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VISCOMETRIC ESTIMATION OF UNPERTURBED CHAIN DIMENSIONS OF POLYMERS

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ABSTRACT

A new expression is proposed to determine the unperturbed dimensions of coil-like polymers viscometrically by use of the Flory and Kratky expression. The unperturbed dimensions so estimated are compared with the results obtained by using different expressions available in the literature. The results are comparable even for stiff chain polymers. The data obtained under theta conditions also fit this expression very well. The effect of molecular weight, its distribution, and that of the solvent has also been studied. It is concluded that the unperturbed dimensions are independent of molecular weight and solvent but depend on the heterogeneity of the system.

INTRODUCTION

The conformational and thermodynamic properties of flexible macromolecules may be described essentially by two independent parameters [1-3]. They are the short-range and long-range interaction parameters are related, respectively, to the unperturbed average dimensions and the excluded volume effect of a given polymer in a given environment. The unperturbed chain dimensions of macromolecules are defined by

$$A = (\langle R_0{}^2\rangle/M)^{1/2}, \tag{1}$$

where $\langle R_0{}^2 \rangle$ is the mean-square end-to-end distance of the chain in an unperturbed state and M is the molecular weight. Different methods are available to determine the parameter A, some of which are direct while others are indirect. Some need different thermodynamic parameters along with the dependence of the intrinsic viscosity $[\eta]$ on molecular weight, while the others need only the dependence of $[\eta]$ on M. All of the methods have certain limitations and have some merits and demerits. A few relevant methods are discussed below.

FLORY-FOX (FF) METHOD

Flory and Fox [4] suggested the following relation for the determination of A:

$$[\eta]^{2/3}/M^{1/3} = K_0{}^{2/3} + 0.858\, K_0{}^{2/3}/\phi_0 (B(M/[\eta])). \tag{2}$$

Here K_0 and B are the Flory constants related to unperturbed dimensions and the polymer solvent interaction parameter, and ϕ_0 is a universal constant. This is a linear equation which, when plotted as $[\eta]^{2/3}/M^{1/3}$ vs $M/[\eta]$ yields an intercept equal to $K_0{}^{2/3}$, and hence A can be determined. This method is found to be inadequate for most of polymers, especially for good solvent systems. However, the theory seems to be quite adequate for poor solvents [5].

KURATA-STOCKMAYER (KS) METHOD

Kurata and Stockmayer [3] correlated viscosity and molecular weight data as shown by the expression:

$$([\eta]^2/M)^{2/5} = K_0{}^{2/3} + 0.363\phi_0 B g(\alpha_\eta)(M^2/[\eta])^{1/3}, \tag{3}$$

where

$$g(\alpha_\eta) = 8\alpha^3{}_\eta/(3\alpha^2{}_\eta + 1)^{3/2}, \tag{4}$$

and α_η is the linear expansion factor, and is expressed as [1]

$$\alpha^3{}_\eta = [\eta]/[\eta_0], \tag{5}$$

where $[\eta_0]$ is the intrinsic viscosity under theta conditions. Equation (3) gives a straight line with intercept $K_0^{2/3}$ when plotted as $([\eta]^2/M)^{1/3}$ vs $(M^2/[\eta])^{1/3}$. However, it has been shown that this equation deviates from linearity in the higher molecular weight region, and this becomes more prominent when the polymer is dissolved in a good solvent [5].

STOCKMAYER-FIXMAN (SF) METHOD

Stockmayer and Fixman [6] proposed the simple relation

$$[\eta]/M^{1/2} = K_0 + 0.51\phi_0 B M^{1/2}. \tag{6}$$

The K_0 value can be obtained by plotting $[\eta]/M^{1/2}$ vs $M^{1/2}$. It is a popular method due to its simplicity, and ir provides better results than the other methods. However, it is subject to the same deviation for high molecular weight polymers, which proves that the KS and SF plots lead to overestimation of K_0 for high molecular weights in good solvents. Moreover, the SF method considers free-draining instead of nondraining molecules.

INAGAKI-SUZUKI-KURATA (ISK) METHOD

Inagaki et al. [7] proposed another relation for the determination of K_0 which, in turn, can be used for the evaluation of A:

$$([\eta]^2/M)^{2/5} = 0.786K_0^{4/5} + 0.454(K_0\phi_0 B)^{2/3}M^{1/3}. \tag{7}$$

ISK plots of $([\eta]^2/M)^{2/5}$ vs $M^{1/3}$ are better when applied to polymers of high molecular weight dissolved in good solvents.

MODIFIED BOHDANECKY (MB) METHOD

A modified form of an equation proposed by Bohdanecky [8] was suggested by Cowie [9]. The equation

$$[\eta]/M^{1/2} = \frac{\phi(\epsilon)}{\phi_0 K_0} + \frac{0.9166\phi(\epsilon)}{\phi_0 K_0 K^{7/10} M^{1/2}} \tag{8}$$

has a solvent-dependent factor (K_0) which varies with the quality of the solvent, and thus the equation may be valid both for good and theta solvents. The parameter $\phi(\epsilon)$ is given as

$$\phi(\epsilon) = \phi_0(1 - 2.63\,\epsilon + 2.86\,\epsilon^2),$$

where ϵ is related to the Mark-Houwink constant a by $a = (1 + 3\,\epsilon)/2$. Thus $\phi(\epsilon) = \phi_0$ in a theta solvent and $k = 0.33B(M/\langle S_0\rangle^2)^{3/2}$.

BERRY (B) METHOD

Berry [10] proposed another relation between molecular weight and intrinsic viscosity for the calculation of unperturbed chain dimensions of flexible polymers:

$$\left[\frac{[\eta]}{M^{1/2}}\right]^{1/2} = K_0{}^{1/2} + 0.42K_0{}^{3/2}B\left(\frac{\langle S_0\rangle^2}{M}\right)^{3/2}\frac{M}{[\eta]} \tag{9}$$

He calculated K_0 for six different polymers and observed deviations in the results. These deviations were more pronounced in the range of lower molecular weight. The results were found to be within 5% of $K_0{}^{1/2}$ determined in a theta solvent. It was further stated that the deviation may become more prominent for polar polymers or solvent, and the difference in $K_0{}^{1/2}$ may increase up to 10% from that determined at theta conditions.

Keeping in view these facts and the importance of unperturbed dimensions, we have tried to develop a new relation between intrinsic viscosity and molecular weight for the estimation of K_0 ($K_0 = \phi_0 A^3$) values. The Kratky and Porod [11] expression relating $[\eta]$ to M of a polymer through ϕ was used for this purpose. This relation was used to find A values for different polymers. The results so obtained are discussed and compared with the results obtained by using the other expressions.

THEORETICAL BACKGROUND

The intrinsic viscosity $[\bar{\eta}]$ of a polydisperse polymer system having wormlike chains is related to the weight-average molecular weight ($\bar{M}_w$) and Z-average radius of gyration $\langle S\rangle$ through

$$[\bar{\eta}] = \frac{\phi(6\langle S^2\rangle)^{3/2}}{M}, \tag{10}$$

where ϕ is the Flory viscosity parameter. $[\bar{\eta}]$ can be replaced by the intrinsic viscosity of a monodisperse system $[\eta]$ of the same material by introducing the heterogeneity correction factor $q_{w,z}$ [12, 19]. Equation (10) will become

$$[\eta] = \frac{\phi(6\langle S^2\rangle)^{3/2}}{q_{w,z}M}. \tag{11}$$

If the system obeys the Schulz-Zimm distribution, $q_{w,z}$ will be equal to [13]

$$q_{w,z} = \frac{1}{(h+1)} \; \frac{\Gamma(h+3+\epsilon)^{3/2}}{\Gamma(h+2)} \; \frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\epsilon}. \tag{12}$$

Here h is the well-known heterogeneity parameter ($= \{(\bar{M}_w/\bar{M}_n) - 1\}^{-1}$), Γ the gamma function, and ϵ has the same meaning as before.

Let us suppose that $q_{w,z}$ is almost equal to unity, i.e., the system is nearly monodisperse. Then $q_{w,z}$ can be neglected and Eq. (11) becomes

$$[\eta] = \frac{\phi(6\langle S^2\rangle)^{3/2}}{M}.$$

The Flory viscosity constant ϕ can be written [11] as

$$\phi = \frac{\phi_0}{\left[\phi(q,L) + \frac{45}{32}\left(\frac{2\pi}{3}\right)^{1/2}\left(\frac{1}{3\sqrt{2}}\right)\frac{(Lq)^{1/2}}{R_H}\right]\langle S^{1/2}\rangle\,(L/q)}, \tag{14}$$

where q and L are the persistence and contour lengths of the chain and R_H is the hydrodynamic radius. Furthermore,

$$S(L/q) = (1 - 3q/L + 6(q/L)^2 - 6(q/L)^3\,[1 - \exp(L/q)] \tag{15}$$

and $\phi(q/L)$ was calculated by Kurata et al. [14] for different values of q/L and N (the degree of polymerization). On the other hand $\langle S^2\rangle^{1/2}$ is related to q through L as follows,

$$\langle S_0{}^2\rangle^{1/2} = \langle S^2\rangle^{1/2}/\alpha \tag{16a}$$

and

$$\langle S_0{}^2\rangle = 1/3LqS(L/q). \tag{16b}$$

The values of $\phi(q,L)$ and $S(L/q)$ approach unity when N is large enough and the system consits of flexible polymers.

By combining Eqs. (13)-(16) we get

$$M^{1/2}/[\eta] = 1/2K_0 + (0.908/\phi_0{}^{1/3}r_0k_0{}^{2/3})M^{-1/2}, \tag{17}$$

where r_0 is equal to R_H/N. A plot of $M^{1/2}/[\eta]$ vs $M^{-1/2}$ gives $1/2K_0$ from the intercept and, hence, A. The slope of the plot will permit the calculation of R_H.

APPLICATION TO EXPERIMENTAL DATA

It is proposed here to compare the results obtained by the different methods to verify the applicability of our equation and to study the effect of molecular weight, its distribution, and the solvent on A. The data for polymers were collected to encompass a range of 1) rigidity, 2) molecular weight, 3) molecular weight distribution, and 4) polydispersity. The polymers selected in this way along with their characteristics are listed in Table 1. The reasons for including such a wide range of polymers are as follows.

Polyhexene-1

Polyhexene-1 is included in the list because five of the above-mentioned methods (FF, KS, SF, ISK, and MB) showed deviations in results either for the lower molecular weights or the higher ones or both [15]. The second reason was that the A values obtained were different in some cases from those obtained under theta conditions. Moreover, the data let us study the solvent effect on A. Due to the difference in $\bar{M}_w/\bar{M}_n$ for different fractions of the sample, it was also possible to see the effect of the polydispersity on A.

Poly(Methyl Methacrylate)

Examples of poly(methyl methacrylate) are considered due to the following reasons: Berry [10] obtained different values of K_0 by using his own expression compared to the results obtained under theta conditions. These values were found to be higher or lower than expected. Moreover, he observed some deviations from his expression in the lower range of molecular weight.

The available data permit study of the effect of molecular weight and solvent on A values and check the applicability of our expression.

Poly(Vinylpyrolidone)

Similarly, poly(vinylpyrolidone) is considered due to its large molecular weight range [16] (6.7×10^4 to 10.2×10^6), thus providing the facility to test the applicability of our expression over a large range.

Sodium Poly(α-L-glutamate)

Sodium poly(α-L-glutamate) (PLGNa) is considered for study because its helix contents change with changing degree of neutralization (α) in aqueous NaCl [17] which affects the rigidity of the polymer. Though data are available for different α values in different concentrations of NaCl and mixtures of aqueous NaCl and dioxane, a selected portion of the data has been included to get a wider range in rigidity of the polymer chain and to include all the data giving negative K_0 values by making use of the SF method [17].

Polystyrene

Samples A and B differ from each other not only in molecular weight but also in molecular weight distribution. On the other hand, Samples A and AB differ only in molecular weight [18]. The same is the case for Samples C and D. Moreover, they cover a wide span in molecular weight and have been studied in different solvents. Similarly, Sample E is included because it has been studied in three different theta solvents [10], and it provides the facility to verify the applicability of our expression in theta conditions.

Cellulose Acetate and Poly[(*p*-Phenylene-2,6-benzobioxazole)] (PBO)

Cellulose acetate is included in the list due to its chain rigidity, and poly(*p*-phenylene-2,6-benzobioxazole) (PBO) is also important due to its rodlike conformation [23]. Thus, we are able to verify the applicability and to see the deviation, if any, from our Eq. (17).

Poly(Vinyl Alcohol)

One of our difficult tasks was to establish the effect of the polydispersity $\bar{M}_w/\bar{M}_n$ on A values. The above-mentioned methods require extrapolation to zero molecular weight. On the other hand, the data available for different polymers normally do not include the polydispersity, and even if they do, the difference is very low, e.g., 0.1-0.4, which does not give the required information. We have considered the data on poly(vinyl alcohol) with the supposition that Sample A (or group of Samples A) has low polydispersity while Sample B has a high value [20].

DISCUSSION

For futher studies we have divided the data of polyhexene [15] and polyethylene [21] into two portions, one with low and the other with high polydispersity. The second advantage of including polyethylene is that the effect of different theta solvents on A values and on the applicability of Eq. (17) can be verified as by polystyrene.

The intrinsic viscosity of all the polymers was plotted according to the different expressions against molecular weight. Some of these plots are shown in Figs. 1-5), which show that the FF and KS expressions give negative intercepts for semiflexible and rigid polymers. Some deviations were also observed from the KS, SF, and MB expressions for the higher molecular weight samples, while the same data fit Eq. (17) very well. But deviations were observed for poly(vinylpyrolidone) and poly(methyl methacrylate) C data even with Eq. (17) in the lower molecular weight range. The data of polyhexene-1 did not show as much deviations when $\bar{M}_n$ was used instead of $\bar{M}_w$. When we tried to find A values by using weight-average molecular weight and Eq. (17), some deviations were observed for the higher molecular weight range, but the deviations were not as pronounced as for the other methods [15]. Some of the PLGNa data gave negative K_0 values by all the methods except Eq. (17). The data plotted according to B and Eq. (17) are shown in Fig. 5, while SF plots have already been given by Saitoh et al. [17].

These results in Table 2 fall in the order of FF < KS < ISK < SF < MB < B, except for stiff and rigid polymers. Comparison of the results obtained by Eq. (17) and the other methods shows that the latter are smaller than that of the SF method and greater than or equal to the ISK one, with the exception of cellulose acetate, PBO, and PLGNa (in the solvent where the polymer has high helix contents), for which higher results were observed. On the other

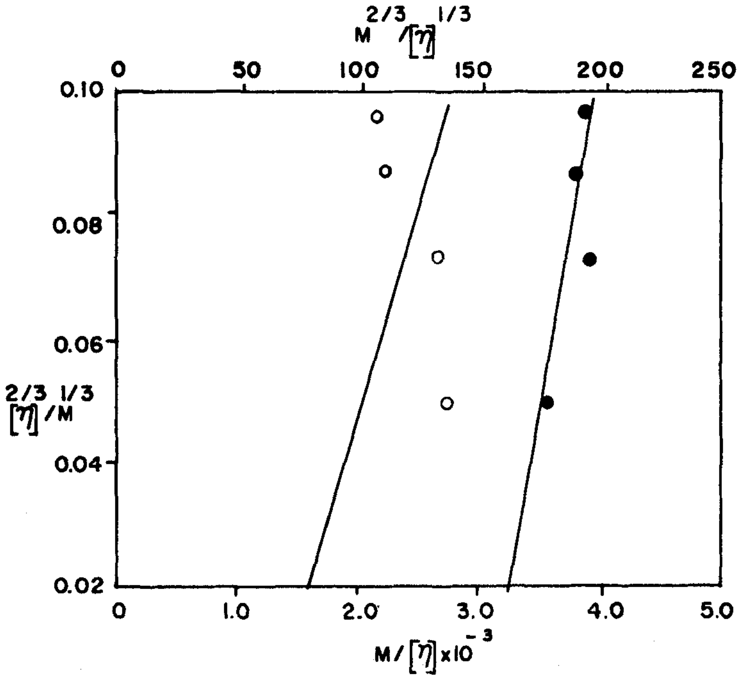

FIG. 1. Plots of $[\eta]^{2/3}/M^{1/3}$ versus (○) $M/[\eta]$ and (●) $M^{2/3}/[\eta]^{1/3}$ of PBO in CH_3SO_3H solvent.

hand, the *A* value obtained by Kamide and Saitoh [26] for cellulose acetate (0.176 nm) is higher than that obtained by our Eq. (17). Similarly the *A* values calculated according to Eq. (17) are comparable to the L_w values obtained by Berry et al. [23] for PBO polymer with the supposition that dimerization had taken place. Moreover, the *A* values calculated for polystyrene by Eq. (17) are in good agreement with the results obtained by light scattering at the theta temperature in cyclohexane [25]. Similarly, the *A* values obtained for poly(methyl methacrylate) were almost the same as those obtained under theta conditions [10], irrespective of the solvent used. The *A* values for polyhexene-1 were also comparable to the experimental results as well as those obtained by the SF method. The above discussion shows that though Eq. (17) was derived particularly for a system with wormlike polymers, it is also applicable to other polymers.

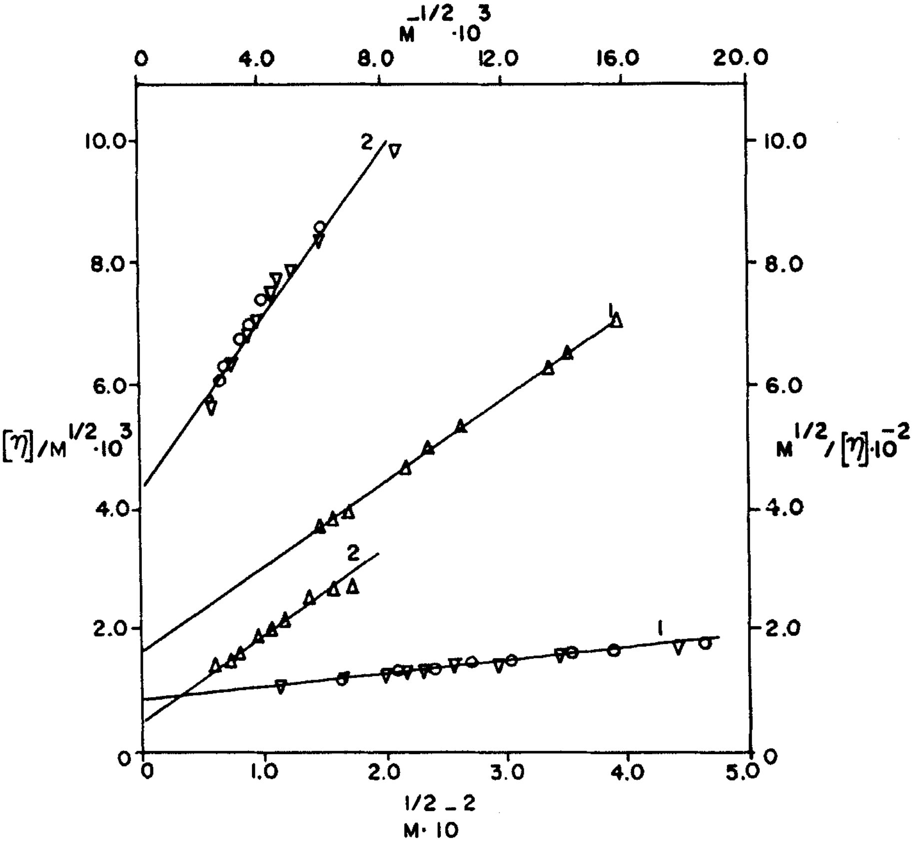

FIG. 2. Plots of (1) $[\eta]/M^{1/2}$ versus $M^{1/2}$ and (2) $M^{1/2}/[\eta]$ versus $M^{-1/2}$ for (○) polystyrene B in toluene, (△) cellulose acetate in acetone, and (▽) polystyrene A-B in toluene.

The introduction of the heterogeneity correction factor $q_{w,z}$ in Eq. (17) leads to the expression

$$\frac{M^{1/2}}{[\eta]} = \frac{1}{2q_{w,z}K_0} + (0.908\phi_0{}^{1/3}r_0K_0{}^{2/3}q_{w,z})M^{-1/2}. \tag{18}$$

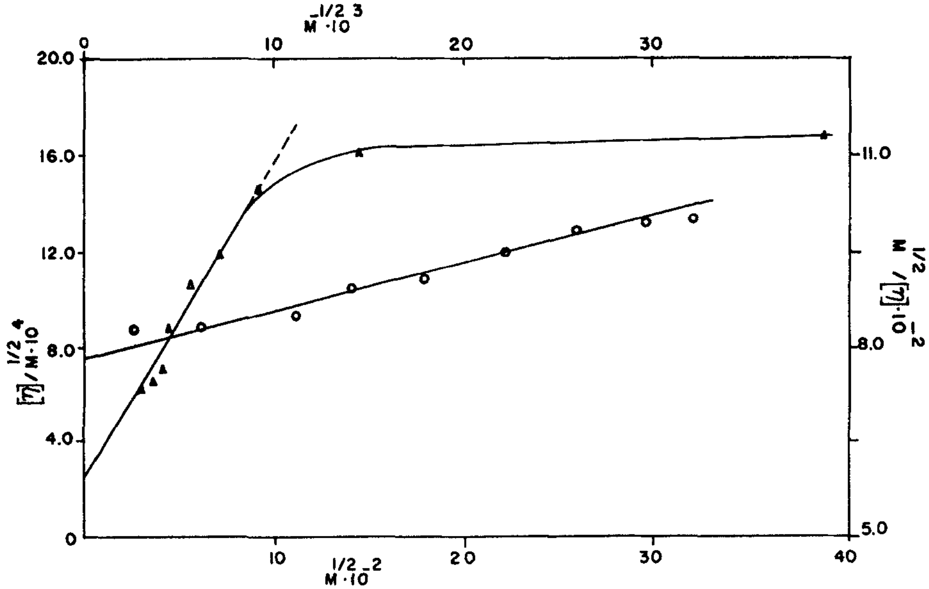

FIG. 3. Plots of (○) $[\eta]/M^{1/2}$ versus $M^{1/2}$ and (△) $M^{1/2}/[\eta]$ versus $M^{-1/2}$ for poly(vinylpyrolidone) in methanol.

This expression proves that neglect of heterogeneity will lead to higher A values. This idea is also supported by the results obtained for poly(vinyl alcohol), polyhexene-1, and polyethylene. In the latter cases, the data were divided into two portions according to their $\bar{M}_w/\bar{M}_n$ values. In this way, two plots were obtained and were extrapolated to zero $M^{-1/2}$ (Fig. 6). The results so obtained show a clear dependence upon $\bar{M}_w/\bar{M}_n$.

The neglect of the excluded-volume effect reduces Eq. (17) to the Tanner and Berry [24] expression in which ϕ_0 (= 2.87×10^{21}) is taken as K'. This will yield double K_0 values and hence higher A values from the same data. This proves that Eq. (17) provides more reliable results than the Tanner and Berry expression and also avoids the assumption of different models for different polymers, as required by the latter.

If Eq. (17) is derived for theta conditions, i.e., taking $\langle S^2 \rangle = \langle S_0{}^2 \rangle$ and $\phi = \phi_0$, then in addition to other changes, the term $1/2K_0$ will become equal to $1/K_0$ and, hence, the intercept of the plots of $M^{1/2}/[\eta]$ vs $M^{-1/2}$ will be equal to $1/K_0$ rather than $1/2K_0$. The data for Polystyrene E in three different

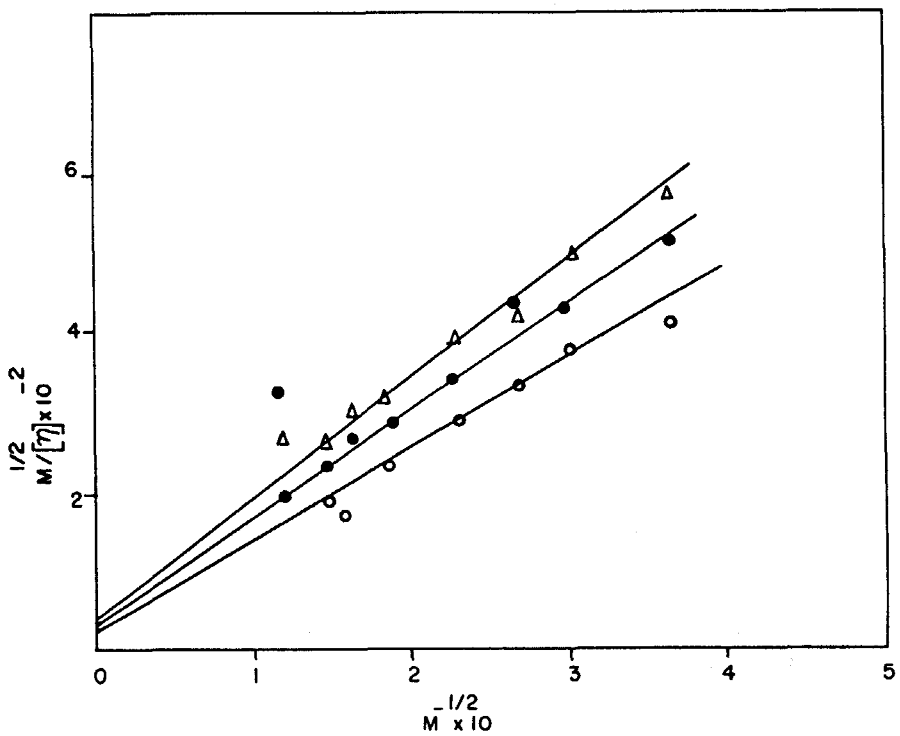

FIG. 4. Plots of $M^{1/2}/[\eta]$ versus $M^{-1/2}$ for polyhexene-1 in (○) cyclohexane, (●) THF, and (△) toluene.

theta solvents, polyethylene in two different solvents, and polyhexene-1 in phenetole (theta solvent) are plotted according to Eq. (17) and the SF expression in Fig. 7. The plots have zero slope in all cases, as expected from the relevant theories. Moreover, the data for polymers of different polydispersity did not fall on the same straight line. The *A* values obtained in this way are listed in Table 2. The *A* values obtained for polystyrene in cyclohexane and dioctyl phthalate are the same, whereas in decalin they are different. Furthermore, these *A* values are less than the values obtained in other solvents or as determined by light scattering [25]. The results obtained by the SF method and Eq. (17) are the same in all the cases studied under theta conditions. On the

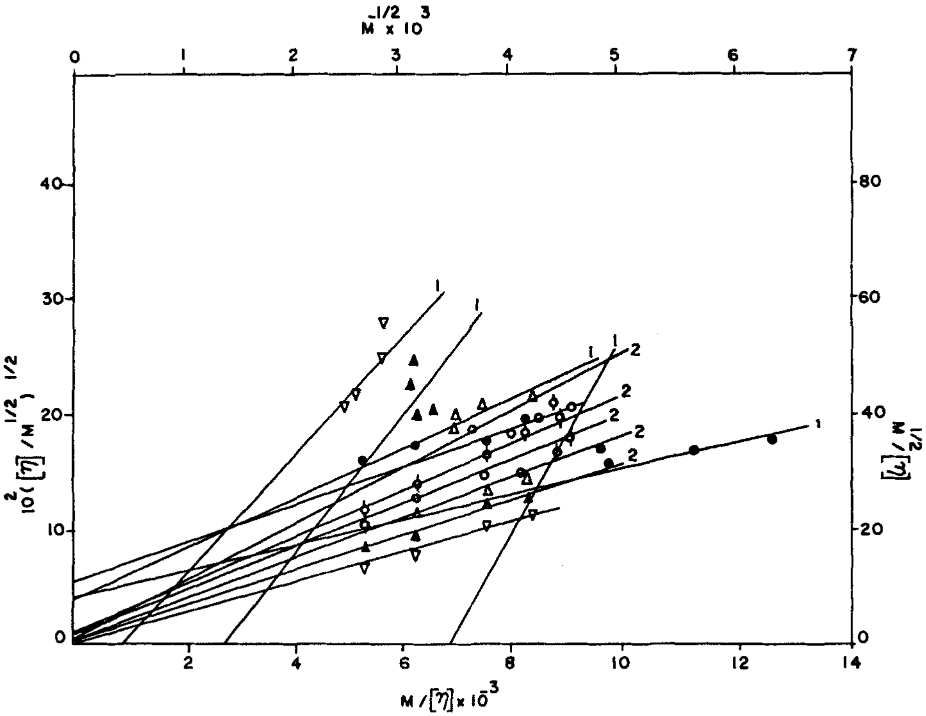

FIG. 5. Plots of (1) $([\eta]/M^{1/2})^{1/2}$ versus $M/[\eta]$ and (2) $M^{1/2}/[\eta]$ versus $M^{-1/2}$ for PLGNa in 1.0 *M* aqueous NaCl (○) $\alpha = 1.0$ and (●) $\alpha = 0.7$, (○) 0.1 *M* aqueous NaCl ($\alpha = 0.3$) and in 0.1 *M* aqueous NaCl/dioxane (70/30 v/v) (△) $\alpha = 0.5$, (▲) $\alpha = 0.4$, and (▽) $\alpha = 0.3$.

other hand, the value obtained for polyhexene-1 in phenetole is almost equal to the results obtained in other solvents. The results for polyethylene by different methods are the same, and these are different in different solvents, as observed by Berry [10]. Furthermore, the result obtained by fractions of low polydispersity are different from those of high polydispersity, and the average of these results is in good agreement with the results obtained by light scattering [27]. The difference in *A* values for different solvents may be due to specific solvent effect on $\langle S_0{}^2\rangle/M$ [10].

BLE 2. The Unperturbed Chain Dimensions Estimated by Various Methods for Solutions of Different Poly

		$A \times 10^8$ $\text{cm}\cdot\text{g}^{-1/2}\cdot\text{mol}^{-1/2}$				
	Solvent	(FF), Eq. (2)	(KS), (Eq. (3)	(SF), Eq. (6)	(ISK), Eq. (7)	(MB), Eq. (8)
ne-1	Cyclohexane	0.771	0.764	0.783	0.793	0.791
ne-1	THF	0.732	0.688	0.702	0.758	0.750
ne-1	Toluene	0.779	0.686	0.722	0.773	0.773
ne-1	Phenetole ($t = \theta = 61.3°\text{C}$)	0.7117	0.963	0.981	–	0.963
hyl methacrylate) A	Chloroform	0.498	0.538	0.562	0.500	0.562
hyl methacrylate) B	Benzene	0.520	0.540	0.562	0.541	0.562
hyl methacrylate) C	Toluene	0.510	0.540	0.571	0.538	0.571
lpyrolidone)	Methanol	0.647	0.657	0.678	0.702	0.678
	1.0 *M* aqueous NaCl, $\alpha = 1.0$	9.321	9.500	9.563	9.621	9.560
	1.0 *M* aqueous NaCl, $\alpha = 0.7$	8.205	8.240	8.806	8.852	8.810
	0.1 *M* aqueous NaCl, $\alpha = 0.3$	x	x	x	x	x
	0.1 *M* aqueous NaCl + 30 vol% dioxane, $\alpha = 0.5$	6.985	7.044	7.083	7.101	7.060
	0.1 *M* aqueous NaCl + 30 vol% dioxane, $\alpha = 0.4$	x	x	x	x	x

	0.1 *M* aqueous NaCl + 30 vol% dioxane, $\alpha = 0.3$	x	x	x	x	x	x
alcohol) A	Water	0.595	0.671	0.828	0.788	0.820	0
alcohol) B	Water	0.740	0.802	0.897	0.844	0.895	0
ne A	Toluene	0.669	0.758	0.742	0.734	0.738	0
ne B	Toluene	0.669	0.758	0.742	0.734	0.738	0
ne AB	Toluene	0.669	0.758	0.742	0.734	0.738	0
ne C	Toluene	0.670	0.760	0.740	0.753	0.738	0
ne D	Benzene	0.670	0.760	0.740	0.753	0.738	0
ne E	Cyclohexane ($t = \theta = 34.8$°C)	–	–	0.664	–	–	–
ne E	Decalin ($t = \theta = 0$°C)	–	–	0.658	–	–	–
ne E	Dioctyl phthalate ($t = \theta = 22.0$°C)	–	–	0.673	–	–	–
acetate	Acetone	x	0.956	0.997	0.837	0.912	0
	CH_3SO_3H	x	x	1.406	1.446	1.381	1
ene A	Decalin ($t = \theta = 135$°C)	–	–	0.955	–	–	–
ene A	Diphenylether ($t = \theta = 163.9$°C)	–	–	1.051	–	–	–

egative results, – = was not calculated.

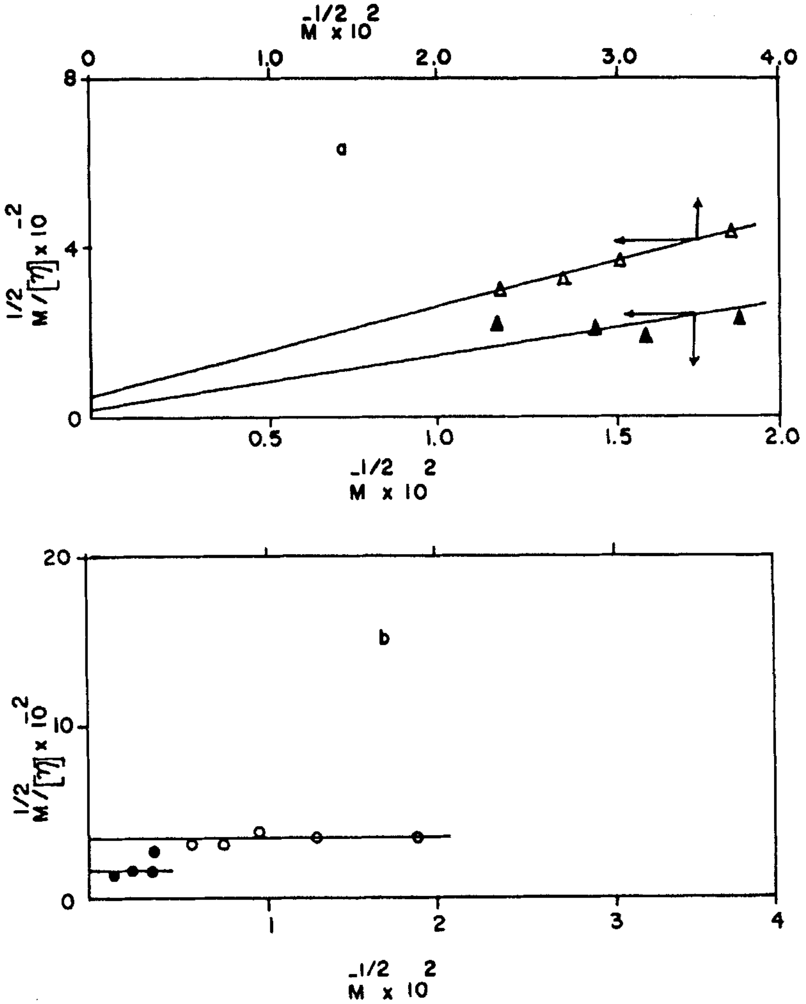

FIG. 6. Plots of $M^{1/2}/[\eta]$ versus $M^{-1/2}$ (a) for polyhexene-1 in cyclohexane (△) fractions having $\bar{M}_w/\bar{M}_n$ = 1.09-1.11 and (▲) fractions having $\bar{M}_w/\bar{M}_n$ = 1.36-1.85 and (b) polyethylene in decalin (○) fractions having $\bar{M}_w/\bar{M}_n$ = 1.30-1.54 and (●) fractions having $\bar{M}_w/\bar{M}_n$ = 2.0-3.50.

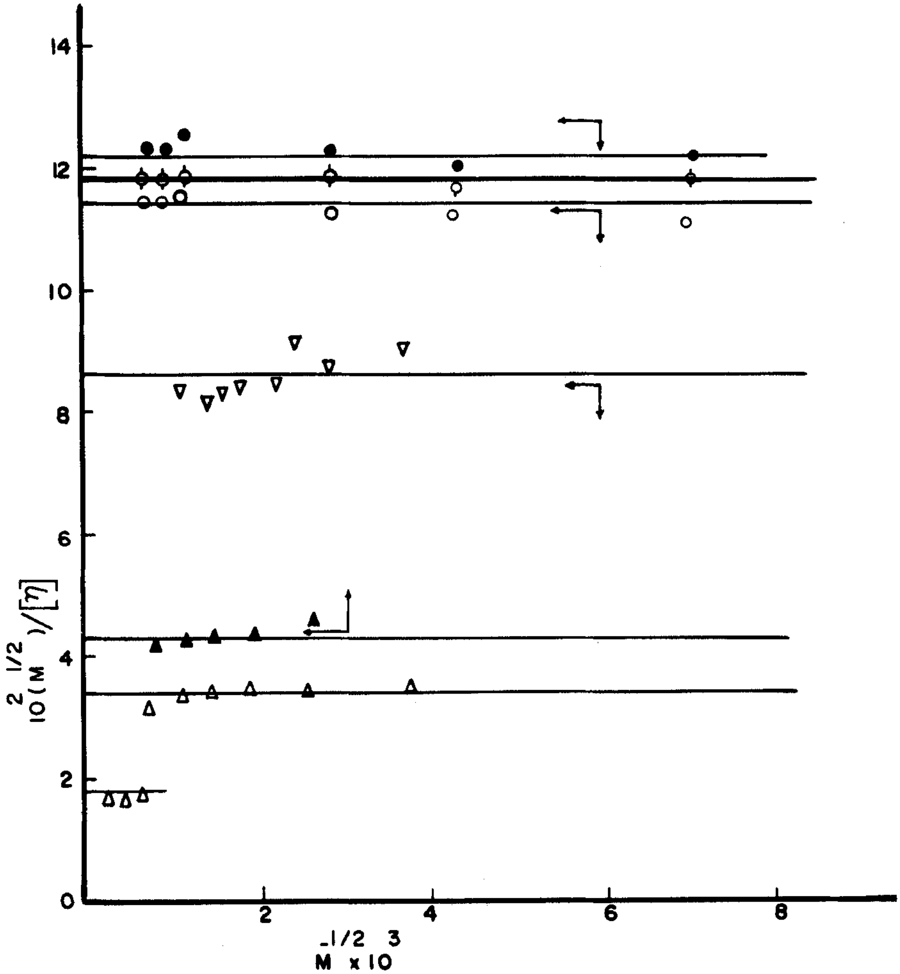

FIG. 7. Plots of $M^{1/2}/[\eta]$ versus $M^{-1/2}$ of Polystyrene E in (○) cyclohexane, (●) decalin, and (○) dioctyl phthalate; polyethylene in (△) decalin and (▲) diphenyl ether; and for (▽) polyhexene-1 in phenetole at theta temperature.

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