# A Note on Intrinsic Viscosity–Molecular Weight Relationships

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It is well known that a simple equation of the form

$$[\eta] = K_m M^a \qquad (1)$$

is of general applicability in describing the relationship between intrinsic viscosity and molecular weight for a wide range of polymeric substances. The values for the constants $K_m$ and $a$ have been obtained for a number of polymer–solvent pairs, and eq. (1) has been used widely for the determination of molecular weights of high polymers. This relation is empirical in origin and its theoretical basis remains an unsettled question. With a few exceptions, however, the theoretical expressions obtained by Flory and Fox[1] can be approximated quite closely by this simple equation.

The purpose of this note lies in demonstrating that there exists a specific relationship between $K_m$



Fig. 1. Relationships between $K_m$ and $a$ obtained for carefully fractionated samples of various polymers: ($\triangle$) polybutadiene, ($\odot$) polyvinyl chloride, ($\oplus$) polyvinyl alcohol, ($\blacktriangledown$) cellulose nitrate, ($\boxdot$) polyvinyl pyrrolidone, ($\bullet$) polystyrene, ($\times$) polymethyl methacrylate.

and $a$, and that this relationship can be derived theoretically. The result furnishes not only some suggestions for the improvement of recent theories on intrinsic viscosity, but also useful information concerning molecular heterogeneity and chain configurations of polymer molecules.

When the values of $K_m$ for a series of well-fractionated polymer homologs in various solvents (mixed or pure solvents)[2–7] are plotted against the corresponding values of $a$, relationships such as those shown in Figure 1 are obtained. Similar relationships are found for the solutions in a single solvent of a series of fractionated polymer samples (for instance, polyvinyl chloride[8] or polybutadiene[9]) polymerized under different conditions. It is of interest that plots of $K_m$ vs. $a$ for various polymeric substances all fall onto either of two typical curves, one for flexible, noncrystallizable polymers and the other for semiflexible, crystalline polymers. This uniformity, however, fails for polymer samples from a different source or for data obtained by different authors.

An attempt will be made in the following pages to put these relationships between $K_m$ and $a$ on a theoretical basis.

Flory and Fox[1] showed that the intrinsic viscosity should depend upon molecular weight in accordance with the formulas

$$[\eta] = KM^{1/2}\alpha^3 \qquad (2)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(\varphi_1 - \kappa_1)M^{1/2} \qquad (3)$$

The quantities occurring in these equations are defined in their paper.[1] Combining eqs. (1) and (2), we obtain

$$\alpha^3 = (K_m/K)M^{(a-1/2)} \equiv AM^\beta \qquad (4)$$

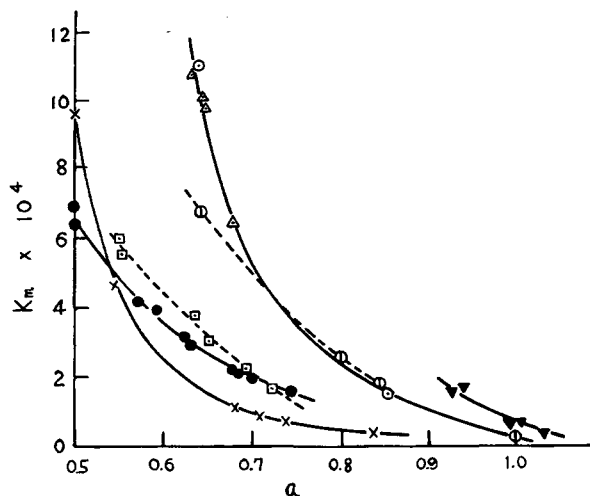We make use of eqs. (3) and (4) to obtain

$$1 + [2C_M(\varphi_1 - \kappa_1)M^{(1/2-\beta)}/A] = (AM^\beta)^{2/3} \quad (5)$$

Differentiation of the logarithms of both sides of eq. (5) with respect to $\ln M$ leads to

$$\beta = 1/[(10/3) + (4/3)(A/x)] \quad (6)$$

where $x = 2C_M(\varphi_1 - \kappa_1)M^{(1/2-\beta)}$.

It is easily seen from eq. (6) that the theoretical expression of Flory and Fox can be reduced by approximation to eq. (1) (the experimental relationship) only when $\beta < 0.3$.

By substitution of this expression for $x$ in eq. (5), we obtain

$$1 + x/A = A^{2/3}M^{2\beta/3} \quad (5a)$$

In the range $0 < \beta < 0.3$, $M^{2\beta/3}$ varies only slightly with $M$ and can be approximated by

$$M^{2\beta/3} = M_0^{2\beta/3}[1 + {}^2/_3\beta\Delta M/M +$$
$$\ldots] \cong M_0^{2\beta/3} \quad (7)$$

where $M_0$ is a type of average molecular weight over the range of concern and $\Delta M = M - M_0$. Making use of eqs. (5a), (6), and (7), we obtain

$$A^{2/3} = (K_m/K)^{2/3} =$$
$$[(^4/_3)(1/\beta - {}^{10}/_3)^{-1} + 1]/M_0^{2\beta/3} \quad (8)$$

Equation (8) is nothing but the theoretical relationship between $K_m$ and $a$ (or $\beta$). In arriving at this result only one approximation has been made, that in eq. (7). It must be noted, however, that strictly speaking, eq. (1) is only an approximate form and should be sufficiently accurate only in a narrow range of molecular weights, insofar as the theory of Flory and Fox is valid (since $M^{2\beta/3}$ in eq. (5a) depends, although slightly, upon molecular weight). The relationship between $K_m$ and $a$ is affected by $K$ and $M_0$ (i.e., the molecular weight range covered by the intrinsic viscosity-molecular weight studies). Since $K$ and $M_0$ do not depend on the type of solvent, however, it is reasonable that such a relationship as was shown in Figure 1 has been obtained for a polymer in several solvents.

In order to confirm quantitatively the validity of eq. (8), we have plotted against $\beta$ the left-hand side of the equation (9):

$$- \ln K_m + {}^3/_2 \ln$$
$$[(^4/_3)(1/\beta - {}^{10}/_3)^{-1} + 1] =$$
$$\beta \ln M_0 - \ln K \quad (9)$$

which is easily obtained from eq. (8). Typical results are shown in Figure 2 for polymethyl

methacrylate[2] and polystyrene.[3] The indicated linear relationships show very good agreement between theory (i.e., eq. (8)) and experiment. Furthermore, $K$ and $M_0$ determined by the intercept and the slope of the plots, respectively, are of reasonable orders of magnitude.

The values of $M_0$ thus determined is nearly equal to the arithmetical average of the upper and lower limits of the molecular weight range covered; for instance, in the case of polymethyl methacrylate, we obtained $M_0 = 2.51 \times 10^6$ from the above graphical method and $M_0 = 2.2 \times 10^6$ as the average of the limits of the molecular weights $4 \times 10^5$ and $4 \times 10^6$. Subsequently, therefore, we employed the latter convenient method of determining $M_0$, although inevitably some error was introduced. Once $K_m$ and $a$ have been obtained for a given polymer-solvent pair, the one unknown constant $K$ can be computed by use of eq. (8).

The above discussion, however, concerns only molecularly homogeneous polymer, as does the theory of Flory and Fox[1] on which the above treatment has been based. For heterogeneous polymers eq. (1) must be rewritten

$$[\eta] = \Psi K_m \bar{M}^a \quad (1a)$$

where $\Psi$ is a numerical constant denoting the molecular heterogeneity and $\bar{M}$ is the average molecular weight (the type of average depending on the method of measurement) of the fractionated or unfractionated, heterogeneous polymer. It must be noticed that in writing $[\eta] = K_m\bar{M}_v^a$, one usually introduces the molecular heterogeneity into the viscosity-average molecular weight, $\bar{M}_v$. Strictly
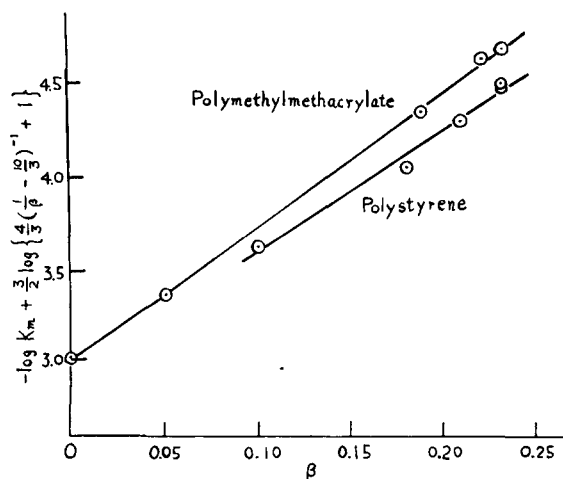


Fig. 2. Examination of the validity of eq. (8): typical plots of the left-hand side of eq. (9) against $\beta$.

TABLE I
Calculation of $K^*$ by Eq. (8) from the Values in the Literature of $K_m$ and $a$
for Various Polymer-Solvent Pairs

| System | | Temp., °C. | Molecular weight × 10^-3, range | $M_0 \times 10^{-3}$ | Re-marks[a] | $K_m \times 10^4$ | $a$ | $K^* \times 10^4$ | $K \times 10^4$ | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Polymer | Solvent | | | | | | | | | |
| Polystyrene | Benzene | 25 | 5-45 | 25 | C, u | 4.40 | 0.65 | 12.13 | | 10 |
| | | 25 | 5-45 | 25 | C, f | 2.92 | 0.65 | 8.05 | 8.05 | 10 |
| | | 30 | 10-600 | 305 | O, u | 1.74 | 0.71 | 9.19 | (30°C.) | 11 |
| Polyisobutylene | Diisobutylene | 20 | 6-1300 | 650 | O, f | 3.59 | 0.64 | 14.92 | | 12 |
| | Carbon tetra-chloride | 30 | 6-1300 | 650 | O, f | 4.52 | 0.64 | 18.78 | | 13 |
| | Cyclohexane | 30 | 6-3200 | 1600 | O, f | 2.77 | 0.69 | 15.35 | 10.7 | 14 |
| | Benzene | 25 | 1-1300 | 650 | O, f | 8.3 | 0.53 | 11.62 | (24°C.) | 15 |
| | | 30 | 1-1300 | 650 | O, f | 6.1 | 0.56 | 11.81 | | 15 |
| | | 40 | 1-1300 | 650 | O, f | 4.3 | 0.60 | 12.48 | | 15 |
| Polymethyl methacrylate | Methyl ethyl ketone | 25 | 770-1440 | 1105 | L, f | 0.68 | 0.72 | 4.77 | | 16 |
| | | 25 | 400-4000 | 2200 | L, f | 0.71 | 0.72 | 5.80 | | 2 |
| | Acetone | 25 | 770-1440 | 1105 | L, f | 0.75 | 0.70 | 5.02 | | 16 |
| | | 25 | 400-4000 | 2200 | L, f | 0.96 | 0.69 | 7.00 | 6.5 | 2 |
| | Toluene | 25 | 400-4000 | 2200 | L, f | 0.71 | 0.73 | 5.80 | (30°C.) | 2 |
| Polybutadiene[b] | Toluene | | | | | | | | | |
| (50°C., 27.1%) | | 25.9 | 30-120 | 75 | O, f | 6.5 | 0.67 | 23.31 | | 9 |
| (5°C., 64.5%) | | 25.9 | 30-1000 | 515 | O, f | 26.4 | 0.55 | 45.48 | | 9 |
| (5°C., 30.5%) | | 25.9 | 30-1000 | 515 | O, f | 10.6 | 0.64 | 42.61 | 23.2 (for gutta-percha) | 9 |
| (-20°C., 65%) | | 25.9 | 30-1000 | 515 | O, f | 10.6 | 0.63 | 36.44 | | 9 |

[a] C indicates cryoscopic measurement, O osmometry, L light scattering, u unfractionated polymer, and f fractionated polymer.

[b] The figures in parentheses indicate the temperature of polymerization and conversion, respectively.

speaking, the nature of $\Psi$ depends on the exponent $a$ of eq. (1a). However, it is not sensitive to the value of $a$ over the range of concern. It is thus concluded that eq. (8) is valid also for heterogeneous polymers if $K$ is simply replaced by $K^*(= \Psi K)$.

In Table I values for $K^*$ are computed from $K_m$ and $a$ obtained for several polymer-solvent pairs[10-16] for which the values of Flory's parameter $K$ are known.[17] Table I provides us with important information on the exact meaning of the arbitrary constants $K_m$ and $a$ and their variation with molecular heterogeneity, structure, and other factors.

At first sight, it is seen that the values thus obtained for $K^*$ do not fluctuate greatly for a polymeric substance in spite of remarkable variation in the corresponding $K_m$-values; this agrees with the behavior predicted on the basis of the above treatment. More close inspection of these values, however, indicates that an "average" molecular heterogeneity of a series of fractionated (or unfractionated) polymer homologs is reflected in these values of $K^*$; for instance, the value found for $K^*$ is obviously greater for the unfrac-

tionated samples than for the fractionated samples of polystyrene.[10] When the osmotic or cryoscopic method is used for absolute molecular weight determination, $K^*$ is usually greater than Flory's parameter $K$, which was obtained for carefully fractionated samples. On the other hand, when the light-scattering method is used (cf. polymethyl methacrylate in Table I), the value of $K^*$ approaches that obtained for $K$ and often becomes smaller than the latter. This is indicative of the well-known fact that the light-scattering method gives the weight-average molecular weight, which is closer than the other average weights to the so-called viscosity-average molecular weight, and hence the efficiency of fractionation is less important.

In view of this effect of molecular heterogeneity, it is rather natural that no consistent relationship was found between $K_m$ and $a$ when comparisons were made between values for polymer from different sources, or between values given in several literature reports on the same polymer-solvent combination. However, this fact can be utilized

to obtain a measure of the molecular heterogeneity of the samples used. Fairly good agreement is obtained between the $K^*$ values computed from the light-scattering data obtained by different authors[2,16] for different samples of polymethyl methacrylate. It may be said, therefore, that the disparities in $K^*$ for polyisobutylene samples from different sources (molecular weights of which were determined by the osmotic method) are due mainly to differences in molecular heterogeneity (see Table I).

The structural features of polymer chains should be reflected in $K$ and, consequently, in $K^*$ obtained in the manner described above. An attempt was made to test the dependence of $K^*$ upon temperature for polyisobutylene solutions in benzene,[15] but an unreasonable result (positive temperature coefficient) was obtained (see Table I), probably owing to the fact that the small temperature dependence was hidden within various errors inevitably introduced. It is evident, however, that the values of $K^*$ obtained for carefully fractionated samples are nearly equal to $K$; and thus they provide information concerning the inherent structural features of the polymer chain, such as flexibility, branching, and so forth.

With this in view, the results on polybutadiene for different polymerization temperatures and conversions have been given in Table I. The value obtained for $K^*$ certainly varies with the polymerization conditions, but this variation does not necessarily imply different degrees of branching. A large amount of branching in the polymers prepared at higher temperatures and conversions would cause a reduction in $K^*$ (defined by the ratio $g^{1/2}$, which is given theoretically by Zimm and Stockmayer[18]). However, the opposite is observed in this case, at least with respect to the dependency of $K^*$ upon the temperature of polymerization. It is not certain, therefore, that branching is responsible for the change in $K^*$, and two other factors must be considered. One is the variation in stereochemical structure (i.e., the proportions of 1,2 addition and cis-trans-1,4 configurations). However, according to Markovitz,[19] the changes in molecular coil dimensions (and, consequently, in $K^*$) resulting from these differences in structure are small and nearly compensate one another. Another factor is the variation in molecular heterogeneity averaged over a series of fractionated samples, which is influenced, more or less, by the heterogeneity of the original samples. In the present case, this might be partly responsible

for the change in $K^*$. Further quantitative discussion of the branching of polymer chains would be possible if examples were available in which the above-mentioned complication had been avoided. Unfortunately, we have no such examples.

We will now discuss features of interest in Figure 1. A few factors can be considered as possible explanations of the fact that the $K_m$-$a$ curves for various polymeric substances are divided into two groups. From eq. (8) it is seen that different curves should be obtained for different values of either $K$ or $M_0$. Indeed, $K_m$ increases with $M_0$ when $K$ is constant (see Table I), but it does not vary so much that the behavior shown in Figure 1 can be accounted for by this factor. The behavior in question must therefore be attributed to changes in $K$, unless the theory of Flory and Fox suffers any deficiency. It seems reasonable that the great disparity between $K$ for flexible, noncrystallizable polymers and $K$ for semiflexible, crystalline polymers (as exemplified in Table I by the remarkable differences in $K^*$ for polybutadiene and $K^*$ for the other more flexible polymers), is responsible for the existence of two distinct groups of curves. The small disparities between the curves in a group may be attributable to small changes in $K$, differences in $M_0$, and differences in molecular heterogeneity, unavoidable even in well-fractionated samples.

Another important factor may help to explain these experimental relationships. It is known that the Flory-Fox theory requires some amendment if it is to be applied to polymers with very poor chain flexibility, such as cellulose derivatives.[20-23] One of the requirements of their theory is that the internal hydrodynamic resistance must be sufficiently large that the universal constant $\Phi$ approximates its asymptotic (maximum) value[17]; however, this condition is not fulfilled for chains of poor flexibility, owing to the high degree of extension of the chains. This restriction in their theory just corresponds to the inapplicability of the present treatment to cases in which $\beta > 0.3$.

Kirkwood and Riseman[24] and Debye and Bueche[25] independently developed quantitative treatments of intrinsic viscosities of polymer solutions. Although their theoretical viewpoints differ somewhat, it may be concluded from both theories that the change of $[\eta]$ with molecular weight is closely associated with the corresponding change in hydrodynamic shielding capacity of elements in the interior of the polymer molecule. As was pointed out by Flory,[17] the effect of this factor vanishes when the total internal resistance to flow is

sufficiently great, as is usually the case. When the situation approaches the partially free-draining case, however, this effect might have to be taken into account, in addition to the volume effect.

In fact, it is seen from Figure 1 that the plots for the extended chains (the upper curve) extends to the region $0.8 < a < 1$. Therefore, an alternative explanation along the line of the Kirkwood-Riseman or Debye-Bueche theories for the existence of two distinguishable groups of curves might be possible. Such an explanation, however, seems less convincing to us than that mentioned previously, because the result obtained from the Flory-Fox theory would not be altered seriously by this factor.

It must be remarked that the above relationship between $K_m$ and $a$ is also applicable to the solution in a common solvent of a series of polymer samples polymerized under different conditions as was shown in Figure 1 for polybutadiene and polyvinyl chloride. This fact can also be interpreted in terms of the theory of Flory and Fox:[1] since $C_M$ in eq. (3) contains the term $\overline{r_0^2}/M$ (where $\overline{r_0^2}$ is the unperturbed value of the mean-square end-to-end length of the polymer chain), the inherent structural features of the chains affect, although indirectly, the long-range, volume effect, causing the differences in the exponent $a$ for these polymer samples even in a common solvent. Branching or some other factors may be considered to produce such differences. However, this line of argument seems somewhat inadequate to account for the observed great changes in $a$. The effect of the factor deduced previously from the Kirkwood-Riseman and Debye-Bueche theories might also have to be taken into account. Further experimental and theoretical studies need to be supplemented before a conclusion is drawn on these points.

Finally, we wish to stress the usefulness of the results of our investigation:

(1) When the empirical relation $[\eta] = K_m M_a$ is obtained for a series of carefully fractionated polymer homologs, the Flory parameter $K$ can be computed from the values for $K_m$ and $a;$ from $K$, quantitative information concerning the inherent structural features of the polymer chain, such as flexibility, the degree of branching, etc., can be obtained.

(2) The value of $K^*$ obtained in the manner described above provides a measure of the molecular heterogeneity inevitably present in a well-fractionated sample. Although this value gives only a measure of average heterogeneity over the series of polymer homologs used, its use furnishes a con-venient means of examining newly obtained $[\eta]$-$M$ data or of choosing the most reliable relationship for a given polymer-solvent combination from among those obtained by various authors. These relationships differ among themselves, in some cases, depending upon the efficiency of fractionation and other factors.

(3) Once $K_m$ and $a$ (and hence $K$) have been established for a given, well-fractionated polymer series in a given solvent, $K_m$ and $a$ can be easily computed for many other solvents from measurements of $[\eta]$. If $K$ is known for a given polymer, we can evaluate $K_m$ and $a$ from measurements of $[\eta]$ and $M$ for a single (carefully fractionated) sample. Only one sample need be used, and thus recourse to the usual more laborious methods is unnecessary; we have, so to speak, a "one-point method" of obtaining an intrinsic viscosity–molecular weight relationship. This method is also applicable to unfractionated polymers; moreover, the molecular heterogeneity of the samples can be estimated. An application of the method to polyacrylonitrile solutions will be reported on in the near future.

(4) It is suggested that for highly extended chains the theory of Flory and Fox may have to be modified to some extent, perhaps by combination with the Kirkwood-Riseman theory. This view is supported by the facts that in the case of greatly extended polymer chains, the intrinsic viscosity increases with $M$ raised to a power a little greater than unity, and that for polymeric substances of molecular weight less than about 30,000 the exponent $a$ often exceeds 0.8.

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## Synopsis

From an examination of experimental data on a number of series of well-fractionated polymer homologs in various solvents, interesting correlations were found between the constants $K_m$ and $a$ in the Mark-Houwink equation often used in describing the relationship between intrinsic viscosity and molecular weight. For a given series of polymer homologs in different solvents, $K_m$ regularly decreases with increasing $a$; moreover, in the $K_m$-$a$ curves, plots for various polymeric substances all conform to one of two typical curves, the one being for flexible, noncrystallizable polymers and the other for semiflexible, crystalline polymers. In this paper an attempt has been made to put these experimental relationships on a theoretical basis. Combination of the theoretical expressions obtained by Flory and Fox with the Mark-Houwink equation yields the equation

$$(K_m/K)^{2/3} = [(4/3)(1/\beta - 10/3)^{-1} + 1]/M_0^{2\beta/3}$$

where $\beta = a - 1/2$, $K$ is a constant characteristic of the polymer chain, and $M_0$ is the arithmetical average of the upper and lower limits of the molecular weight range covered. The experimental relations between $K_m$ and $a$ mentioned above can be quite adequately accounted for by this equation. Although eq. (1) was originally derived for molecularly homogeneous polymers, it has been shown to be valid also for molecularly heterogeneous polymers if $K$ is replaced by $K^*$, which reflects the molecular heterogeneity of a series of fractionated (or unfractionated) polymer homologs. Although this value gives only an average heterogeneity over a series of the polymer homologs used and depends upon the method of molecular weight determination, its use furnishes a convenient method either for the examination of newly obtained $[\eta]$ vs. $M$ data or for the choice of the most reliable relationship among those obtained by various authors for a given polymer-solvent combination. When the theory of Flory and Fox is applicable and $K$ is known for a given polymer, the Houwink constants can be easily computed through use of eq. (1) from the measurements of $[\eta]$ and $M$ for only one (carefully fractionated) sample, without recourse to more laborious methods usually used. This is, so to speak, a "one-point method" of obtaining the intrinsic viscosity-molecular weight relationship.

## Résumé

L'examen des données expérimentales sur dess éries de polymères homologues bien fractionnés dans différents solvants montre des corrélations intéressantes entre les constantes $K_m$ et $a$ de l'équation de Mark-Houwink souvent utilisée pour la relation entre la viscosité intrinsèque et le poids moléculaire. Pour une série donnée de polymères homologues dans différents solvants, $K_m$ diminue régulièrement avec l'accroissement de $a$, et de plus, dans un diagramme $K_m$ vs. $a$, tous les points pour différentes substances polymériques tombent sur deux courbes typiques, l'une pour les polymères flexibles, non cristallisables et l'autre pour les polymères semiflexibles, cristallins. Dans cet article un essai a été fait pour expliquer ces relations expérimentales sur une base théorique. En combinant les expressions théoriques obtenues par Flory et Fox avec l'équation Mark-Houwink, on obtient:

$$(K_m/K)^{2/3} = [(4/3)(1/\beta - 10/3)^{-1} + 1]/M_0^{2\beta/3} \quad (1)$$

où $\beta = a - 1/2$, $K$ est une constante caractéristique d'une chaine polymérique et $M_0$ est la moyenne arithmétique entre les limites supérieures et inférieures du domaine de poids moléculaire envisagé. Les relations expérimentales entre $K_m$ et $a$ mentionnées ci-dessus peuvent être suffisamment expliquées par cette équation. On montre que bien qu'elle ait été dérivée originairement pour les polymères homogènes, eq. (1) conserve sa validité pour les polymères hétérogènes si $K$ est remplacé par $K^*$, et l'hétérogénéité moléculaire d'une série de polymères homologues fractionnés (ou non fractionnés) se reflète elle-même dans la valeur de $K^*$. Bien que cette valeur donne seulement un hétérogénéité moyenne pour une série de polymères homologue et bien que cette valeur dépende de la méthode utilisée pour la détermination du poids moléculaire, son emploi fournit une méthode convenable pour l'examen des données nouvellement obtenues de $[\eta]$ vs. $M$ ou bien pour le choix de la relation la plus acceptable pour une combinaison polymère-solvant donnée à partir de celles obtenues par différents auteurs aui parfois diffèrent l'une de l'autre. Lorsque la théorie de Flory et Fox est applicable et lorsque $K$ est connue pour un polymère donné, les constantes de Houwink peuvent être facilement calculées au moyen de eq. (1) à partir des mesures de $[\eta]$ et de $M$ pour un seul échantillon (soigneusement fractionné) sans avoir recours aux méthodes plus laborieuses utilisées habituellement. C'est pour ainsi dire la "one point method" pour obtenir la relation viscosité intrinsèque-poids moléculaire.

## Zusammenfassung

Bei der Prüfung der experimentellen Daten einer Reihe von gut fraktionierten Polymerhomologen in verschiedenen

Lösungsmitteln wurden interessante Zusammenhänge zwischen den Konstanten $K_m$ und $a$ der zur Beschreibung von Viskositätszahl-Molekulargewichts-abhängigkeiten oft benützten Mark-Houwink-Gleichung gefunden. Für eine gegebene Reihe von Polymerhomologen nimmt $K_m$ in verschiedenen Lösungsmitteln mit steigendem $a$ in regelmässiger Weise ab und darüber hinaus fallen bei den $K_m$ vs. $a$-Kurven alle Diagramme für verschiedenartige polymere Substanzen auf zwei typische Kurvenzüge, nämlich einen für flexible nichtkristallisierbare Polymere und den anderen für semiflexible, kristalline Polymere. In der vorliegenden Mitteilung wird der Versuch unternommen die empirischen Beziehungen auf eine theoretische Grundlage zu stellen. Durch Kombination der theoretischen Ausdrücke von Flory und Fox mit der Mark-Houwink-Gleichung erhält man:

$$(K_m/K)^{2/3} = [(^4/_3)(1/\beta - {}^{10}/_3)^{-1} + 1]/M_0^{2\beta/3} \quad (1)$$

wo $\beta = a - {}^1/_2$, $K$ eine für eine bestimmte Polymerkette charakteristische Konstante und $M_0$ das arithmetische Mittel zwischen der oberen und unteren Grenze des betreffenden Molekulargewichtsbereiches ist. Die oben erwähnten empirischen Beziehungen zwischen $K_m$ und $a$ können befriedigend durch diese Gleichung wiedergegeben werden. Es wurde gezeigt, dass Gl. (1), obgleich sie ursprünglich für

molekular homogene Polymere abgeleitet wurde, ihre Gültigkeit auch für molekular heterogene Polymere beibehält, wenn nur $K$ durch $K^*$ ersetzt wird, in dessen Wert sich die molekulare Heterogenität einer Reihe von fraktionierten (oder nicht fraktionierten) Polymeren wiederspiegelt. Obwohl dieser Wert nur eine mittlere Heterogenität für die Reihe der untersuchten Polymerhomologen liefert und von der zur Molekulargewichtsbestimmung benützten Methode abhängt, liefert seine Benützung doch eine bequeme Methode, sowohl für die Überprüfung neu erhaltener $[\eta]$ vs. $M$-Daten, als auch für die Auswahl der verlässlichsten Beziehung für ein gegebenes Polymer-Lösungsmittelsystem aus den von verschiedenen Autoren erhaltenen Beziehungen, die manchmal von einander abweichen. Falls die Theorie von Flory und Fox angewendet werden kann und $K$ für ein bestimmtes Polymeres bekannt ist können die Houwink-Konstanten leicht mittels Gl. (1) aus Messungen von $[\eta]$ und $M$ an einer einzigen (sorgfältig fraktionierten) Probe, ohne Zuhilfenahme der gewöhnlich benützten, einen grösseren Aufwand erfordernden Methoden, berechnet werden. Man kann diese Methode als die "Einpunktmethode" zur Ermittlung der Viskositätszahl-Molekulargewichtsbeziehung bezeichnen.