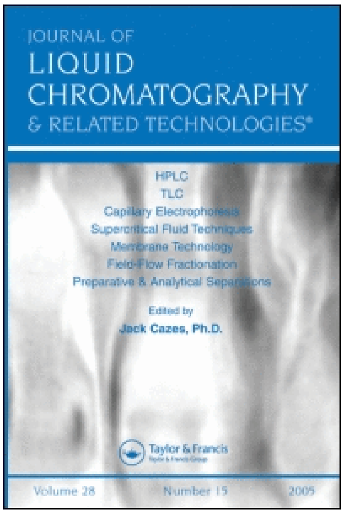

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Analysis of Block and Statistical Copolymers by Gel Permeation Chromatography: Estimation of Mark-Houwink Constants

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Abstract

A method is introduced for the estimation of Mark-Houwink constants of block and statistical copolymers. The homopolymer Mark-Houwink constants and copolymer composition are required. Use of estimated Mark-Houwink constants in GPC analyses gives results which agree well with those calculated with experimentally determined constants. Comparisons between this method and those of Runyon and coworkers (11) and Chang (12) are made for block copolymers. Chang's method was also extended to statistical copolymers, and where it compared closely with the one introduced here. The use of copolymer Mark-Houwink constants as a qualitative measure of polymer compatibilities in different solvents is also discussed.

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Introduction

Gel permeation chromatography (GPC) has become a very powerful tool in the analysis of polymer samples. Fundamental to the interpretation of a chromatogram is the ability to translate the elution volume at which a polymer fraction appears into molecular weight. This was originally done by constructing a calibration curve of ln M vs. elution volume (ve) where M is the molecular weight of a narrow molecular weight version of the polymer being studied (1-3). The more recent universal calibration method relates ve to the hydrodynamic volume (Vh), which is a function of the product of intrinsic viscosity and molecular weight ($[\eta]M$) and permits the use of a single set of calibration standards for the GPC analysis of virtually any polymer system for which the Mark-Houwink constants are known in the GPC solvent (4-6).

The analysis of copolymers by GPC presents a very difficult problem because the Mark-Houwink constants are not generally known. Although it is possible to determine these constants either through the tedious method of fractionation or by other means (7-10), their values will change as a function of copolymer composition, and consequently would have to be redetermined for each composition of copolymer present. This problem becomes intractable in cases where the copolymer composition is heterogeneous, i.e. drifts with molecular weight. Runyon and coworkers (11) and Chang (12) have suggested methods for the calculation of the molecular weight distribution of copolymers which require the calibration curves or Mark-Houwink constants of the constituent homopolymers and the copolymer composition. These methods, however, have been applied only to diblock copolymers and not to multiblock systems or to statistical copolymers.

In this article, we propose a means for facilitating the interpretation of GPC chromatograms of copolymers of either block or statistical structures. This entails the calculation of the copolymer Mark-Houwink constants which can be accomplished with the knowledge of the copolymer composition and the Mark-Houwink constants of the contributing segments.

This method can be applied not only to binary but also to higher order copolymers provided that reliable composition analyses can be achieved.

Theory

The hydrodynamic volume of a solvated polymer coil can be defined as

$$Vh = \frac{4\pi}{3} r_H^3 \tag{1}$$

where r_H is the hydrodynamic radius. It can be deduced from the Einstein equation (13) that

$$r_H^3 = \frac{3}{10\pi N_o} [\eta]M \tag{2}$$

at infinite dilution, where N_o is Avogadro's constant. As a result, Vh can be expressed as:

$$Vh = \frac{4\pi}{3\phi''} [\eta]M \tag{3}$$

where $\phi'' = 6.3067 \times 10^{24}$ (cgs units) and is related to Flory's universal constant ϕ' through the relationship between r_H and the radius of gyration, r_G, and the Flory-Fox equation (14,15).

The Mark-Houwink relation is:

$$[\eta] = K\ M^a \tag{4}$$

where K and a are the Mark-Houwink constants. Therefore,

$$Vh = \frac{4\pi}{3\phi''} K\ M^{a+1} \tag{5}$$

This is the widely accepted universal calibration expression, and is applicable at infinite dilution. Appropriate allowances can be made where necessary to account for concentration effects (6,16-18).

In general, one may express the hydrodynamic radius of any polymer coil according to Flory (19) as follows

$$\bar{r}_H^2 = \bar{r}_{Ho}^2\ \alpha^2 \tag{6}$$

where the subscript zero refers to the unperturbed radius that exists under Theta conditions, and α is the chain expansion factor. This is a measure of the extent to which polymer-solvent "long range interactions" perturb the molecular dimensions of the polymer coil. One may express α according to the following relationship (20)

$$\alpha = \sigma M^{\varepsilon/2} \tag{7}$$

where σ and ε are constants characteristic of the polymer and solvent in question.

The mean square end-to-end radius, $\bar{r}^2$, and consequently $\bar{r}_G^2$ and $\bar{r}_H^2$ of a polymer are the sum of the contributions of all the constituent segments of the coil. A suitable functional form (see Appendix I) is:

$$\bar{r}_H^2 = \Sigma(\bar{r}_H^2)_i = \Sigma(\bar{r}_{Ho}^2)_i \, \alpha_i^2 \tag{8}$$

where the subscript, i, which refers to a segment, may represent any group of monomer units. For copolymers, segments are defined as the different moieties present whose contributions determine the coil size. For a binary copolymer these include runs of homopolymer units as well as hetero segments. The chain expansion factor of a copolymer, α_c, is a function of the molecular weight of the entire chain, M_c. The coefficients σ_i and ε_i of the relation in eq. (7) are, however, assumed to be composition dependent. Consequently, we recast eq. (8) as follows:

$$(\bar{r}_H^2)_c = \Sigma(\bar{r}_{Ho}^2)_i \, \sigma_i^2 \, M_c^{\varepsilon_i} \tag{9}$$

where the subscript c refers to copolymer. The molecular weight of the ith segment of the copolymer is M_i where

$$M_i = w_i M_c \tag{10}$$

and w_i is the corresponding weight fraction of the whole copolymer. Then

$$(\bar{r}_H^2)_c = \Sigma w_i \left(\frac{\bar{r}_{Ho}^2}{M}\right)_i \sigma_i^2 M_c^{\varepsilon_i+1} \tag{11}$$

From Flory (19):

$$K_\theta = \phi'' \left(\frac{\bar{r}^2_{Ho}}{M} \right)^{3/2} \tag{12}$$

and

$$K = K_\theta \sigma^3 \tag{13}$$

while

$$(a + 1) = 3/2(\varepsilon + 1) \tag{14}$$

where K_θ is the Mark-Houwink constant under Theta conditions. Then the following expression describes Vh:

$$Vh = \frac{4\pi}{3} (\bar{r}^2_H)^{3/2} = \frac{4\pi}{3\phi''} [\Sigma w_i (K_i M_c^{(a_i+1)})^{2/3}]^{3/2} \tag{15}$$

In the case of an A-B block copolymer, there would be only two segments, poly-A and poly-B, which represent the two types of interactions present, and characterize the expansion of their corresponding homopolymer coils. The influence of the A-B interactions have been shown to be minimal and may usually be ignored (21-25). However, for statistical copolymers, one must take into account the A-B heterointeractions which have been observed to contribute to coil size and consequently there would be three segments included in the calculation (25-29).

Results and Discussion

The Mark-Houwink constants for polystyrene (PS), poly(methyl methacrylate) (PMMA) and the alternating styrene-methyl methacrylate copolymer are recorded for several solvents in Table I. These constants were then used to calculate copolymer Mark-Houwink constants for both block and statistical copolymers of these components. This was done for several compositions and solvent systems as will be discussed.

Block Copolymers

The Mark-Houwink constants were determined for several compositions of styrene-methyl methacrylate block copolymers by calculating the Vh of those

Table I

Mark-Houwink Coefficients

Polymer	Solvent	K (x 10^3) (mL/g)	a	Reference
Polystyrene	tetrahydrofuran (THF)	6.82	0.766	30
	methyl ethyl ketone (MEK)	19.5	0.635	31
	toluene	7.5	0.750	32
	n-chlorobutane	15.1	0.659	33
Poly(methyl methacrylate)	THF	12.8	0.69	34
	MEK	6.80	0.72	35
	toluene	7.10	0.73	36
	n-chlorobutane	50.5	0.5	37
Alternating poly(styrene-co-methyl methacrylate)	THF	7.75	0.76	29
	MEK	11.5	0.69	29
	toluene	10.9	0.73	29
	n-chorobutane	10.8	0.70	29

copolymers at different molecular weights according to equation (15). A linear regression of the log Vh vs log M_c plot was then performed. The Mark-Houwink pre-exponential constant for the copolymer, K_c, was obtained from the intercept of the line and exponent, a_c, was estimated from the slope according to equation (5). These values are tabulated for four solvents in Table II. Because there are no heterointeractions involved in the coil expansion, the values obtained for both K_c and a_c lie between those for the two homopolymers in all cases. These constants are also composition dependent, with the values progressing linearly in a and with a slight curvature in K from near those of polystyrene to near PMMA as the methacrylate content increased in the copolymer. This is illustrated in Figures 1 to 4 for the tetrahydrofuran and n-chlorobutane solvent systems.

The Mark-Houwink constants for 1:1 styrene-methyl methacrylate block copolymer have been determined previously for the solvent systems reported in this study (29). Table III reports these values and a comparison of the molecular weights that one obtains upon conversion from hydrodynamic volume using the experimental and calculated values for the applicable molecular weight range for the experimental values, i.e. between 10^5 and 10^6 for the n-chlorobutane solvent system and between 10^4-10^6 for the others. Agreement in all cases is within 10%. This may be considered quite good when one considers the possible error in the reported values of the homopolymer Mark-Houwink constants and experimental error in the measured block copolymer Mark-Houwink constants. In addition, discrepancies may also have arisen because in some cases fractionation was incomplete, and $\bar{M}_w/\bar{M}_n$ was as high as 1.6.

Other workers have also suggested ways of relating the molecular weight of an eluting block copolymer to those of the homopolymer which comprise it. Runyon and coworkers have empirically postulated that

$$M_c = M_A^{w_A} M_B^{w_B} \tag{16}$$

where M_A and M_B are the molecular weights of the homopolymers A and B which elute at the same time as the copolymer with molecular weight, M_c (11).

Table II

Calculated Mark-Houwink Constants for Poly(styrene-co-methyl methacrylate)

Block Copolymers at Several Compositions in Different Solvents

Copolymer Composition	THF		MEK		Toluene		n-Chlorobutane	
(wt. fraction styrene)	K ($x10^3$ mL/g)	a	K ($x10^3$ mL/g)	a	K ($x10^3$ mL/g)	a	K ($x10^3$ mL/g)	a
0.2	11.239	0.705	8.647	0.700	8.850	0.719	38.313	0.537
0.3	10.541	0.714	9.689	0.691	9.789	0.715	53.637	0.554
0.4	9.891	0.721	10.814	0.682	10.771	0.710	29.671	0.570
0.5	9.287	0.729	12.026	0.674	11.795	0.706	26.283	0.586
0.6	8.723	0.736	13.327	0.665	12.858	0.703	23.371	0.602
0.7	8.197	0.744	14.722	0.657	13.961	0.699	20.857	0.617
0.8	7.707	0.751	16.214	0.650	15.103	0.696	18.673	0.631

Table III

Experimental Mark-Houwink Constants and Comparison of Molecular Weights Obtained from Hydrodynamic Volumes Using Experimental and Calculated Mark-Houwink Constants for 1:1 Block Poly(styrene-co-methyl methacrylate)

Solvent	K (x10^3 mL/g)$^{(a)}$	a$^{(a)}$	Molecular Weight$^{(a)}$	Molecular Weight$^{(b)}$	Hydrodynamic Volume
THF	6.41	0.76			
			1.0×10^4	0.952×10^4	4.668×10^{-20}
			1.0×10^5	0.942×10^5	2.686×10^{-18}
			1.0×10^6	1.034×10^6	1.546×10^{-16}
MEK	14.66	0.67			
			1.0×10^4	1.101×10^4	4.660×10^{-20}
			1.0×10^5	1.095×10^5	2.180×10^{-18}
			1.0×10^6	1.089×10^6	1.020×10^{-16}
Toluene	13.18	0.69			
			1.0×10^4	0.979×10^4	5.037×10^{-20}
			1.0×10^5	0.958×10^5	2.467×10^{-18}
			1.0×10^6	0.938×10^6	1.208×10^{-16}
n-Chlorobutane	44.46	0.55			
			1.0×10^5	1.073×10^5	1.661×10^{-18}
			1.0×10^6	1.018×10^6	5.892×10^{-16}

(a) reference (29) (b) this work

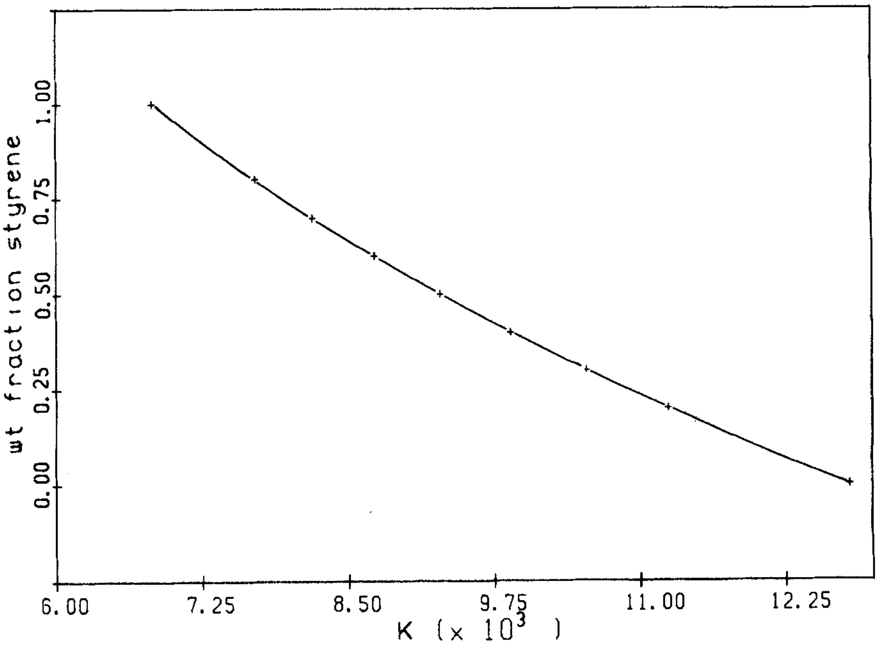

Figure 1. Styrene-Methyl Methacrylate Block Copolymer Composition vs. K in THF.

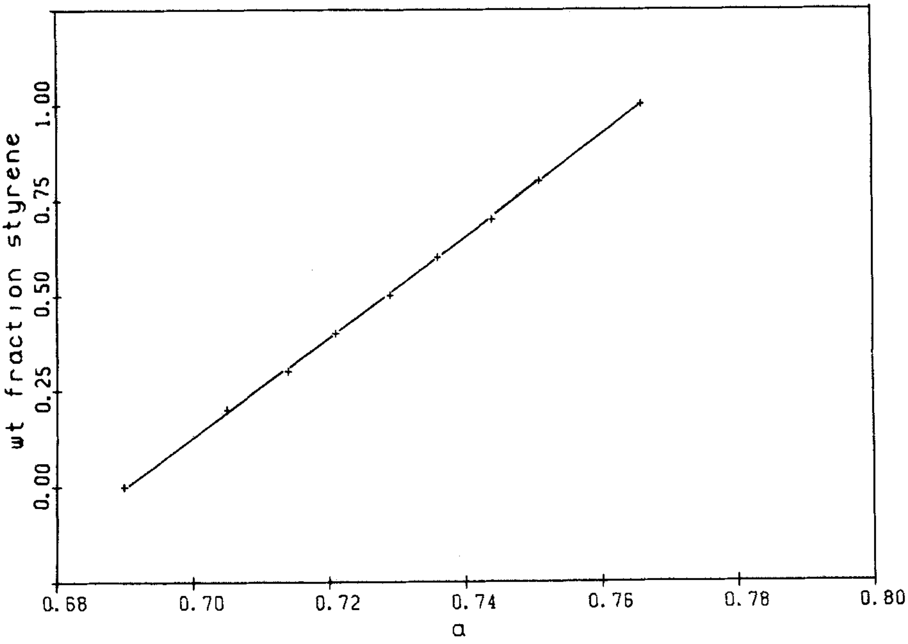

Figure 2. Styrene-Methyl Methacrylate Block Copolymer Composition vs. a in THF.

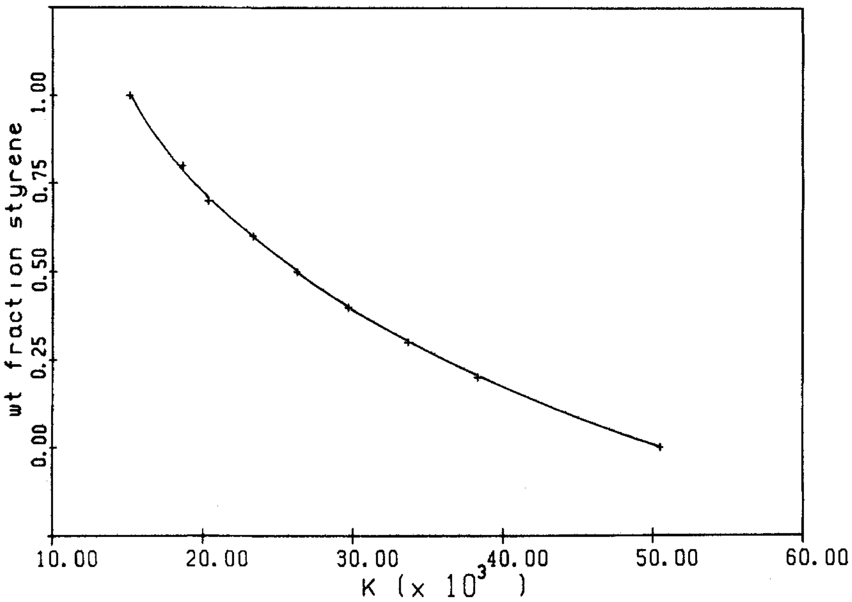

Figure 3. Styrene-Methyl Methacrylate Block Copolymer Composition vs. K in n-Chlorobutane.

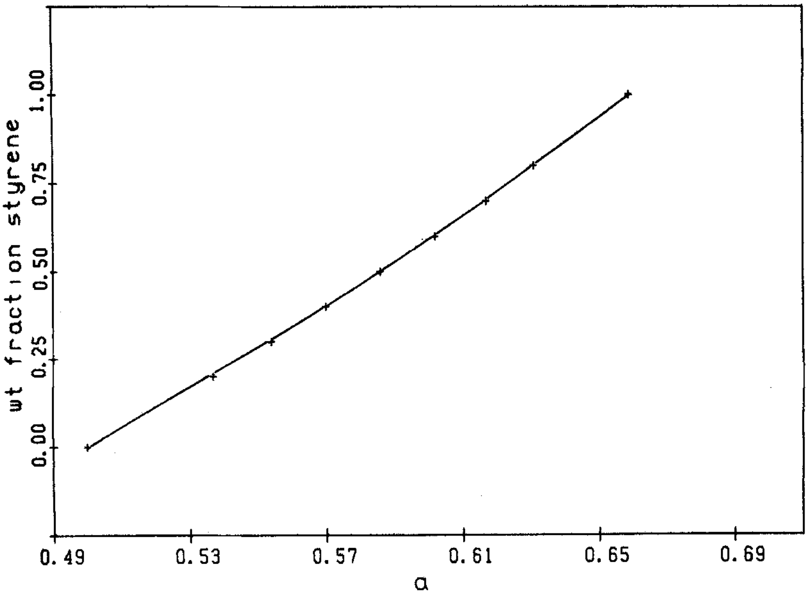

Figure 4. Styrene-Methyl Methacrylate Block Copolymer Composition vs. a in n-Chlorobutane.

Chang proposed (12) that since two homopolymers will elute at the same time when

$$M_1 = \left[\frac{K_2}{K_1} M_2^{(a_2+1)}\right]^{1/(a_1+1)} \qquad (17)$$

where the subscripts 1 and 2 refer to different polymers, one may assume a block copolymer with molecular weight M_c will have the same elution volume as a homopolymer with molecular weight M_A when

$$M_c = M_1 + M_2 \qquad (18)$$

and

$$M_A = M_1 + \left[\frac{K_2}{K_1} M_2^{(a_2+1)}\right]^{1/(a_1+1)} \qquad (19)$$

Mark-Houwink constants were calculated for the different composition styrene-methyl methacrylate block copolymers as described before using these two methods and are presented in Tables IV and V. Comparison of these constants and those in Table II show excellent agreement for each of the solvent systems with the exception of n-chlorobutane. Molecular weights calculated from Vh's using the Mark-Houwink constants derived from these three methods are within 2% of each other for the range of 10^4-10^6. For the n-chlorobutane system, disparities between this work and Runyon's range up to 10% but only 5% between this work and Chang's. However, the disagreement between the values calculated according to Runyon and Chang range up to 15%. This probably results from the large difference in Mark-Houwink constants of the homopolymers in this solvent and is a manifestation of the difference of methods for determination of copolymer constants. It is in cases such as this that the weakness of the empirical method begins to appear. Even so, when applied to the GPC analysis of a broad distribution polymer of $\bar{M}_n \approx 178{,}000$ and $\bar{M}_w \approx 450{,}000$, the total discrepancy is reduced to about 6%.

Table IV

Calculated Mark-Houwink Constants for Poly(styrene-co-methyl methacrylate) Block Copolymers at Several Compositions in Different Solvents after the Method of Runyon et al (11)

Copolymer Composition	THF		MEK		Toluene		n-Chlorobutane	
(wt. fraction styrene)	K ($x10^3$ mL/g)	a	K ($x10^4$ mL/g)	a	K ($x10^3$ mL/g)	a	K ($x10^3$ mL/g)	a
0.2	11.335	0.705	8.468	0.702	8.533	0.722	40.423	0.529
0.3	10.658	0.712	9.434	0.694	9.348	0.718	36.046	0.544
0.4	10.016	0.720	10.498	0.685	10.237	0.714	32.071	0.560
0.5	9.408	0.727	11.670	0.676	11.206	0.710	28.466	0.575
0.6	8.832	0.735	12.959	0.668	12.261	0.706	25.206	0.592
0.7	8.286	0.742	14.375	0.660	13.410	0.701	22.263	0.608
0.8	7.770	0.750	15.929	0.651	14.660	0.698	19.613	0.624

Table V

Calculated Mark-Houwink Constants for Poly(styrene-co-methyl methacrylate) Block Copolymers at Several Compositions in Different Solvents after the Method of Chang (12)

Copolymer Composition	THF		MEK		Toluene		n-Chlorobutane	
(wt. fraction styrene)	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a
0.2	11.412	0.706	8.513	0.700	8.752	0.720	39.737	0.535
0.3	10.774	0.713	9.496	0.691	9.652	0.715	35.482	0.552
0.4	10.169	0.721	10.572	0.682	10.601	0.711	31.771	0.568
0.5	9.590	0.728	11.748	0.673	11.602	0.707	28.488	0.583
0.6	9.033	0.736	13.031	0.665	12.656	0.703	25.542	0.598
0.7	8.493	0.743	14.430	0.657	13.765	0.699	22.853	0.613
0.8	7.962	0.750	15.957	0.649	14.932	0.696	20.340	0.627

Statistical Copolymers

The application of equation (15) to the estimation of Mark-Houwink constants of statistical copolymers is much more difficult than for block copolymers. Because heterointeractions play an important role in the determination of coil size in solution, it is necessary to know the fractions of homo and hetero diads present in the polymer chain as well as the homo and hetero Mark-Houwink constants.

The fractions of homo and heterodiads may be either determined spectroscopically (37) or calculated from the reactivity ratios and feed composition assuming a simple copolymer (39) or other model. If the Mayo-Lewis (39) copolymer equation applies then the mole fractions (N_{ii}) of the various diad types can be calculated from the following well-known expressions (40):

$$N_{12} = \frac{P_{12}P_{21}}{0.5(P_{12} + P_{21})} \tag{20}$$

$$N_{11} = 0.5N_{12}\left[\frac{1}{P_{12}} - 1\right] \tag{21}$$

$$N_{22} = 0.5N_{12}\left[\frac{1}{P_{21}} - 1\right] \tag{22}$$

where the subscripts 12 and 21 refer to the heterodiads, 11 refers to the homodiad of monomer 1, and 22 refers to the homodiad of monomer 2, and

$$P_{12} = \frac{1}{r_1\dfrac{[M]_1}{[M]_2} + 1} \tag{23}$$

$$P_{21} = \frac{\dfrac{[M_1]}{[M_2]}}{\dfrac{[M_1]}{[M_2]} + r^2} \tag{24}$$

The term, P_{ij}, denotes the probability of occurrence of an M_iM_j sequence, $[M_1]/[M_2]$ denotes the ratio of concentration or mole fractions of monomers 1 and 2 in the feed, and r_1 and r_2 are the reactivity ratios. The mole fractions of homo and heterodiads may then be converted into weight fractions for use in equation (15). These calculations were done for several compositions of styrene-methyl methacrylate statistical copolymers, where $r_1 = 0.449$, $r_2 = 0.480$ (41). The results are tabulated in Tabel VI. The importance of taking into account the contributions of the heterointeractions is well illustrated for this case. The proportion of heterodiads present ranges to nearly 70% for the 1:1 copolymer. Even for copolymers of high content in either styrene or methyl methacrylate the amount of heterodiads present exceeds 35%.

The Mark-Houwink constants for hetero segments may be estimated in two ways. An alternating copolymer may be prepared and constants determined either classically or as described by Dobbin et al (9, 10). These constants are to be considered as equivalent to those which determine the heterointeraction contribution in a statistical copolymer. Conversely, a statistical copolymer of one composition may be prepared and its Mark-Houwink constants determined. Equation (15) could then be employed to solve for the heteroconstants from the copolymer and contributing homopolymer Mark-Houwink constants, the weight fractions of homo and heterodiads present, and Vh at several molecular weights. The copolymer Mark-Houwink constants could then be determined for any composition of the statistical copolymer as described before.

The Mark-Houwink constants for alternating poly(styrene-co-methyl methacrylate) and those for polystyrene and poly(methyl methacrylate) which are listed in Table I were used with the weight fractions of homo and heterodiads from Table VI to calculate the copolymer Mark-Houwink constants for statistical copolymers at several compositions in different solvents. These values are recorded in Table VII.

A comparison of molecular weights obtained from hydrodynamic volume using the calculated Mark-Houwink constants and values obtained experimentally (28) are presented in Table VIII for three different compositions of statistical poly(styrene-co-methyl methacrylate) in toluene and n-chlorobutane. The

Table VI

Weight Fraction of Homo and Heterodiads Present in Statistical Poly(styrene-co-methyl methacrylate) of Various Compositions

Copolymer Composition (wt. fraction styrene)	wt. Fraction Homostyrene diads (w_{11})	wt. Fraction Homomethacrylate diads (w_{22})	wt. Fraction Hetero diads (w_{12})
0.20	0.012	0.619	0.369
0.30	0.033	0.444	0.523
0.40	0.076	0.288	0.636
0.50	0.152	0.165	0.683
0.60	0.271	0.083	0.646
0.70	0.426	0.036	0.537
0.80	0.606	0.013	0.381

Table VII

Calculated Mark-Houwink Constants for Poly(styrene-co-methyl methacrylate)

Statistical Copolymers at Several Compositions in Different Solvents

Copolymer Composition	THF		MEK		Toluene		n-Chlorobutane	
(wt. fraction styrene)	K (x10^3 mL/g)	a	K (x10^3 mL/g)	a	K (x10^3 mL/g)	a	K (x10^3 mL/g)	a
0.2	10.437	0.718	8.503	0.707	8.544	0.729	26.263	0.585
0.3	9.532	0.731	9.440	0.700	9.320	0.728	20.225	0.619
0.4	8.789	0.742	10.457	0.693	10.159	0.727	16.375	0.647
0.5	8.213	0.750	11.570	0.686	11.081	0.723	14.168	0.665
0.6	7.787	0.756	12.819	0.677	12.121	0.718	13.190	0.675
0.7	7.473	0.760	14.218	0.667	13.282	0.712	13.056	0.677
0.8	7.220	0.763	15.791	0.657	14.570	0.705	13.437	0.673

Table VIII

Experimental Mark-Houwink Constants and Comparison of Molecular Weights Obtained from Hydrodynamic Volumes Using Experimental and Calculated Mark-Houwink Constants for Different Composition Statistical Poly(styrene-co-methyl methacrylate) Samples

Copolymer Composition (wt. fraction styrene)	Solvent	K ($\times 10^3$ mL/g) (experimental)	a (experimental)	Molecular Weight (from experimental values)	Molecular Weight (from calculated values)	Hydrodynamic Volume
0.30	toluene	11.4	0.70	1×10^{5}	0.932×10^{5}	2.394×10^{-18}
				1×10^{6}	0.898×10^{6}	1.200×10^{-16}
	n-chlorobutane	26.5	0.60	1×10^{5}	1.032×10^{5}	1.760×10^{-18}
				1×10^{6}	1.005×10^{6}	7.007×10^{-17}
0.57	toluene	13.2	0.71	1×10^{5}	0.999×10^{5}(a)	3.111×10^{-18}
				1×10^{6}	0.986×10^{6}(a)	1.595×10^{-16}
	n-chlorobutane	24.9	0.63	1×10^{5}	1.078×10^{5}(b)	2.336×10^{-18}
				1×10^{6}	1.016×10^{6}(b)	9.965×10^{-17}
0.71	toluene	8.32	0.75	1×10^{5}	0.982×10^{5}	3.107×10^{-18}
				1×10^{6}	1.034×10^{6}	1.747×10^{-16}
	n-chlorobutane	17.6	0.67	1×10^{5}	1.151×10^{5}	2.617×10^{-18}
				1×10^{6}	1.146×10^{6}	1.224×10^{-16}

calculated values of (a) $K = 11.785 \times 10^{-3}$ $a = 0.720$

(b) $K = 13.384 \times 10^{-3}$ $a = 0.673$

applicable molecular weight range of the experimental constants is ~10^5-10^6, and consequently the comparison is restricted to that range. The agreement of molecular weights obtained from the calculated and experimental constants is excellent. Only in one case, the 7:3 styrene-methyl methacrylate copolymer in n-chlorobutane, is there deviation between the two values of about 15%; in all other cases agreement is within 10%. Again, the discrepancies may perhaps be ascribed to the experimental limitations in determining the Mark-Houwink constants as described before.

Although no other methods have been postulated for the correlation of hydrodynamic volume to molecular weight of statistical copolymer, Chang's hypothesis for block copolymers (12) may be extended towards application for statistical copolymer analysis. This can be done by inserting the heterodiad contributions into equations (18) and (19) as follows:

$$M_c = M_{11} + M_{22} + M_{12} \tag{25}$$

$$M_A = M_{11} + \left[\frac{K_{22}}{K_{11}} M_{22}^{(a_{22}+1)}\right]^{1/(a_{11}+1)} + \left[\frac{K_{12}}{K_{11}} M_{12}^{(a_{12}+1)}\right]^{1/(a_{11}+1)} \tag{26}$$

The copolymer Mark-Houwink constants may then be calculated from these equations as previously described. Table IX lists the results of these calculations for several compositions of statistical poly(styrene-co-methyl methacrylate) in four solvents. The values obtained according to this method are almost identical to those calculated according to equation (15) in all cases except for the n-chlorobutane solvent system. Even so, a comparison of molecular weights calculated from hydrodynamic volumes in the applicable range using the two methods show agreement within 5% in all cases. The method of Runyon and coworkers (11) does not lend itself for application in a statistical copolymer system, because of its empirical nature.

The values of both K and a, as determined from equation (19) for statistical copolymers are composition dependent as in the block copolymers

Table IX

Calculated Mark-Houwink Constants for Poly(styrene-co-methyl methacrylate) Statistical Copolymers at Several Compositions in Different Solvents after Chang (12)

Copolymer Composition	THF		MEK		Toluene		n-Chlorobutane	
(wt. fraction styrene)	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a	K ($\times 10^3$ mL/g)	a
0.2	10.740	0.718	8.107	0.707	8.295	0.729	28.050	0.581
0.3	9.877	0.730	9.003	0.700	9.052	0.728	22.037	0.614
0.4	9.113	0.741	10.038	0.693	9.904	0.727	17.937	0.641
0.5	8.473	0.749	11.199	0.685	10.850	0.723	15.331	0.660
0.6	7.970	0.756	12.489	0.676	11.906	0.718	13.922	0.671
0.7	7.584	0.760	13.906	0.667	13.068	0.712	13.416	0.674
0.8	7.284	0.763	15.496	0.656	14.360	0.705	13.521	0.672

case. However, because of the influence on coil size of the heterointeractions, both constants are weighted towards those of the heterodiads. This is especially true at compositions approaching 1:1 styrene-methyl methacrylate where the proportion of heterodiads is greatest. This manifests itself in a significant deviation in the plots of copolymer composition vs. both K and a from those obtained for the block copolymers. This is shown for both tetrahydrofuran and n-chlorobutane in Figures 5-8.

The values of the hetero Mark-Houwink constants, relative to those of the homopolymers, provide a comparative measure of the compatibility of the two components in a particular solvent system. The interaction of two components which are incompatible will expand the coil size relative to the non-interactive, i.e. block case, because of segmental repulsions. Conversely, attractive interactions will contract the coil size relative to the non-interactive case. The solvent, of course, plays a large role in these interactions. As a result, a solvent system which is of approximately the same quality for both homopolymer components would expand the copolymer coil (where repulsive interactions are present) to a substantially smaller extent than when it is a good solvent for one component and a poor solvent for the other. This is because the solvated segments of the heterodiad are of increased incompatibility in the latter case.

Table X shows the fraction of volume increase of the statistical poly(styrene-co-methyl methacrylate) over those of the block copolymers at different compositions in the four solvents studied. In all cases, the amount of volume increase was composition dependent, and reached a maximum where the proportion of heterodiads was greatest, at about 1:1 styrene-methyl methacrylate content. In addition, the maximum volume increase ranged from about 14% in methyl ethyl ketone, a solvent which is of approximately the same quality for polystyrene as poly(methyl methacrylate), to about 61% in n-chlorobutane which is a fairly good solvent for polystyrene but a Theta solvent for poly(methyl methacrylate). Maximum increases in volume for tetrahydrofuran and toluene were both about 19%.

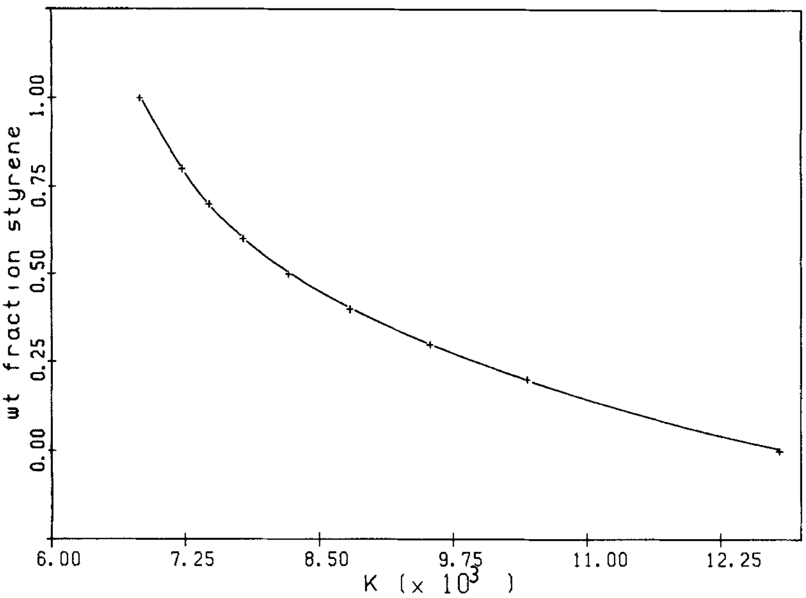

Figure 5. Statistical Copolymer Composition vs. K in THF.

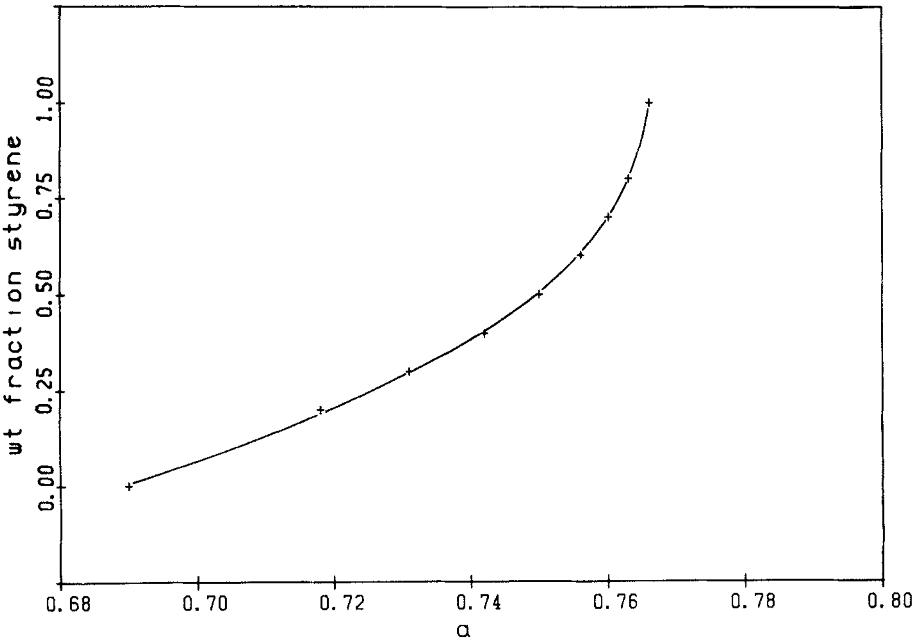

Figure 6. Statistical Copolymer Composition vs. a in THF.

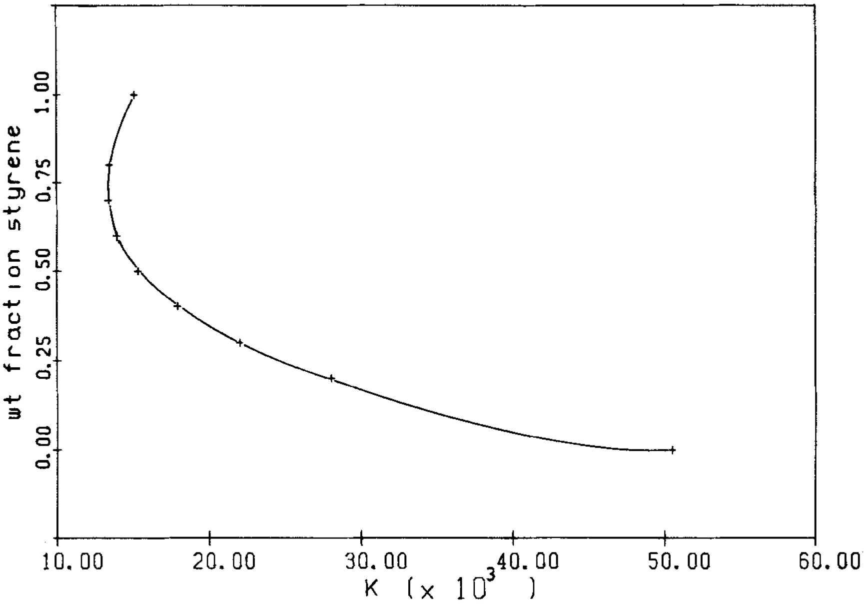

Figure 7. Statistical Copolymer Composition vs. K in n-Chlorobutane.

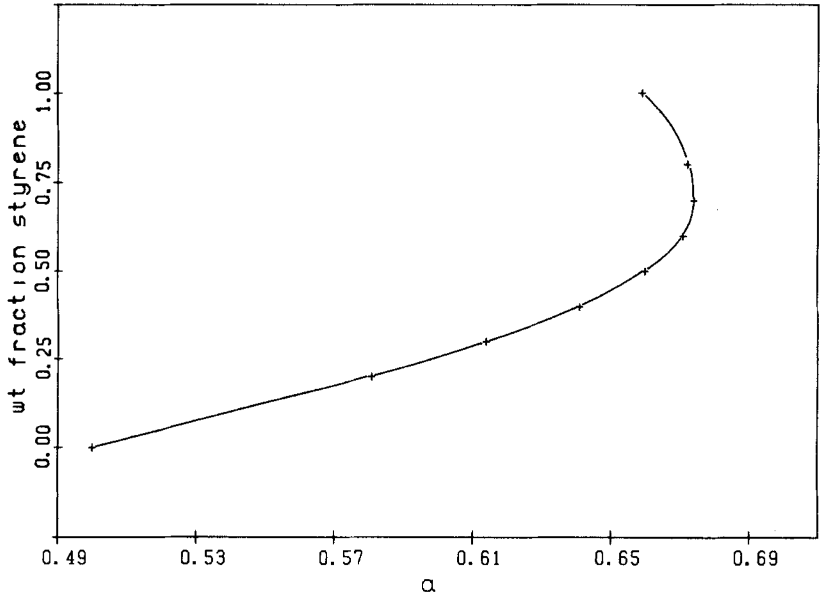

Figure 8. Statistical Copolymer Composition vs. a in n-Chlorobutane.

Table X

Comparison of Hydrodynamic Volumes Calculated from Mark-Houwink Constants of Block and Statistical Poly(styrene-co-methyl methacrylate) of Different Compositions in Several Solvents for Molecular Weight of 1 x 10^6

Solvent	Copolymer Composition (wt. frac. St.)	Hydrodynamic Volume		Fraction Volume Increase
		Block Copolymers (x10^{16})	Statistical Copolymers (x10^{16})	
THF	.2	1.268	1.409	.1113
	.3	1.347	1.540	.1436
	.4	1.392	1.653	.1876
	.5	1.460	1.726	.1820
	.6	1.510	1.778	.1768
	.7	1.585	1.803	.1372
	.8	1.642	1.815	.1057
MEK	.2	0.910	0.986	.0831
	.3	0.901	0.994	.1032
	.4	0.888	0.999	.1256
	.5	0.884	1.004	.1355
	.6	0.865	0.982	.1353
	.7	0.856	0.949	.1088
	.8	0.855	0.918	.0728
toluene	.2	1.212	1.343	.1084
	.3	1.268	1.445	.1394
	.4	1.302	1.553	.1928
	.5	1.349	1.603	.1881
	.6	1.411	1.637	.1597
	.7	1.450	1.651	.1385
	.8	1.505	1.644	.0924
n-chlorobutane	.2	0.424	0.564	.3304
	.3	0.471	0.695	.4759
	.4	0.518	0.829	.5990
	.5	0.573	0.920	.6055
	.6	0.635	0.983	.5472
	.7	0.697	1.000	.4340
	.8	0.758	0.974	.2855

It should be possible, therefore, to exploit this phenomenon to obtain a qualitative measure of relative compatibilities or incompatibilities of different polymers in different solvent systems. This may be done simply by estimating the Mark-Houwink constants of the statistical copolymers whose constitutive homopolymers are to be studied in the desired solvents. Plots of the copolymer composition vs. K or a are then constructed. A concave distortion from the block copolymer plot would indicate repulsive interactions and hence incompatibility and convex deviation would indicate attractive interactions and compatibility. The relative degree of deviation is an expression of the relative degree of compatibility or incompatibility between the two polymers. A comparison of Figures 5 and 6 with Figures 7 and 8 shows that for the styrene/methyl methacrylate system, incompatibility in n-chlorobutane is much more acute than in tetrahydrofuran.

GPC Analysis

The use of copolymer Mark-Houwink constants, determined as described above is most easily applied to the GPC analysis of samples with homogeneous composition, i.e. low conversion, constant feed or azeotropically produced copolymers. This is because only one detector and a single set of Mark-Houwink constants are then required. The situation becomes more complex for copolymers of heterogeneous composition. In that case, one requires a method for converting the GPC trace into weight fraction of eluting copolymer and following the composition change with elution volume. The first requirement may be fulfilled with the use of a densimeter detector whose response factor has been shown to be composition independent to a first approximation (42). The second requirement can be fulfilled if one uses a calibrated second detector such as infrared (IR).

GPC analysis of ternary and higher order copolymers may be accomplished even with heterogeneous samples provided that one can follow the copolymer composition--with e.g. a multiband or Fourier transform IR detector--and determine accurately the weight fractions of homo and heterodiads present at each weight fraction in a statistical system. This would entail expanding equations (19-23) to accommodate higher order copolyerizations.

Conclusions

A method for the calculation of Mark-Houwink constants for both block and statistical copolymers has been successfully applied to the styrene methyl methacrylate system in several solvents. Agreement of molecular weights calculated from Vh using these constants and experimental values is very good. Comparison between this and other predictive methods yield results which are also in good agreement. Plots of copolymer composition vs. K or a may be used as a qualitative measure of relative polymer compatibilities in solution. The ability to calculate Mark-Houwink constants at any copolymer composition enables GPC analysis of those copolymers provided that the weight fraction of eluting copolymer and copolymer composition can be followed. Application of GPC to the analysis of higher order copolymers is possible but becomes increasingly more complex as the number of components increases.

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Appendix I

The mean squared end-to-end distance of a freely orienting chain consisting of x_a segments each of length ℓ_a is:

$$\bar{d}_a^2 = x_a \ell_a^2 \qquad \text{(I-1)}$$

where $d_a = 2r_a$.

Similarly, the mean squared end-to-end distance of a freely orienting macromolecule with x_b segments of length ℓ_b is:

$$\bar{d}_b^2 = x_b \ell_b^2 \qquad \text{(I-2)}$$

If one end of the first molecule were attached to an end of the second polymer the mean squared end-to-end distance of the combined chain would be:

$$\bar{d}_{a+b}^2 = x_a \ell_a^2 + x_b \ell_b^2 \qquad \text{(I-3)}$$

Similarly, for a macromolecule comprising n subsections, each consisting of x_i segments of length ℓ_i:

$$\bar{d}_n^2 = \sum_{i=1}^{n} x_i \ell_i^2 = \sum_{i=1}^{n} \bar{d}_i^2 \qquad \text{(I-4)}$$

The relations quoted above apply also to copolymers if ℓ is taken to mean an average bond length.

Equation (I-4) shows that the squared end-to-end distance of a random coil macromolecule equals the sums of the squares of the end-to-end distances of its segments.

The mean squared end-to-end distance of a real polymer chain is given by the same formulas as those above with β_i^2 substituted for the ℓ_i^2 of a freely orienting chain. Here β_i^2 is a constant characteristic of the particular polymer to take account of restricted bond angles and preferred conformations.

In the unperturbed state the mean squared end-to-end distance is often represented as:

$$\bar{d}_o^2 = \sum_{i=1}^{n} x_i \beta_i^2 = \sum_{i=1}^{n} (\bar{d}_i^2)_o \qquad \text{(I-4a)}$$

In solution the dimensions of the polymer coil are perturbed by the solvent and the relations operating are amended by including Flory's chain expansion factor α. In the case of interest here each segment may have a different expansion factor, α_i, with a common solvent. Considering solvent-perturbed dimensions:

$$\bar{d}^2 = \sum_{i=1}^{n} x_i \beta_i^2 \alpha_i^2 = \sum_{i=1}^{n} \bar{d}_i^2 \qquad \text{(I-5)}$$

For random coil polymers the radius of gyration is related to the end-to-end distance by:

$$\bar{r}_G^2 = \frac{\bar{d}_o^2}{6} \qquad \text{(I-6)}$$

It is also expected theoretically (43) and experimentally (44) that the hydrodynamic radius is related by a constant factor to the radius of gyration and hence to the hydrodynamic radius.

As a result, equation (8) of this paper follows directly from equation (I-5). Equation (8) applies rigorously to polymers in which the segmental dimensions are described by equation (I-1) (with β substituted for ℓ). This includes block and graft copolymers with long, flexible segments. In a more general sense, equation (8) provides a suitable functional form for describing copolymers. For a statistical copolymer, the equation serves as a framework for group contribution calculations, as in this article, although the individual segment sizes may have no physical meaning.