DIMENSIONS OF LONG CHAIN MOLECULES IN DILUTE SOLUTIONS: THERMODYNAMIC EFFECTS AND INTRINSIC VISCOSITY MEASUREMENTS

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ABSTRACT

DIMENSIONS OF LONG CHAIN MOLECULES IN DILUTE SOLUTIONS: THERMODYNAMIC EFFECTS AND INTRINSIC VISCOSITY MEASUREMENTS

By

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The purpose of this work was to study different theoretical approaches which have been proposed to explain the "excluded volume" effect which is observed when studying the properties of dilute solutions of polymer molecules. In theory the polymer molecule is described statistically as a random coil of connected beads. The excluded volume effect may be thought of as an osmotic swelling of the randomly coiled chain by the polymer-solvent interactions.

This work is divided into two parts. Part one contains a discussion of excluded volume theories and the behavior of the equations resulting from theories at very large (asymptotic) and very low (near to unity) values of α, a factor expressing the linear expansion of a polymer molecule owing to polymer-solvent

interaction compared with that at the Flory (theta) temperature condition. At the Flory (theta) temperature, the polymer-solvent interaction vanishes, the excluded volume effect is not present, and the random coil end-to-end distance is a minimum similar to its dimensions in the bulk, undissolved polymer. At the theta condition the expansion factor, α is unity. The equations are

Flory: $\alpha^5 - \alpha^3 = (4/3)\ Z$

KSR: $(\alpha^3 - \alpha)(1 + 1/3\alpha^2)^{3/2} = (32/3^{5/2})\ Z$

Kurata: $(\alpha^3 - 1) + 3/8\ (\alpha^5 - \alpha^3) = (5/2)\ Z$

Fixman: $\alpha^3 - 1 = (2)\ Z$

Ptitsyn: $(4.68\,\alpha^2 - 3.68)^{3/2} - 1 = (9.36)\ Z$

FON: $\alpha^5 - 0.4931\alpha^3 - 0.2499\alpha^{-1.332} \sin(1.073 \ln\alpha)$
$- 0.5069\alpha^{-1.332} \cos(1.073 \ln\alpha) = (2.603)\ Z$

where

$$Z = (3/2\pi)^{3/2}\,\beta a^{-3}\,N^{1/2}$$

for a chain of N links of the effective chain length a. β represents the binary cluster integral, an integral function of the polymer-solvent pair potential energy function, e.g. Lennard Jones potential

for nonpolar systems. These equations were expanded in the form of power series and each equation was compared to the exact power series obtained by the perturbation theory of the excluded volume effect. This exact series is

$$\alpha^2 = 1 + (4/3)\,Z + 2.075\,Z^2 + \ldots$$

Part two contains the comparison of expansion factor calculated from these equations with experimental data for expansion factor obtained from dilute solution viscosity data from the literature. The experimental observation of dilute solution viscosity for several polymers of various molecular weights in a number of solvents along with that at the Flory (theta) temperature yields the expansion factor α for these solutions. Thus the theory and data may be compared and the influence of polymer molecular weight and polymer-solvent thermodynamics on molecular size in solution may be studied.

The conclusions as summarized are that at least for the nonpolar polymer-nonpolar solvent systems, Flory's thermodynamic equation predicts expansion factor in reasonable agreement with intrinsic viscosity measurements. The discrepancy between the experimental expansion factor function $(\alpha^5 - \alpha^3)$ and the theoretical calculation from thermodynamic parameters at low values of α.

(near to 1) could be reduced if not eliminated by the use of a function $(1 - Be^{-M})$ where B is a constant which might be related to the binary cluster integral β. For the polar systems exact values of Flory thermodynamic parameters, χ_S and χ_H, are very important in the success of the expansion factor predictions and the use of a universal entropy parameter, χ_S, equal to 0.34 in general warrants further investigation. In spite of the better success of some of the newer theories in correlating molecular weight dependence of α with experimental α values, Flory's theory offers the maximum applicability to the study of the polymer-solvent thermodynamic interactions, because the thermodynamic parameters are available from nonviscometric data sources.

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To my parents

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INTRODUCTION

During the last three decades much effort has been devoted to the development of a quantitatively adequate statistical mechanical theory of the large deviations found in polymer solutions from the ideal theormodynamic behavior represented by Raoult's law. Despite the considerable success achieved by the lattice theory of Flory[1] and Huggins,[2] the inherent complexity of the problem has so far prevented the achievement of a rigorous and complete treatment for sufficiently detailed models. For this reason the comparison of theory and experiment is still a matter of importance in apprising the adequacy of approximations made in the various derivations.

The "excluded volume" effect which is observed when studying the properties of dilute solutions of polymer molecules may be thought of as an osmotic swelling of the randomly coiled chain by the polymer-solvent interactions. In theory the polymer molecule is described statistically as a random coil of connected beads. The problem of the "excluded volume" effect has essential importance for the structural interpretation of the solution properties of linear polymer molecules because the molecular weight, temperature, and intermolecular thermodynamic interaction dependencies of solution properties are markedly influenced by the existence of this effect. Thus the study of the volume effects has been a central problem of polymer solution theory since its discovery by Flory.

The exact statistical mechanical calculation of the average dimensions of a linear polymer molecule in nonideal solvent is one of the ultimate goals of the theory of dilute polymer solutions. Unfortunately this calculation is a formidably difficult problem, even with a greatly simplified model of polymer chain such as the pearl necklace model. Since the pioneering work of Flory, a number of investigators have attempted to solve this problem by introducing various simplifying assumptions. The results so far reported are at variance with each other and with experiment, depending mainly on the assumptions used to evaluate the interaction energy of chain elements in the molecule.

PART I

THEORETICAL CONSIDERATIONS

CHAPTER I

FLORY THEORY

The dimensions of long chain molecules in solution are greatly influenced by the interactions between chain elements. The interactions may be divided into two classes:[1] The "short-range" interactions and the "long-range" interactions. Short-range interactions are those between atoms or groups separated by only a small number of valence bonds; and because of them, there is an effective constancy of bond angles.[2] The "long-range" interactions are those between nonbonded groups which are separated in the basic chain structure by many valence bonds.[2] The discussion here is limited to nonbranched chains. Polyelectrolytes are not considered.

In the absence of both types of interaction, long chain molecules would obey Gaussian or random flight statistics.[1] Of course covalent binding forces are present which fix the lengths of the chain links. Under these conditions the mean square value of the spherical radius of gyration of the random flight macromolecule is given by[1]

$$< S^2 >_{00} = l^2 n/6 \qquad (I-1)$$

where n is the number of bonds in the chain, l is the bond length, and the double zero subscript denotes lack of both kinds of interaction.

The chain without long-range interaction may be called the "unperturbed" chain,[1] and the mean square radius of gyration may be written as[2]

$$< S^2 >_0 = s l^2 n/6 \qquad (I-2)$$

where s is a "structural" parameter independent of n and accounting for the effects of the "short-range" interactions. "Long-range" interactions, on the other hand, give rise to "excluded volume" effect[1] which can be thought of as an osmotic swelling of the randomly coiled chain by the polymer-solvent interactions.[2] As a result of both types of interaction, the mean square radius of gyration of a real linear macromolecule in dilute solution is written as[1]

$$< S^2 > = \alpha^2 < S^2 >_0 = (\alpha^2 s)\, l^2 n/6 \qquad (I-3)$$

where. α is the linear expansion factor which depends on the number of bonds n as well as s and temperature. The factor s primarily represents the molecular structural features of the polymer chain while α depends upon the effects of interactions of the polymer with the solvent. For a clear understanding of the conformational properties of chain molecules in solution, separate determination of the factor α and the factor s is necessary.

It is well known that the excluded volume effect vanishes under a special condition of temperature or solvent, which is usually known as the Flory (theta) condition. Certain measurements performed on solutions under theta conditions can furnish direct knowledge of the "unperturbed" dimensions and the factor s. With the aid of Flory-Fox[3, 4] equations, viscosity measurements can furnish information on long-range interaction and the factor α. These equations are

$$[\eta] = 6^{3/2} \Phi < S^2 >^{3/2} / M \qquad \text{(I-4)}$$

$$[\eta] = [\eta]_\theta \, \alpha^3 \qquad \text{(I-5)}$$

$$[\eta]_\theta = \Phi K M^{1/2} \qquad \text{(I-6)}$$

$$K = 6^{3/2} \Phi \, (< S^2 >_0 / M)^{3/2} \qquad \text{(I-7)}$$

where $[\eta]$ and $[\eta]_\theta$ represent intrinsic viscosities in ordinary and theta solvents respectively. M is the molecular weight of the polymer and Φ and K are constants independent of M.

The ratio between the efflux times of solvent (t_0) and of solution (t) from a capillary viscometer for the same densities of the two gives relative viscosity η_{rel}. Specific viscosity $\eta_{sp} = \eta_{rel} - 1$.

The concentration dependence of the viscosity of polymer solutions is eliminated by the extrapolation of measured values of the reduced viscosity $\frac{\eta_{sp}}{C}$ or of the logarithm of the reduced viscosity $\frac{\ln \eta_{rel}}{C}$, to infinite dilution. The extrapolated value is called the intrinsic viscosity $[\eta]$. Since ϕ is supposed to be a universal constant[1] for all the flexible linear polymers, the unperturbed mean square radius of gyration $< S^2 >_0$ can readily be calculated from K. The unperturbed dimensions of various chain molecules thus determined are found in very many cases to be practically independent of the particular theta solvent employed and are thus characteristic of the chain under consideration apart from a usually slight downward trend with increasing temperature.[5] The unperturbed dimensions of various polymers in different theta solvents are listed in reference 23 and one can see that for the same polymer there is a slight variation in unperturbed dimension in different theta solvents. Table I-1 shows, from reference 23, sample entries for unperturbed end-to-end distance $(< r^2 >_0/M)^{1/2}$. The quantity $< r^2 >_0/M$ is independent of molecular weight.

Table I-1

Unperturbed End-to-End Distance $(\langle r^2 \rangle_0 / M)^{1/2}$ for the Polymers Polystyrene and Poly(methyl Methacrylate) in Different θ Solvents

Polymer	Solvent	θ Temp. ^{0}C.	$(\langle r^2 \rangle_0 / M)^{1/2}$
Polystyrene Atactic	Ethyl or Methyl Cyclohexane	~70	650 ± 15
	Cyclohexane	34	690 ± 10
	73% - trans - decalin	18	655
	100% - trans - decalin	24	670
Poly(methyl methacrylate)	Butyl Chloride	35.4	537
	3-Octanone	72	560 ± 10

Once the values of K or $\langle S^2 \rangle_0 / M$ are known, the expansion factor α can be evaluated from the ratio $([\eta]/[\eta]_\theta)^{1/3}$ or from $(\langle S^2 \rangle / \langle S^2 \rangle_0)^{1/2}$ or from $(\langle r^2 \rangle / \langle r^2 \rangle_0)^{1/2}$ where $\langle r^2 \rangle$ is the mean square end-to-end distance of a chain at the temperature of measurement and $\langle r^2 \rangle_0$ is the same at the theta temperature. For Gaussian chains the mean radius of gyration and mean square end-to-end distance are related by

$$\langle S^2 \rangle = \langle r^2 \rangle / 6 \qquad \text{(I-8)}$$

Thermodynamic analysis of the polymer-solvent system may then be accomplished with the aid of an appropriate theory such as that of Flory.[1]

$$\alpha^5 - \alpha^3 = 2C_M (1/2 - \chi) M^{1/2} \qquad \text{(I-9)}$$

or

$$\alpha^5 - \alpha^3 = 2C_M \psi [1 - \theta/T] M^{1/2} \qquad \text{(I-9a)}$$

where C_M is an essentially numerical factor for a particular polymer-solvent pair.

$$C_M = (27/2^{5/2}\pi^{3/2})(\bar{v}^2/N_A V_1)(6 < S^2 >_0/M)^{-3/2} \qquad \text{(I-10)}$$

where $\bar{v}$ is the partial specific volume of polymer, V_1 is the molar volume of solvent and N_A is the Avogadro number. According to Guggenheim's[6] more refined lattice treatment, χ is a parameter related to the local free energy of the polymer rather than simply a heat-of-mixing parameter as used by Flory.[1] The parameter χ is a dimensionless quantity which includes the interaction energy characteristic of a given solvent-solute pair. Thus χ is often written as

$$\chi = \chi_H + \chi_S \qquad \text{(I-11)}$$

where the two terms refer to a heat parameter and entropy parameter respectively. χ is a parameter characterizing the entropy of dilution of polymer with solvent. θ is defined as

$$\theta = K\,T/\psi \qquad \text{(I-12)}$$

where K is a heat parameter such that

$$\Delta \bar{H}_1 = R\,T\,K\,v_2^2 \qquad \text{(I-13)}$$

$\Delta \bar{H}_1$ is partial molar heat of dilution; and v_2 is volume fraction of polymer. Similarly

$$\Delta \bar{S}_1 = R\,\psi v_2^2 \qquad \text{(I-14)}$$

where $\Delta \bar{S}_1$ is partial molar entropy of solution.

K, ψ and χ are related as

$$K_1 - \psi = \chi - 1/2 \qquad \text{(I-15)}$$

In a poor solvent, where both K and K/ψ generally are positive, θ also will be positive. At the temperature $T = \theta$, the chemical potential due to polymer segment-solvent interactions is zero, and deviations from ideality vanish.

Equation (I-9) directs attention to a number of important characteristics of the molecular expansion factor α. In the first place α is predicted to increase slowly with molecular weight (assuming $T > \theta$) and without limit even when the molecular weight becomes very large. Secondly, α depends on the intensity of the thermodynamic interactions between solvent and polymer. The larger the factor $(1/2 - \chi)$, the greater the value of α for a given M and thus, the better the solvent, the greater the "swelling" of the molecule. χ is less than 1/2 for soluble system, approaches 1/2 at the theta condition where α tends to 1.0, and decreases when the strength of polymer solvent interaction increases, i.e. by hydrogen bonding. Ordinarily for positive θ, therefore, $\alpha^5 - \alpha^3$ may be expected to decrease as temperature is decreased in a poor solvent. Phase separation sets a practical limit on how poor a solvent may be and yet permit the existence of a stable homogeneous dilute solution.[1] θ represents the lowest temperature for complete miscibility in the given poor solvent.

Several assumptions were made in arriving at Equation (I-9). Tompa[24] discusses these assumptions quite thoroughly. Guggenheim[25] and Tompa[24] have discussed the refinements to Flory's lattice theory in detail. Most of the refinements are toward improvement of the theory. However, their approach does not remove inherent imperfections in the lattice model on which the whole theory is based.

CHAPTER II

OTHER THEORIES

Kurata, Stockmayer and Roig (KSR) Theory

Kurata, Stockmayer and Roig[26] proposed a new approximate theory of the excluded volume effect in an attempt to resolve some of the discrepancies observed in Flory's equation (I-9). Their equation is

$$\alpha^3 - \alpha = (1 + \frac{1}{3\alpha^2})^{-3/2} (4/3)^{5/2} (3/2\pi)^{3/2} \beta N^{1/2}/a^3 \quad \text{(II-1)}$$

where a is an effective bond length, and β is the binary cluster integral (see Chapter IV) of each chain element. This treatment uses an equivalent ellipsoid model for the linear polymer molecule in deriving Equation (II-1). The closed expression for excluded volume effect in terms of parameters used by Flory can be written as

$$(\alpha^3 - \alpha)(1 + \frac{1}{3\alpha^2})^{3/2} = (4/3)^{5/2} C\psi(1 - \frac{\theta}{T}) M^{1/2} \quad \text{(II-2)}$$

where C is a constant different from that of Flory's in Equation (I-9).

Fixman Theory

Fixman[11] derived an approximate differential equation to get a closed form of excluded volume effect on the basis of quite different statistical considerations. His differential equation is

$$Z\alpha (d\alpha/dZ) = 1 - \alpha^2 + 2(Z/\alpha) \qquad \text{(II-3)}$$

where α* refers to the change in end-to-end distance of a macromolecule from that of the unperturbed dimension. Fixman did not solve or analyze the above equation. When the above equation is solved with proper boundary condition ($\alpha(Z) = 1$ for $Z = 0$ at $T = \theta$), one obtains

$$\alpha^3 - 1 = 2Z \qquad \text{(II-4)}$$

Kurata Theory

An approximate closed expression for the excluded volume effect has been developed by Kurata[29] with the help of the uniform expansion model of perturbed chains. His equation is

$$(\alpha^3 - 1) + (3/8)(\alpha^5 - \alpha^3) = (5/2) Z \qquad \text{(II-5)}$$

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*See Chapter IV for difference between α and α_L.

The uniform expansion approximation consists in replacing the perturbed chain by an equivalent Gaussian chain whose average dimension is chosen so as to coincide with that of the original chain. Undoubtedly the uniform expansion model becomes increasingly poor as Z is increased toward infinity.

Kurata's equation was derived in closed form from the basic equation developed by Fujita et al.[30] This equation is a simple hybrid form between the Flory equation

$$\alpha^5 - \alpha^3 = (4/3)\, Z$$

and the Fixman equation

$$(\alpha^3 - 1) = 2Z$$

The proportion of hybridization is 73% for the Fixman character and 27% for the Flory character.[29]

Fujita, Okada and Norisuye (FON) Theory

Fujita, Okada and Norisuye[30] derived a closed expression for excluded volume effect subject to the condition that interaction of a pair of chain segments is characterized by the binary cluster integral β. Starting with this expression and estimating the total number of segmental collisions in such a chain by use of the approximation of uniform distribution of segments and of the ellipsoid approximation to the overall shape of the molecule, an approximate closed expression for α was obtained. The result is

$$\alpha^5 - 0.4931\alpha^3 + 0.2499\alpha^{-1.332} \sin(1.073 \ln\alpha)$$
$$- 0.5069\alpha^{-1.332} \cos(1.073 \ln\alpha) = 2.630\, Z \qquad \text{(II-6)}$$

The validity of the above relation is attributed almost entirely to the appropriateness of the physical assumptions used to estimate the total number of two-body collisions of chain segments in the perturbed polymer molecule. Those assumptions were:

a. The approximation of uniform distribution of chain segments in the molecule considered,

b. The use of an ellipsoid model to represent the average shape of such a molecule, and

c. The uniform expansion approximation to obtain expressions for the major and minor axis of the ellipsoid.

In fact all the treatments of the excluded volume effect which are approximate have had recourse to approximations similar to those mentioned above.

Ptitsyn Theory

The approximate theory of Ptitsyn,[33] which takes interaction between segments of the chain roughly into account, leads to an equation differing substantially from that of Flory. Ptitsyn's equation is

$$(4.8\,\alpha^2 - 3.68)^{3/2} - 1 = 9.36\,Z \qquad \text{(II-7)}$$

It was derived by means of a somewhat artificial modification of the approach which was used by Fixman for the derivation of his equation. Ptitsyn took into account that the volume effects lead to a non-Gaussian distribution function $w(h)$ for the end-to-end distance. The non-Gaussian character of the function $w(h)$ implies that the influence of the volume effects on the chain dimensions cannot be considered as a simple increase in the length of a statistical element of the chain.

CHAPTER III

ASYMPTOTIC BEHAVIOR OF DIFFERENT THEORIES

The behavior of an equation in the limit of large Z and hence large α is considered. In summary the appropriate equations are:

Flory:[31] $$\alpha^5 - \alpha^3 = (2.60)\,Z \qquad \text{(III-1)}$$

KSR:[26] $$(\alpha^3 - \alpha)\left(1 + \frac{1}{3\alpha^2}\right)^{3/2} = (32/3^{5/2})\,Z \qquad \text{(III-2)}$$

Kurata:[29] $$(\alpha^3 - 1) + \frac{3}{8}(\alpha^5 - \alpha^3) = (5/2)\,Z \qquad \text{(III-3)}$$

Fixman:[32] $$(\alpha^3 - 1) = (2)\,Z \qquad \text{(III-4)}$$

Ptitsyn:[33] $$(4.68\alpha^2 - 3.68)^{3/2} - 1 = (9.36)\,Z \qquad \text{(III-5)}$$

FON:[30] $$\begin{aligned} &\alpha^5 - .4931\alpha^3 - .2499\alpha^{-1.332}\sin(1.073\ln\alpha) \\ &- .5069\alpha^{-1.332}\cos(1.073\ln\alpha) \\ &= (2.630)\,Z \end{aligned} \qquad \text{(III-6)}$$

In the limit of large Z, the well known equation of Flory yields α^5 proportional to Z whereas the KSR equation yields α^3

proportional to Z. All the equations fall in either of the above two categories. Equation (III-4) of Fixman, Equation (III-5) of Ptitsyn and Equation (III-2) of KSR belong to the same category in the sense that all these yield α^3 proportional to Z in the limit of indefinitely large Z, and hence they are called the third power type. On the other hand, in the asymptotic limit Equation (III-1) of Flory, Equation (III-6) of FON and Equation (III-3) of Kurata yield α^5 proportional to Z and hence they are called fifth power type. A new equation of Flory and Fisk[34] also belongs to this latter type, but it will not be considered here because it refers to the expansion factor defined in terms of the root mean square radius of gyration of the molecule.

Comparison of Equations (III-3) and (III-6) with Equation (III-1) indicates that asymptotic behavior is reached at a smaller value of Z by Equation (III-3) than by Equations (III-1) and (III-6). In the asymptotic limit

$$\alpha^5 = (6.67)\ Z \qquad \text{for Equation (III-3)}$$

$$\alpha^5 = (2.630)\ Z \qquad \text{for Equation (III-6)}$$

$$\alpha^5 = (2.60)\ Z \qquad \text{for Equation (III-1)}$$

Thus Equations (III-6) and (III-1) have a remarkable similarity in the asymptotic limit. Similarly, asymptotic relations for the other category are

$$\alpha^3 = (2.05)\,Z \qquad \text{for Equation (III-2)}$$

$$\alpha^3 = (2)\,Z \qquad \text{for Equation (III-4)}$$

$$\alpha^3 = (.92)\,Z \qquad \text{for Equation (III-5)}$$

Kurata Equation (III-3) is numerically closer to Ptitsyn Equation (III-5) in the ordinary range of α (i.e. for $1 \leq \alpha \leq 2$) as found by Kurata.[25] Again Kurata equation has been found[29] to be practically closer to the equations of Fixman and Ptitsyn in behavior than to that of Flory, in the ordinary range of α values, but it is in contrast to the equations of Fixman and Ptitsyn as far as asymptotic behavior is concerned. This shows that it is practically impossible to argue from the experimental data concerning the asymptotic dependence of α on Z, because in the ordinary range of α values, some theories show similar behavior to each other even though they do not belong to the same category.

The asymptotic behavior of KSR equation has a remarkable resemblance to that of Fixman's equation. In fact it has been found[2] that the KSR equation is also in good agreement with numerical solution of Fixman differential equation (II-3) for intermediate values of Z.

This is reflected in almost coinciding positions of plots from KSR and Fixman equations, both showing the quantity $(\alpha^5 - \alpha^3)/Z$ to be an increasing function of Z rather than constant as expected from Flory's equation. This agreement between the KSR and Fixman equations is all the more remarkable in view of their apparently totally different methods of derivation; and it is therefore tempting to regard this agreement as additional support for their validity.

The really accurate experimental determination of α as a function of Z, actually of molecular weight, with a well defined system of polymer and solvent is one of the most crucial tasks required of the experimentalist in the field. On the other hand, since the range of Z accessible to experiment is rather limited, it is beyond the problem of experimental work to determine what is the correct asymptotic form of α in the limit of large Z. Edwards[35] has developed a sophisticated theory on this form and reached a conclusion which favored the fifth-power type mentioned above. However, it must be noted that this fact does not necessarily imply the correctness of Flory's equation.

CHAPTER IV

COMPARISON OF DIFFERENT THEORIES WITH ACTUAL SERIES

The long-range interactions between chain elements, i. e. interactions between nonbonded segments of polymer chains, are represented in sufficiently dilute solutions by the binary cluster integral,

$$\beta = \int_0^{\infty} \left\{ 1 - \exp \left[- w(l)/k\,T \right] \right\} 4\pi l^2 dl \qquad \text{(IV - 1)}$$

provided that pair potential of average force w(l) as a function of the intersegmental distance l is assumed to be of short-range nature as required by the inequality[2]

$$\beta < < < r^2 >^{3/2}$$

Here k T has its usual meaning and r is the displacement length of chain considered. The expansion factor α is then a function of a single parameter which may be written

$$Z = (3/2\pi)^{3/2} \beta a^{-3} N^{1/2} \qquad \text{(IV - 2)}$$

for a chain of N links of the effective length a. In the absence of this type of interaction, i.e. at $T = \theta$, where $\beta = 0$, the mean-square dimensions of the chain are simply written

$$< r^2 >_0 = 6 < S^2 >_0 = a^2 N \qquad \text{(IV - 3)}$$

which is identical to Equation (I-2).

For small values of Z, exact expressions for expansion factors can be obtained by means of perturbation treatments of the interactions (see Zimm, stockmayer and Fixman[9] and Yamakawa and Kurata[39]). These are, for example, for mean square radius of gyration

$$\alpha_L^2 = < S^2 >/< S^2 >_0 = 1 + (134/105)\, Z - \ldots \qquad \text{(IV - 4)}$$

and for mean square end-to-end distance

$$\alpha^2 = < r^2 >/< r^2 >_0 = 1 + (4/3)\, Z - 2.075\, Z^2 + 6.459\, Z^3 + \ldots \qquad \text{(IV - 5)}$$

The difference between α and α_L is caused by the non-Gaussian character of the chain, but it is rather small and negligible for most purposes. These equations can be effectively applied to systems in poor solvents near the theta temperature, but not to systems in good solvents because of slow convergence of the series. The expansion factor α for long chains is a function of single variable Z provided that clusters of three or more segments can be ignored.[9]

When notations are brought into correspondence,[10] we find that for Flory's equation

$$\beta = 2 V_1 \psi_1 (1 = \theta / T) \qquad \text{(IV - 6)}$$

and finally we have

$$\alpha^5 - \alpha^3 = C Z \qquad \text{(IV - 7)}$$

where constant C has the value $3^{3/2}/2 = 2.60$ or about twice that needed to secure agreement with the linear term in Equation (IV - 5).

It is found[13] that if C in Flory's equation is set equal to (4/3), thus forcing agreement with the linear term in Equation (IV - 5), the coefficient of Z^2 in the expansion of Flory's equation is in fair agreement (-2.667 compared to -2.075) with the correct value; and coefficient of Z^3 is 9.778 compared with 6.459 in Equation (IV - 5).

The proposal to adopt this new value of C, in general was not accepted by Orofino and Flory[14] who supposed that at higher values of α and Z, the original constant would be superior.

Fixman[11] proposed to generalize the Flory theory by using more realistic segment density distribution. But Casassa and Orofino[12] have shown that the coefficient of Z is made even larger by the use of the more realistic segment density distribution. This lends support to Flory's surmise that the use of a single Gaussian function has a relatively minor effect in comparison with other approximations made in the derivation.

The KSR equation can be written as

$$\alpha^3 - \alpha = C\, g(\alpha)\, Z \qquad \text{(IV - 8)}$$

where

$$g(\alpha) = 8\alpha^3 / (3\alpha^2 + 1)^{3/2} \qquad \text{(IV - 9)}$$

In deriving this equation, the constant C was set equal to 4/3 to make an agreement with the coefficient of Z in the exact series expansion. The KSR equation then gives a value of -0.2 for the coefficient of Z^2.

The Fixman equation when expanded in the series form for small values of Z corresponds to the linear term of the precise equation but it leads to the coefficient of Z^2 considerably lower than the precise coefficient (-0.67 instead of -2.075).

The Ptitsyn equation when expanded gives the coefficients 4/3 for Z, -2.075 for Z^2 and 8.611 for Z^3 in which first and second coefficients are given correctly but third is slightly overestimated in comparison with exact values.

The Kurata equation has the three coefficients as 4/3, -8/9 and 88/81. Thus here there is a large deviation of second and third coefficients from actual values, -2.075 and 6.459 for second and third coefficients respectively as in Equation (IV - 5).

The FON equation gives the first coefficient as 4/3.

Thus if we judge the theories by the values of the coefficients, the Ptitsyn theory should be ranked highest, followed by the Flory theory and then the other theories. However, this kind of criterion is practically meaningless because it should be remarked that the inferiority of these equations to Flory's in predicting the numerical coefficients in expansion series need not be regarded as a serious matter, since the convergence of the series is so slow that for all but the smallest value of Z, terms well beyond the second play quite a dominant role.

CHAPTER V

RELATION BETWEEN EXPANSION FACTOR α, INTRINSIC VISCOSITY $[\eta]$, AND INTRINSIC VISCOSITY AT THE FLORY (THETA) TEMPERATURE $[\eta]_\theta$.

In 1949, Flory[31] developed an approximate theory of the excluded volume effect in a polymer chain and indicated that the mean square radius of gyration $< S^2 >$ of a chain of N links becomes asymptotically proportional to a power of N higher than first. It has been concluded that the dependence of intrinsic viscosity on molecular weight arises from the excluded volume effect rather than the draining effect of solvent molecules.[18, 38] The essential correctness of this view is now widely accepted, but there remain several deviations of the theory from experiments. For example, in the case of solutions of polystyrene in cyclohexane, if the theory is tested by plotting the intrinsic viscosity against the radius of gyration using a log log scale, the points fall on a line of slope 2.2, instead of three as anticipated.[20] This implies that the hydrodynamic radius of a polymer coil is not always proportional to the statistical radius.

According to Flory and Fox[4, 16]

$$[\eta]/[\eta]_\theta = \alpha^3 \qquad \text{(V - 1)}$$

But Kurata and Yamakawa[17] have developed a perturbation theory of the intrinsic viscosity, taking the non-Gaussian character of chains into account and derived

$$[\eta]/[\eta]_\theta = \alpha^n , \; n = 2.43 \qquad \text{(V - 2)}$$

That the exponent n is lower than 3 has also been confirmed by the experiment of Schulz, Kirste and Inagaki[40] for the polymethyl methacrylate-butylchloride system.

Since the equation of Kurata and Yamakawa is now known to be theoretically correct at least for values of α close to unity, this difference implies that Equation (V - 1) cannot be a generally valid relation. Also there exists no theory which justifies the validity of Equation (V - 1) for larger values of α. Thus at present no general relation is available which permits unambiguous calculation of α from measurements of limiting viscosity number alone. Nevertheless, numerous existing data appear to support the empirical validity of the Flory-Fox viscosity relation given by Equation (V - 1).

In view of this somewhat confusing situation, all the proposed equations for excluded volume effect will be tested by calculating α from Equation (V - 1) as well as Equation (V - 2).

PART II

COMPARISON OF DIFFERENT THEORIES WITH EXPERIMENT

CHAPTER VI

SYSTEMS AND SCHEME OF COMPARISON

Systems Studied

Broadly the systems of polymers and solvents can be classified into two categories--polar and nonpolar. Again the sub-classification may be made as,

a. nonpolar polymer and nonpolar solvent,

b. nonpolar polymer and polar solvent,

c. polar polymer and nonpolar solvent,

d. polar polymer and polar solvent.

The data for all the systems studied in this work were obtained from the literature. The systems studied are:

1. Nonpolar polymer and nonpolar solvent

Polystyrene-benzene (P-B) at 30° C. (Reference 44), same at 25° C. (Reference 51).

Polystyrene-toluene (P-T) at 25° C. (References 45 and 52), same at 30° C. (Reference 53).

2. Polar polymer and nonpolar solvent

   Polymethyl methacrylate-toluene (PMMA-T) at 27° C. (Reference 46).

3. Polar polymer and polar solvent

   Polymethyl methacrylate-methyl isobutyrate (PMMA-MIB) at 27° C. (Reference 47).

All the polymers studied were quite narrow-molecular-weight-distribution polymers. An attempt was made to get as wide a range of molecular weights as possible. Accurate intrinsic viscosity data at temperatures very near to the Flory temperature are hard to find.

Two sets of data for α from light scattering were used as "control data." They are polystyrene-toluene (PS-T) at 20° C. (Reference 48) and polyvinyl acetate-methyl ethyl ketone (PVA-MEK) at 25° C. (Reference 36).

The χ values used for comparing Flory's theory with experiment were obtained from References 49 and 50.

Scheme of Comparison

The equations are

Flory: $$\alpha^5 - \alpha^3 = C Z \qquad \text{(VI-1)}$$

KSR: $$(\alpha^3 - \alpha)(1 + 1/3\,\alpha^2)^{3/2} = C\,Z \qquad \text{(VI-2)}$$

Kurata: $$(\alpha^3 - 1) + 3/8\,(\alpha^5 - \alpha^3) = C\,Z \qquad \text{(VI-3)}$$

Fixman: $$\alpha^3 - 1 = C\,Z \qquad \text{(VI-4)}$$

Ptitsyn: $$(4.68\,\alpha^2 - 3.68)^{3/2} - 1 = C\,Z \qquad \text{(VI-5)}$$

FON: $$\alpha^5 - 0.4931\,\alpha^3 - 0.2499\,\alpha^{-1.332}\sin(1.073\ln\alpha) - 0.5069\,\alpha^{-1.332}\cos(1.073\ln\alpha) = C\,Z \qquad \text{(VI-6)}$$

where the constant C for each equation is different. Flory's equation may be written as

$$\alpha^5 - \alpha^3 = 2\,C_M\,(1/2 - \chi)\,M^{1/2} \qquad \text{(VI-7)}$$

For comparison of this equation with experiment, one must calculate the expansion factor function $(\alpha^5 - \alpha^3)$ from experimental α values and the theoretical calculation from the known theoretical or experimental (other than viscosity measurements) values of χ.

The most straightforward manner to examine these equations is to make the following plots and study the deviations from the expected shapes of the plots. The plots are made using the α values from

$$\alpha^3 = [\eta]/[\eta]_\theta$$

and

$$\alpha^{2.43} = [\eta]/[\eta]_\theta$$

to test these latter two equations also.

1. Expansion factor functions of all the equations against $M^{1/2}$. It is expected that these plots should give straight lines passing through the coordinate origin because the form of each equation is $y = mx$ although there is no physical meaning to the extrapolation of the line to the zero molecular weight.
2. Expansion factor function/$M^{1/2}$ against M, molecular weight. These plots should give horizontal lines because the quantities on the right hand side are independent of molecular weight and characteristic of a particular polymer-solvent system.
3. Expansion factor function/$M^{1/2}$ against α, the expansion factor. These plots also should give horizontal lines for the same reason as in 2 above.

It was thought desirable to have some "control plots." These plots were made using above equations (VI-1 to VI-6) using the α values from light scattering, thus avoiding the doubtful α values from $\alpha^3 = [\eta]/[\eta]_\theta$ or $\alpha^{2.43} = [\eta]/[\eta]_\theta$. Thus one can make the comparison of different equations with experiment irrespective of the above α values since the exact value of the exponent n in $\alpha^n = [\eta]/[\eta]_\theta$ is unknown.

CHAPTER VII

FLORY THEORY

Flory's equation is

$$\alpha^5 - \alpha^3 = 2C_M \psi (1 - \theta / T) M^{1/2} \qquad \text{(VII-1)}$$

or
$$\alpha^5 - \alpha^3 = 2C_M (1/2 - \chi) M^{1/2} \qquad \text{(VII-2)}$$

or
$$\alpha^5 - \alpha^3 = 2C_M (1/2 - \chi_S - \chi_H) M^{1/2} \qquad \text{(VII-3)}$$

For nonpolar systems according to Hildebrand-Scatchard[43] regular solution theory

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \qquad \text{(VII-4)}$$

where χ_H is the heat parameter, χ_S is the entropy parameter of the total parameter χ (χ is fully described in Chapter I), V_1 is the molar volume of the solvent, and δ is the solubility parameter, subscript 1 and 2 referring to solvent and solute respectively. For the system of nonpolar polymer and nonpolar solvent the Flory equation is

$$\alpha^5 - \alpha^3 = 2C_M \left[1/2 - \chi_S - \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \right] M^{1/2} \quad \text{(VII-5)}$$

A similar equation for polar systems is also available[49] but it will not be considered here. For nonpolar systems χ_S equal to 0.34 was taken as suggested by Blanks[50] and V_1 and δ values were obtained from Reference 49. From α values from the literature expansion factor function was calculated and thus both sides of the equation were compared. Tables VII-1, VII-2 and VII-3 show this for nonpolar systems. It was observed that the theoretical calculation of the Flory equation was very sensitive to χ values. It can be seen that in most of the nonpolar systems of a polymer and a solvent, the theoretical calculation is greater than the expansion factor function. Also this difference is found to decrease in general as the value of α increased. Tables VII-1, VII-2 and VII-3 show this. The general trend, at least for the nonpolar systems, is that below the value of α equal to about 1.2, the theoretical calculation is twice or more than twice the expansion factor function. However, this must be determined carefully in the future by running a series of experiments at different values of α. This sort of experimental data at low values of α is hard to find and also it is liable to serious experimental errors.

For polar systems (Table VII-4) the theoretical calculation of the equation was done by finding the χ values as shown in

Table VII-1

Comparison of Flory's Equation with Experiment[a]

$M \times 10^{-4}$[b]	$[\eta]$ dl/g	$[\eta]_\theta$[c] dl/g	α^3	$(\alpha^5 - \alpha^3)$	$2C_M[1/2 - \chi]\ M^{1/2}$[d]
Atactic Polystyrene in Benzene at 25° C. (Reference 51)					
110	2.72	.86	3.16	3.65	4.37
90	2.36	.78	3.03	3.32	3.95
50	1.56	.58	2.69	2.52	2.94
29	1.13	.44	2.56	2.23	2.24
16	.71	.33	2.16	1.45	1.67
9.4	.48	.25	1.92	1.05	1.28
7.2	.39	.22	1.77	.83	1.12

[a] $(\alpha^5 - \alpha^3)$ is calculated from α values from literature.

$2C_M\left[1/2 - \chi_S - \frac{V_1}{RT}(\delta_1 - \delta_2)^2\right]M^{1/2}$ for nonpolar systems; V_1, δ_1 and δ_2 from Reference 50; χ from Reference 49.

[b] Molecular weights by osmotic solution.

[c] $[\eta]_\theta = 82 \times 10^{-5} M^{1/2}$ for polystyrene.

[d] Note: $\chi = \chi_S + \chi_H$. $\chi_S = .34$, $\chi_H = \frac{V_1}{RT}(\delta_1 - \delta_2)^2$ for nonpolar systems.

Table VII-2

Comparison of Flory's Equation with Experiment

$M \times 10^{-4}$[a]	$[\eta]$ dl/g	$[\eta]_\theta$[b] dl/g	α^3	$\alpha^5 - \alpha^3$	$2C_M[1/2 - \chi]\ M^{1/2}$
Anionic Polystyrene in Benzene at 30°C. (Reference 44)					
153	3.72	1.04	3.58	4.79	5.12
109	2 8	.866	3.23	3.84	4.32
82	2.21	.760	2.91	3.02	3.75
50	1.6	.592	2.7	2.54	2.93
34.5	1.25	.492	2.54	2.19	2.43
23.5[c]	.9	.408	2.21	1.53	2.01
21	.85	.386	2.2	1.52	1.90
15	.67	.325	2.06	1.28	1.60
8.3[c]	.42	.242	1.74	.77	1.19
7.5[c]	.387	.23	1.68	.7	1.13
5.5	.197	.197	1.55	.52	.97

[a] Molecular weights by vapor pressure osmometry.

[b] $[\eta]_\theta$ values are experimental in Reference 54.

[c] Unfractionated, $\overline{M}_w / \overline{M}_n \approx 1.1$.

Note: In above calculations value of χ_H at 25° C. was used since δ values were available at 25° C. According to Hildebrand and Scott[43] $(\delta_1 - \delta_2)^2$ in $\chi_H = \frac{V_1}{RT}(\delta_1 - \delta_2)^2$ does not change much with temperature even though δ values change.

Table VII-3

Comparison of Flory' s Equation with Experiment

$M \times 10^{-3}$[a]	$[\eta]$ dl/g	$[\eta]_\theta$[b] dl/g	α^3	$\alpha^5 - \alpha^3$	$2C_M[1/2 - \chi]\ M^{1/2}$
Polystyrene in Toluene at 25° C. (Reference 52)					
940	2.320	0.795	2.92	3.04	3.80
830	2.040	0.747	2.73	2.61	3.57
372	1.140	0.500	2.28	1.67	2.39
325	1.040	0.468	2.23	1.57	2.24
115	0.465	0.278	1.67	0.68	1.33
Polystyrene in Toluene at 30° C. (Reference 53)					
580	1.37	0.55	2.49	2.09	2.93
500	1.15	0.52	2.21	1.54	2.72
380	1.00	0.44	2.27	1.66	2.73
170	0.51	0.30	1.70	0.72	1.59
100	0.38	0.23	1.65	0.66	1.22
40	0.19	0.14	1.36	0.31	0.77

[a] Molecular weights by light scattering.

[b] $[\eta]_\theta = 82 \times 10^{-5} M^{1/2}$ for the system at 25° C. and for the system at 30° C., $[\eta]_\theta$ is experimental.

Table VII-4

Comparison of Flory's Equation with Experiment

$M \times 10^{-4}$	$[\eta]$ dl/g	$[\eta]_\theta$ dl/g	α^3	$(\alpha^5 - \alpha^3)$	$2C_M[1/2 - \chi]\ M^{1\ 2}$
Polymethyl methacrylate in Methylisobutyrate at 30 C. (Reference 46)					
261	1.98	0.78	2.54	2.19	11.82
172	1.42	0.63	2.26	1.62	9.55
97	1.00	0.47	2.12	1.37	7.18
60	0.74	0.37	1.99	1.16	5.64
31	0.45	0.27	1.69	0.71	3.97
19	0.35	0.21	1.66	0.67	3.19

$(\alpha^5 - \alpha^3)$ is calculated from α values from literature. $\chi = \chi_S + \chi_H$, $\chi_S = 0.34$, χ_H from Reference 49.

Reference 49 using χ_S equal to 0.34 as suggested therein. It was observed that the theoretical calculation was consistently throughout the range of α values far greater than (4 to 5 times) the experimental value of the expansion factor function. Also the theoretical calculation of the equation was extremely sensitive to the χ values. This implies that χ_S may not be 0.34 for the systems where the above fact was observed. It should be kept in mind that the calculation of the χ_H value is subject to the limitations of the Hildebrand-Scatchard theory. From the above observations one may suggest that the correction terms which may be incorporated in Flory's equation to improve it may be different in different cases depending on the type of the polymer-solvent system. It was observed that a small change in the value of χ altered the value of the theoretical calculation to a large extent. This observation warrants a new investigation in the value of χ_S, since χ_S is a function of the size and shape of the molecules in solution.

Stockmayer[10] has strongly suggested that the factor C_M in Flory's equation should be replaced by 0.49 C_M for temperatures near the Flory (theta) temperature on the basis of the calculation of χ from Flory's equation and by some method other than the viscosity measurements. He found that Flory's equation gave the value of $(1/2 - \chi)$ exactly half the value of $(1/2 - \chi)$ obtained by the other method. He[7] has also shown that the Montê Carlo calculations of Wall and his co-workers[15] are in distinctly better agreement with the lower value of the constant in Flory's equation. This seems to be quite valid as can be observed from Tables VII-1, VII-2 and VII-3. One cannot say that the same is true for the polar systems also without having the correct values of χ to compare the value of the expansion factor function with theoretical calculations. Thus no conclusion can be made for the nonpolar systems regarding the value of C_M without having the correct values of χ.

The proposal to adopt the new value of the constant C_M in general was not accepted by Orofino and Flory[14] who supposed that at higher values of the expansion factor α, the original constant would be superior. Tables VII-1, VII-2 and VII-3 support the conclusion of Flory and Orofino. It seems, however, that over a certain range of α values, the original constant would be superior and the determination of this range α values for different systems requires exhaustive experimentation.

Plot of the Expansion Factor Function Against $M^{1/2}$ With $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

Figure 1 shows this plot for P-B with α calculated from $[\eta]/[\eta]_\theta = \alpha^3$. The data with the Flory equation reasonably

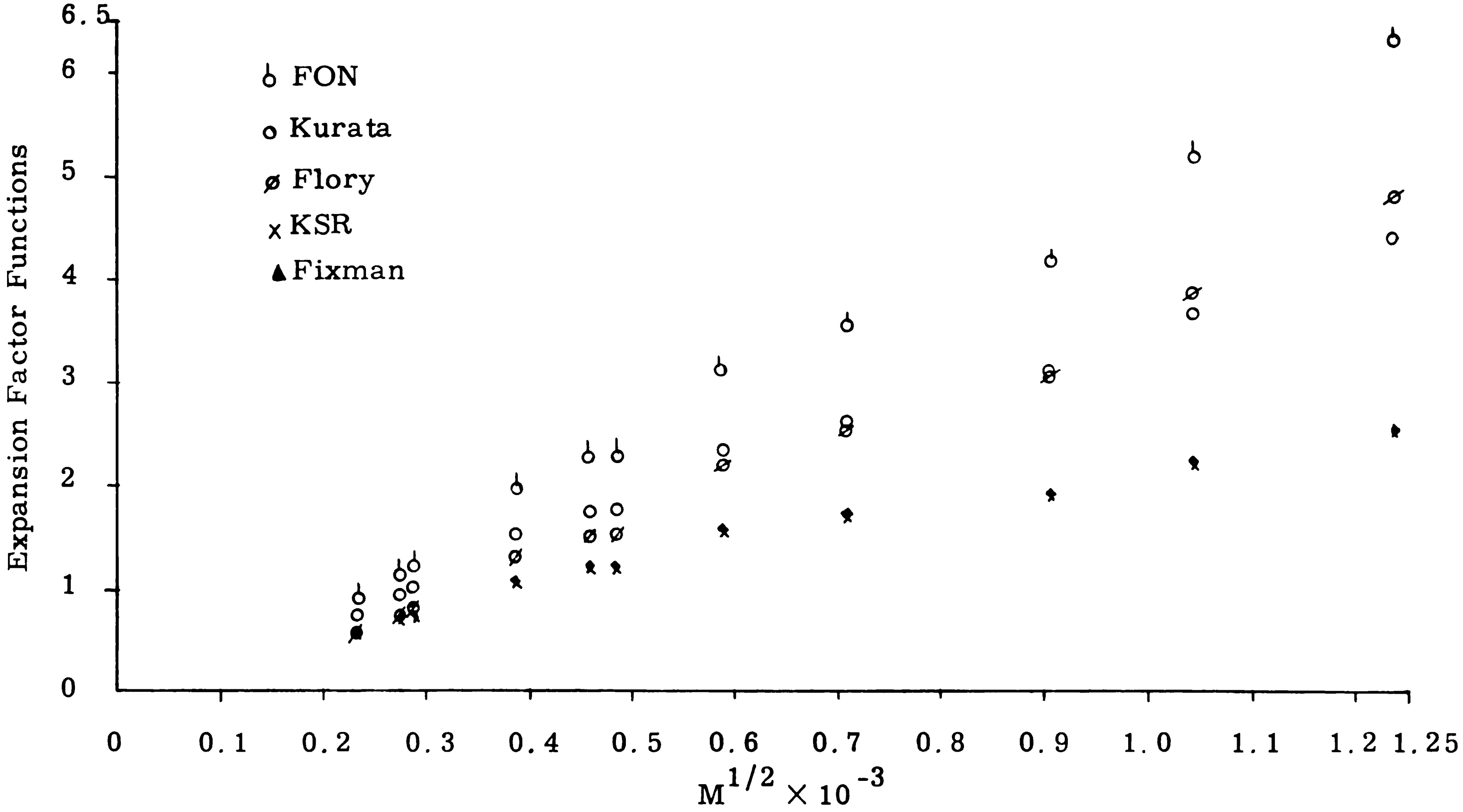


Figure 1. --Expansion factor functions vs $M^{1/2}$ for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

fall on a straight line; however, the line does not pass through the coordinate origin. The observation is similar for P-T in Figure 2. Here higher α values are not available. For PMMA-T in Figure 3 also the observation is similar except that the point with the highest value of α falls outside of the straight line. This could be due to an experimental error. For PMMA-MIB in Figure 4, there is a slight scatter of the points from the straight line. In all but the last case, there is a small positive intercept on the abscissa if the lines are extended towards the coordinate origin. The lines have not been extended towards the origin because very low values of α (near to 1) are not available. Okada et al.[41] have observed downward as well as upward curvature at extremely low values of α. The positive intercepts on the abscissa axis indicate that Flory's equation is adequate only in the region of molecular weights above a certain value which depends on the kind of solvent (and probably on temperature also). Below the molecular weight corresponding to the intercept on the abscissa axis, the factor α is sensibly equal to unity independent of molecular weight. For PMMA-MIB (Figure 4), the intercept on abscissa axis is negative. It is not clear whether this is due to experimental error or whether it reflects a certain specific interaction between methyl methacrylate monomer and methyl isobutyrate molecule. One has to note that in the region of α close to unity,

Figure 2. --Expansion factor functions <u>vs</u> $M^{1/2}$ for polystyrene-toluene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

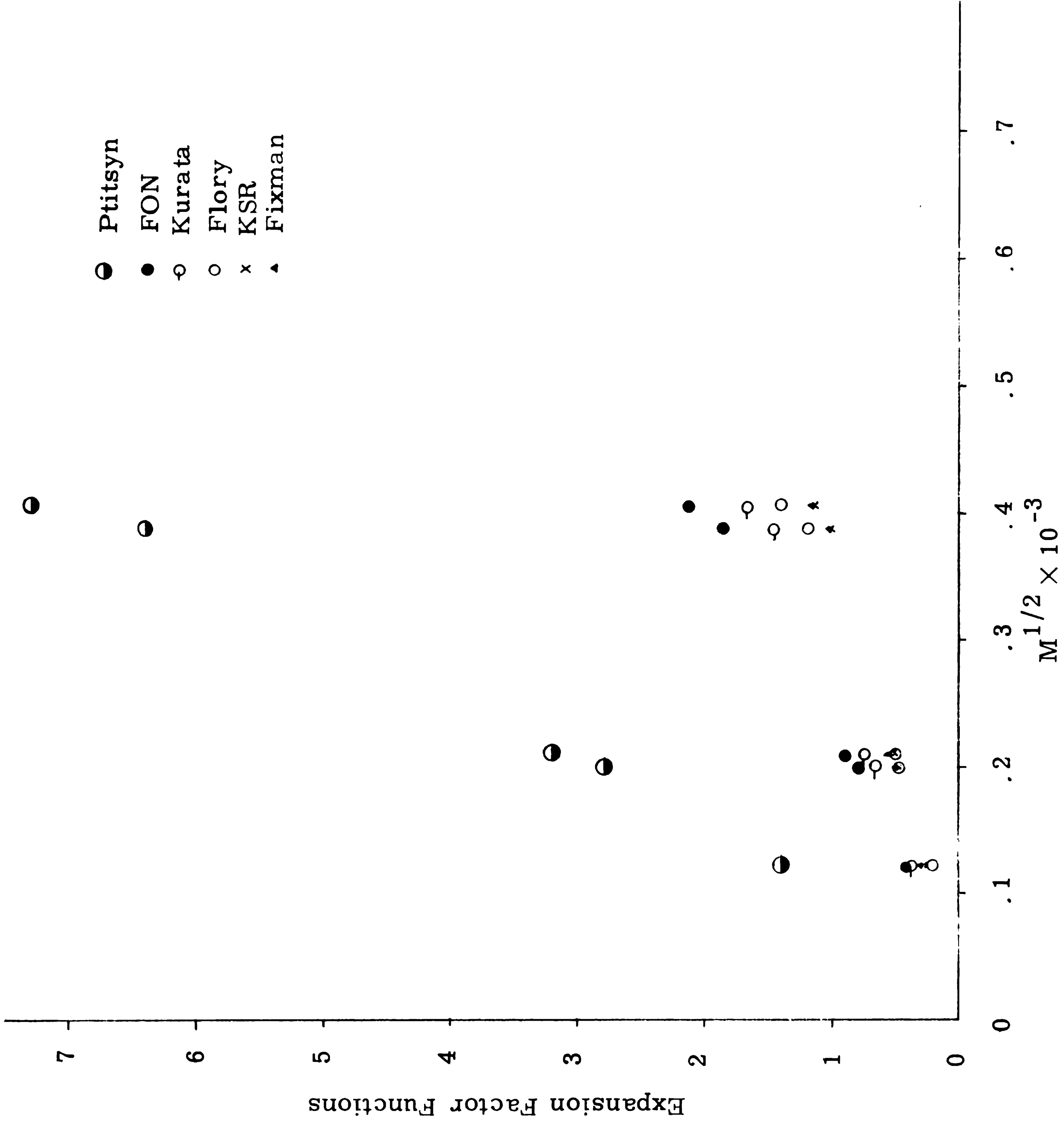

Ptitsyn
FON
Kurata
Flory
KSR
Fixman
Expansion Factor Functions
0
1
2
3
4
5
6
7
0
.1
.2
.3
.4
.5
.6
.7
$M^{1/2} \times 10^{-3}$

Figure 2.

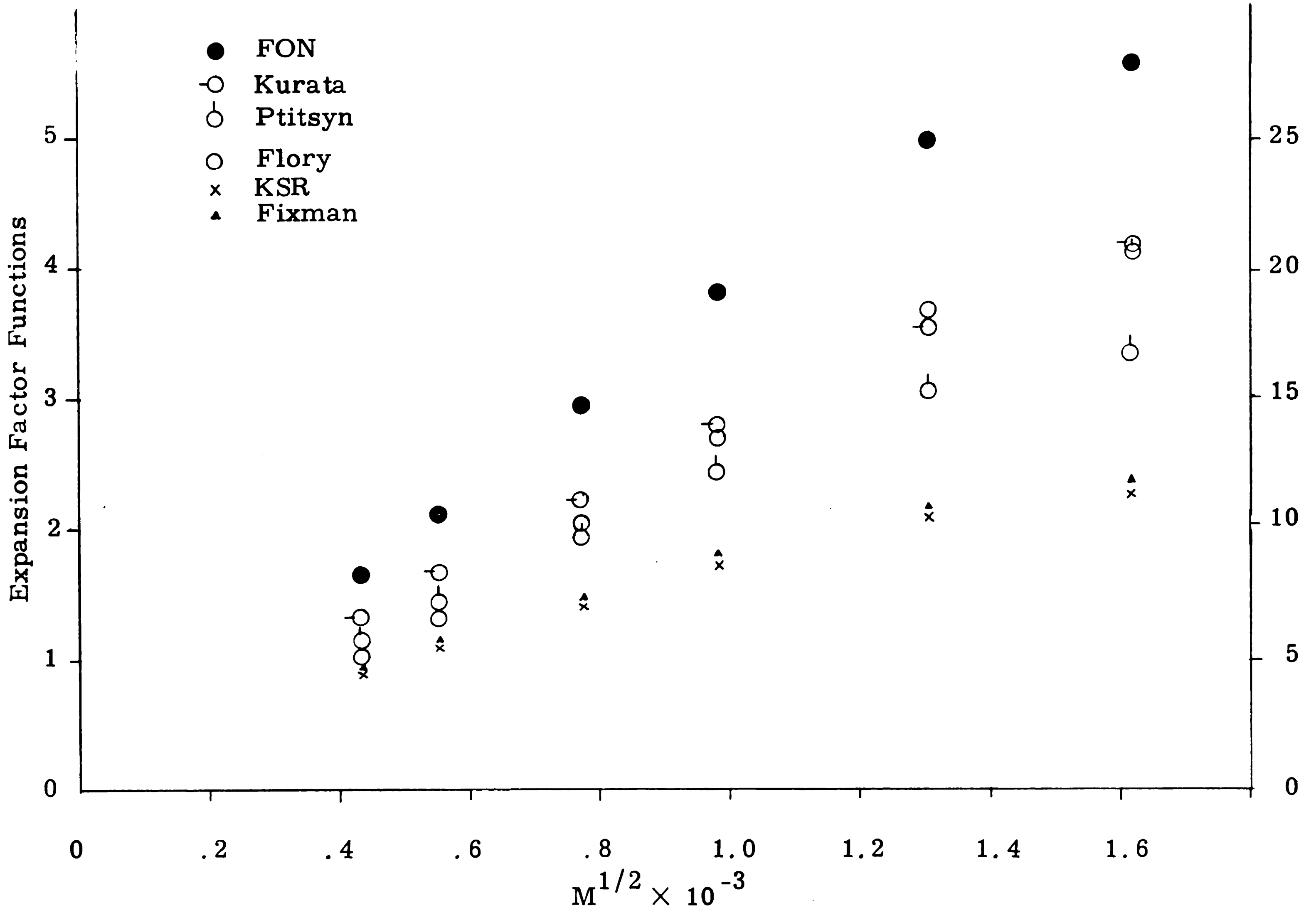
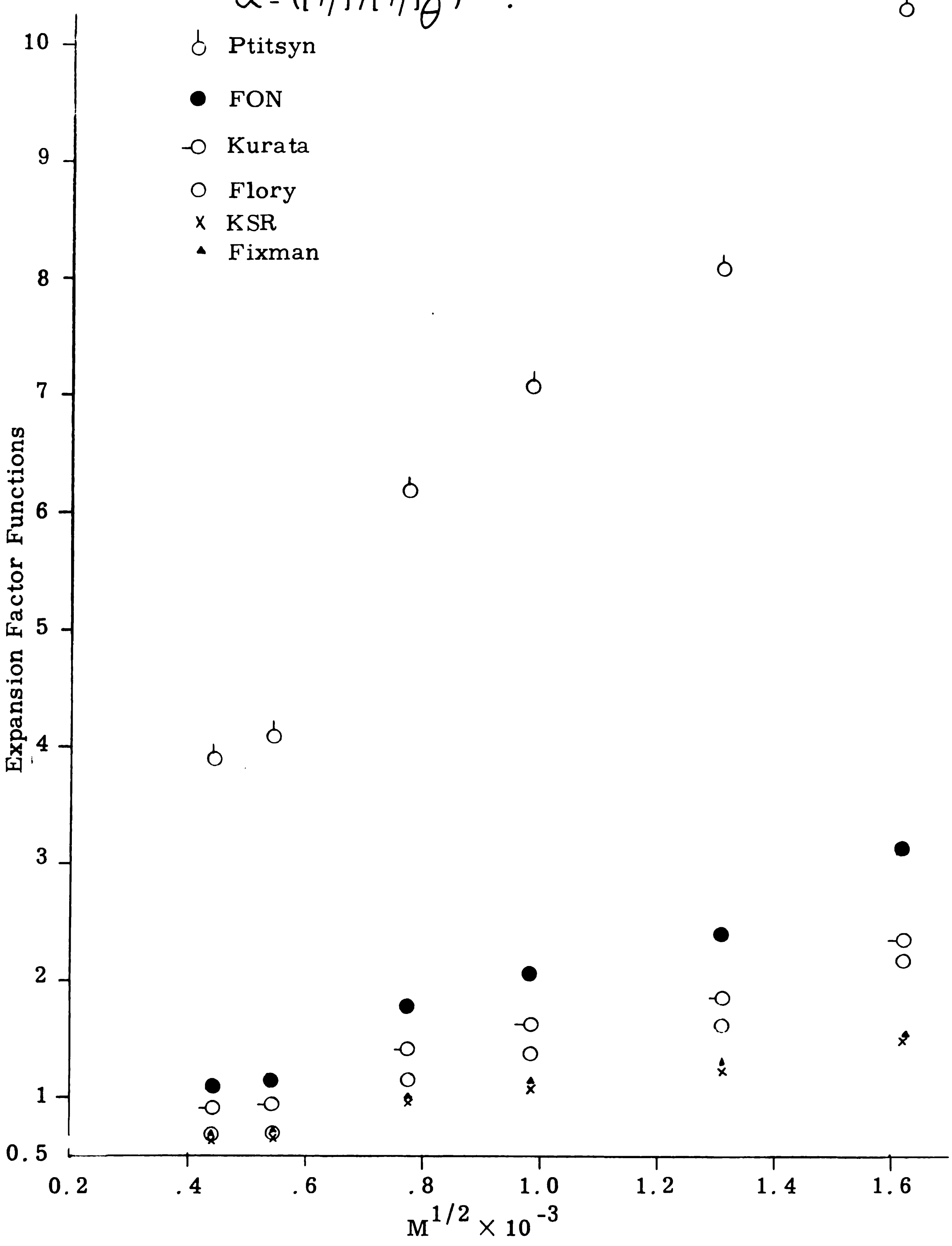


Figure 3. --Expansion factor functions vs $M^{1/2}$ for polymethyl methacrylate-toluene at 27° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/3}$.

Figure 4. --Expansion factor functions vs $M^{1/2}$ for polymethyl methacrylate-methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.



plots of this type are very sensitive to small errors in the measurement of $[\eta]$. It appears therefore a little hazardous to extend the curves to the coordinate origin in absence of data at values of α close to unity.

Plot of (Expansion Factor Function)/$M^{1/2}$ Against M with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

Flory's equation predicts that if one plots $(\alpha^5 - \alpha^3)/M^{1/2}$ against M, the quantity should be independent of M at every given temperature. However, a marked dependence of $(\alpha^5 - \alpha^3)/M^{1/2}$ on M has been observed for several polymer solvent systems by Krigbaum and Flory.[42] Figures 5, 6, 7 and 8 show these plots for P-B, P-T, PMMA-T and PMMA-MIB respectively. Figure 5 for P-B shows that the points are widely scattered. Figure 6 for P-T shows that there is a continuous rise in the value of $(\alpha^5 - \alpha^3)/M^{1/2}$ as M increases. Figure 7 for PMMA-T shows that there is a uniform marked dependence of $(\alpha^5 - \alpha^3)/M^{1/2}$ on M as observed by Krigbaum and Flory.[42] Figure 8 for PMMA-MIB shows a somewhat different behavior than that observed above. Here data show a drooping line as molecular weight increases. However there is a scatter of points about this line. It appears that χ is a function of M for nonpolar-nonpolar systems but not for polar polymers.

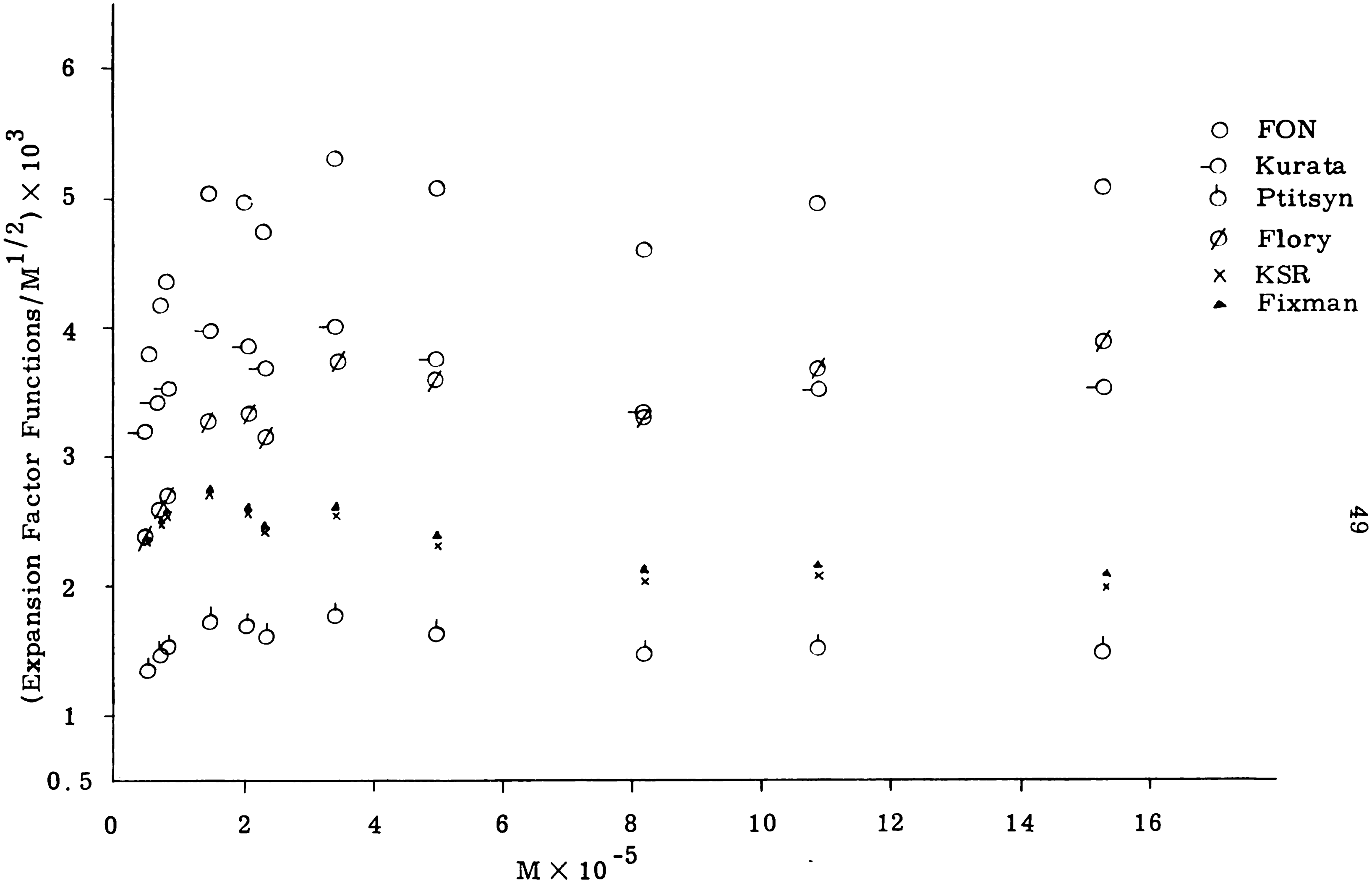


Figure 5. --Expansion factor functions/$M^{1/2}$ vs M for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

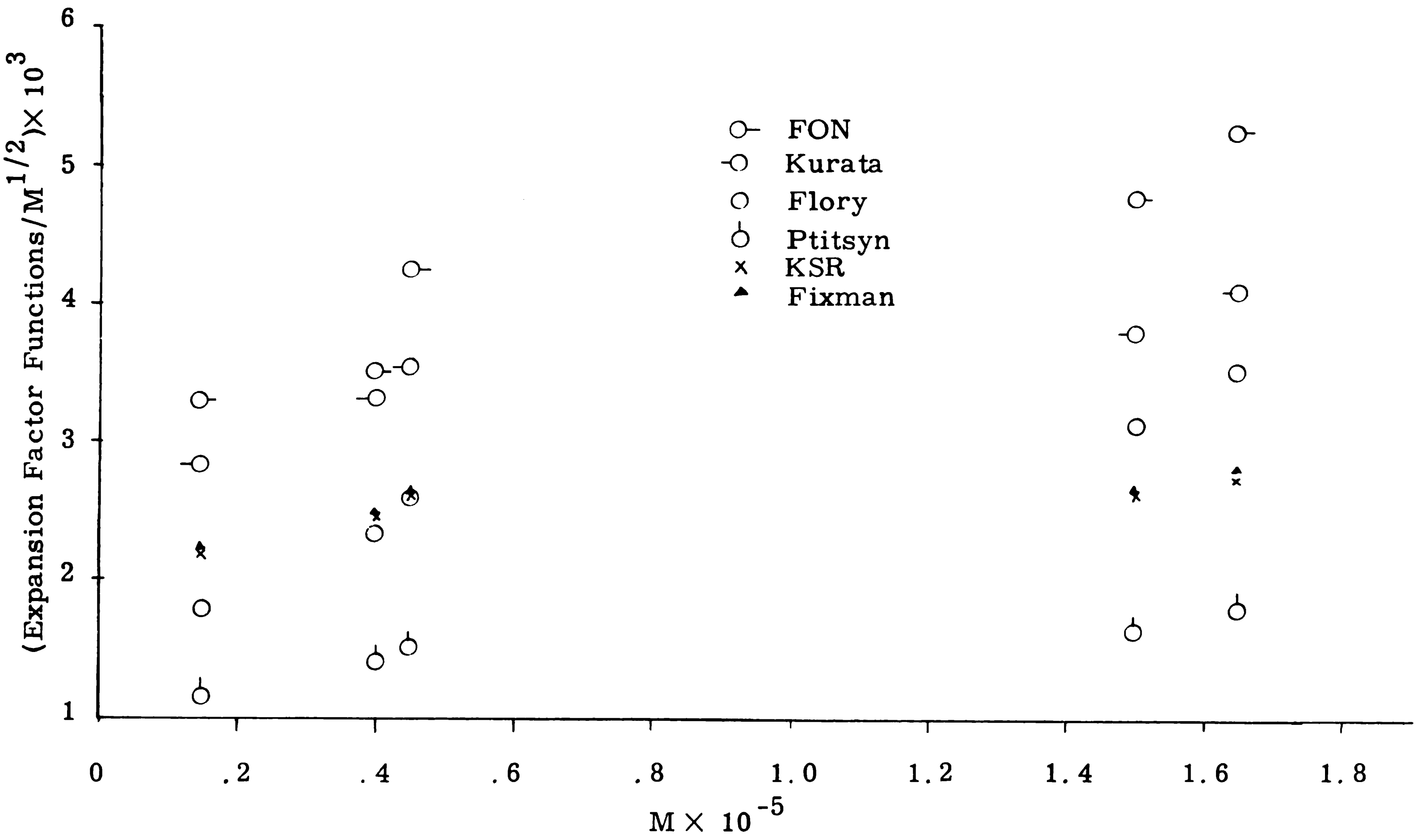


Figure 6. --Expansion factor functions/$M^{1/2}$ vs M for polystyrene-toluene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

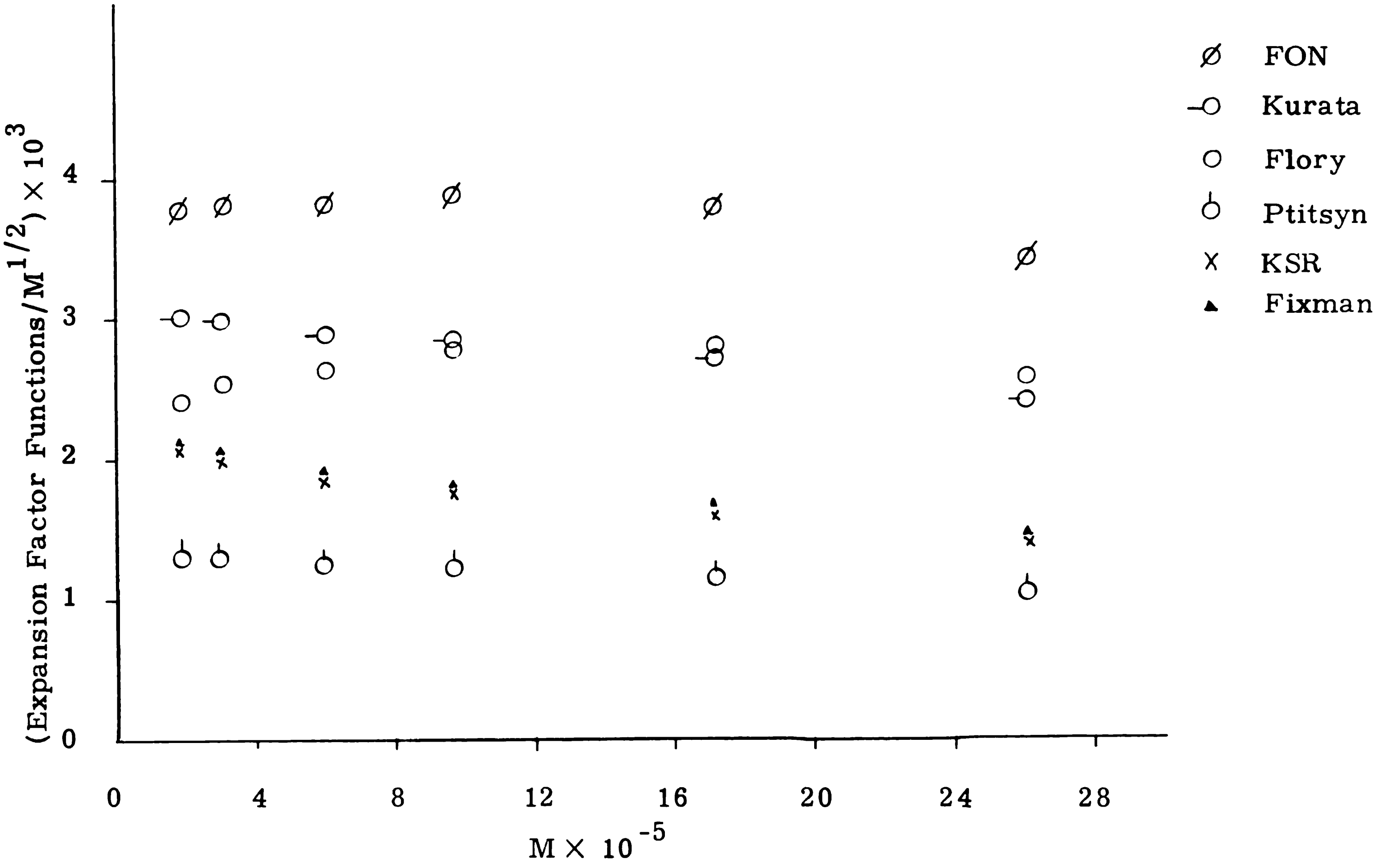


Figure 7. --Expansion factor functions/$M^{1/2}$ vs M for polymethyl methacrylate-toluene at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

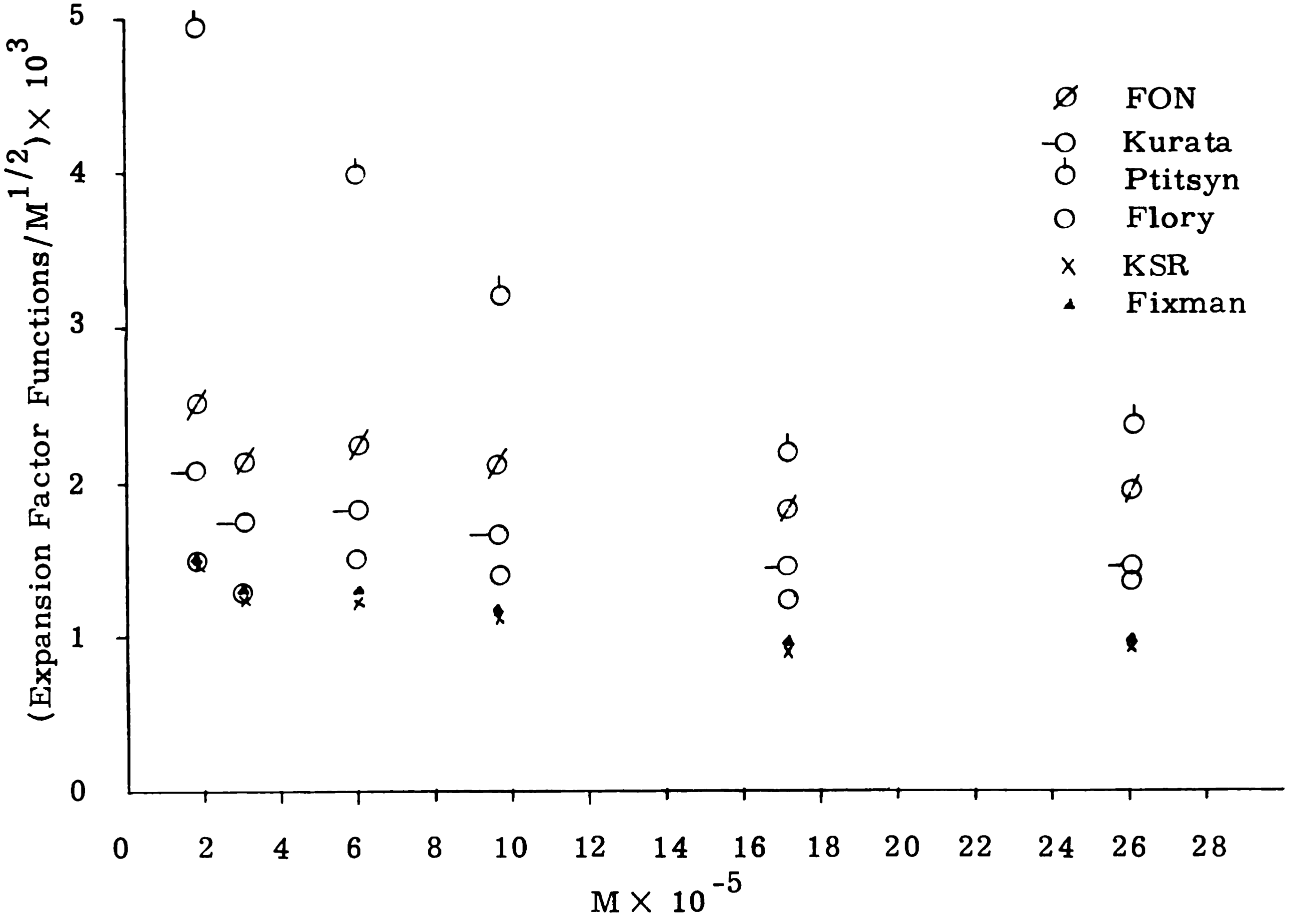


Figure 8. --Expansion factor functions/$M^{1/2}$ vs M for polymethyl methacrylate-methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

Plot of (Expansion Factor Function)/$M^{1/2}$ Against α with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

A plot of this kind should give a horizontal line. Figures 9, 10, 11, and 12 show these plots for all the four systems. For P-B (Figure 9) there is a wide scatter of points while for P-T (Figure 10), the points show an increase in value as α increases. For PMMA-T (Figure 11), first the plot increases gradually and then decreases gradually, thus showing a distinct maximum as in the case of a plot of $(\alpha^5 - \alpha^3)/M^{1/2}$ vs M. For PMMA-MIB (Figure 12), the plot shows points falling downward as α increases. Thus in all cases, these plots are similar to the plots of $(\alpha^5 - \alpha^3)/M^{1/2}$ against M as expected.

All the three kinds of plots show deviations from the expected shapes. This discrepancy may be attributed first of all to the incorrectness of α-values obtained by $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$ from the viscosity data and secondly to the imperfection of Flory's equation. This imperfection could be corrected by obtaining a correct α value from $[\eta]$ and $[\eta]_\theta$ or by incorporating a molecular weight dependence on χ since χ_S is a function of size and shape of a molecule.

Plots with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$

The expansion factor function with the above value of α is far different from the theoretical calculations with χ values as

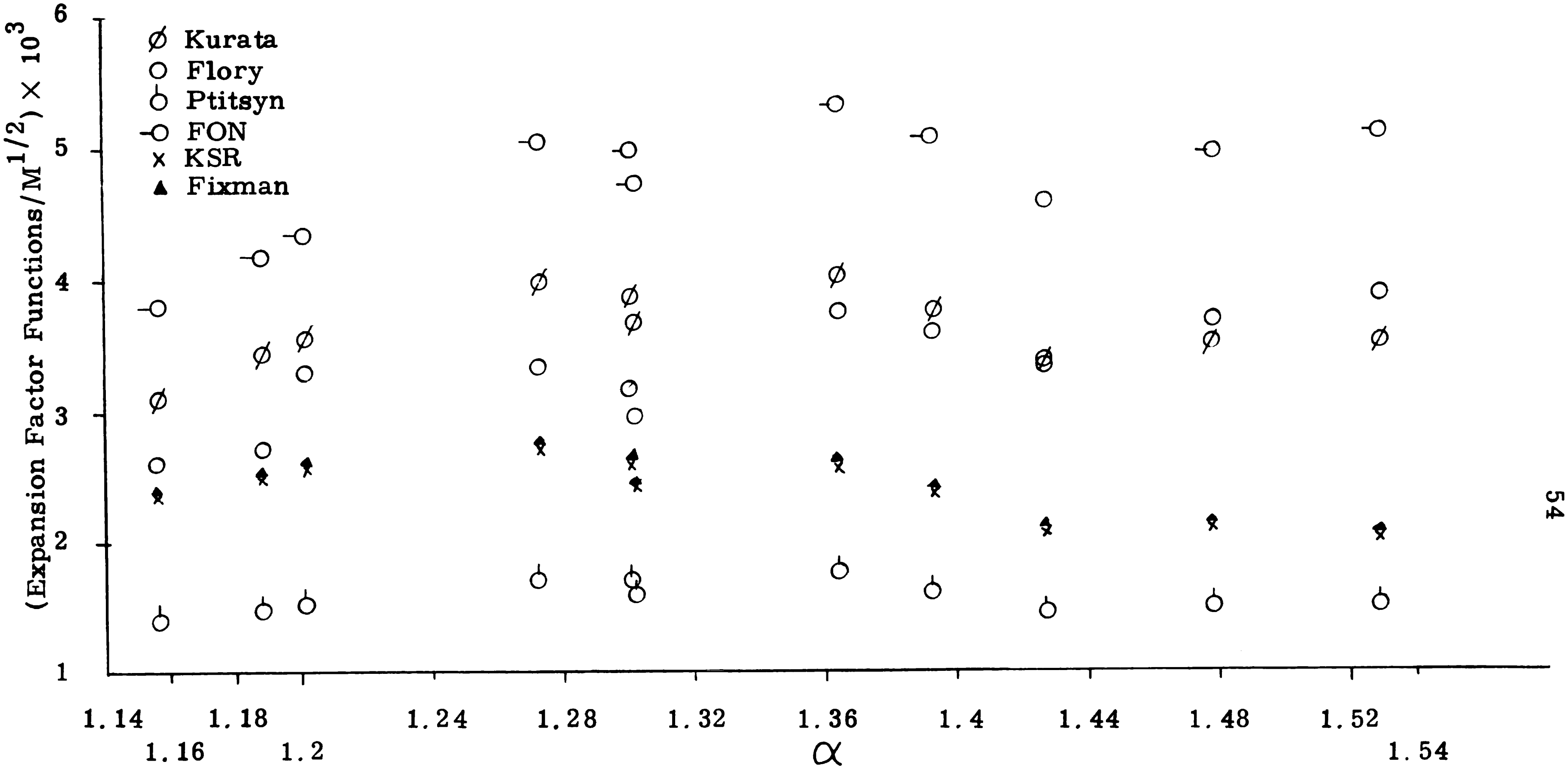


Figure 9. --Expansion factor functions/$M^{1/2}$ vs α for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

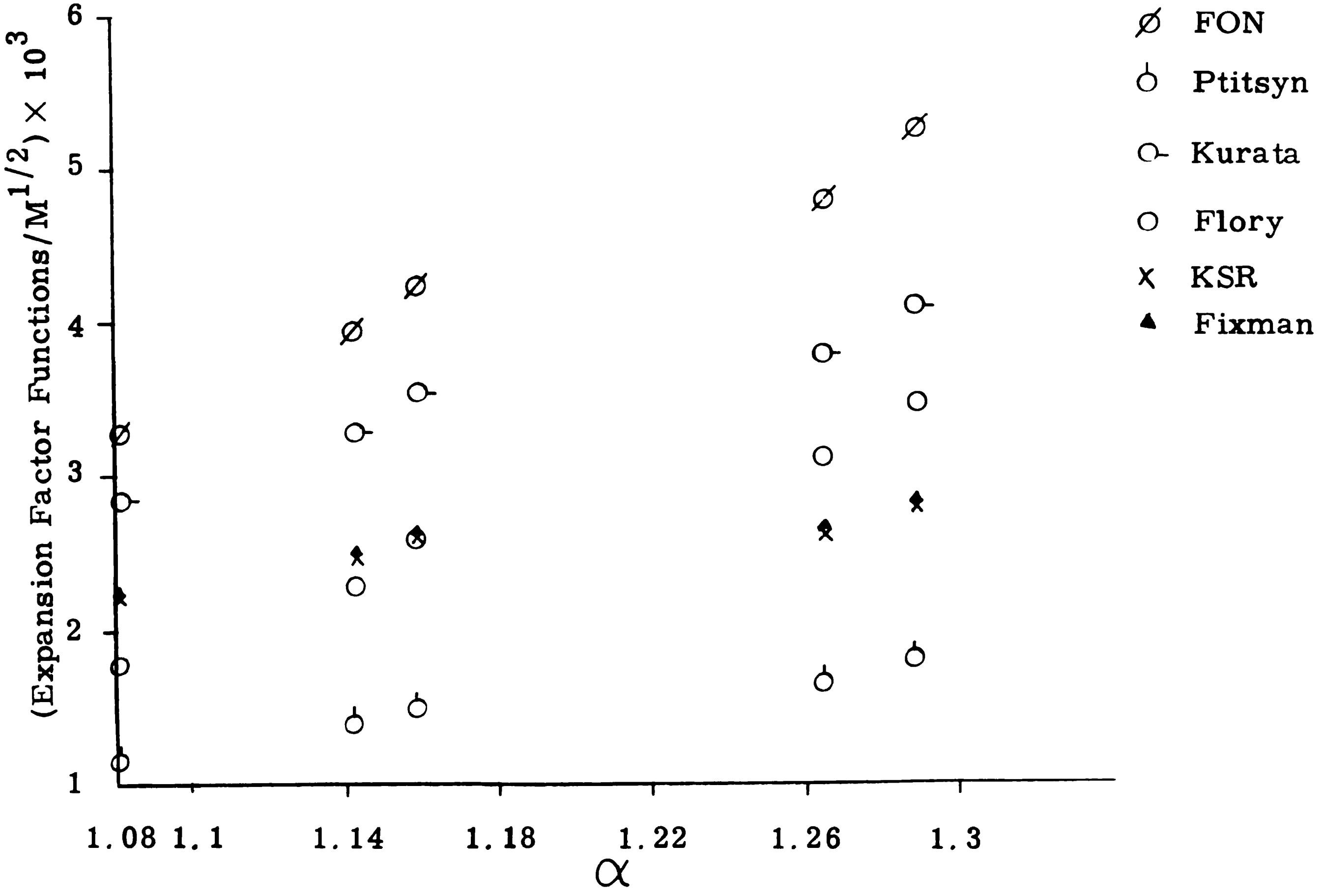


Figure 10. --Expansion factor functions/$M^{1/2}$ vs α for polystyrene-toluene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

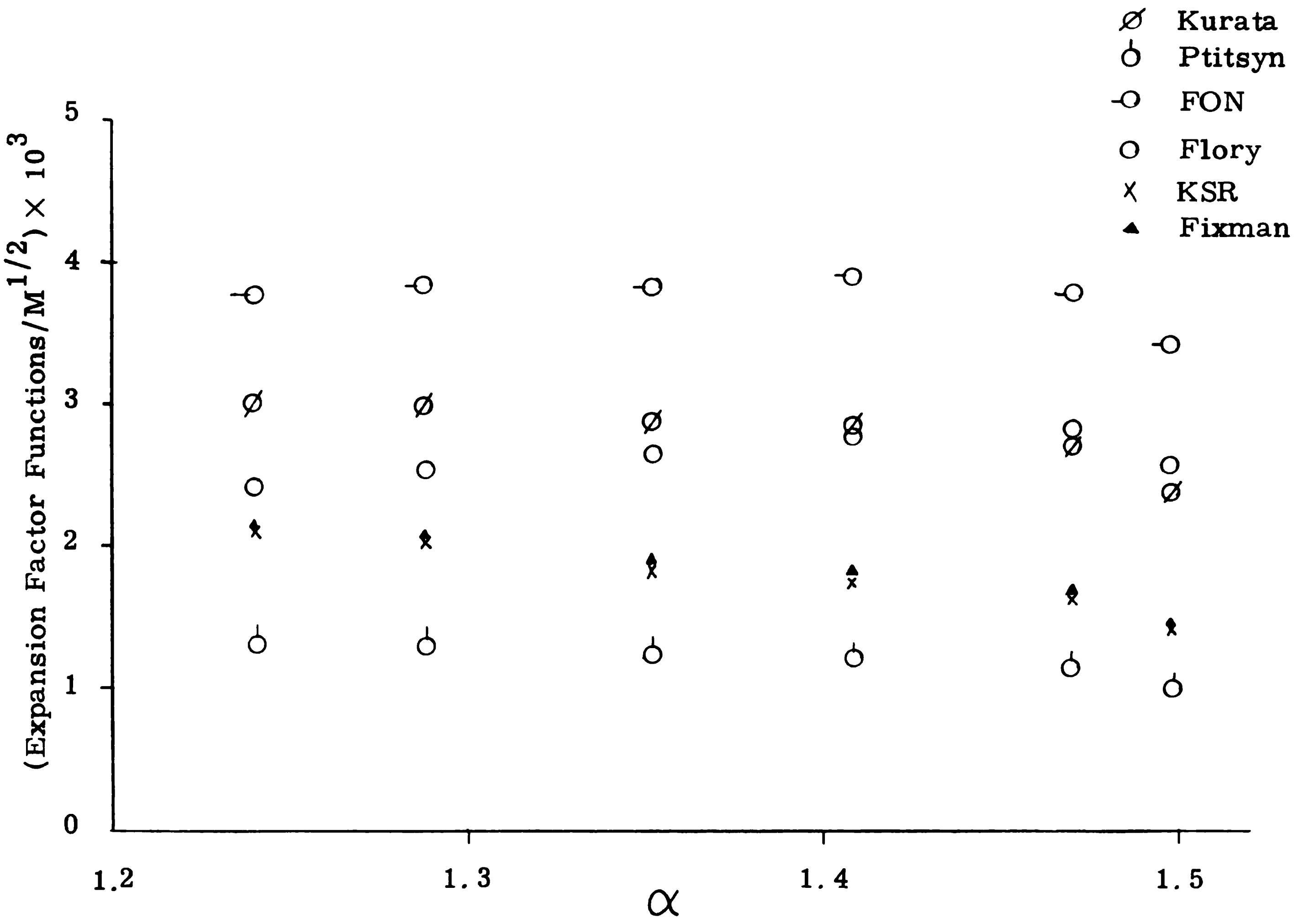


Figure 11. --Expansion factor functions/$M^{1/2}$ vs α for polymethyl methacrylate-toluene at 27° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/3}$.

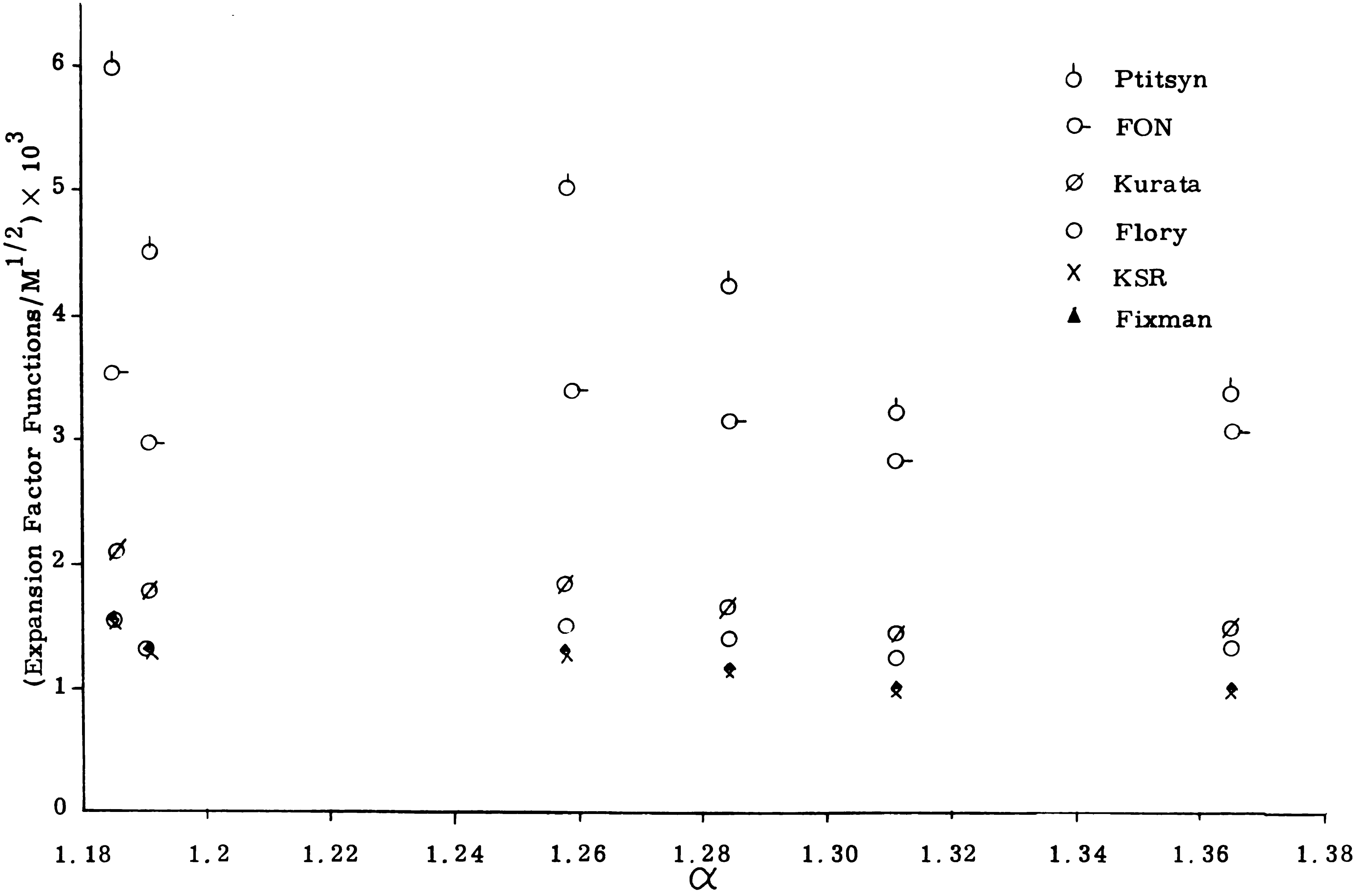


Figure 12. -- Expansion factor functions/$M^{1/2}$ vs α for polymethyl methacrylate-methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$.

compared to the calculations with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$ (this is quite obvious), thus opposing the new value of α. Figures 13, 14, 15, and 16 show plots of $(\alpha^5 - \alpha^3)$ against $M^{1/2}$ and it is observed that the scatter of the points is much more than the case where $\alpha^3 = [\eta]/[\eta]_\theta$. The same is true with all the other plots (Figures 17-24). The points are more widely scattered.

Plots with α Values from Light Scattering

Figures 25 and 26 show the plots of the expansion factor function against $M^{1/2}$ for PS-T and PVA-MEK respectively with α values from light scattering obtained from the literature. Unfortunately the data are not available over a wide range. In both the cases, the points are far from a straight line passing through the coordinate origin. Figures 27 and 28 show $(\alpha^5 - \alpha^3)/M^{1/2}$ against M for the two systems. The plots do not show any horizontal line. Thus Flory's equation does not show any good correlation with α values obtained from the light scattering. This is also the case with the plots of $(\alpha^5 - \alpha^3)/M^{1/2}$ against α as shown in the Figures 29 and 30.

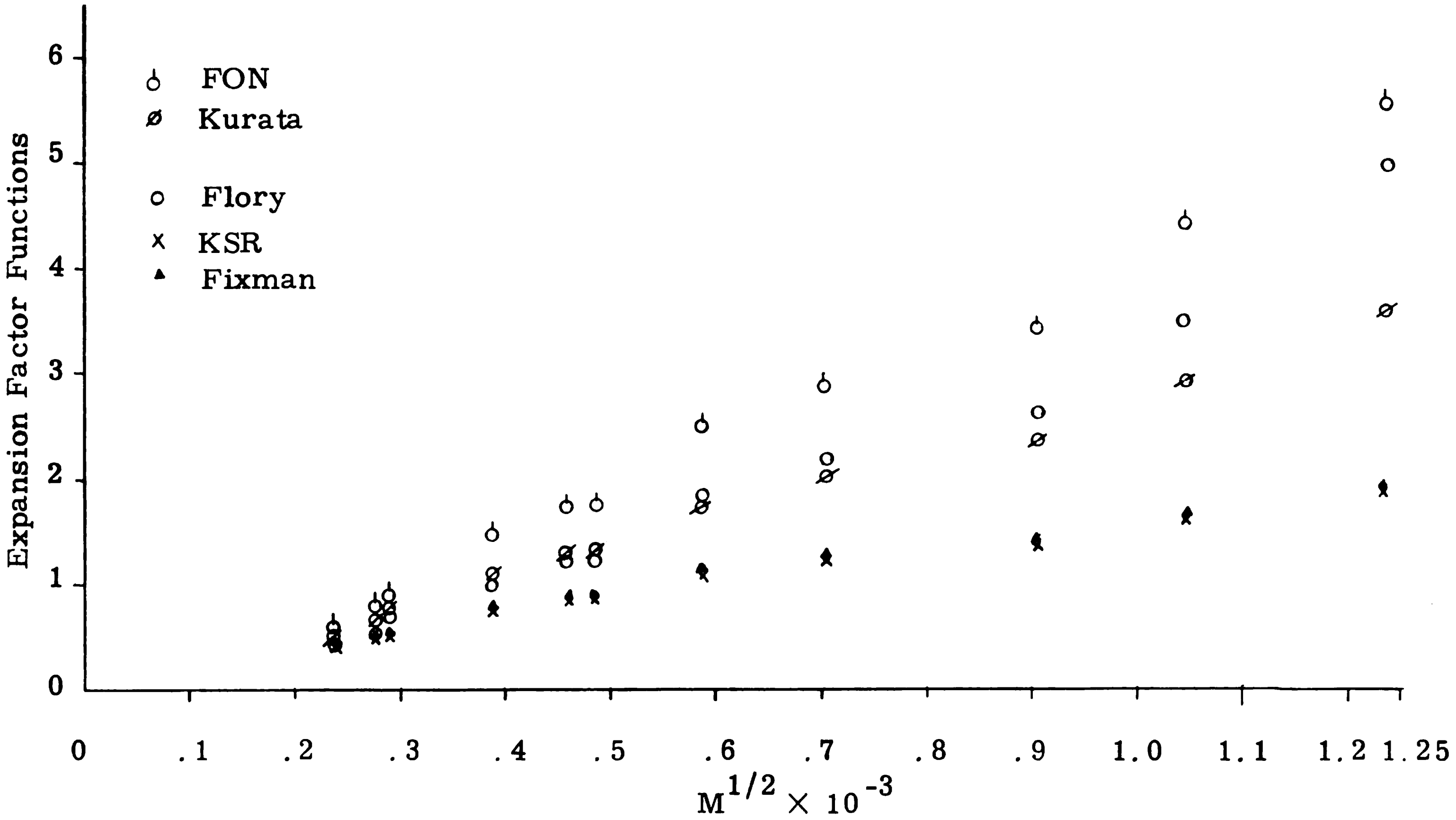


Figure 13. --Expansion factor functions vs $M^{1/2}$ for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

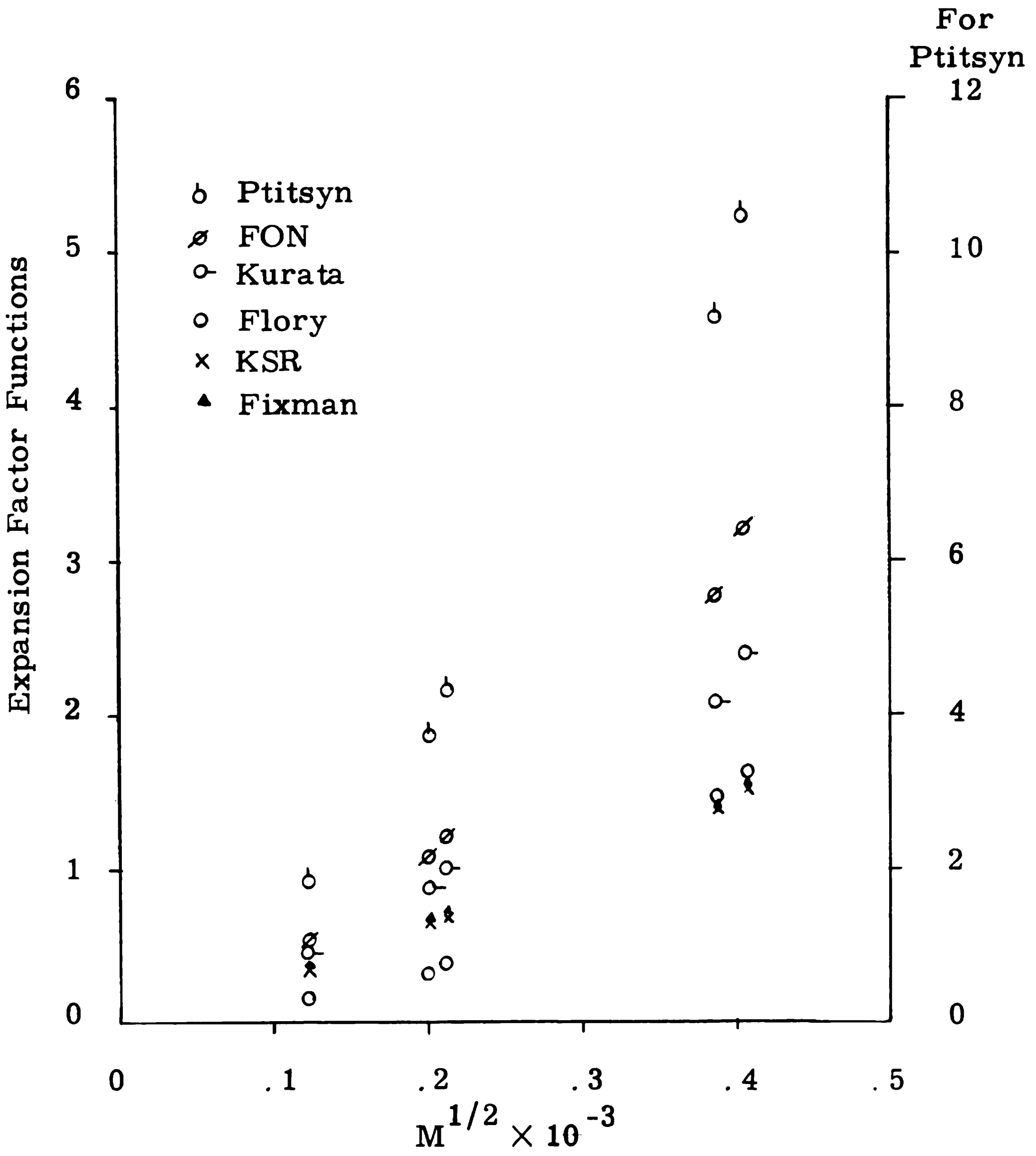
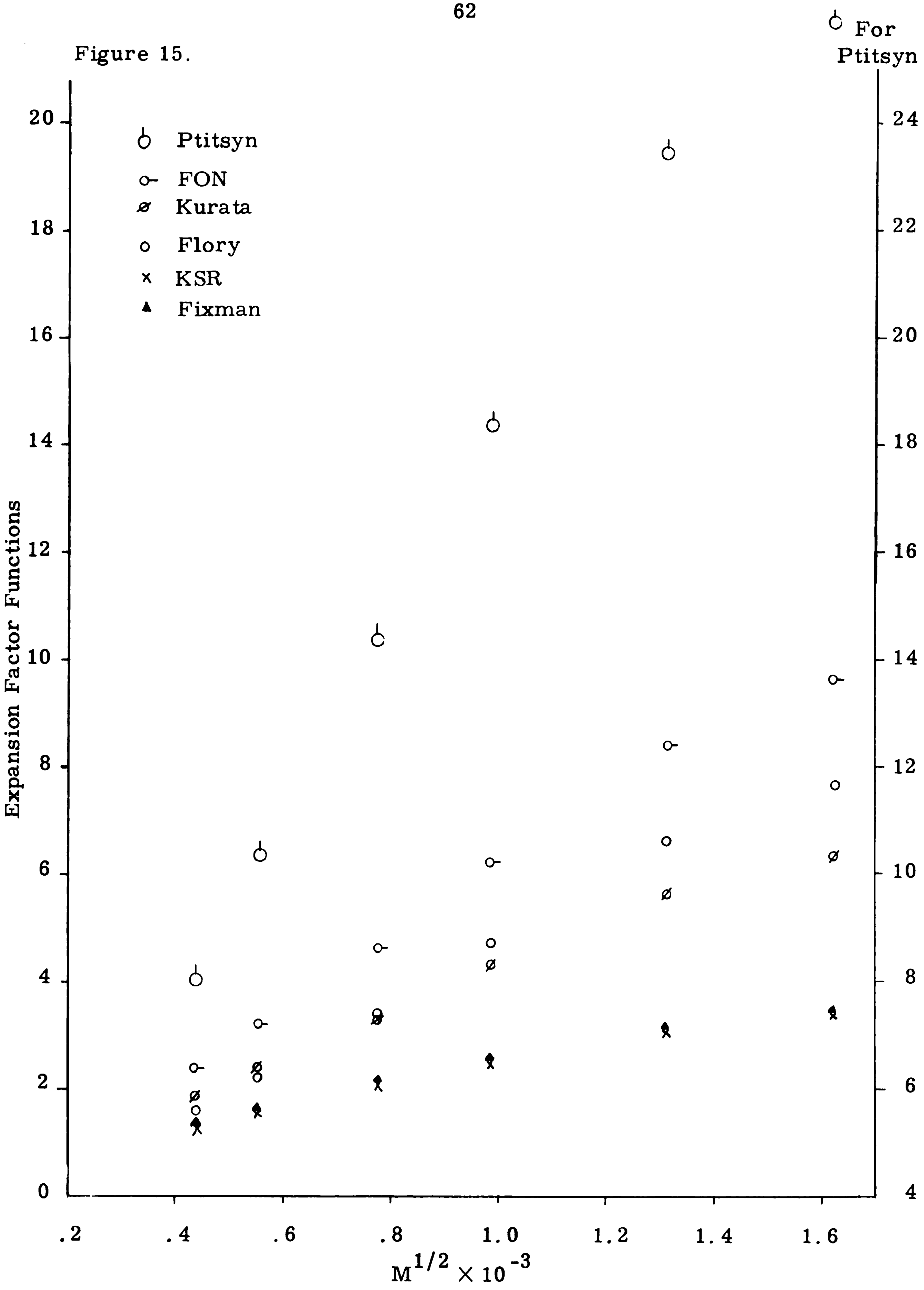


Figure 14. --Expansion factor functions vs $M^{1/2}$ for polystyrene-toluene at 30° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/2.43}$.

Figure 15. --Expansion factor functions vs $\overline{M}^{1/2}$ for polymethyl methacrylate in toluene at 27° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/2.43}$.

Figure 15.


For Ptitsyn
Ptitsyn
FON
Kurata
Flory
KSR
Fixman
Expansion Factor Functions
0
2
4
6
8
10
12
14
16
18
20
4
6
8
10
12
14
16
18
20
22
24
.2
.4
.6
.8
1.0
1.2
1.4
1.6
$M^{1/2} \times 10^{-3}$

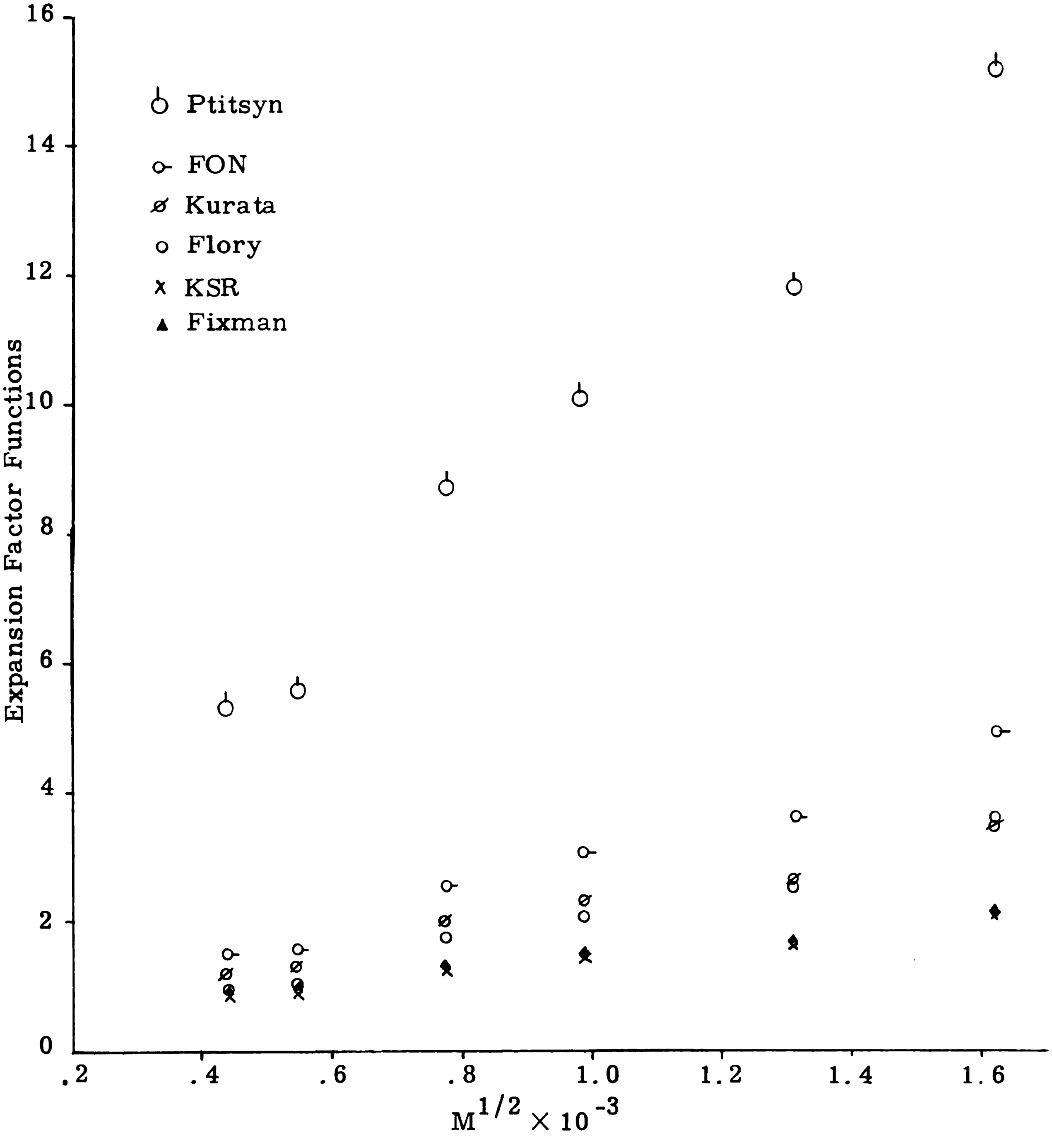


Figure 16. --Expansion factor functions vs $M^{1/2}$ for polymethyl methacrylate in methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

Figure 17. -- Expansion factor functions/$M^{1/2}$ vs M for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

Figure 17.

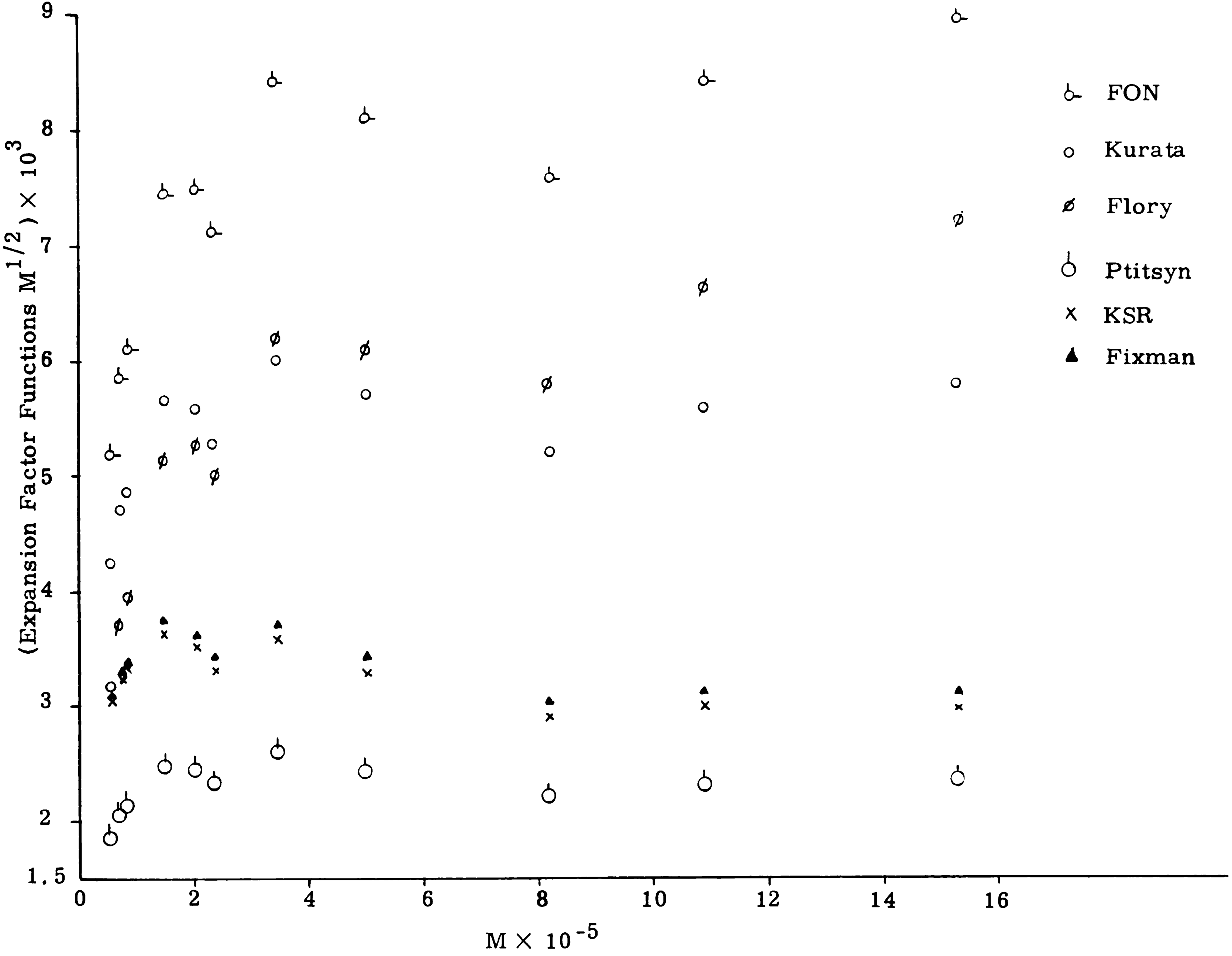

(Expansion Factor Functions $M^{1/2}$) × 10^3
9
8
7
6
5
4
3
2
1.5
0
2
4
6
8
10
12
14
16
M × 10^{-5}
FON
Kurata
Flory
Ptitsyn
KSR
Fixman

Figure 18. --Expansion factor functions/$M^{1/2}$ vs M for polystyrene-toluene at 30° C with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

Figure 18.

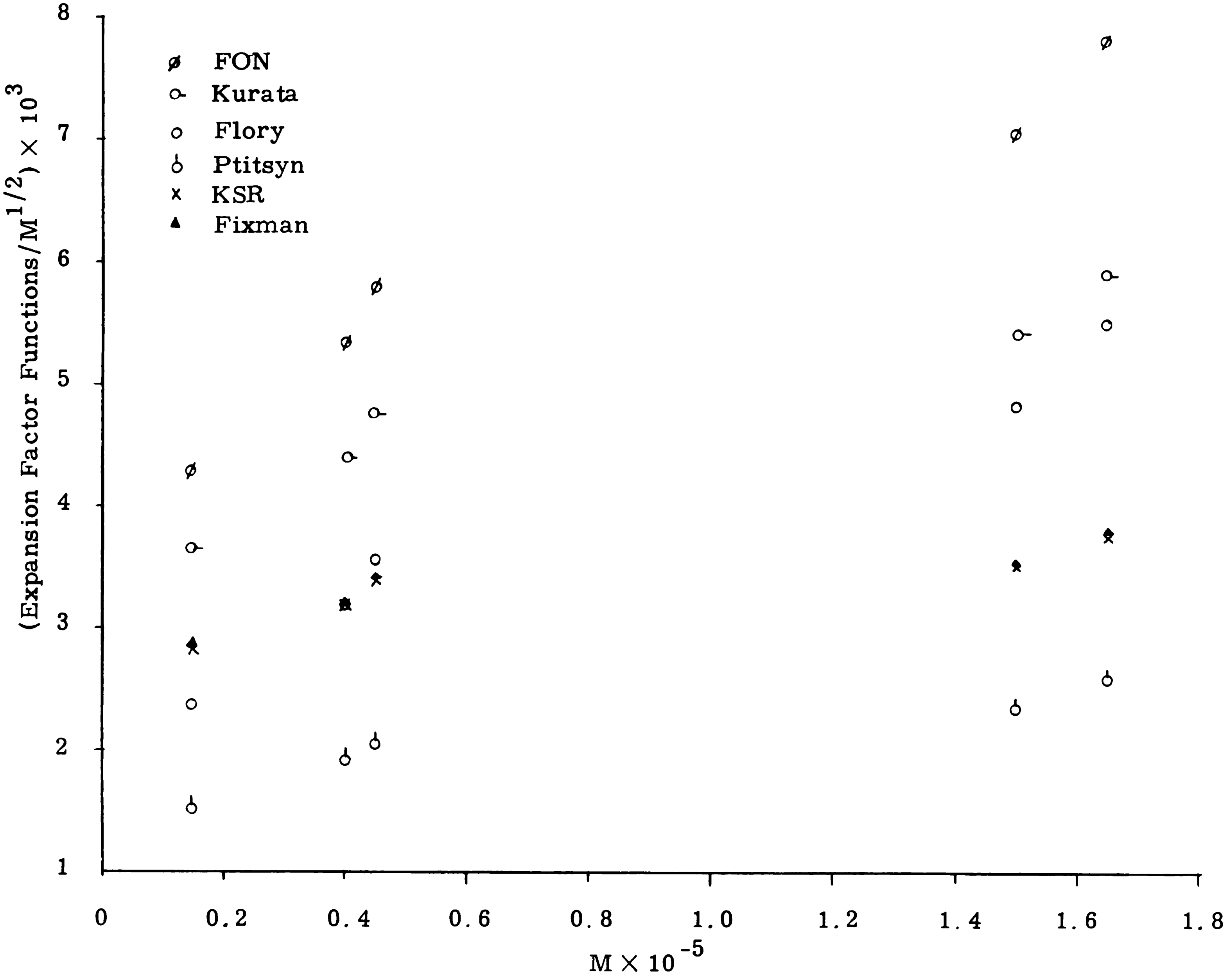
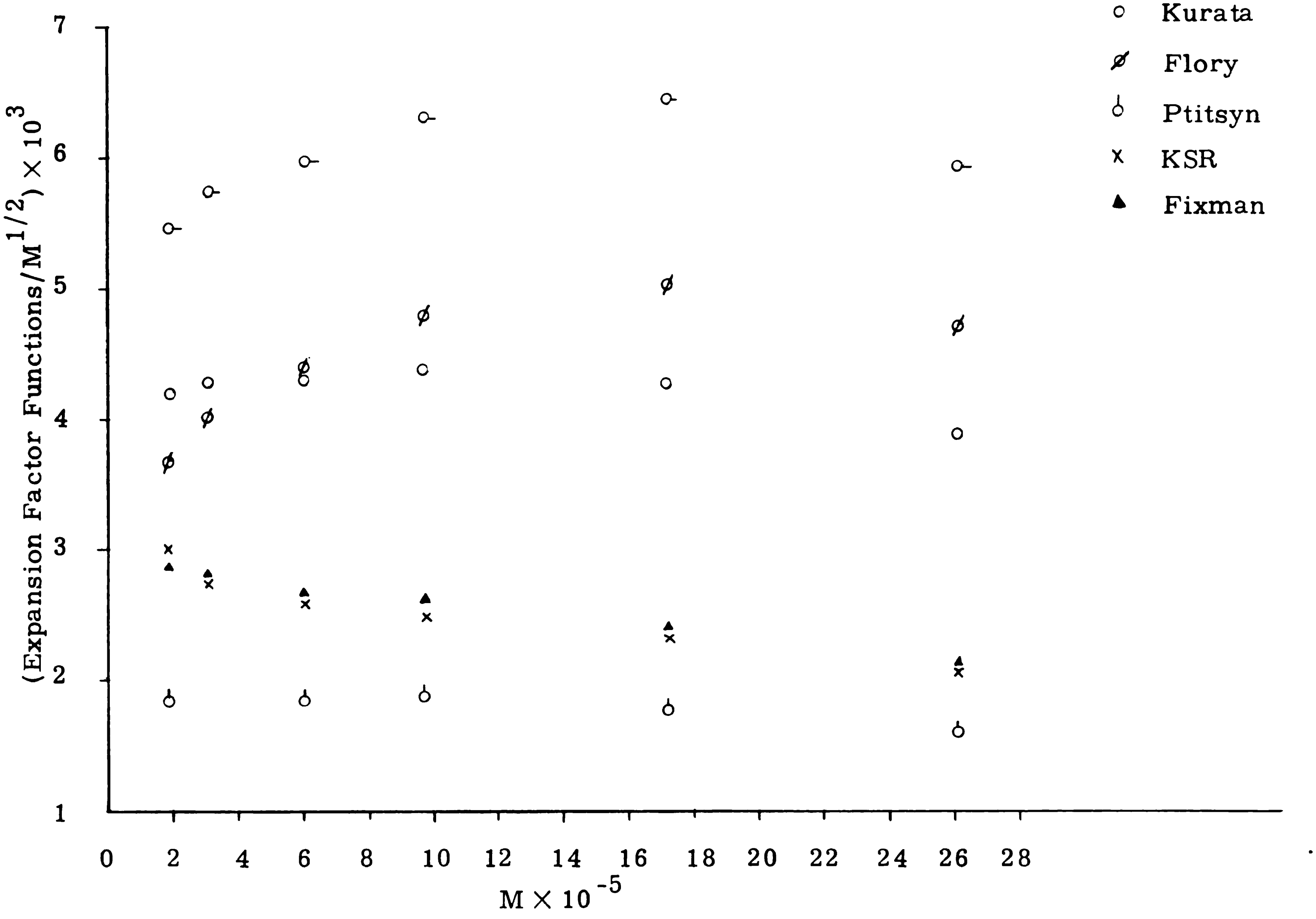

(Expansion Factor Functions/$M^{1/2}$) × 10^3
8
7
6
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
M × 10^{-5}
FON
Kurata
Flory
Ptitsyn
KSR
Fixman

Figure 19. --Expansion factor functions/$M^{1/2}$ vs M for polymethyl methacrylate-toluene at 27° C with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.



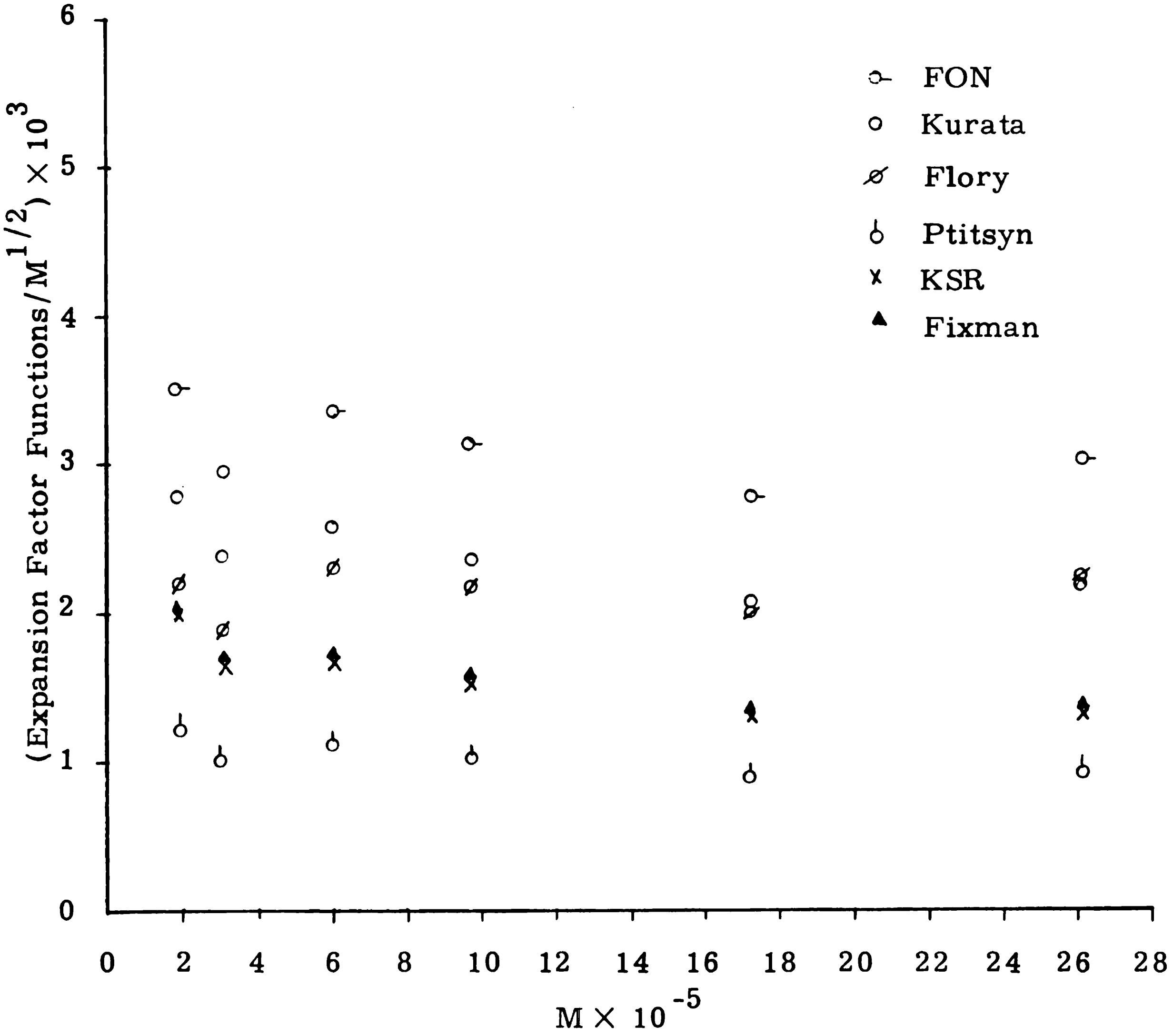


Figure 20. --Expansion factor functions/$M^{1/2}$ vs M for polymethyl methacrylate-methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

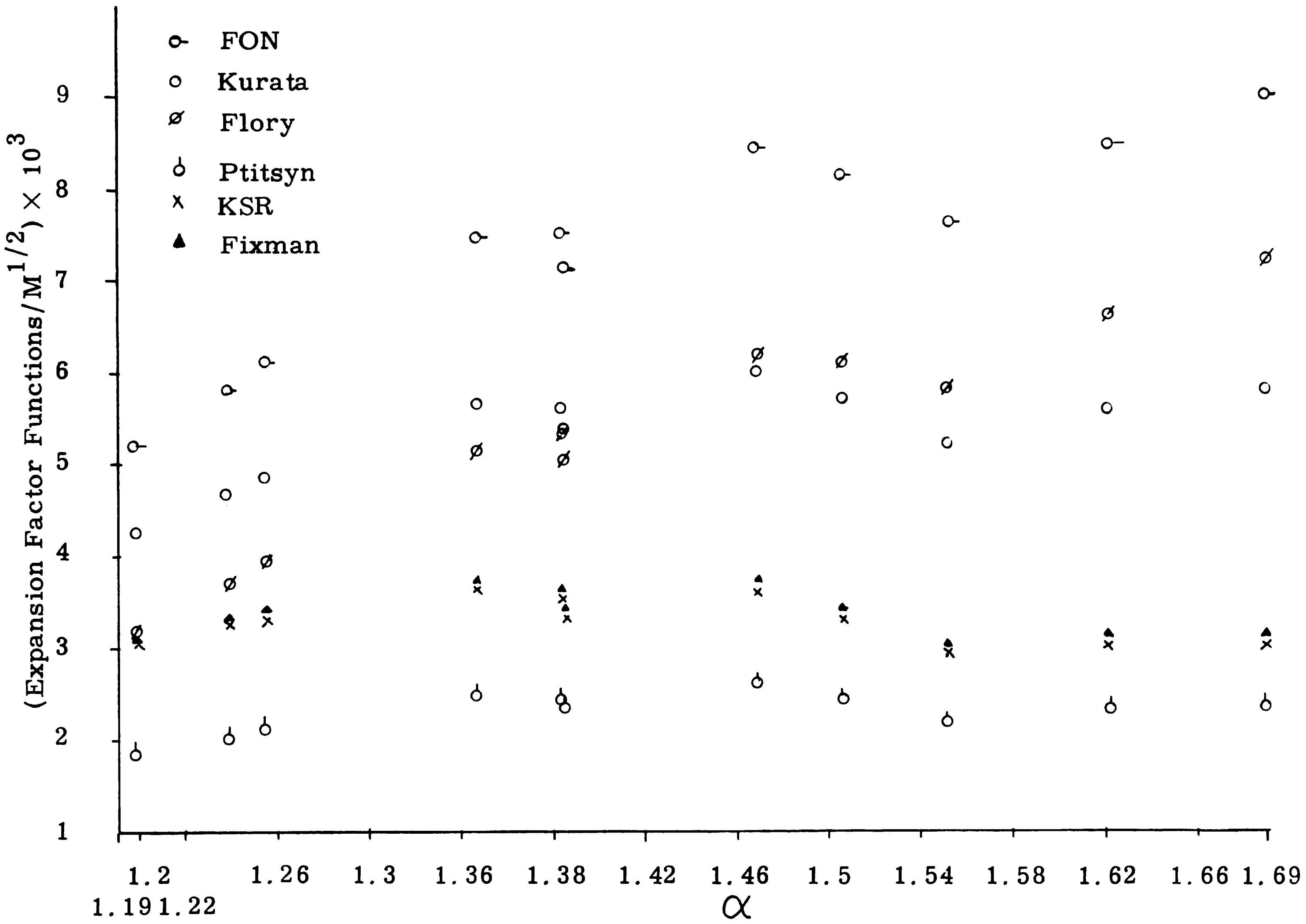


Figure 21. --Expansion factor functions/$M^{1/2}$ vs α for polystyrene-benzene at 30° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/2.43}$.

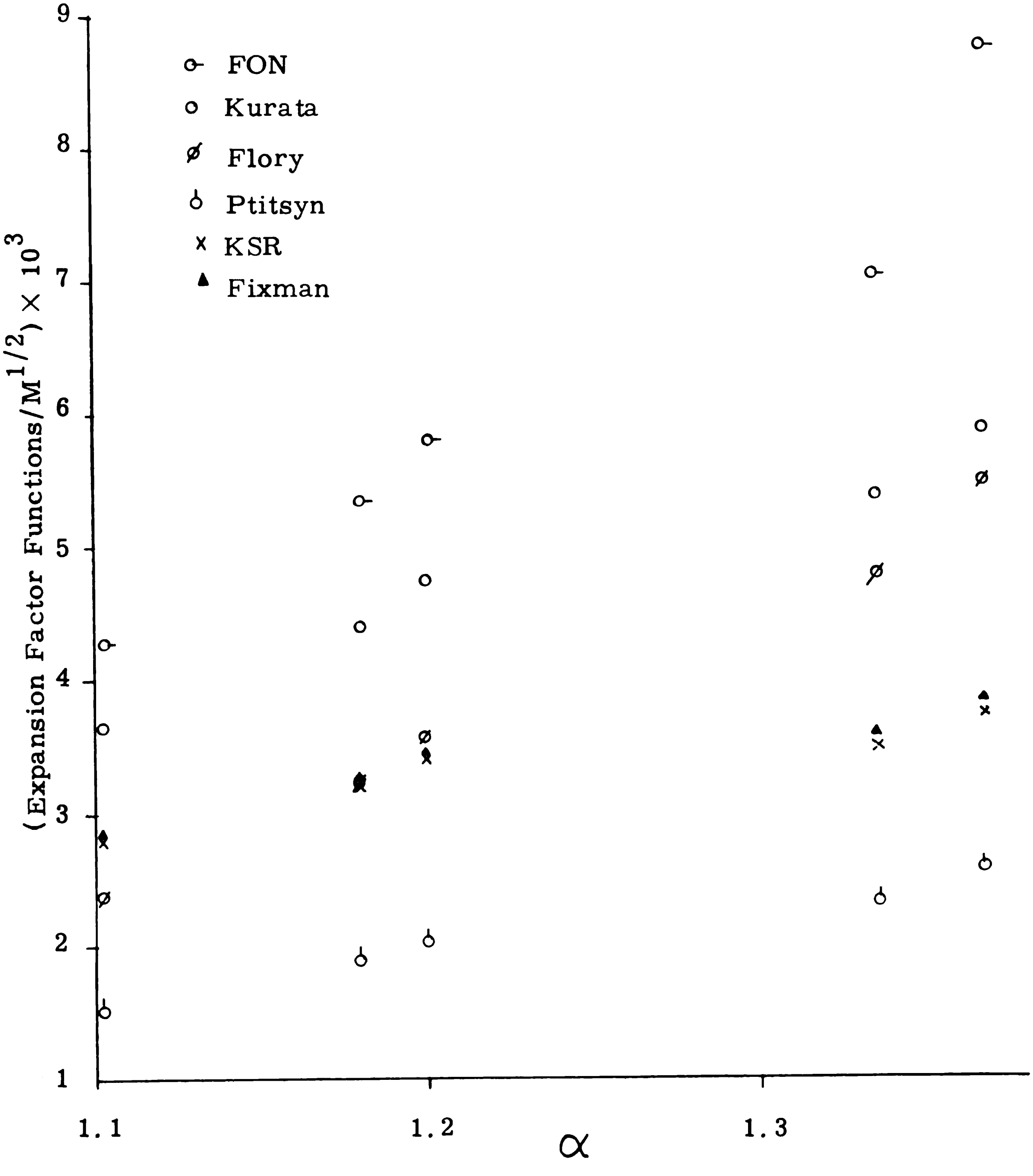


Figure 22. --Expansion factor functions/$M^{1/2}$ vs α for polystyrene-toluene at 30° C with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

Figure 23. --Expansion factor functions/$M^{1/2}$ vs α for polymethyl methacrylate-toluene at 27° C. with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$.

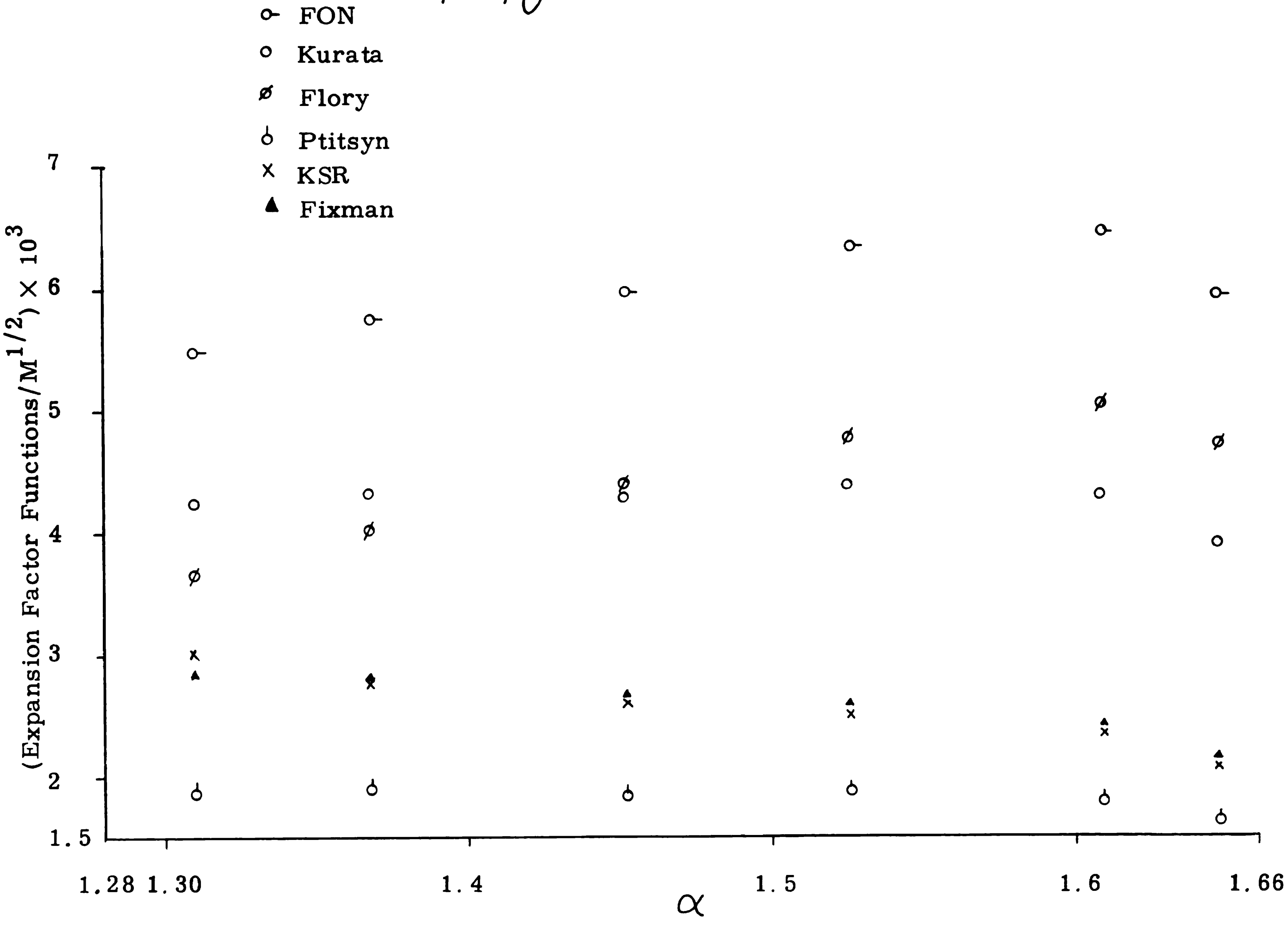


Figure 24. --Expansion factor functions/$M^{1/2}$ vs α for polymethyl methacrylate-methyl isobutyrate at 27° C. with $\alpha = ([\eta]/[\eta]_{\theta})^{1/2.43}$.

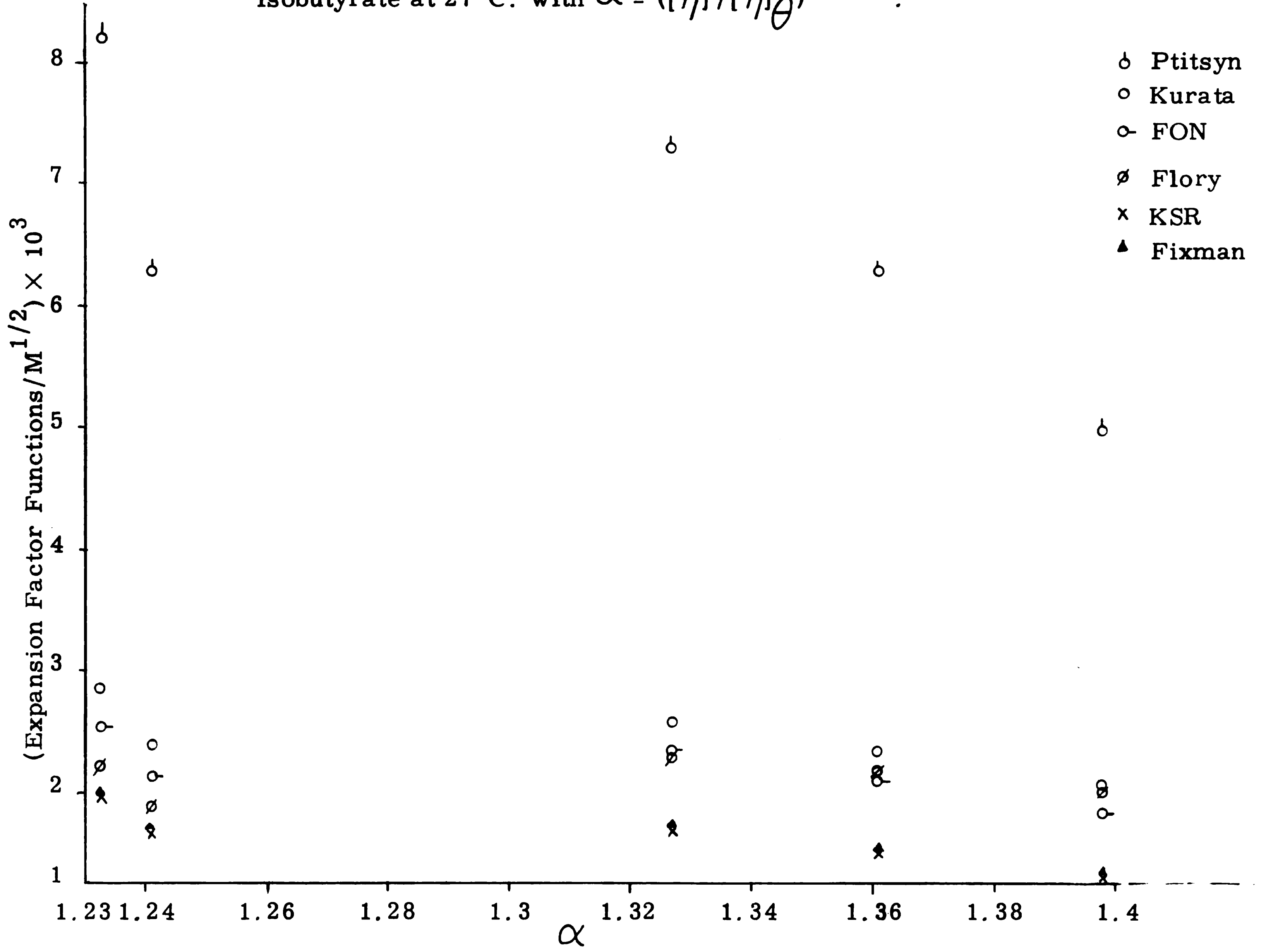
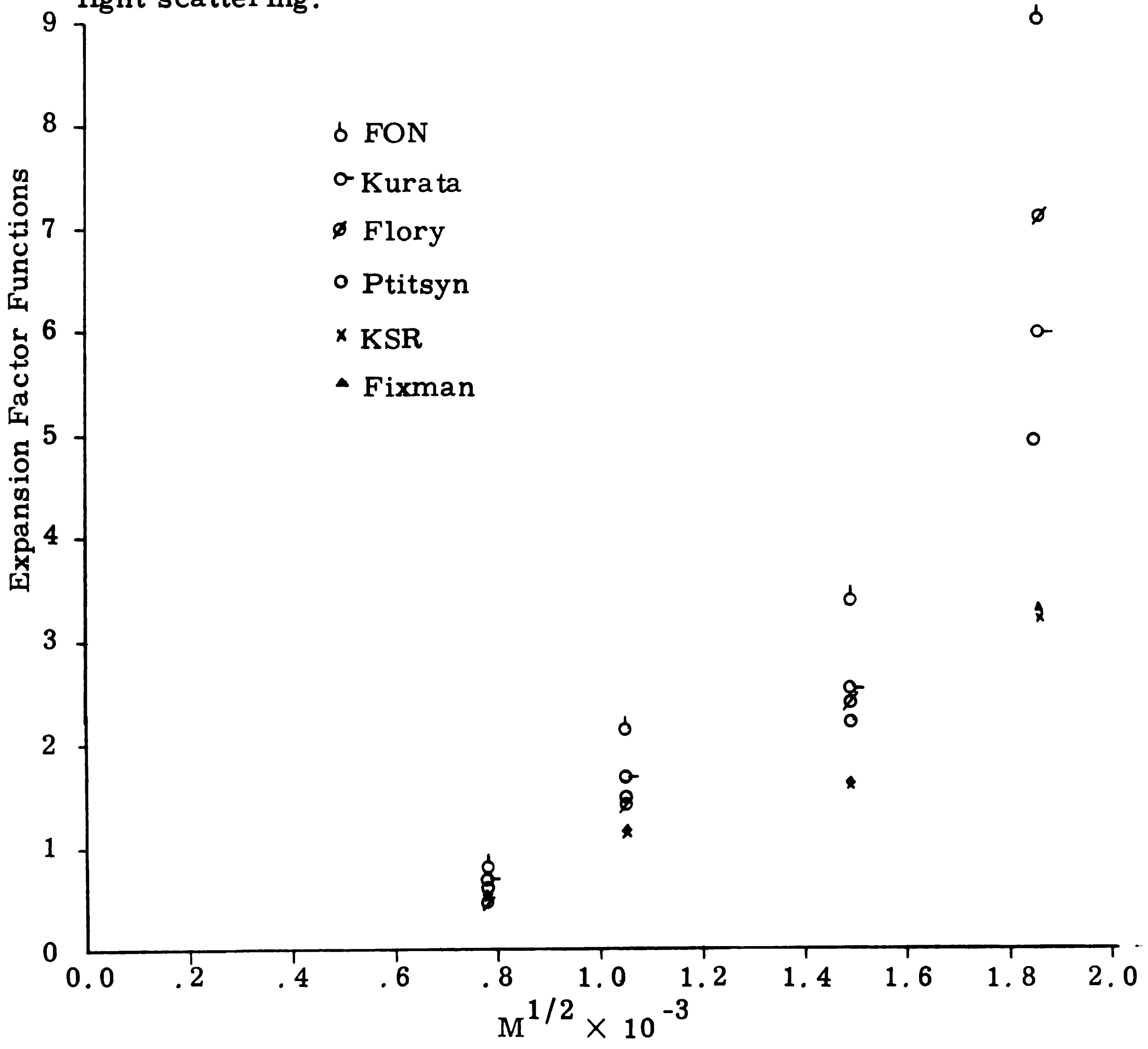


Figure 25. --Expansion factor functions vs $M^{1/2}$ for polystyrene-toluene at 20° C. with α from light scattering.



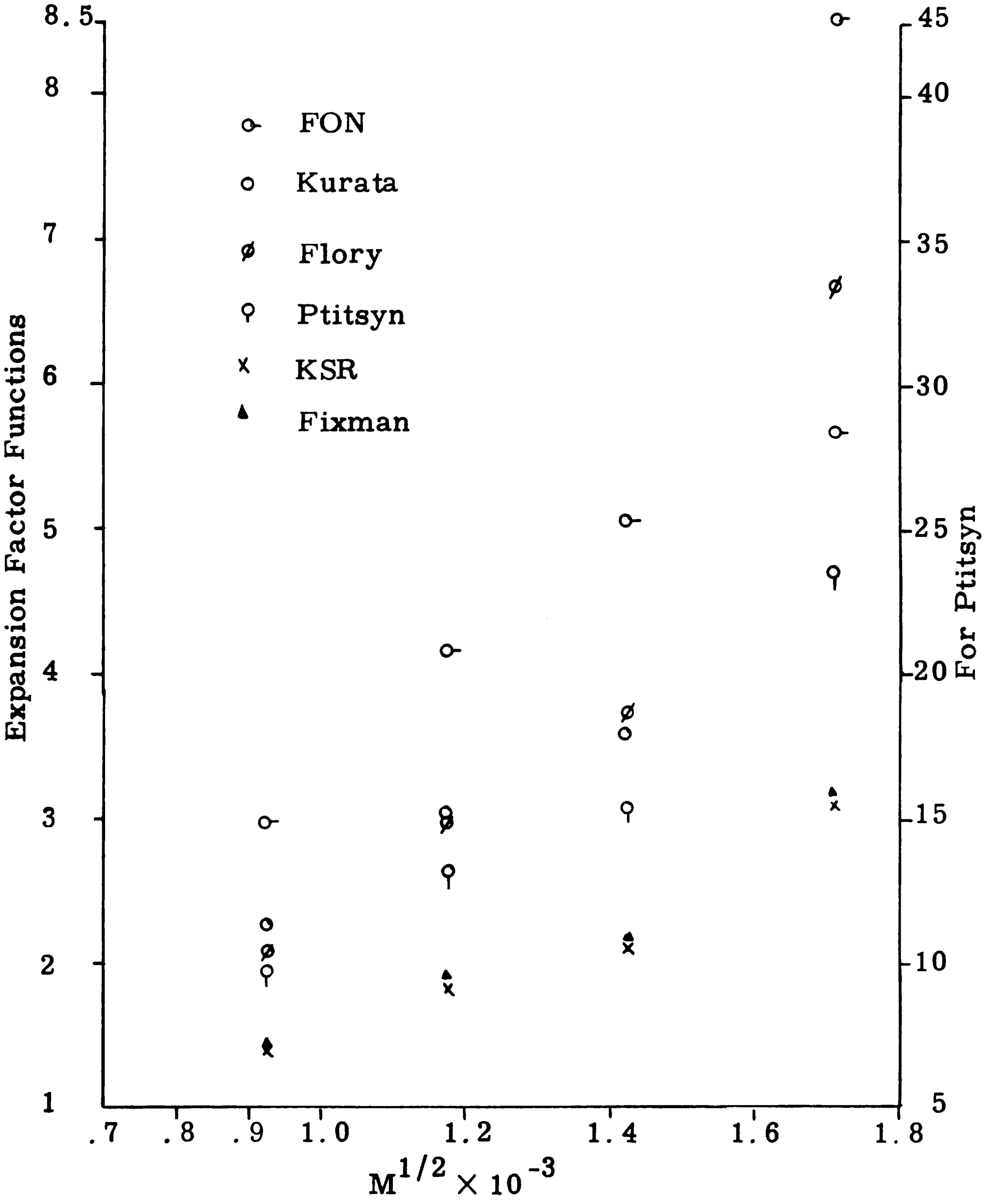


Figure 26. --Expansion factor functions vs $M^{1/2}$ for polyvinylchloride-methyl ethyl ketone at 25° C. with α from light scattering.

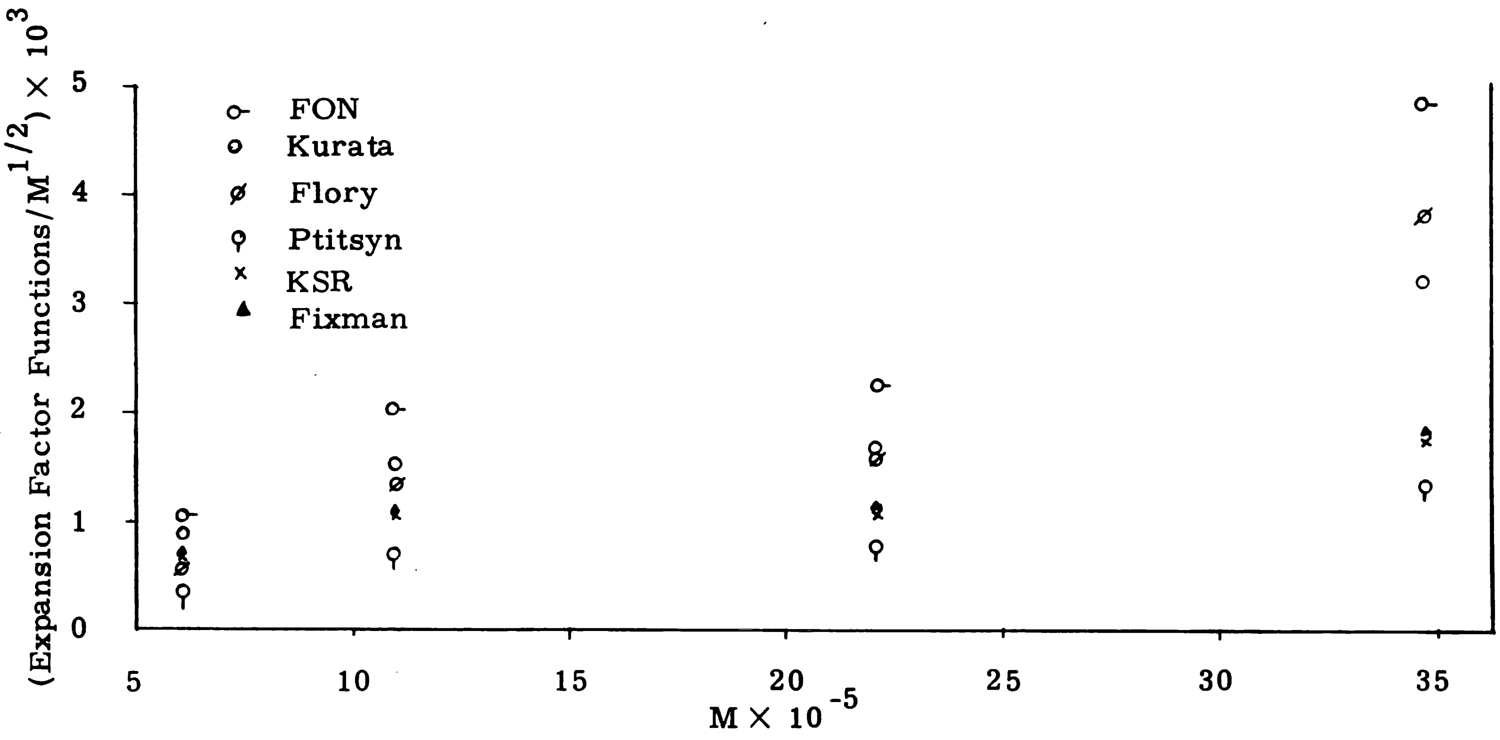


Figure 27. --Expansion factor functions/$M^{1/2}$ vs M for polystyrene-toluene at 20° C. with α from light scattering.

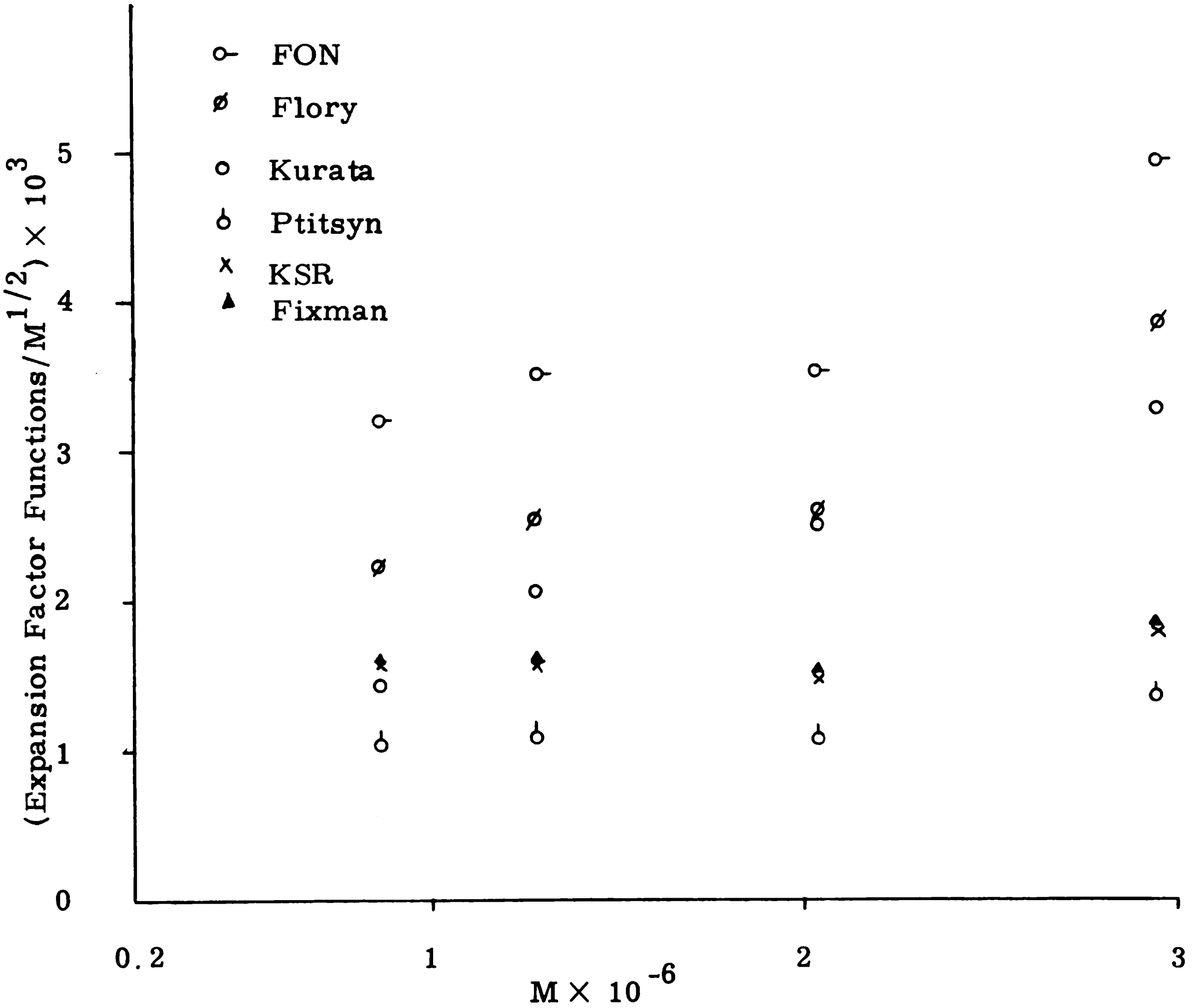


Figure 28. --Expansion factor functions/$M^{1/2}$ vs M for polyvinylchloride-methyl ethyl ketone at 25° C. with $\overline{\alpha}$ from light scattering.

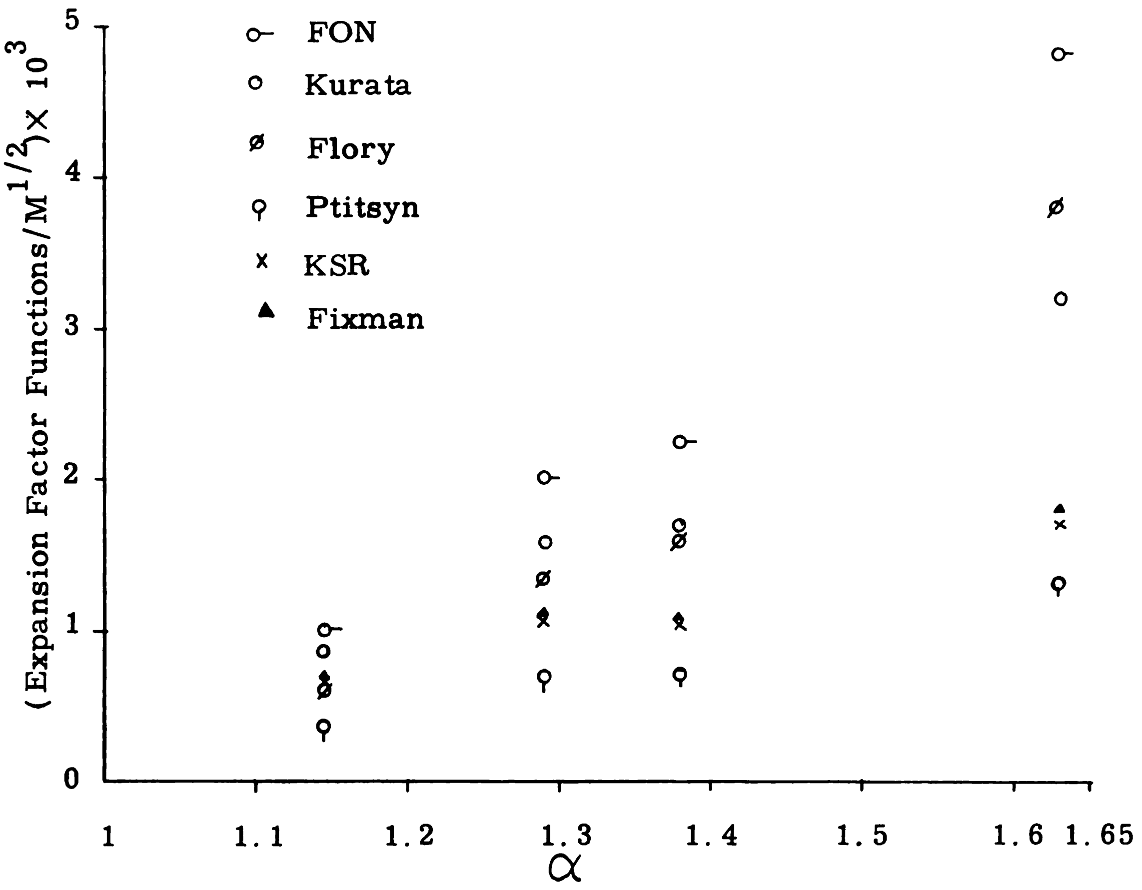


Figure 29. --Expansion factor functions/$M^{1/2}$ vs α for polystyrene-toluene at 20° C. with α from light scattering.

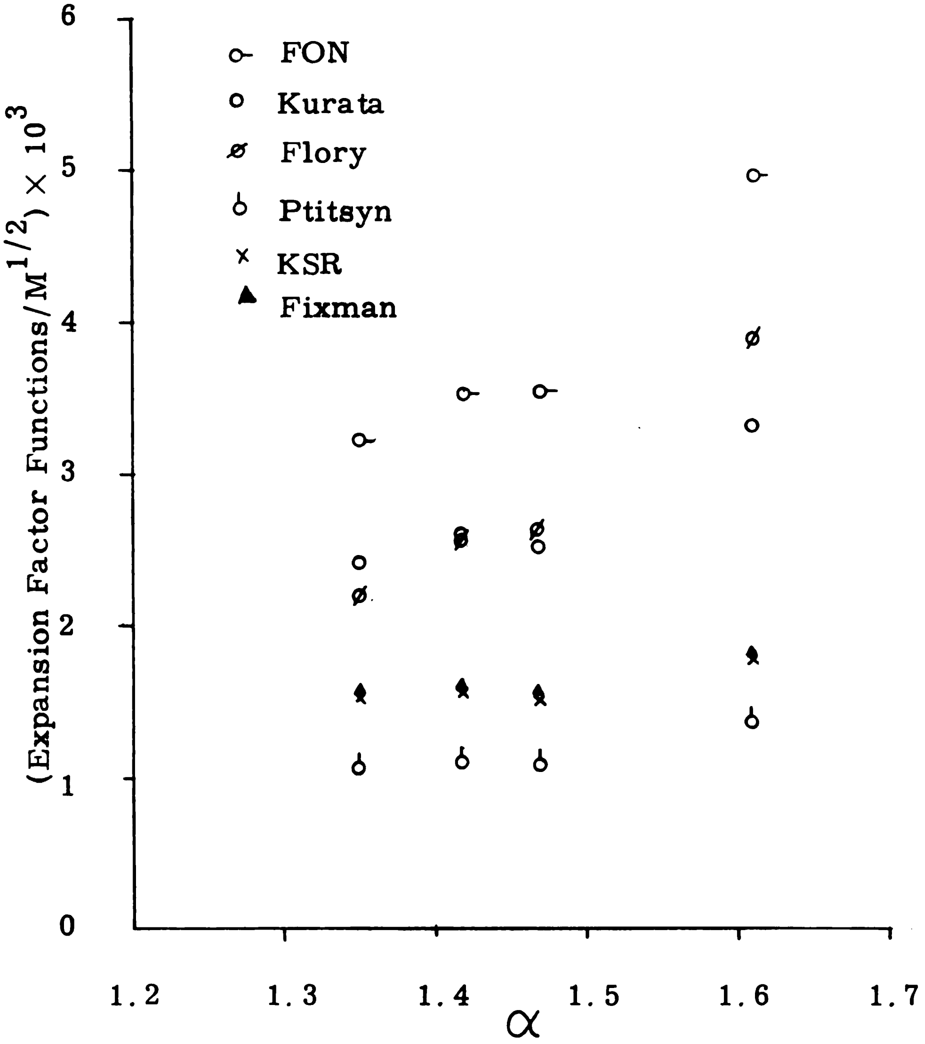


Figure 30. --Expansion factor functions/$M^{1/2}$ vs α for polyvinylchloride-methyl ethyl ketone at 25° C. with $\overline{\alpha}$ from light scattering.

CHAPTER VIII

OTHER THEORIES

Kurata, Stockmayer and Roig (KSR) and Fixman Theories

The KSR and Fixman equations will be discussed together since it can be seen from the figures that both equations give points very close to each other.

Plots of Expansion Factor Functions Against $M^{1/2}$ with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

In the cases of P-B and PMMA-T, as shown in Figures 1 and 3, it can be observed that at high values of α or for higher molecular weights, the points give a curve. From this it seems that the KSR and Fixman equations are appropriate for relatively low molecular weights. The data for P-T (Figure 2) and PMMA-MIB (Figure 4) fall reasonably on a straight line. The lines do not pass through the coordinate origin and in the cases of PMMA-T (Figure 3) and PMMA-MIB (Figure 4) they show negative intercept on the abscissa axis. Other observations are similar to those observed in plots from Flory's equation.

Plots of Expansion Factor Functions/$M^{1/2}$ Against M

Figures 5-8 show these plots for P-B, P-T, PMMA-T and PMMA-MIB respectively. In these plots the points are much less scattered above the horizontal lines than the points in plots from Flory's equation. In the plot for P-B (Figure 5), for small values of molecular weight, one can observe an upward curve. This may be due to an error in the values of intrinsic viscosities at low values of molecular weight. As the molecular weight increases, there is a slight fall in the curve which finally becomes a horizontal line at higher molecular weights. This observation supports the validity of these equations at higher molecular weights which is quite in contrast to the observation made for plots of expansion factor function against $M^{1/2}$. In the plot for P-T (Figure 6), the deviation of points is much less as compared to Flory's theory, although the points do not fall on a horizontal line. Here the line slowly rises with molecular weight with a slight scattering of the points about this line. For PMMA-T (Figure 7) and PMMA-MIB (Figure 8), the line slowly falls with an increase in the molecular weight.

Plot of (Expansion Factor Function)/$M^{1/2}$ Against α with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

Figures 9-12 show these plots. For P-B (Figure 9) one observes a slight upward curvature about the horizontal line and then a fall with a final horizontal line. For P-T (Figure 10) one observes a rise in the plot with increasing α values. For PMMA-T and PMMA-MIB (Figures 11 and 12) there is a uniform fall in the plot with increasing α values.

From all the above plots, it can be seen that the KSR and Fixman equations represent the experimental observation better than the Flory equation.

Plots with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$

No noticeable improvement in the plots is observed with the above α values (Figures 13-24).

Plots with α Values Direct from Light Scattering

Figures 25-30 show different plots for both the systems. Figures 25 and 26 show the plots of expansion factor function against $M^{1/2}$ for PS-T and PVA-MEK respectively. The plots are far from expected shapes and are no better than those obtained with

Flory's equation. Figures 27 and 28 show the plots of (expansion factor function)/$M^{1/2}$ against M. The representation is much better than Flory's equation. Similar is the case with the plots of (expansion factor function)/$M^{1/2}$ against α as shown in Figures 29 and 30.

Kurata Theory

The Kurata equation shows a slight upward curvature for P-B and PMMA-T in the plots of expansion factor function against $M^{1/2}$ as shown in Figures 1 and 3 respectively. This is similar to that observed in the same plots for the KSR and Fixman equations (Figures 1 and 3). In other plots (Figures 2 and 4) the shape is similar to the plots of KSR and Fixman equations (Figures 2 and 4), but the scattering of points is slightly more. From most of the plots one can see that the Kurata plots are similar to the KSR and Fixman plots with slightly magnified error.

The Kurata and KSR-Fixman plots have much different shapes when (expansion factor function)/$M^{1/2}$ against M is plotted for PVA-MEK (Figure 28) and the same against α is plotted for PS-T (Figure 29) and PVA-MEK (Figure 30) with α calculated from light scattering. In most of the other plots one observes a little more deviation in the Kurata plots than in the KSR-Fixman plots.

Fujita, Okada and Norisuye (FON) Theory

Figure 1 shows a plot of expansion factor function against $M^{1/2}$ for P-B with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$. It can be seen that at higher values of molecular weight, the points are so scattered that it is hard to draw a line through them. While for the same plot, a considerable improvement is observed with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$ as shown in Figure 13.

Other plots shown in Figures 2, 14, 15, and 16 show shapes similar to those obtained before.

The plot of (expansion factor function)/$M^{1/2}$ against M (Figure 5) shows a wide scatter about a horizontal line and this is even worse when $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$, as can be seen in Figure 17, for P-B. Similar is the case for the same plots for P-T as shown in Figures 6 and 18. For PMMA-T, the plot shows a good horizontal line as shown in Figure 7; but the same plot with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$ shows an upward curve with a distinct maximum (Figure 19). The plot for PMMA-MIB (Figure 20) shows a downward curve.

Figure 9 shows a plot of (expansion factor function)/$M^{1/2}$ against α for P-B with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$. There is an upward curve with the points widely scattered about the curve. The same plot when made with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$ gives points scattered at random as shown in Figure 21. Figures 10 and 22 show plots for P-T with both values of α respectively. Both plots show an increase in the plot with increasing α.

Figure 11 shows a surprisingly good horizontal line with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$, with the point with highest α falling out of the line. Figure 23 shows the same plot with $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$. There is an upward curve. Figures 12 and 24 show plots for PMMA-MIB with both values of α respectively. There is a fall in the line with increasing α.

Figures 25-30 show plots of FON equation with α values from light scattering. It can be seen that the FON equation shows the maximum deviation from the expected shapes.

Ptitsyn Theory

Expansion Factor Function Against $M^{1/2}$ with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

Figure 31 shows this plot for P-B. At the low values of M, the plot is a straight line, but not passing through the coordinate origin. At high values, there is a smooth curve, with points slightly scattered about this curve. Figure 2 shows the plot for P-T. The behavior here is similar to that observed with other equations. Figure 3 shows the plot for PMMA-T. The plot is a straight line at low values of M, almost passing through the coordinate origin.

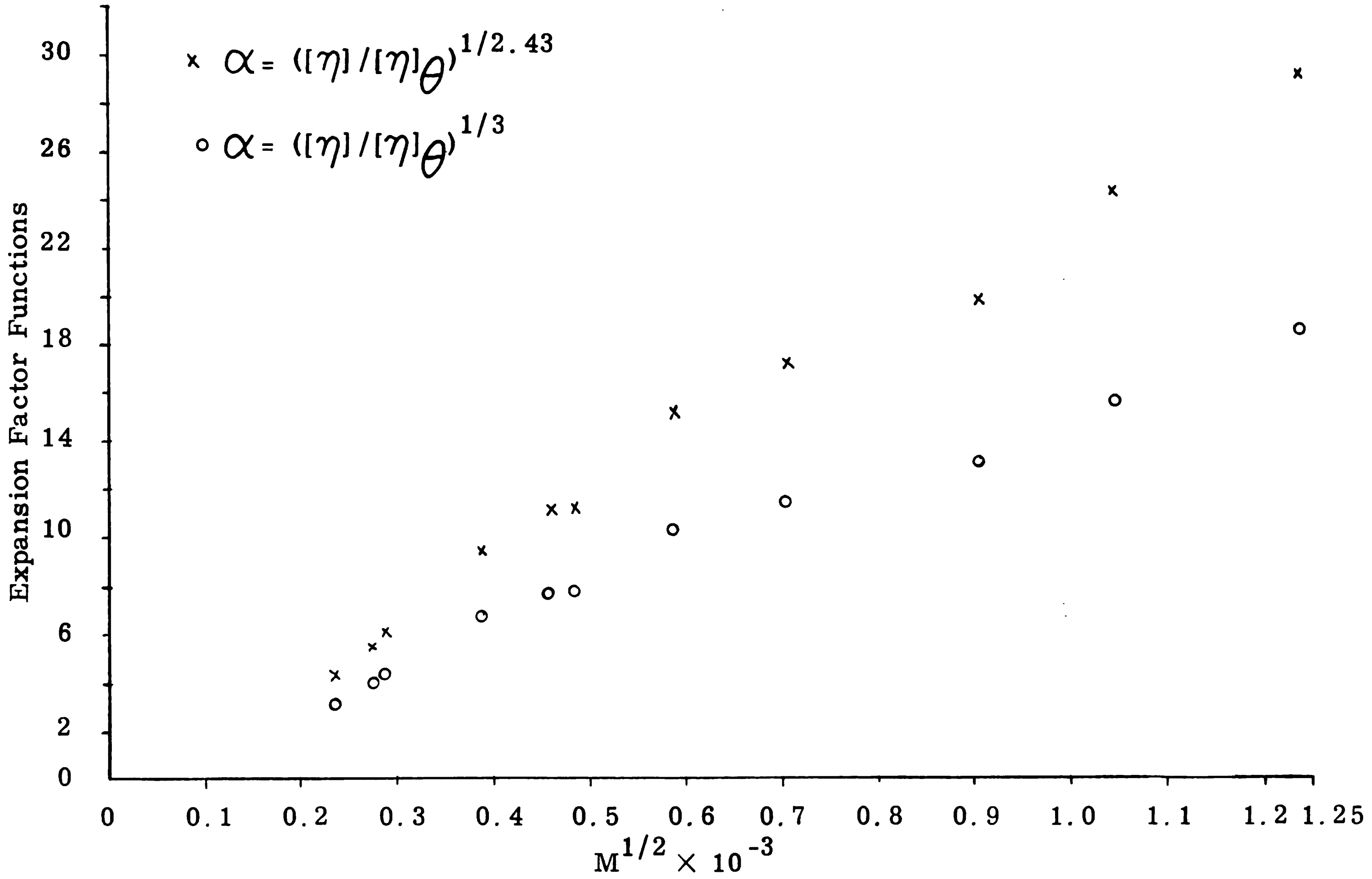


Figure 31. --Expansion factor function of the Ptitsyn equation vs $M^{1/2}$ for polystyrene-benzene at 30° C. with α from $([\eta]/[\eta]_\theta)^{1/3}$ and $([\eta]/[\eta]_\theta)^{1/2.43}$.

At high values, it shows a curve. Figure 4 shows the plot for PMMA-MIB. Here the points are too scattered to draw any line or curve.

(Expansion Factor Function)/$M^{1/2}$ Against M with $\alpha = ([\eta]/[\eta]_\theta)^{1/3}$

Figures 5-8 show these plots. For P-B and P-T (Figures 5 and 6), the deviation from a horizontal line is the least for Ptitsyn equation in comparison with all the other equations. Figure 7 shows this plot for PMMA-T where the curve continuously falls as molecular weight increases. Similar is the case with PMMA-MIB (Figure 8), where there is a downward curve.

(Expansion Factor Function)/$M^{1/2}$ Against α

Figure 9 shows an almost horizontal line for P-B. In the case of P-T (Figure 10), there is a very gradual rise with increasing α values. Figure 11 shows practically a horizontal line for PMMA-T, the point with the highest value of α falling out slightly. For all the above cases, the behavior of the Ptitsyn equation is closest to the expected behavior. But in the case of PMMA-MIB, as shown in Figure 12, the behavior of the Ptitsyn equation is the worst. It is not clear why it is so.

No improvement is observed when all the plots are made with α values from $\alpha^{2.43} = ([\eta]/[\eta]_\theta)$ (Figures 14, 24, and 31).

Plots with α from Light Scattering

Figures 25-30 show these plots. Plots of (expansion factor function)/$M^{1/2}$ against M and the same against α (Figures 27-30) show much less deviation from a horizontal line as compared to other equations except the equations of KSR and Fixman where the behavior is pretty much the same.

CHAPTER IX

DISCUSSION OF DIFFERENT THEORIES

Flory Theory

The comparison of the values of the expansion factor function with the experimental α values and the theoretical calculations with the χ values shows that for the nonpolar polymer-nonpolar solvent systems, the theoretical calculation is usually greater than the expansion factor function by a factor of 2 or more for the α values roughly less than 1.2.

In the light of the above observations and other defects observed in the Flory equation when compared with the experiment, one has the following remarks and discussion when examining this equation.

Flory and Orofino[14] observed the values of the quantity $(1/2 - \chi)$ exhibiting a slight dependence on the molecular weight, although no such account is taken care of in this equation. In most cases $(1/2 - \chi)$ decreases as the molecular weight increases. This could be due to:

(a) deviation of the spatial distribution of the molecule from the assumed Gaussian form,

(b) failure to consider the contiguity of molecular segments in space,

(c) neglect of higher terms in derivation of the expression for excluded volume effect,

(d) effects of molecular heterogeneity which may increase with molecular weight of fraction.

(a) is investigated by Flory[14] and he believes it to be an unlikely source of the variation observed. No satisfactory theory is available for dealing with (b). Possibility (c) may be responsible at least in part for the apparent molecular weight dependence of the quantity $(1/2 - \chi)$. With regard to possibility (d), if the molecular heterogeneity of the polymer fraction increases with molecular weight owing to the decreasing efficiency in separation, then accordingly this would be reflected in values of $(1/2 - \chi)$.

As is well known, Fox and Flory[16] have pointed out that the constant Φ takes a common value, 2.1×10^{21}, not only for sufficiently large values of M, but also down to low values of M. Kurata and Yamakawa[17] have shown that the counter contributions of the draining effect and the volume effect make Φ approximately independent of M over wide ranges insofar as the argument X, the draining parameter of Kirkwood and Riseman[18] theory takes a value larger than about ten. However, they[17] say that as X decreases beyond ten, the balance inclines toward the draining effect and a decrease of the ϕ values becomes significant. Kurata and Yamakawa[17] further predict two kinds of deviations of ϕ from the constancy; one is related to the volume effect and the other is related to the draining effect and often is observed for relatively short chains or rigid molecules such as the cellulose derivatives. They concluded that the draining effect is important for quantitative interpretation of intrinsic viscosity as well as the excluded volume effect.

According to Flory and Fox[16]

$$[\eta] = \frac{6^{3/2} \phi \left(< S^2 >_0\right)^{3/2} \alpha^3}{M}$$

Numerical Value of ϕ

Kurata, Yamakawa and Utiyama[19] predict the value of as 2.87 × 10^{21} instead of 2.1 × 10^{21}. About half this difference, according to them, is explainable from the polydisperity effect, but the other half is not by this means.

Dependence of ϕ on Temperature

Krigbaum and Carpenter[20] showed that the Flory constant ϕ should be a decreasing function of temperature, at least in the vicinity of the theta temperature.

Dependence of ϕ on the Solvent Nature

The value of ϕ decreases with the increasing expansion of the polymer coil or the increasing solvent power.

In the vicinity of the Flory temperature, the parameter Z, hence α, increases rather markedly with the temperature. Therefore the constant ϕ is expected to decrease with the temperature and/or the solvent power.[21] On the other hand, at temperatures far above the θ point, this tendency generally becomes weak, although not completely vanished; and accordingly, the ϕ would behave, at least approximately, like a constant as claimed by Flory and Fox.

Krigbaum[22] made an attempt to explain the variation in $(\alpha^5 - \alpha^3)/M^{1/2}$ by means of a theory that assumes that $< r^2 >$ and $< S^2 >$ differ to a different extent on swelling. In conclusion it may be said that it may be possible to improve Flory's equation, at least for the nonpolar systems, so that it can represent the experimental observations better by multiplying $2C_M (1/2 - \chi) M^{1/2}$ by

$(1 - Be^{-M})$ where B is a constant and M is molecular weight, such that at high values of M, Be^{-M} would be much less than 1 while at low values of M, $(1 - Be^{-M})$ would tend to 1/2.

Kurata, Stockmayer and Roig (KSR) and Fixman Theories

In all the plots it is observed that the points due to equations from the above two theories nearly coincide. In fact, the KSR equation is also in good agreement with the numerical solution of Fixman differential equation, Equation (II-3). Both the equations show $(\alpha^5 - \alpha^3)/M^{1/2}$ to be an increasing function of Z unlike Flory's equation, as observed experimentally. In comparison with the Flory plots, the plots from the above two equations show much less scattering of points. There is no definite evidence in the improvement of the plots when α was calculated from $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$, as strongly suggested by Ohyanagi and Matsumoto.[28]

In the derivation of the KSR equation, instead of a spherical symmetrical model, an ellipsoidal model with three radii of inertia

$$R_x^2 = \frac{1}{36} Na^2 + \frac{1}{12} < r^2 >, \quad R_y^2 = R_z^2 = \frac{1}{36} Na^2$$

was used, where $< r^2 >$ is the mean square distance between the ends of the chain, N is the number of segments of the chain, a is the effective length of the link joining neighboring segments, and x, y, and z denote the three axes. (The axis x coincides with the vector joining the ends of the chain.) The KSR equation was derived for the Gaussian chain and its use for chains with volume effects means that the latter increase only the distance between the ends of the chain and have no effect on its cross sectional dimensions. This would lead to a strong dependence of the shape of the chain on volume effects, which is contrary to the strict theory and experiment. Thus KSR equation does not in fact involve a more precise model of the chain (ellipsoidal instead of spherical) but introduces a physically unjustified assumption that in the limit, the swelling of the chain is anisotropic. But Kurata, Stockmayer and Roig[26] claim that their equation is in excellent agreement with the Monte Carlo calculations of Wall and Erpenbeck for a diamond lattice chain and also with viscosity data for various polymer solutions.

Kurata Theory

The Kurata equation shows characteristics somewhere between the Flory equation and the Fixman equation, as can be seen from the plots, leaning more toward the Fixman equation. It shows more scattering than Fixman's equation but less than Flory's equation, and scattering is more for $\alpha = ([\eta]/[\eta]_\theta)^{1/2.43}$. Since this equation is a hybrid of Flory's and Fixman's equations, it has inherent weaknesses of both and does not show much improvement on either of the other two. On the contrary, it seems Fixman's equation is closer to the experiment than Kurata's equation.

Ptitsyn Theory

The plots of (expansion factor function)/$M^{1/2}$ against M and the same against α show that the Ptitsyn equation shows characteristics very much similar to those of KSR and Fixman equations. (The only difference being that the Ptitsyn equation shows much less scatter of the points. In fact, the Ptitsyn equation gave the best plots in most of the cases.) This is because the Ptitsyn equation is an artificial modification of the Fixman equation. It seem, the allowance for the non-Gaussian character of the function W(h) has led to considerably improved agreement between this theory and experiment. Kurata[29] has observed that in a plot of α^3 against Z, his equation is closer to that of Fixman and Ptitsyn rather than to that of Flory. This is quite evident since the Ptitsyn equation is an artificial modification of the Fixman equation.

Fujita, Okada and Norisuye (FON) Theory

The FON equation deviates the most from the experiment. Fujita et al.[30] observed that in the region of α^3 up to about 3, their equation when plotted for α^3 against Z gives a curve which nearly coincides with that predicted by the Ptitsyn equation; but beyond this, the latter yields α^3 which increases more rapidly with increasing Z.

CHAPTER X

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Flory's Equation

The most important factors that focus one's attention on Flory's equation $\alpha^5 - \alpha^3 = 2C_M (1/2 - \chi) M^{1/2}$ for improvement are C_M and χ. For the nonpolar polymer-nonpolar solvent systems, the theoretical calculations using χ values changed from nearly the same (in fact a little less) value as that of the expansion factor function calculated from the experimental values of α to twice or more than twice the value of the expansion factor function as α decreased. Accepting Flory's theory, the theoretical calculation requires an α dependent adjustment. This adjustment could either depend on M or χ or both.

The expansion factor function $(\alpha^5 - \alpha^3)$ when plotted against $M^{1/2}$ gives in most cases nearly a straight line. From this one can conclude that $2C_M (1/2 - \chi) M^{1/2}$ is not a function of M.

The plot of $(\alpha^5 - \alpha^3)/M^{1/2}$ against M deviated from the horizontal line at comparatively low values of M. $2C_M (1/2 - \chi) M^{1/2}$ is not independent of M for polystyrene if M is less than about 3×10^5 but it seems independent of M for M greater than 3×10^5. It may be possible to rectify this situation by multiplying $2C_M (1/2 - \chi) M^{1/2}$ by $(1 - Be^{-M})$ where B is a constant such that at high values of M, Be^{-M} would be much less than 1, while at low values of M $(1 - Be^{-M})$ would tend to 1/2. It may be possible to relate the constant B to the binary integral β.

For polar systems no clear conclusion can be drawn as in the case of nonpolar systems unless the independent values of χ are available to make a comparison between the experimental value of the expansion factor function $(\alpha^5 - \alpha^3)$ and the theoretical calculation of $2C_M (1/2 - \chi) M^{1/2}$. Complete data for only one system were obtained from the literature. The χ values were obtained from Reference 49. The value of the entropy parameter χ_S is suggested as 0.34 and a method of calculation of the heat parameter χ_H is shown in the same reference. The use of this χ value made the theoretical calculation of $2C_M (1/2 - \chi) M^{1/2}$ four to five times larger than the experimental expansion factor function $(\alpha^5 - \alpha^3)$ for the system investigated. Also it was observed that a small variation in the χ value altered the value of the theoretical calculation to a large extent. This observation warrants a new investigation in the value of χ_S. Since χ_S is a function of the size and shape of the molecules in solution, it seems this dependence is very strong in the polar systems.

Relation Between $[\eta]$, $[\eta]_\theta$ and α

Many workers have strongly suggested that the value of n in $\alpha^n = [\eta]/[\eta]_\theta$ should not be 3 but a little less than that. One suggested value for n is 2.43. With this value of n, α was calculated and the different plots were made, but there was hardly any improvement observed in the plots. On the contrary, the plots with n = 3 were closer to the experiment. This shows that n = 3 is the best so far.

The evaluation of n by light scattering is not strictly possible because light scattering gives the change in the radius of gyration from that at the theta temperature, i.e. one gets $\alpha_L^2 = < S^2 >/< S^2 >_0$ whereas the expansion factor α in the equation $\alpha^n = [\eta]/[\eta]_\theta$ refers to the change in the end-to-end distance of a chain, i.e. $\alpha^2 = < r^2 >/< r^2 >_0$. α_L and α are slightly different as can be seen from the exact series expansion of the two

$$\alpha^2 = < r^2 >/< r^2 >_0 = 1 + (4/3)\,Z - \ldots$$

$$\alpha_L^2 = < S^2 >/< S^2 >_0 = 1 + (134/105)\,Z - \ldots$$

This shows the limitation of the light scattering data in evaluation of n.

Ranks of Different Theories

If the various theories are ranked on the basis of the plots made to compare the molecular weight dependence of the expansion factor with the experiment, then the old theory of Flory is certainly not the best. Some of the newer theories like the Ptitsyn theory and the KSR-Fixman theories are closer to the experiment than the Flory theory, the Kurata and FON theories deviating the most from the experiment. In spite of this little shortcoming of the Flory theory, it is the only theory which relates the expansion factor α to independently determined thermodynamic parameters of polymer-solvent interactions, thus rendering it the mose widely applicable theory currently available.

Future Work Recommended

Reliable experimental data is very important to test the different equations of excluded volume. For this purpose data over a wide range of α values at different temperatures for all kinds of systems are necessary. The basic measurement is intrinsic viscosity for different systems at different temperatures. Measurement of intrinsic viscosity is very sensitive to slightest experimental error. Good temperature control is also very important. Viscosity of polymer solutions, as determined in capillary viscometers, depends on the rate of flow of the solution. Depending on the rate of shear, the viscosity of the polymer solution will be higher or lower. The viscosities of polymer solutions of the same molecular weight in the same solvent and at the same temperature, as given in the literature, show unsatisfactory agreement. This is because the viscometers used by the different workers had different efflux times for the same solvent, because the shear rate was different in each case. The shear rate, however small, has an effect on intrinsic viscosity. Therefore the use of a multiple bulb Cannon-Ubbelhode type viscometer is strongly recommended. All the bulbs have different shear rates. From this, the viscosity at zero shear rate can be found out by extrapolation. There are anomalies in the concentration dependence of viscosity at high dilutions. Rafikov et al.[27] have described them elaborately. These must be carefully studied before extrapolation to zero concentration.

Light scattering data for different systems are necessary over a wide range along with the intrinsic viscosity data to find the best value of the exponent n in $[\eta]/[\eta]_\theta = \alpha^n$.

For the comparison of both sides of the Flory equation, values measured by some method other than intrinsic viscosity measurements are necessary, and for this osmometer measurements are highly recommended.

NOMENCLATURE

NOMENCLATURE

a	Effective length of a link
B	Constant
c	Concentration in gms/100 c.c.
C	Constant in the Flory, KSR, Kurata, Fixman, Ptitsyn and FON equations (Chapter VI)
C_M	Constant in Flory's equation
e	Base of natural logarithm
$\Delta \overline{H}_1$	Partial molar heat of dilution
k	Boltzman constant
K	Constant in the theoretical intrinsic viscosity relationship $[\eta]_\theta = KM^{1/2}$
l	Intersegmental distance
M	Molecular weight

$\overline{M}_n$, $\overline{M}_w$	Number and weight average molecular weights respectively
n	Exponent on α in $\alpha^n = [\eta]/[\eta]_\theta$
n	Number of bonds in a chain
N	Number of links or segments
N_A	Avagadro' s number
$< r^2 >$, $< r^2 >_0$	Mean square and unperturbed mean square distance between ends of a chain
R	Gas constant
R_x, R_y, R_z	Radii of inertia in x, y, and z directions respectively
s	Structural parameter accounting short
$\Delta \overline{S}_1$	Partial molar entropy of dilution
$< S^2 >$, $< S^2 >_0$, $< S^2 >_{00}$	Mean square radius of gyration, the same in absence of long range interactions, the same in absence of both long range and short range interactions
t, t_0	Efflux time of solution and solvent respectively out of a capillary viscometer
T	Absolute temperature

$\bar{v}$	Partial specific volume of polymer
v_2	Volume fraction of polymer
V_1	Molar volume of solvent
w(h)	Radial distribution function for end-to-end coordinates of a polymer chain (usually Gaussian)
w(r)	Pair potential of average force
Z	A parameter of which expansion factor α is a single valued function

Greek Symbols

α, α_L	Factor expressing the linear deformation of a polymer molecule owing to solvent interaction, i.e. $\alpha = (< r^2 >/< r^2 >_0)^{1/2}$, and the same for radius of gyration, i.e. $\alpha_L = (< S^2 >/< S^2 <_0)^{1/2}$
β	Binary cluster integral representing the mutually excluded volume per segment pair.
δ_1, δ_2	Solubility parameters of solvent and polymer respectively
η, η_0	Viscosity of solution and solvent respectively
η_{rel}	Relative viscosity, η / η_0

η_{sp}	Specific viscosity, $\eta_{rel} - 1$
$[\eta]$	Intrinsic viscosity, dl/g
$[\eta]_\theta$	Intrinsic viscosity at the Flory temperature, dl/g
θ	Temperature at which chemical potential due to polymer segment-solvent interactions is zero and $\alpha = 1$
κ	Parameter expressing the energy, divided by kT, of interaction between a solvent molecule and polymer
ϕ	Flory's constant
χ, χ_H, χ_S	Flory interaction parameter, heat parameter and entropy parameter of the same
ψ	Parameter characterizing the entropy of dilution of polymer with solvent

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