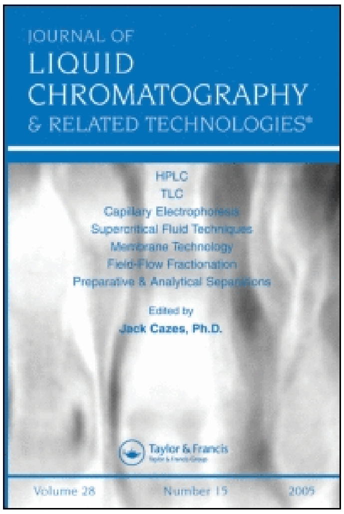

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Molecular Weight Calibration in Steric Exclusion Chromatography of Diblock Copolymers of Polystyrene and Poly (Ethylene Oxide)

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To cite this Article Dawkins, J. V. , Guest, M. J. and Jeffs, G. M. F.(1984) 'Molecular Weight Calibration in Steric Exclusion Chromatography of Diblock Copolymers of Polystyrene and Poly (Ethylene Oxide)', Journal of Liquid Chromatography & Related Technologies, 7: 9, 1739 — 1751

To link to this Article: DOI: 10.1080/01483918408068833
URL: http://dx.doi.org/10.1080/01483918408068833

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(9), 1739-1751 (1984)

MOLECULAR WEIGHT CALIBRATION IN STERIC EXCLUSION CHROMATOGRAPHY OF DIBLOCK COPOLYMERS OF POLYSTYRENE AND POLY(ETHYLENE OXIDE)

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ABSTRACT

The molecular weight calibration curve in steric exclusion chromatography of a diblock copolymer of polystyrene and poly (ethylene oxide) is obtained by a method involving the universal calibration principle. The method is developed from the experimental observation that calibration curves for homopolymers of polystyrene and poly(ethylene oxide) in N,N-dimethylacetamide at 353 K are parallel. It is assumed that the size of the diblock copolymer in solution is linearly related to the sizes of the corresponding homopolymers. The method requires the experimental determination of copolymer composition. Reasonable results for the number average molecular weights of diblock copolymers were obtained with this calibration method.

INTRODUCTION

Grubisic, Rempp and Benoit (1) suggested that hydrodynamic volume can be used for universal calibration in steric exclusion

0148-3919/84/0709-1739$3.50/0

chromatography (SEC), showing that a plot of log[η]M against retention volume V_R (in counts) was the same for homopolymers and copolymers having various structures. Here, [η] is the intrinsic viscosity (dl g^{-1}) of the polymer in the SEC solvent and M is the molecular weight of the polymer. At a given V_R, it is assumed that all polymers have the same value of [η]M so that we can write

$$\log[\eta]_{ps} M_{ps} = \log[\eta]_p M_p \tag{1}$$

where ps refers to a calibration established experimentally with polystyrene standards and p to the calibration for the polymer requiring analysis. It is also assumed that the column combination, solvent and temperature remain constant. Equation (1) therefore permits the determination of M_p from an experimental polystyrene calibration. This may be accomplished with an on-line viscometric detector (2) by establishing the dependence of $[\eta]_{ps}$ and $[\eta]_p$ on V_R as a polymer elutes from the chromatograph. Alternatively, if a viscometric detector is not available, [η] and M are related by the Mark-Houwink equation given by

$$[\eta] = KM^{a} \tag{2}$$

in which K and a are constants for a particular homopolymer-solvent-temperature system. Substitution of equation (2) for homopolymers ps and p into equation (1) and rearrangement gives

$$\log M_p - [(1+a_{ps})/(1+a_p)]\log M_{ps} = [1/(1+a_p)]\log(K_{ps}/K_p) \tag{3}$$

In the molecular weight characterisation of block copolymers, a viscometer may be included in a multidetector system comprising one or more concentration detectors selected from refractive index, ultraviolet and infrared detectors (3), so that the dependence of the intrinsic viscosity $[\eta]_c$ of the block copolymer on V_R may be established. Provided that hydrodynamic volume is a valid universal calibration parameter for a block copolymer (4), then the molecular weight calibration M_c for the block copolymer may be calculated with the equation

$$\log M_c - \log M_{ps} = \log[\eta]_{ps}/[\eta]_c \tag{4}$$

from an experimental calibration for polystyrene, as in equation (1).

If no viscometer detector is available, then the relation for $\log M_c$ against V_R has to be derived from the experimental M_{ps} and M_p calibration curves. Tung and co-workers (5,6) proposed a calibration method which assumed that the size of the copolymer molecule is the sum of the two segments of the molecule considering each block to behave as a separate homopolymer. Their method involved a simple expression for $\log M_c$ in terms of the homopolymer calibrations $\log M_{ps}$ and $\log M_p$ which were weighted according to the copolymer composition. Tung and co-workers (5,6) also reported that their experimental calibration curves M_{ps} and M_p were parallel. Chang (7,8) proposed a molecular weight calibration method for block copolymers, requiring homopolymer calibrations and Mark-Houwink constants as defined in equation (3). Chang (7,8) observed that his method in practice would often involve parallel calibration curves for the homopolymers. This follows because many SEC separations are performed with good solvents for homopolymers (9-11), when $a_{ps} \approx a_p$ so that the right hand side of equation (3) becomes a shift factor between the parallel M_p and M_{ps} calibration curves. When polymers in good solvents have similar polymer-solvent interactions, then this shift factor for universal calibration may be considered in terms of the unperturbed mean-square end-to-end distance $\langle r^2\rangle_0$ of a polymer (10-12). In this paper we demonstrate how universal calibration based on $\langle r^2\rangle_0$ may be extended to the determination of the calibration M_c for diblock copolymers of polystyrene and poly(ethylene oxide) designated PS-PEO.

CALIBRATION METHOD

The intrinsic viscosity for a polymer solution may be expressed in terms of $\langle r^2\rangle_0$ for a polymer (9-11) according to the Flory-Fox equation

$$[\eta] = \Phi[\langle r^2\rangle_0/M]^{3/2} \alpha^3 M^{1/2} \tag{5}$$

where α is the linear expansion factor and Φ is the viscosity constant. Substituting equation (5) into equation (1) and rearranging gives

$$\log M_p - \log M_{ps} = \log[\langle r^2\rangle_0/M]_{ps}[M/\langle r^2\rangle_0]_p + \log[\alpha_{ps}{}^2/\alpha_p{}^2] \tag{6}$$

assuming that Φ is the same for two polymers when $\alpha_{ps} = \alpha_p$. Results have been presented showing that $\alpha_{ps} \sim \alpha_p$ for homopolymers in good solvents when polymer-solvent interactions are very similar (13). Consequently, equation (6) may be simplified to

$$\log M_p - \log M_{ps} = \log[\langle r^2\rangle_0/M]_{ps}[M/\langle r^2\rangle_0]_p \tag{7}$$

Since $\langle r^2\rangle_0/M$ is a characteristic constant for a homopolymer whose conformation may be represented by a random coil, the shift factor on the right hand side of equation (7) is easily calculated.

Recent studies of diblock copolymers in solution suggest that the conformation may be considered to be that for homopolymers (14,15). Thus, molecular size for an individual block, represented by the mean-square radius of gyration, is the same in the block copolymer as that in the equivalent homopolymer, i.e. the molecular size of a block in the diblock copolymer is not affected by the presence of the second block. Consequently, the molecular size of a diblock copolymer in solution may be linearly related to the sizes of the homopolymers (16) according to the relation

$$[\langle r^2\rangle_o/M]_c = W_s[\langle r^2\rangle_o/M]_{ps} + (1 - W_s)[\langle r^2\rangle_o/M]_p \qquad (8)$$

where W_s is the weight fraction of styrene in the diblock copolymer. By analogy with the derivation of equation (7) from equation (1), it can be shown that equation (4) for a diblock copolymer may be transformed to

$$\log M_c - \log M_{ps} = \log[\langle r^2\rangle_o/M]_{ps}[M/\langle r^2\rangle_o]_c \qquad (9)$$

where $[\langle r^2\rangle_o/M]_c$ may be calculated from equation (8) as long as the copolymer composition has been determined.

EXPERIMENTAL

Block Copolymers and PEO Homopolymers

All polymers were prepared by anionic polymerisation techniques in order to produce samples with narrow molecular weight distributions. Solvents and monomers were extensively dried and purified, and the polymerisations were performed under conditions of rigorous purity using a high vacuum technique. Ampoules containing the various reactants were equipped with breakseals and were sealed onto an all-glass reactor similar to a reactor described previously (17).

The synthesis of PS-PEO diblock copolymers involving the formation of polystyrylpotassium in tetrahydrofuran followed by the addition of ethylene oxide was performed according to the method described by O'Malley and Marchessault (18). Polymerisations were initiated with cumylpotassium. The synthesis of this initiator involved firstly the preparation of methyl cumyl ether from α-methyl styrene, methanol and hydrochloric acid, and secondly the reaction of this ether with sodium-potassium alloy in tetrahydrofuran. A predetermined volume of a standardised solution of cumyl potassium in tetrahydrofuran was placed into an all-glass ampoule which was evacuated and sealed. Both monomers and methanol were rigorously dried before sealing in ampoules. Tetrahydrofuran which had been dried with calcium hydride, disodium (α-methyl styrene tetramer), and a sodium mirror was distilled into the reactor. Polystyrylpotassium was formed by reaction at 273 K for 30 min. and then initiated the polymerisation of ethylene oxide which was performed at room temperature for 3-4 days before terminating with methanol. Block copolymer was recovered by precipitating the reaction mixture in a five-fold excess of 60/80 petroleum ether. Similar procedures were used to prepare PEO homopolymers by the initiation of the anionic polymerisation of ethylene oxide with cumylpotassium in tetrahydrofuran using an all-glass reactor. Copolymer composition was determined from infrared measurements with a Perkin Elmer 457 spectrometer. Calibration plots of absorbance versus concentration were obtained for absorption peaks at 700 cm^{-1} (PS) and 1105 cm^{-1} (PEO) with solutions of the homopolymers dissolved in trichloroethylene. From the spectrum for each PS-PEO diblock copolymer in trichloroethylene and the calibration plots, the weight fraction of each block was calculated. Trichloroethylene (SLR, Fisons, with 0.2% triethylamine added) was destabilised by shaking with 10% v/v hydrochloric acid, washed three times with distilled water, and dried by stirring with fused calcium chloride for 30 min. before distillation, taking the middle fraction for use.

Steric Exclusion Chromatography

PS-PEO diblock copolymers and PEO homopolymers were characterised by SEC with a Waters Associates model 200 chromatograph at ICI Organics Division, Blackley, Manchester. A series arrangement of columns containing crosslinked polystyrene gels was used at 353 K with N,N-dimethylacetamide as solvent as described in the paper by Dawkins and Hemming (19). The molecular weight calibration for polystyrene was established with standards supplied by Pressure Chemical Co., Pittsburgh, and Waters Associates. The molecular weight calibration for poly (ethylene oxide) was established with PEO homopolymers prepared by anionic polymerisation and with samples of poly(ethylene glycol) designated PEG assuming values of molecular weight provided by the suppliers (Shell Chemicals, BDH, ICI). The PEO homopolymers were characterised by measuring the solution viscosity of PEO in water with an Ubbelohde-type viscometer at 303 K. Data at several polymer concentrations were extrapolated linearly by the Huggins and Kraemer plots to find $[\eta]$ at infinite dilution. The value of the viscosity average molecular weight $\bar{M}_v$ of PEO for plotting the GPC calibration was calculated from the relation reported by Bailey and co-workers (20)

$$[\eta] = 1.25 \times 10^{-4}\bar{M}_v^{\,0.78} \qquad (10)$$

The polydispersity, defined as the ratio of weight and number average molecular weights $\bar{M}_w/\bar{M}_n$, was calculated from the chromatograms of the PEO homopolymers without corrections for chromatogram broadening. Values of $\bar{M}_w/\bar{M}_n$ were below 1.3, so that construction of a PEO calibration curve with $\bar{M}_v$ by the peak retention volume procedure should be accurate (10).

RESULTS AND DISCUSSION

Experimental calibration curves for PS standards, PEO homopolymers and PEG samples are shown in Figure 1. Straight line behaviour was assumed for the range of V_R from 16.5 to 22.0

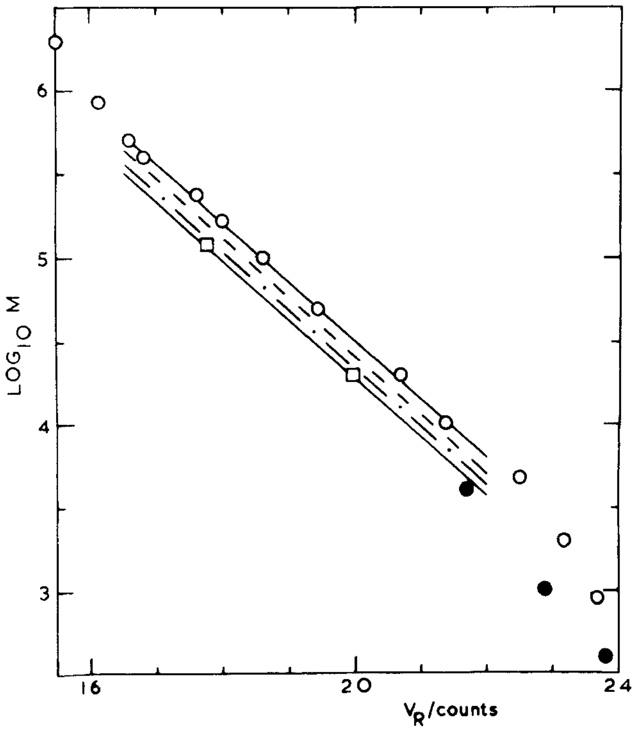

FIGURE 1

Molecular weight calibration plots for N,N-dimethylacetamide at 353 K. ○ polystyrene standards, □ poly(ethylene oxide) homopolymers, ● poly(ethylene glycol) samples. -□-□- predicted M_p calibration for PEO with equation (7) and a shift factor $\log_{10}$ 0.593. --- predicted M_c calibration for PS-PEO (W_s = 0.68) with equation (9) and a shift factor $\log_{10}$ 0.82. -·-·- predicted M_c calibration for PS-PEO (W_s = 0.37) with equation (9) and a shift factor $\log_{10}$ 0.70.

counts. The calibration curves for PS and PEO homopolymers may be related with equation (7). The value of $[\langle r^2\rangle_o/M]_{ps}^{1/2}$ was assumed to be 0.67 Å, as in previous universal calibration studies (9,12,19). The calibration curve for PEO predicted with equation (7) superimposes with the experimental data for PEO in Figure 1 when the shift factor is $\log_{10} 0.593$, so that $[\langle r^2\rangle_o/M]_p^{1/2}$ for PEO is then 0.87 Å. This value is very close to the value of 0.84 Å reported by Beech and Booth (21). The difference between these two values of $[\langle r^2\rangle_o/M]_p$ is close to experimental error. The shift factor in equation (7) is presumed to be unaffected by possible small differences in α_{ps} and α_p in equation (6) for PS and PEO in N,N-dimethylacetamide. The results indicate that equation (7) is a satisfactory method for determining the calibration curve for PEO homopolymers. Therefore, it is reasonable to assume that the calibration curves for PS and PEO homopolymers are parallel which is a requirement in the procedure for determining the calibration curve for a PS-PEO diblock copolymer.

In the synthesis of a PS-PEO diblock copolymer, part of the polystyrylpotassium was removed from the polymerisation reactor and deactivated with methanol. A chromatogram for such a sample which corresponds therefore to the PS block is shown in Figure 2. A chromatogram for the PS-PEO diblock copolymer resulting from the same polystyrylpotassium is also shown in Figure 2. The positions of these chromatograms on the V_R axis clearly indicate the success of the sequential polymerisation procedure for forming PS-PEO and also indicate that there is no measurable PS homopolymer in the sample of diblock copolymer. Residual PS homopolymer would have arisen from premature termination of some of the polystyrylpotassium on addition of ethylene oxide monomer, generating a second peak at $V_R = 20.15$ counts in the chromatogram for the diblock copolymer in Figure 2. If it is assumed that the sample of diblock copolymer does not contain homopolymer, then

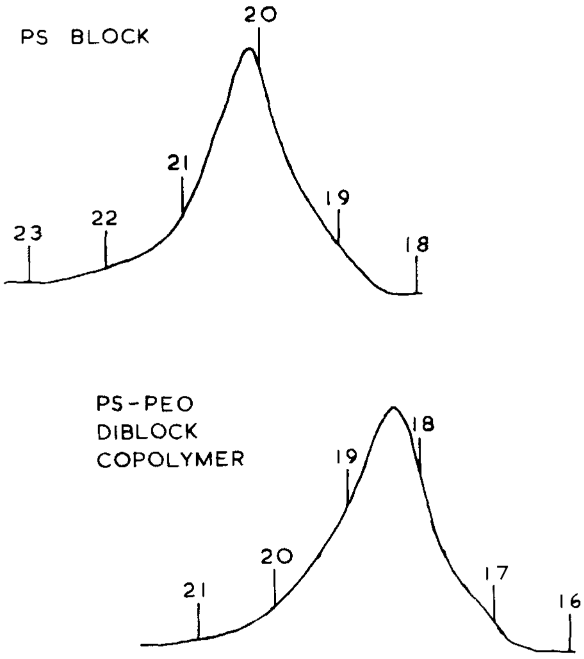

FIGURE 2

Chromatograms for diblock copolymer PS-PEO-4 and the PS block from elution with N,N-dimethylacetamide at 353 K.

values of $\bar{M}_n$ (PS) and $\bar{M}_n$ (PS-PEO) for the polystyrene block and the diblock copolymer respectively are related by

$$W_s = \bar{M}_n\,(\mathrm{PS})/\,\bar{M}_n\,(\mathrm{PS\text{-}PEO}) \qquad (11)$$

A value of $\bar{M}_n$ (PS) is determined from the chromatogram for the polystyrene sample in Figure 2 with the PS calibration curve in Figure 1. Since W_s is known from infrared spectroscopy measurements, the value of $\bar{M}_n$ (PS-PEO) may be estimated with equation (11), and results are given in Table 1.

SEC calibration curves for PS-PEO diblock copolymers were determined with equation (9), having calculated $[\langle r^2\rangle_0/M]_c$ with

TABLE 1

Characterisation Data for PS-PEO Diblock Copolymers

Copolymer	W_s	$\bar{M}_n$(PS)	$\bar{M}_n$(PS-PEO)	$\bar{M}_n$(SEC)	$\bar{M}_w/\bar{M}_n$
PS-PEO-1	0.72	36200	50300	53900	1.40
PS-PEO-2	0.68	43900	64600	64500	1.50
PS-PEO-3	0.42	36200	86200	76100	1.44
PS-PEO-4	0.37	22100	59700	54900	1.47

equation (8) employing $[\langle r^2\rangle_o/M]_{ps}^{1/2}$ = 0.67 Å, $[\langle r^2\rangle_o/M]_p^{1/2}$ = 0.87 Å for PEO, and the values of W_s given in Table 1. The copolymer calibrations M_c are parallel to and between the curves for the homopolymers, as shown by the selected copolymer examples in Figure 1. With the calibration curve and chromatogram for a diblock copolymer, values of $\bar{M}_n$(SEC) and the polydispersity were calculated and are listed in Table 1. The SEC method gives values of $\bar{M}_n$ for the copolymers in fair agreement with $\bar{M}_n$(PS-PEO) obtained with equation (11).

In summary, the proposed calibration method is simple to use and provides reasonable values of molecular weight for PS-PEO diblock copolymers. It is likely that many SEC separations of homopolymers and copolymers will be performed with good solvents having similar polymer-solvent interactions because solute-gel interactions are more likely when the eluent becomes less compatible with the gel and when the eluent is a poor or theta solvent for the polymeric solute (22). In this work we have assumed no change in copolymer composition with V_R. It follows from equation (8) that when W_s varies across the chromatogram the M_c calibration calculated with equation (9) must be non-parallel to the calibration curves for the homopolymers. Results for diblock copolymers having a copolymer composition distribution will be reported in a separate paper.

ACKNOWLEDGEMENTS

The authors thank the Science Research Council for the award of a research studentship.

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