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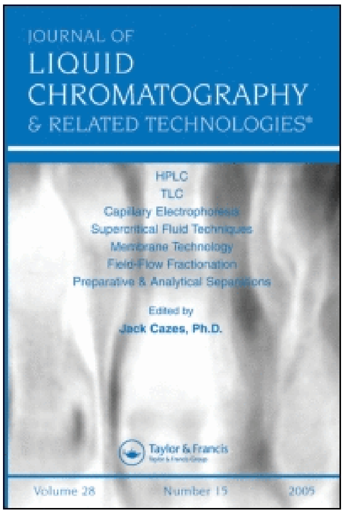

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Generalized Universal Molecular Weight Calibration Parameter in GPC

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To cite this Article Hamielec, A. E. and Ouano, A. C.(1978) 'Generalized Universal Molecular Weight Calibration Parameter in GPC', Journal of Liquid Chromatography & Related Technologies, 1: 1, 111 — 120

To link to this Article: DOI: 10.1080/01483917808068382

URL: http://dx.doi.org/10.1080/01483917808068382

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JOURNAL OF LIQUID CHROMATOGRAPHY, 1(1), 111-120 (1978)

GENERALIZED UNIVERSAL MOLECULAR WEIGHT CALIBRATION PARAMETER IN GPC

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ABSTRACT

In this report we show by experimental and theoretical investigations that the commonly used GPC universal calibration parameter, the intrinsic viscosity multiplied by the weight average molecular weight ($[\eta]\ M_w$) is incorrect. The error which can arise by using $[\eta]\ M_w$ to calculate the molecular weight across the GPC chromatogram for nonuniformly branched polymers [poly(vinyl acetate) and low density polyethylene] and copolymers with compositional drift, could be very large. We also show conclusively that the number average molecular weight M_n is the correct average to use for the universal calibration parameter. We therefore recommend that our general universal calibration parameter $[\eta]\ M_n$ be used for calculating the molecular weight across the chromatogram for all polymer systems (linear and branched homopolymers, copolymers with or without compositional drift and for polymer blends).

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INTRODUCTION

In this letter it is shown that the universal calibration curve concept for GPC as proposed by Benoit, et al.(1) has been incorrectly applied. Earlier investigations(1-4) plot the product of the intrinsic viscosity, and the weight average molecular weight ($[\eta]\ M_w$) to correct for polydispersity of the polymer in the detector cell which may contain a mixture of polymer molecules having the same hydrodynamic volume, $[\eta]_i M_i$, but of different molecular weights. This occurs with polymers of nonuniform long chain branching, copolymers with compositional drift and mixture of different homopolymers, such as polystyrene-poly(phenylene oxide) blends. The use of $[\eta]\ M_w$ as the universal parameter is incorrect as we shall now show.

Herein is reported experimental data on branched poly(vinyl acetate) which clearly shows that the use of $[\eta]\ M_w$ as a universal calibration parameter is incorrect. We also refer to the study by Williams and Cervenka(2) who showed that branched low density polyethylene did not conform with the universal calibration curve using $[\eta]\ M_w$. In addition we give a theoretical analysis which confirms that $[\eta]\ M_w$ is incorrect and shows conclusively that the product of $[\eta]$ and the number average molecular weight (M_n) is

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the correct and general form of the universal calibration parameter.

EXPERIMENTAL

Poly(vinyl acetate) (PVAC) samples with various frequency of long chain branching (LCB) were synthesized using bulk free radical polymerization with AIBN initiator at various temperatures and monomer conversion levels. These polymers were characterized as follows: (1) $\bar{M}_w$ and the $[\bar{\eta}]$ of the whole polymers were measured by a low angle laser light scattering (LALLS) photometer and Ubbelohde viscometer, (2) GPC with LALLS and DRI detectors were used to measure the instantaneous M_w and weight fraction (W) variations with the retention volumes. The details of the LALLS detector and its application with GPC has been described elsewhere(5&6). The detailed experimental procedures used for a large number of PVAC with LCB will be given in a future publication.

RESULTS AND DISCUSSION

Figure 1 shows typical M_w versus the retention volume variations for 2 PVAC samples with different frequency of LCB. In the free radical polymerization of vinyl acetate the frequency of LCB increases markedly with increasing monomer conversion(7) and

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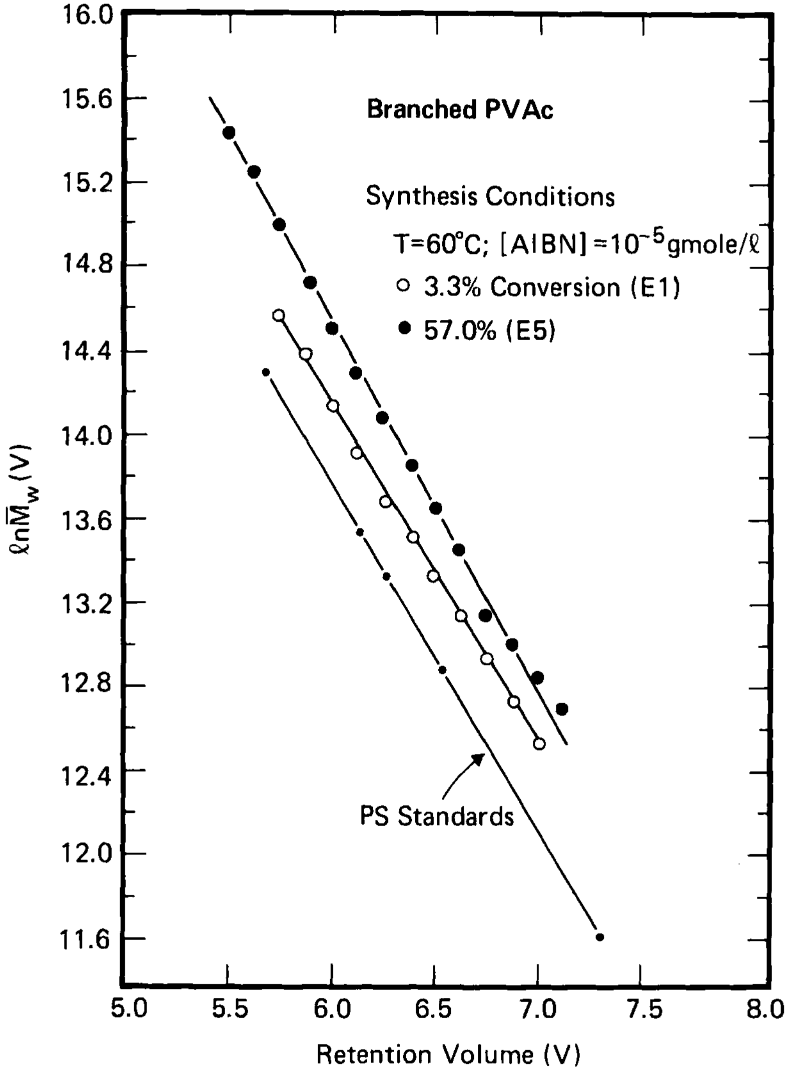

Figure 1. Weight average molecular weight variation across GPC chromatograms.

that at all levels of conversion, the polymer is a mixture of linear chains and chains with widely different branching frequency. Also shown is the usual molecular weight calibration obtained using narrow MWD polystyrene (PS) standards. Several facts are immediately obvious from these data. At the same retention volume (hydrodynamic volume) for the PVAC samples, it is clear that polymer chains of higher branching frequency have a much higher M_w. It may therefore be concluded that when branched PVAC is eluted from the GPC columns into the detector cell, the detector is instantaneously sensing a sample which is very heterogenous in molecular weight even though the molecular species have the same hydrodynamic volume. This presents a difficulty of choosing a molecular weight average for use with the universal calibration curve. Following the usual practice of employing the $[\eta]\ M_w$, we calculated the $[\eta]$ at various retention volumes for the 2 PVAC samples. These calculated data are given in Table 1 along with the measured $[\bar{\eta}]$ viscosities of the whole polymers.

Compare $[\eta]$ versus retention volume variations with the whole polymer $[\bar{\eta}]$. It is clear that there is an inconsistency. $[\eta]$ values found using the universal calibration curve based on polystyrene ($[\eta]_{ps}M_{ps}$), and the parameter $[\eta]\ M_w$ are much too small relative to whole polymer intrinsic viscosity $[\bar{\eta}]$. This is particularly true for sample E-5 which has higher LCB

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TABLE 1

Use of the Universal Calibration Curve Based on Polystyrene to Generate Intrinsic Viscosities Across Branched Poly(vinyl acetate) Chromatograms.

Retention Volume Counts	$(M[\eta])_{ps}$ $(\times 10^{-6})$	PVAC Sample - E1 $M_w \times 10^{-6}$	PVAC Sample - E1 $[\eta]$	PVAC Sample - E5 $M_w \times 10^{-6}$	PVAC Sample - E5 $[\eta]$
5.5	8.87	...	...	5.13	1.729
5.625	6.21	...	...	4.20	1.478
5.75	4.35	2.13	2.04	3.20	1.359
5.875	3.05	1.758	1.735	2.47	1.235
6.0	2.14	1.383	1.547	2.00	1.070
6.125	1.498	1.099	1.363	1.623	0.923
6.25	1.050	0.882	1.190	1.316	0.798
6.375	0.736	0.737	0.999	1.045	0.704
6.5	0.515	0.622	0.828	0.856	0.602
6.625	0.361	0.514	0.702	0.694	0.520
6.75	0.253	0.417	0.607	0.514	0.492
6.875	0.1773	0.344	0.515	0.442	0.401
7.0	0.1243	0.279	0.446	0.381	0.326
		$[\bar{\eta}]_{E1} = 2.20$		$[\bar{\eta}]_{E5} = 3.00$	

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frequency. This is an indication that using M_w in the universal parameter, $[\eta]\, M_w$ may be incorrect and that some other molecular weight average of the polydispersed sample in the detector cell should be employed. We are confident that our M_w values are accurate for the following reason. M_w values integrated with respect to weight fractions are in agreement with off line LALLS measurement for the whole polymer. We will now provide a convincing theoretical proof that M_w is indeed the incorrect average and will define the correct universal calibration parameter which has general applicability.

THEORETICAL DERIVATION

In the analysis to follow we neglected band broadening and assumed that the polymer molecules in the detector cell all have the same hydrodynamic volumes. One can therefore write,

$$[\eta]_{ps}M_{ps} = [\eta]_1 M_1 = [\eta]_2 M_2 = \ . \ . \ . \qquad (1)$$

Where species 1, 2 etc. may refer to linear, branched, copolymers or blends of homopolymers. The intrinsic viscosity of the polymer solution in the detector cell is given by:

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$$[\eta] = W_1\,[\eta]_1 + W_2\,[\eta]_2 + \ldots W_n\,[\eta]_n \qquad (2)$$

Where W_1, W_2, etc. are the weight fractions of the species in the detector cell. Equation (2) may be written as follows:

$$[\eta] = \frac{W_1}{M_1}\,[\eta]_1 M_1 + \frac{W_2}{M_2}\,[\eta]_2 M_2 + \ldots \qquad (3)$$

By virtue of Equation (1), Equation (3) may be rewritten as:

$$[\eta] = [\eta]_{ps} M_{ps}\left(\frac{W_1}{M_1} + \frac{W_2}{M_2} + \ldots \frac{W_n}{M_n}\right) \qquad (4)$$

By definition the number average molecular weight M_n, is given by:

$$M_n = \frac{1}{\frac{W_1}{M_1} + \frac{W_2}{M_2} + \ldots \frac{W_m}{M_m}} \qquad (5)$$

Thus the correct universal calibration parameter is given by:

$$[\eta]\,M_n = [\eta]_{ps} M_{ps} = [\eta]_1 M_1 = [\eta]_2 M_2 \ldots \qquad (6)$$

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RECOMMENDATION

It is therefore recommended that: (1) our universal calibration parameter $[\eta]\ M_n$ be used when applying the principle of universal molecular weight calibration. (2) That on-line viscometer and DRI detectors be used with GPC to measure the variation of M_n with retention volume and thus the $\bar{M}_n$ of the whole polymer. (3) That the LALLS, viscometer and DRI detectors be used with GPC to measure the variation of M_n and M_w with retention volume and thus provide a measure of the $\bar{M}_n$ and $\bar{M}_w$ of the whole polymer. In addition two molecular weight distribution will be provided (M_n vs W and M_w vs W). Although this does not give a complete characterization, it does provide a deeper insight into the MWD and the molecular architecture of polymers, heretofore not possible.

ACKNOWLEDGEMENT

One of the authors (A.E.H.) thanks IBM Canada and the IBM World Trade Corporation for support as a Summer Visiting Professor at the IBM San Jose Research Lab in 1977.

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