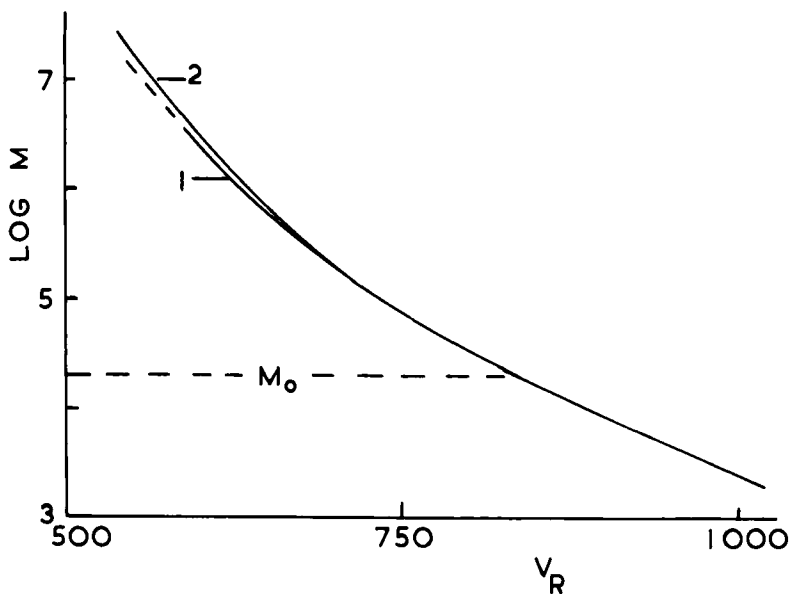calibration curves generated for the fractions and whole polymers

FIGURE 4

SEC calibration curves for PVA computed by the Ram and Miltz method with M_0 = 20,000. Curve 1, fractions and reacetylated whole polymers B3R and B4R; Curve 2, as-polymerised whole polymers B3M and B4M; -----, curve for linear PVA.

are displayed in Figures 4, 5, 6 and 7, and it can be seen that the calibrations for the branched species do not deviate from the linear calibration until a molecular weight of about 100,000, almost irrespective of the choice of value for M_0. The higher molecular weight end of the calibration curves for M_0 = 100,000 are displayed enlarged in Figure 8 to show how differing degrees of branching influence the M_b calibration. The identification of M_0 is not straightforward because the onset of branching will depend on polymerisation conversion (1). Park and Graessley (8) estimated M_0 to be about 300,000 for conversions of 41 and 71%; other workers have proposed values of at least 70,000 (23) and about 200,000 (24). In Figure 8 it is evident from the calibration curves that samples B160T and B500T contain the highest LCB which is presumed to arise
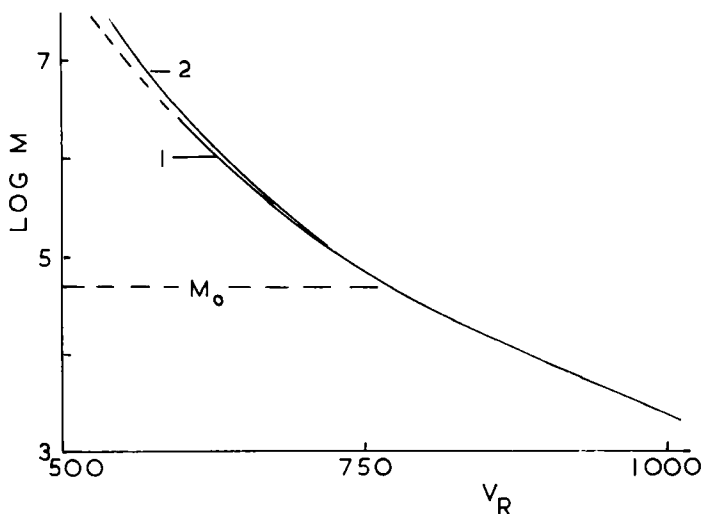
FIGURE 5

SEC calibration curves for PVA computed by the Ram and Miltz method with M_0 = 50,000. Curve 1, fractions and reacetylated whole polymers B3R and B4R; Curve 2, as-polymerised whole polymers B3M and B4M; -----, curve for linear PVA.
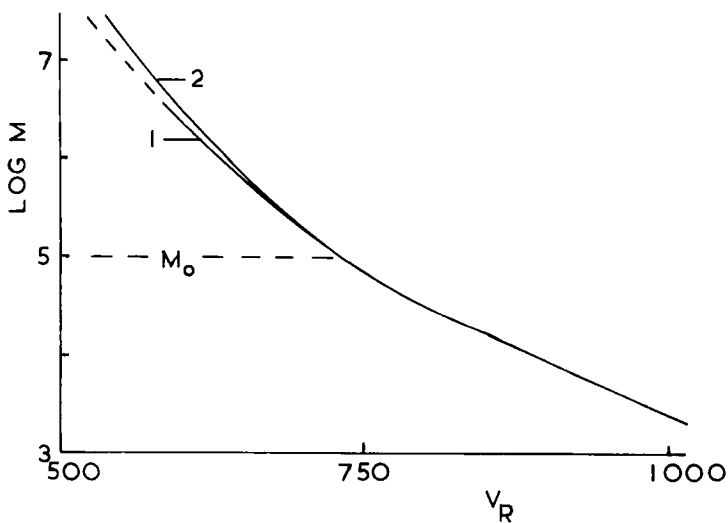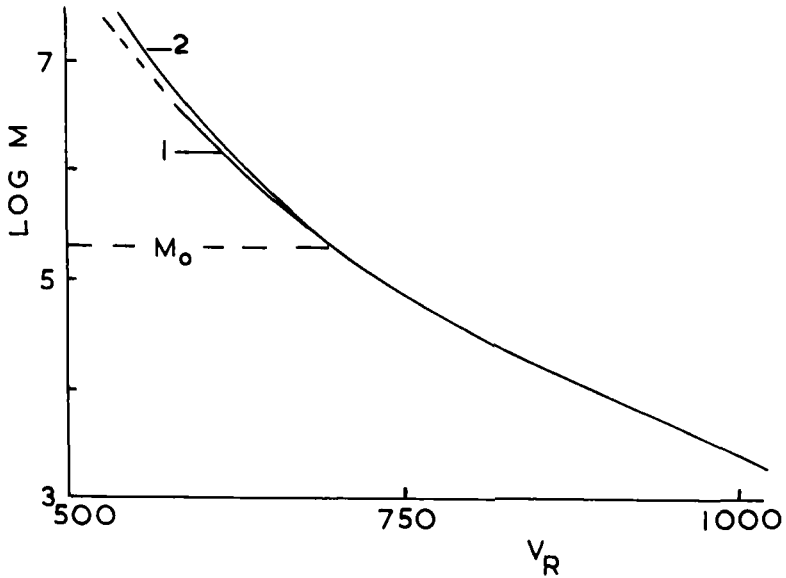

FIGURE 6

SEC calibration curves for PVA computed by the Ram and Miltz method with M_0 = 100,000. Curve 1, fractions and reacetylated whole polymers B3R and B4R; Curve 2, as-polymerised whole polymers B3M and B4M; -----, curve for linear PVA.

FIGURE 7

SEC calibration curves for PVA computed by the Ram and Miltz
method with M_o = 200,000. Curve 1, fractions and reacetylated
whole polymers B3R and B4R; Curve 2, as-polymerised whole polymers
B3M and B4M; -----, curve for linear PVA.

because these commercial samples should have been polymerised to a
higher conversion than our laboratory-prepared samples. The
retention volume data in Figure 3 were based on a molecular weight
calibration curve established with polystyrene standards. It is
now possible to use the calibration curves generated by the RM
method to find $\bar{V}_w$ for the PVA whole polymers. These results are
plotted in Figure 9 where the positions of the branched polymers
have moved to lower V_R as a consequence of the higher $\bar{M}_w$ in Table 5,
whereas the positions of the reacetylated whole polymers have stayed
relatively constant. Therefore, the observations regarding the
influence of branching on the plot in Figure 3 in which the reten-
tion parameter $\bar{V}_w$ was used for polydisperse samples are confirmed
to be satisfactory. Finally, it should be noted that the RM method
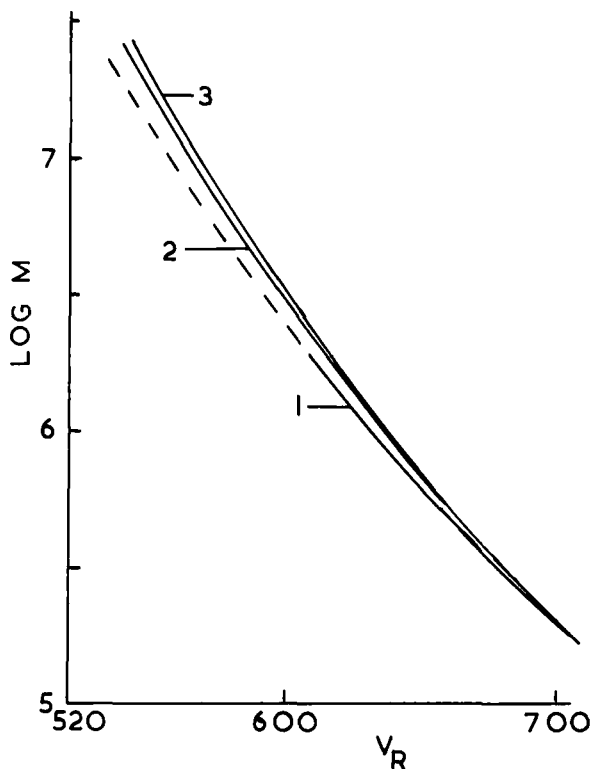
FIGURE 8

SEC calibration curves for PVA computed by the Ram and Miltz method with M_0 = 100,000. Curve 1, fractions and reacetylated whole polymers B3R and B4R; Curve 2, as-polymerised whole polymers B3M and B4M; Curve 3, whole polymers B160T and B500T; -----, curve for linear PVA.

includes equation (2) which assumes that the constants K and a are independent of molecular weight. Whilst this should be a satisfactory assumption for narrow distribution samples, it is possible for K and a to change for a polydisperse whole polymer whose chromatogram extends over a wide range of V_R (25). Our results suggest that even if the values of K and a are not truly constant over a wide range of M the RM method will provide reasonable calibration data. On the other hand, it is possible that the errors in
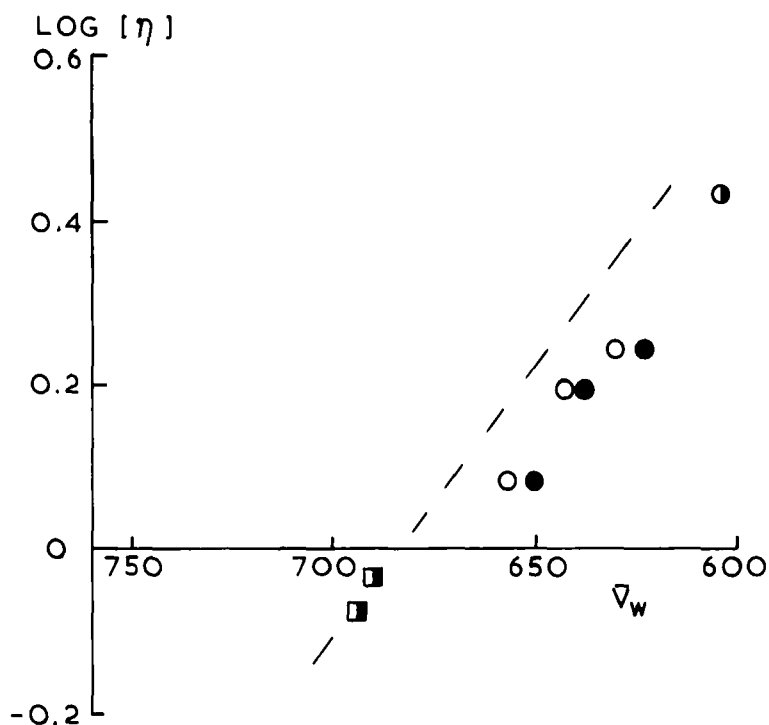
LOG [η]

FIGURE 9

SEC calibration of intrinsic viscosity against weight average
retention volume for PVA whole polymers. ○ ●, as-polymerised
whole polymers B3M, B4M, B160T and B500T; □ ■, whole polymers
B3R and B4R after hydrolysis and reacetylation; open symbols,
$\bar{V}_w$ determined with ps calibration; filled symbols, $\bar{V}_w$ determined
with PVA calibration computed by the Ram and Miltz method;
-----, curve for linear PVA fractions from Figure 3.

our determinations of K and α for our polydisperse whole polymers obtained by the calibration procedure proposed by Weiss and Cohn-Ginsberg (22) may arise because K and α are not constants over a wide range of V_R.

CONCLUSIONS

It has been demonstrated that fully reacetylated samples of hydrolysed linear PVA display identical SEC behaviour to the as-polymerised linear samples, confirming the reliability of the hydrolysis and reacetylation techniques. PVA samples produced by high conversion polymerisation at high temperature have been hydrolysed and reacetylated. SEC results on these samples before and after chemical modification show that long-chain branching in PVA is of the hydrolysable type, and that non-hydro-lysable branching if present in the molecular weight range examined here is not detected by the calibration method involving [n]. It is proposed that a calibration method involving [n] and the reten-tion parameter $\bar{V}_w$ is valid for fractions and polydisperse samples permitting a comparison of linear and branched PVA. For branched polymers the SEC calibration method of Ram and Miltz, which involves no initial assumption on the extent of branching in a sample, was found to provide satisfactory molecular weight data for PVA.

ACKNOWLEDGEMENTS

REFERENCES

1. Lindemann, M. K., in Vinyl Polymerization, Ham, G. E., ed., Vol. 1, Part 1, Marcel Dekker, New York, 1967, Chap. 4.

2. Pritchard, J. G., Polyvinyl Alcohol, MacDonald, London, 1970.

3. Finch, C. A., Polyvinyl Alcohol, John Wiley, New York, 1973.

4. Scholte, Th. G., and Meijerink, N. L. J., Brit. Polym. J., 9, 133, (1977).

5. Scholte, Th. G., in Developments in Polymer Characterisation-4, Dawkins, J. V., ed., Applied Science Publishers, London, 1983, Chap. 1.

6. Drott, E. E., and Mendelson, R. A., J. Polym. Sci., A-2, 8, 1361, 1373, (1970).

7. Morishima, Y., Kim, W-S., and Nozakura, S-I., Polym. J., 8, 196, (1976).

8. Park, W. S., and Graessley, W. W., J. Polym. Sci., Polym. Phys. Ed., 15, 71, 85, (1977).

9. Ram, A., and Miltz, J., J. Appl. Polym. Sci., 15, 2639, (1971).

10. Wild, L., Ranganath, R., and Barlow, A., J. Appl. Polym. Sci., 21, 3331, (1977).

11. Grubisic, Z., Rempp, P., and Benoit, H., J. Polym. Sci., B, 5, 753, (1967).

12. Dawkins, J. V., J. Liq. Chromatogr., 1, 279, (1978).

13. Fettes, E. M., Chemical Reactions of Polymers, Interscience, New York, 1964.

14. Braun, D., Cherdron, H., and Kern, W., Techniques of Polymer Synthesis and Characterization, Wiley-Interscience, New York, 1972.

15. Atkinson, C. M. L., and Dietz, R., Eur. Polym. J., 15, 21, (1979).

16. Dawkins, J. V., in Steric Exclusion Liquid Chromatography of Polymers, Janca, J., ed., Marcel Dekker, New York, 1984, Chap. 2.

17. Dawkins, J. V., Maddock, J. W., and Nevin, A., Eur. Polym. J., 9, 327, (1973).

18. Wheeler, O. L., Lavin, E., and Crozier, R. N., J. Polym. Sci., 9, 157, (1952).

19. Graessley, W. W., Hartung, R. D., and Uy, W. C., J. Polym. Sci., A-2, 7, 1919, (1969).

20. Nozakura, S-I., Morishima, Y., and Murahashi, S., J. Polym. Sci., A-1, 10, 2853, (1972).

21. Spychaj, T., Lath, D., and Berek, D., Polymer, 20, 437, (1979).

22. Weiss, A. R., and Cohn-Ginsberg, E., J. Polym. Sci., B, 7, 379, (1969).

23. Aggarwal, S. H., Jenkins, R. F., and Porter, R. S., J. Appl. Polym. Sci., 27, 113, (1982).

24. Melville, H. W., and Sewell, P. R., Makromol. Chem., 32, 139, (1959).

25. Dawkins, J. V., and Maddock, J. W., Eur. Polym. J., 7, 1537, (1971).