

CHROM. 5123

MOLECULAR WEIGHT ANALYSIS OF BLOCK COPOLYMER
BY GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A method is introduced for converting the experimental elution volume to molecular weight of linear block copolymer by use of the calibration curves for homopolymers. The basis of this method is the linear relationship between the logarithm of molecular weight and the elution volume. In a comparison of the results obtained by this method and those calculated, according to a method recently suggested by RUNYON and coworkers¹, it has been found that this method gives lower molecular weight than the latter method does. In the case of styrene-butadiene block copolymer in tetrahydrofuran, the difference is negligible for all practical purposes. It can be deduced, however, that in some extreme cases the RUNYON correction can give a molecular weight 80% higher than that calculated by the suggested method.

INTRODUCTION

Gel permeation chromatography (GPC) has been developed into a most convenient technique for the determination of molecular weight distribution (MWD) of polymers. For homopolymers the interpretation of experimental GPC curve is now standard procedure. The relation between the GPC curve of a block polymer and its MWD is yet to be established. The interpretation in this case is complicated by the presence of a composition distribution along with MWD. RUNYON and coworkers¹ have recently suggested a method to calculate the MWD of styrene-butadiene block polymer from GPC and UV data; the latter being obtained by adding a UV spectrometer to the GPC instrument. In this paper a slightly different method for calculating the molecular weight of block polymer from elution volume is introduced and compared with the above method.

PARALLEL CALIBRATION CURVES

The most useful part of a molecular weight *vs.* elution volume calibration curve from a gel permeation chromatogram is a straight line on a semi-log plot which can be expressed as

$$V - V_0 = k(\log M - \log M_0) \quad (1)$$

where M is the molecular weight eluted at solvent volume V and k is a constant. The subscript zero designates the reference point. When the calibration curves for two homopolymers A and B are parallel to each other, *i.e.*, when they have the same slope, at any elution volume the following is true:

$$M_A = rM_B$$

where M_A and M_B are the molecular weights of A and B respectively at elution volume V and r is the ratio of M_A to M_B at the reference elution volume V_0 . This relation shows that so far as elution volume is concerned M_A and rM_B are equivalent. Let us assume that this equivalence can be applied to the component blocks in a block copolymer. That is to say, it is assumed that a homopolymer with molecular weight $M_{A'}$ will elute at the same solvent volume as a block copolymer $M_1 + M_2$ when $M_{A'} = M_1 + rM_2$, where M_1 and M_2 are the molecular weights of the blocks of monomers A and B respectively. Since the molecular weight of the block copolymer $M_c = M_1 + M_2$, $M_1 = W_1M_c$ and $M_2 = W_2M_c$, it follows that

$$M_c = M_{A'} / (1 + [r - 1]W_2) \quad (2)$$

where W_2 is the weight fraction of monomer B in the copolymer M_c . Therefore, the molecular weight of the block polymer can be calculated by (1) evaluating r from the two calibration curves for homopolymer, (2) reading $M_{A'}$ at the elution volume of the homopolymer from the calibration curve for homopolymer A, (3) determining W_2 by UV spectrum in a case such as styrene-butadiene copolymer, and (4) calculating M_c by use of eqn. 2.

UNPARALLEL CALIBRATION CURVES

When the calibration curves of two homopolymers under the same experimental conditions are not parallel to each other, the case can be stated mathematically as follows:

$$\begin{aligned} V - V_0 &= k_1 (\log M_A - \log M_{A0}) \\ &= k_2 (\log M_B - \log M_{B0}) \end{aligned} \quad (3)$$

$$k_1 \neq k_2$$

It is assumed that the B block in the copolymer can be substituted by a block $M_{1'}$ of monomer A, without changing the elution volume if

$$M_{1'} = \left(\frac{M_2}{M_{20}} \right)^{k_2/k_1} M_{10}$$

Then the homopolymer A having the same elution volume as the block polymer has a molecular weight $M_{A'}$.

$$M_{A'} = M_1 + \left(\frac{M_2}{M_{20}} \right)^{k_2/k_1} M_{10}$$

Subtracting $M_c = M_1 + M_2$ and rearranging terms, we have

$$k_3(W_2M_c)^{k_2/k_1} - (1 + W_2)M_c + M_{\Lambda}' = 0 \quad (4)$$

where $k_3 = M_{10}M_{20}^{-k_2/k_1}$ is a constant. With k_1 , k_2 and k_3 calculated from the calibration curves of the two homopolymers, W_2 determined experimentally and M_{Λ}' read from the calibration curve at the same elution volume as the copolymer in question, eqn. 4 can be solved for M_c , the molecular weight of the block copolymer. For instance, when $k_2/k_1 = 2$, eqn. 4 is quadratic and can be solved. For other values of k_2/k_1 , it may be more convenient to find M_c by trial and error. In the special case when $k_2 = k_1 = k$ the two calibration curves are parallel to each other and $k_3 = r$. Eqn. 4 reduces to eqn. 2.

Eqn. 3 can be rewritten as

$$\log M_B = \frac{k_1}{k_2} \log M_{\Lambda} + \log M_{B0}M_{\Lambda0}^{-k_1/k_2}$$

Based on the universal calibration curve and the Mark-Houwink equation it can be derived (e.g. see ref. 2)

$$\log M_B = \frac{1 + a_1}{1 + a_2} \log M_{\Lambda} + \frac{1}{1 + a_2} \log \frac{K_1 f(e_2)}{K_2 f(e_1)}$$

where K and a are the constants in the Mark-Houwink equation and $f(e)$ is a function of a . A comparison of these two equations reveals

$$\frac{k_1}{k_2} = \frac{1 + a_1}{1 + a_2}$$

and

$$M_{B0}M_{\Lambda0}^{-k_1/k_2} = [K_1 f(e_2) / K_2 f(e_1)]^{1/(1+a_2)}$$

In trichlorobenzene at 135°, the values of k_1/k_2 for poly- α -methylstyrene, polypropylene², and polyethylene, compared to polystyrene, are 1.021, 0.975, and 0.990 respectively — close enough to 1 to justify the use of eqn. 2 instead of eqn. 4, even though the calibration curves are not strictly parallel to each other. Since the value of a varies in a narrow range from 0.5 to 0.8 (ref. 3) one can anticipate that eqn. 2 can be applied to most solvent and block copolymers and eqn. 4 will be needed less frequently for higher precision.

DISCUSSION

Although the derivations are done for diblock polymers, the treatment can be readily extended to triblock cases. The third block is treated in the same manner as the second block. Thus, $M_{\Lambda}' = M_1 + r_2M_2 + r_3M_3$, and $M_c = M_{\Lambda}' / (1 + [r_2 - 1]W_2 + [r_3 - 1]W_3)$ for the ABC type of block polymer. It can be readily deduced that this treatment makes no distinction between ABA and ABAB types

TABLE I
COMPARISON OF CORRECTION FACTORS

W_2	$r = 2$		$r = 5$		$r = 10$	
	$W_2 \log r$	$\log (1 + W_2)$	$W_2 \log r$	$\log (1 + 4 W_2)$	$W_2 \log r$	$\log (1 + 9 W_2)$
0.20	0.061	0.079	0.140	0.255	0.20	0.447
0.30	0.091	0.114	0.210	0.342	0.30	0.568
0.40	0.121	0.146	0.280	0.415	0.40	0.663
0.50	0.152	0.176	0.349	0.477	0.50	0.740
0.60	0.182	0.204	0.419	0.531	0.60	0.806
0.70	0.212	0.230	0.489	0.580	0.70	0.863
0.80	0.242	0.255	0.559	0.623	0.80	0.914

of copolymers, both of which are treated as AB type diblock cases. If we carry this reasoning one step further, a random copolymer of comonomers A and B would be treated as an AB type block polymer. It would be interesting to find out experimentally whether GPC would not distinguish a random copolymer from a diblock or triblock polymer of the same composition and molecular weight.

This can be readily observed from eqn. 2, $M_c = M_A' / (1 + [r - 1]W_2)$. It shows that a homopolymer A of molecular weight M_A' , if it is present in the block polymer sample, will be fractionated at the same elution volume as the block polymer M_c . Since this equation can be expressed in terms of M_B' as well, the homopolymer M_B' would be also separated at this elution volume. So will other structures of various values of W_2 . For example, in a styrene-butadiene block polymer S(100000), S(90000) B(5000), S(88000) B(6000) and B(50000) would all be eluted at the same elution volume, if they are present. [S(m)B(n) stands for a polymer consisting of a block of polystyrene of molecular weight m and a block of polybutadiene of molecular weight n .] Therefore, what we have obtained from GPC fractionation is a GPC average molecular weight and a GPC average composition. Further work is needed to convert the GPC average MWD of block polymer to its true MWD. This is a subject being currently studied in our laboratory.

RUNYON and coworkers¹ suggested that the molecular weight of a block copolymer is related to the molecular weights of the homopolymers at the same elution volume according to the following equation:

$$M_c = M_A'^{W_1} M_B'^{W_2}$$

Since $W_1 + W_2 = 1$ and $M_A'/M_B' = r$,

$$M_c = M_A' / r^{W_2} \quad (5)$$

Comparing this equation with eqn. 2 one can see that the difference between the two corrections is in the form of the function of r . In one the correction factor is r^{-W_2} , and in the other it is $(1 + [r - 1]W_2)^{-1}$. A comparison is made in Table I of the actual values calculated according to these two methods for various values of r and W_2 .

It can be seen from Table I that for low values of r , say $r = 2$, the two methods

of correction give almost the same results. The difference amounts to only 4% at the most, probably well within experimental error. Only at high value of r the difference is appreciable. In the case of $r = 10$ and $W_2 = 0.20$, eqn. 5 will give a molecular weight about 80% higher.

ACKNOWLEDGEMENT

The author expresses his gratitude to Borg-Warner Corporation for permission to publish this work.

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