

TEST OF VISCOSITY THEORIES OF FLORY, KURATA, PTITSYN AND PALIT FOR DILUTE POLYMER SOLUTIONS

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ABSTRACT. The linear expansion factor α for the fractions of different types of macromolecules in a number of solvents at different temperatures have been determined using Stockmayer-Fixman's and in some cases Kurata's relationship. The validity of (1) Flory, (2) Kurata et al and (3) Ptitsyn theories have been tested in terms of the dependence of the function α on molecular weight. From available research data it has been found that Flory's theory is of limited applicability, while Kurata and Ptitsyn theories are in good agreement. The same data have been utilised to test Palit's theory which predicts linear dependence of $100\rho_0[\eta] + \ln M$ on $M^{2/3}$ with a slope of the order of 10^{-2} . Palit's equation has been found to be in very good agreement in practically all cases.

INTRODUCTION

Flory (1948, 1949, 1951) treated the interaction of chain segments with their environment as a mixing problem and was led to the following equation

$$\alpha^5 - \alpha^3 = 2\psi_1 C_M (1 - \theta/T) M^\dagger \quad (1)$$

where α is the linear expansion factor, defined as the ratio of the root-mean-square values of perturbed and unperturbed radii of gyration, ψ_1 is an entropy of dilution factor, θ represents the temperature at which the second virial coefficient vanishes for the solvent-polymer pair, and

$$C_M = (27/2.5/2.\pi^{3/2}N)(\bar{v}^2/V_1)(M/\bar{r}_0^2)^{3/2}$$

where N is Avogadro's number and \bar{v} and V_1 are the partial specific volume of the polymer and molar volume of the solvent respectively. In this theory the macromolecule is considered to be equivalent to a cluster of unconnected segments for which there is a spherically symmetrical Gaussian distribution around the centre of mass.

Kurata, Stockmayer and Roig (1960) proposed a new theory of excluded volume effect assuming an equivalent ellipsoid model, in which the polymer chain with fixed ends is replaced by a uniform distribution of unconnected segments within an ellipsoid whose dimensions are chosen to give the correct principal

radii of gyration of the chain and derived the following relationship for a Gaussian chain

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

where α is the effective bond length, β the binary cluster integral, and N is the number of segments in the polymer chain.

Taking into account segment-segment interaction and on consideration of a non-Gaussian distribution function for α , Ptitsyn (1962) derived the following equation

$$[(4.68\alpha^2 - 3.68)^{3/2} - 1] = C'N^{\frac{1}{2}} \quad \dots (3)$$

The validity of eqs. (1), (2) and (3) is tested in this paper in terms of available literature values of α calculated for solutions of well defined fractions of a number of polymers in different solvents of varying solvent power at different temperatures.

Based on Eyring's Rate Theory and the 'hole' theory of liquids, Palit (1955, 1963) derived the following equation correlating intrinsic viscosity, $[\eta]$ and molecular weight of polymers.

$$100\rho_0[\eta] = K_1M^{2/3} - \ln M + K_2 \quad \dots (4)$$

where ρ_0 is the density of the polymer at infinite dilution and $K_1 = 1.09N^{1/3}\gamma v_{sp}^{2/3}/RT \simeq$ order of 10^{-2} and K_2 are constants. We have used $\rho_0 = 1$ as a rough approximation.

The same literature data have been utilised to test equation (4).

DETERMINATION OF α

The linear expansion factor α , is obtained by either of the following three procedures :

Procedure (1) depends on the Flory-Fox (1951) relationship

$$[\eta] = KM^{\frac{1}{2}}\alpha^3 \quad \dots (5)$$

$$\frac{[\eta]}{[\eta]_{\theta}} = \alpha^3 \quad (6)$$

where $[\eta]_{\theta}$ is the intrinsic viscosity in θ -solvent. Eq. (6) is directly used if $[\eta]_{\theta}$ values are known.

Procedure (2) where data on $[\eta]_{\theta}$ are not available α is calculated by a modified relationship proposed by Kurata *et al* (1963) :

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363B\phi_0g(\alpha_{\eta})(M^{2/3}/[\eta]^{1/3}) \quad \dots (7)$$

where $\phi_0 = 2.87 \times 10^{21}$ and $B = \beta/m_0^2$ in which β represents the binary cluster integral and m_0 is the molar weight of a polymer segment, and

$$g(\alpha_{\eta}) = 8\alpha_{\eta}^3(3\alpha_{\eta}^2 + 1)^{-3/2}$$

A rough value of $K^{2/3}$ is obtained from eq. (7) graphically after assuming $g(\alpha_\eta)$ to be unity. Using this value of K , values of α_η for all the fractions are obtained from eq. (5). With the help of these values of α_η and consequently of $g(\alpha_\eta)$ a more accurate value of $K^{2/3}$ is obtained by a second graphical intercept method.

Procedure (3) involves a more direct evaluation of K as suggested by Stockmayer and Fixman (1963). Their equation reads

$$[\eta] = KM^{1/2} + 0.51\phi_p BM \quad \dots (8)$$

in which B is the polymer-solvent interaction parameter. Because of the simplicity of eq. (8), K values were obtained in most cases from the ordinate intercept of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ graphs. Unless otherwise indicated procedure (3) has been utilised for evaluation of K .

EXPERIMENTAL RESULTS AND DISCUSSION
A. ADDITION POLYMERS

1. *Poly-p-Chloro Styrene.* Our method of treatment of the experimental data is illustrated here in this case, in some details. The \bar{M}_n and $[\eta]$ values (Table I) of Kuwahara *et al* (1965) at 30°C are utilised to calculate K and α values of Table II.

TABLE I
Results for Poly-p-Chloro Styrene fractions

Fraction	$\bar{M}_n \times 10^{-4}$	$[\eta]$, dl./g.		
		Chlorobenzene	M.E.K.	Toluene
1	268	3.18	2.40	2.06
2	107	1.53	1.22	1.07
3	59.0	0.888	0.76	0.676
4	46.9	0.756	0.623	0.550
5	28.4	0.486	—	0.406
6	17.0	0.327	0.296	0.274

TABLE II
Values of K and α

Solvent	Temp. °C	α						$K \times 10^5$ (Procedure 2)
		1	2	Fraction		5	6	
				3	4			
Chlorobenzene		1.571	1.435	1.322	1.302	1.222	1.166	
M.E.K.	30	1.431	1.330	1.255	1.221	—	1.128	50
Toluene		1.360	1.274	1.207	1.170	1.148	1.100	

The values of α are found to increase with increase of M and solvent power in all the solvent-polymer pairs studied, indicating increased expansion of the molecule.

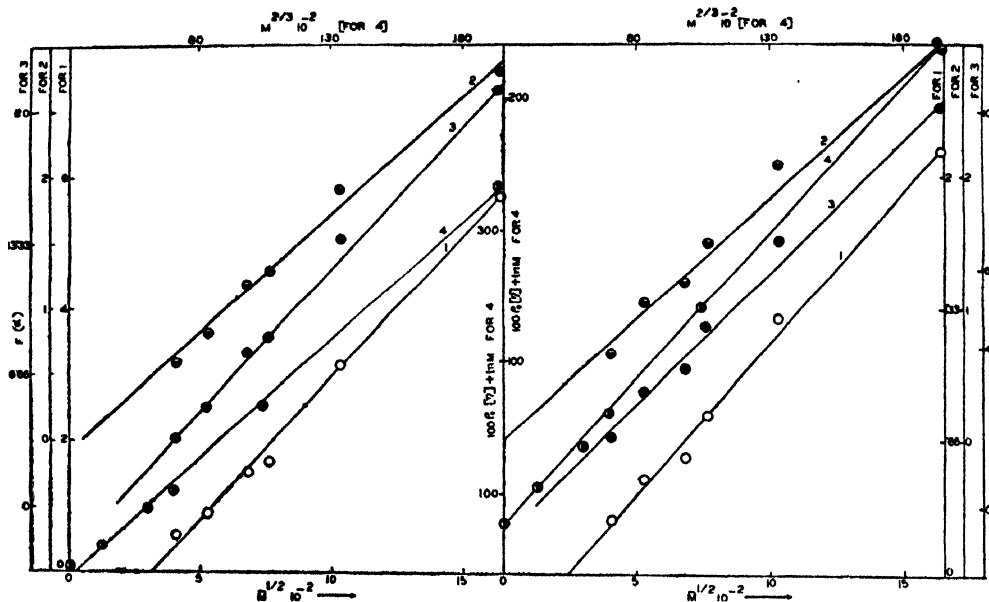


Fig. 1. Poly-p-Chlorostyrene in Chloro benzene at 30°C

Fig. 2. Poly-p-Chlorostyrene in Toluene at 30°C.

GRAPHICAL TEST OF THE FOUR EQUATIONS

Analysis of Flory Relation : According to eq. (1) plots of $\alpha^5 - \alpha^3$ ag. $M^{\frac{1}{2}}$ are expected to give straight lines passing through the origin. Graphs of $\alpha^5 - \alpha^3$ vs. $M^{\frac{1}{2}}$ in all the solvents show a good linear monotonic increase but they do not pass through the origin. Abscissa intercepts correspond to about 99000, 57000 and 60000 Ms with chlorobenzene (Fig. 1), toluene (Fig. 2) and M.E.K. (Fig. 3) as respective solvents. This is in contradiction to Flory's eq. (1) according to which α should approach unity as the M approaches zero. Again from eq. (1) one can expect that $\alpha^5 - \alpha^3 / M^{\frac{1}{2}}$ values should be invariant with M ; evidently they increase with M . So, Flory's equation is inadequate for these systems.

Analysis of Kurata et al's relation : Plots of $(\alpha^2 - \alpha) (1 + 1/3\alpha^2)^{3/2}$ vs. $M^{\frac{1}{2}}$ (eq. 2) are fairly good linear in case of chlorobenzene, poorly linear in case of toluene and very poorly linear in case of M.E.K. and pass through the origin in case of M.E.K. and toluene. In case of chlorobenzene, however, a small abscissa intercept corresponding to 2500M is obtained by the least square method. It is apparent that the data fit better in the K-S-R. equation.

Analysis of Ptitsyn's Relation : According to eq. (3) plots of $[(4.68\alpha^2 - 3.68)^{3/2} - 1]$ ag. $M^{\frac{1}{2}}$ are expected to give straight lines passing through the origin. Such graphs although very good linear, in case of chlorobenzene, fairly good linear in

case of toluene and good linear in case of M.E.K., do not pass through the origin but give abscissa intercepts, as obtained by the least square method, corresponding to about 28000, 13000 and 10000 Ms in chlorobenzene, toluene and M.E.K. as respective solvents. This indicates that like Flory's eq., Pittsyn eq. has also got limited applicability in this case but in a sense it is better as its range of applicability is greater.

Analysis of Palit's Relation : According to eq. (4) plots of $100\rho_0[\eta] + \ln M$ ag. $M^{2/3}$ are expected to give straight lines. Good linear plots are obtained with chlorobenzene and very good linear plots are obtained with toluene and M.E.K. with 1.79×10^{-2} , 1.10×10^{-2} and 1.97×10^{-2} as corresponding slopes.

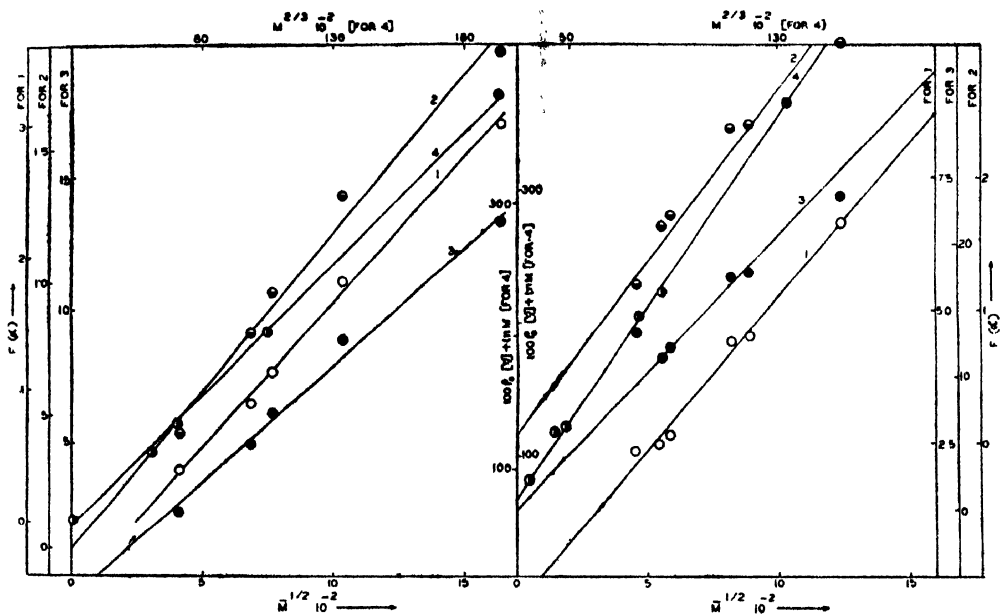


Fig. 3. Poly-p-Chlorostyrene in M.E.K. at 30°C.

Fig. 4. Poly-p-Methylstyrene in Toluene at 30°C.

2. *Poly-p-Methyl Styrene:* The \bar{M}_n and $[\eta]$ data of Kuwahara *et al.* (1965) at 30°C are utilised. K is evaluated by procedure 2. The Flory eq. gives fairly good, good and poorly linear plots in case of toluene (Fig. 4), cyclohexane (Fig.5) and M.E.K. (Fig. 6) as respective solvents but it has got an abscissa intercept of about 9000, 63000 and 53000 Ms respectively with these three solvents. The K-S-R eq gives poor linear plot in the case of toluene as solvent while good linear plots are obtained in the case of the other two solvents. In case of poorer solvents such as cyclohexane and M.E.K. it passes through the origin whereas, with a better solvent such as toluene a small ordinate intercept is obtained. The Ptitsyn eqn. gives fairly good linearity in toluene and good linear plots in cyclohexane and M.E.K. as solvents and passes through the origin in case of toluene whereas

in cyclohexane and M.E.K. it has an abscissa intercept of about 9000 and 14000 Ms respectively. Palit's plot is excellently linear in all these cases with respective slopes of 2.9×10^{-2} , 2×10^{-2} and 1.35×10^{-2} .

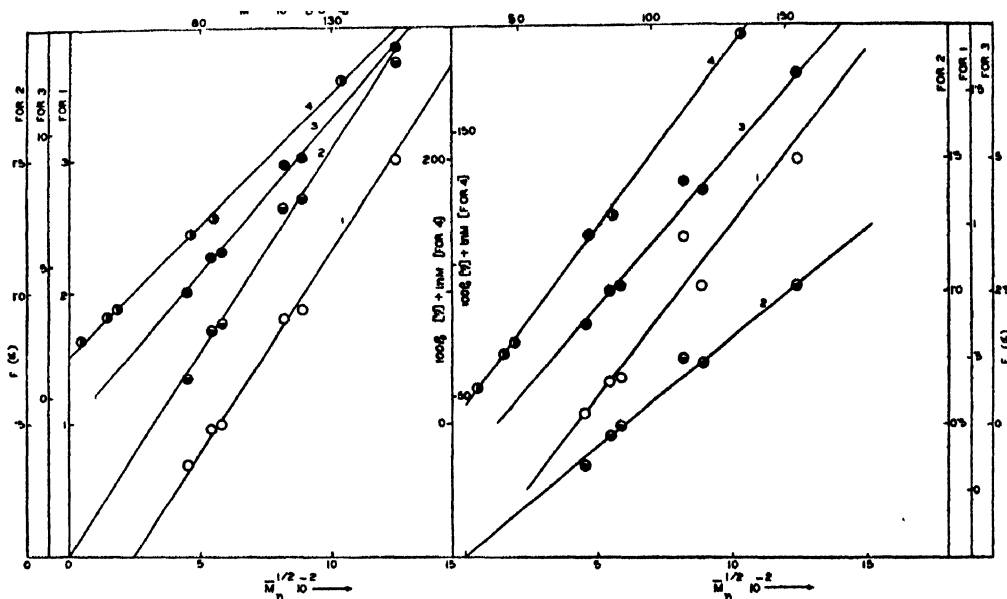


Fig. 5. Poly-p-Methylstyrene in Cyclohexane at 30°C.

Fig. 6. Poly-p-Methylstyrene in M.E.K. at 30°C.

3. *Poly-m-Methyl Styrene* : Source of data is an unpublished work done by Choudhury *et al* (1967) in this laboratory. K is evaluated by procedure 2. At 30°C, Flory plot gives good, fairly good and poor linear plots with benzene (Fig. 7), cyclohexane (Fig. 8) and ethyl acetate (Fig. 9) as respective solvents but it has got an abscissa intercept corresponding to about 12000, 5000 and 8100 Ms. The K-S-R eq. gives poor linear plots in case of benzene and ethyl acetate whereas in case of cyclohexane it is out of linearity but all of them pass through the origin. Ptitsyn eq. gives poor linear plots in case of benzene and ethyl acetate whereas in case of cyclohexane as solvent fairly good linearity is obtained. However, all of them pass through the origin. At 40° and 50°C also K-S-R- and Ptitsyn theories are more or less satisfactory. Palit eq. gives good linearity in case of benzene and cyclohexane as solvents and in ethyl acetate also the linearity is fairly good with respective slopes of 2.75×10^{-2} , 1.83×10^{-2} and 1.35×10^{-2} .

4. *Poly-α-Methyl Styrene* (Fig. 10) : The \bar{M}_n and $[\eta]$ data of McCormick (1959) in toluene at 25°C are utilised. The Flory plot is too widely scattered to give any linearity. The K-S-R and Ptitsyn eqs. pass through the origin though

they give fairly good linear and poorly linear plots respectively. Palit's eq. gives very good linear plot with a slope of 1.88×10^{-2} .

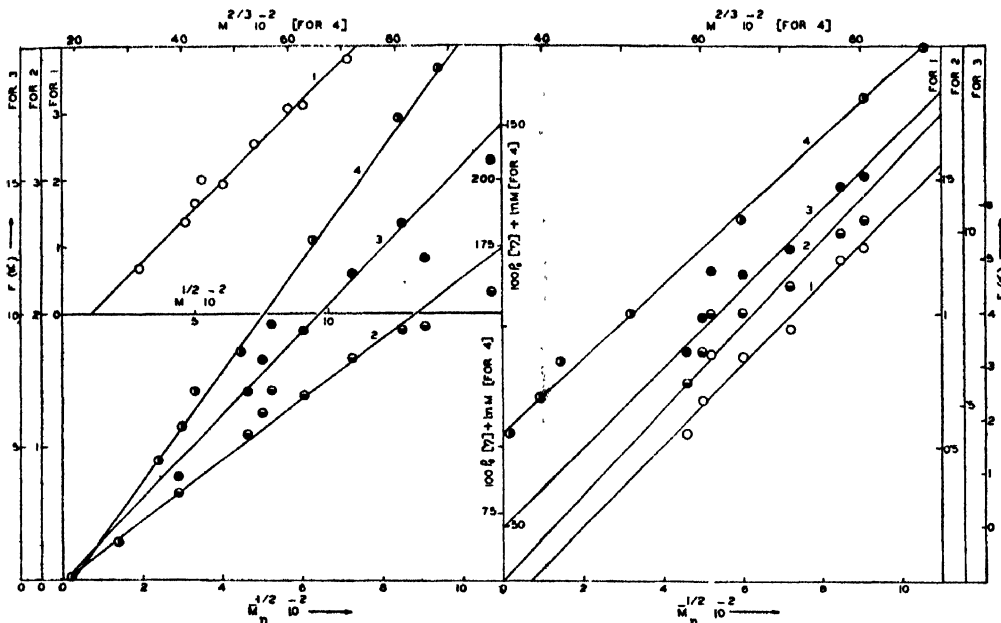


Fig. 7. Poly-m-Methylstyrene in Benzene at 30°C.

Fig. 8. Poly-m-Methylstyrene in Cyclohexane at 30°C.

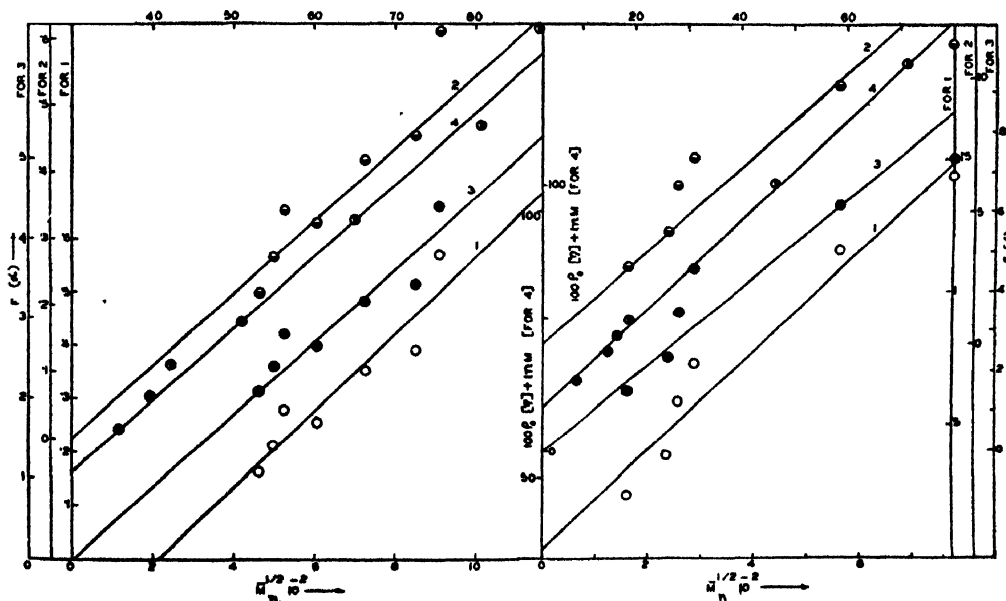


Fig. 9. Poly-m-Methylstyrene in Ethyl Acetate at 30°C.

Fig. 10. Poly-α-Methyl styrene in Toluene at 25°C.

5. *Polystyrene*: Fujita *et al* (1963) took eleven polystyrene fractions in toluene, in M.E.K. and in cyclohexane at 34.5°C. α is evaluated by procedure 1. With M.E.K. (Fig. 11) as solvent, poorly linear Flory plot is obtained with an abscissa intercept of about 40,000 M. The K-S-R and Ptitsyn plots are too much scattered to give any linearity. The least square straight lines have abscissa intercepts at about 12100 and 25600 Ms respectively. Excellent linear Palit plot is obtained with a slope of 1.45×10^{-2} .

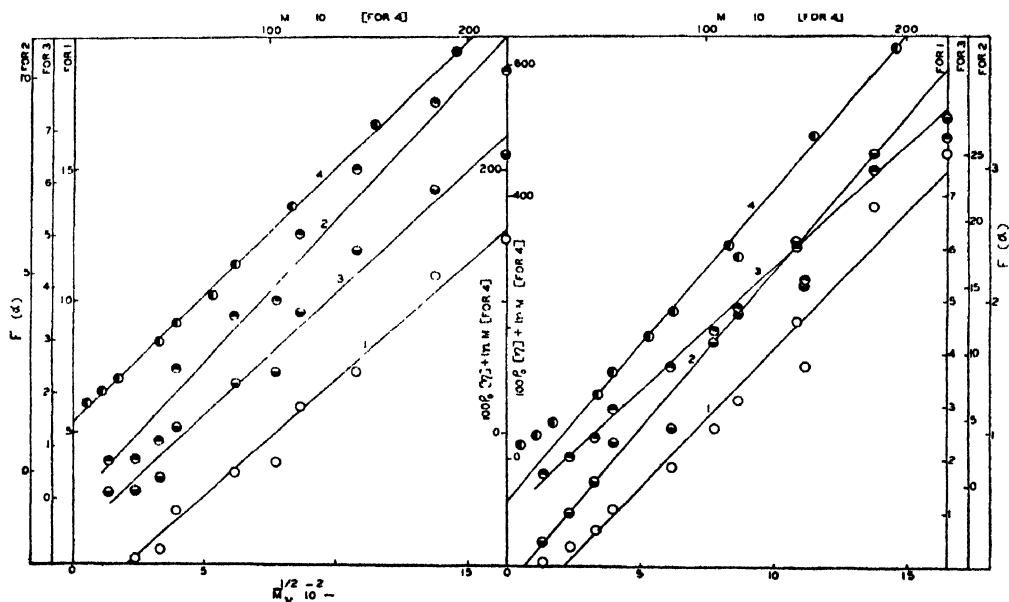


Fig. 11. Polystyrene in M.E.K., at 34.5°C. Ref. (12).

Fig. 12. Polystyrene in Toluene at 34.5°C (Ref. 12).

With toluene (Fig. 12) as solvent very poorly linear Flory plot is obtained with an abscissa intercept at about 44100 M. Good linear K-S-R plot is obtained with an abscissa intercept at 4220 M. Excellent linear plot is obtained in case of Ptitsyn eq., but it has an abscissa intercept at about 12100 M. Good linear Palit plot is obtained with a slope of 2.56×10^{-2} .

When the data of Rossi *et al* (1965) in M.E.K. (Fig. 13) are utilised the Flory and Ptitsyn plots are found to be not linear at all. The least square straight lines give abscissa intercepts corresponding to about 1600 and 6400 Ms. Very poor linearity is observed in case of K-S-R eq., but the least square straight line passes through the origin. Fairly good linear Palit plot is obtained with a slope of 1.47×10^{-2} .

6. *Polymethyl Methacrylate*: The \bar{M}_w , $[\eta]_0$ and $[\eta]$ data of Chinai *et al* (1955) at 25°C are utilised. With toluene as solvent, the Flory plot is too much scattered to give any linearity (Fig. 14) and the least square straight line gives a small ordinate intercept while with M.E.K. fairly good linearity is obtained

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(Fig. 15) with an abscissa intercept of about 96000 M. The K-S-R plot give poor linearity with M.E.K. and passes through the origin while in case of toluene

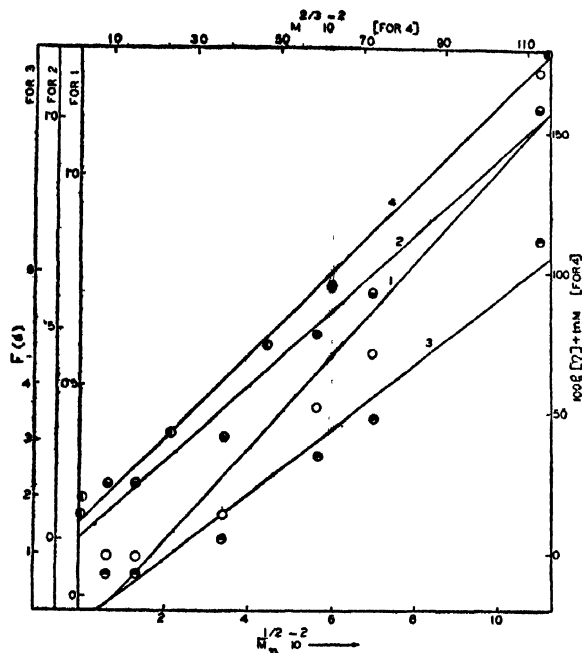


Fig. 13. Polystyrene in M.E.K., at 34.5°C (Ref. 13).

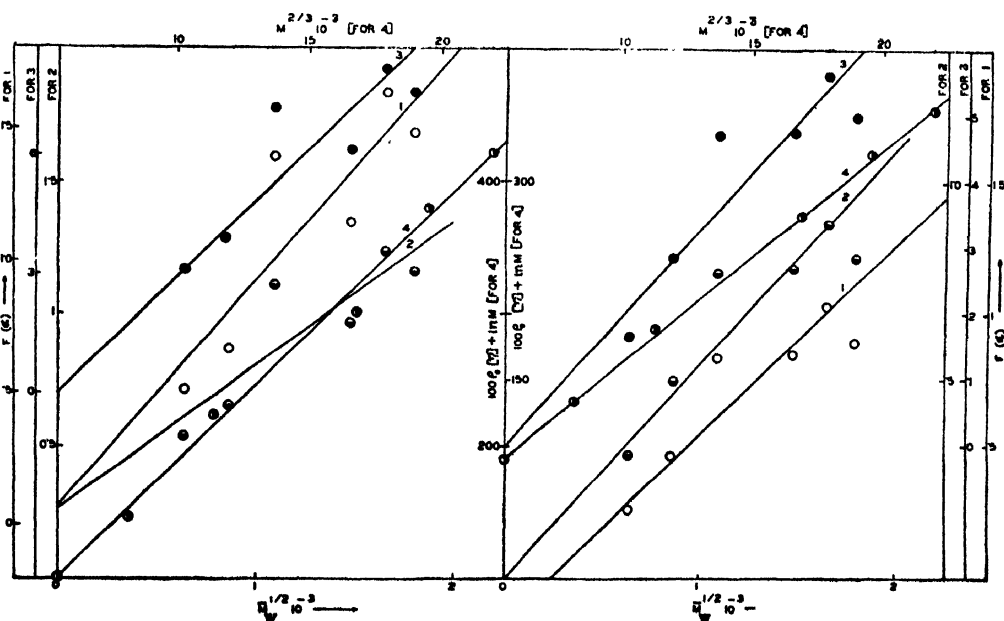


Fig. 14. Polymethyl Methacrylate in Toluene at 25°C.

Fig. 15. Polymethyl Methacrylate in M.E.K., at 25°C.

the plot is out of linearity and the least square straight line gives a large ordinate intercept. Ptitsyn plot passes through the origin though poor linearity is obtained in both the solvents. Palit's plot is fairly good linear with toluene and very good linear with M.E.K. with slopes of 1.94×10^{-2} and 1.62×10^{-2} respectively.

7. *Polyethyl-Methacrylate* (Fig. 16) : The \bar{M}_w , $[\eta]_0$ and $[\eta]$ data of Chinai *et al.* (1956) in M.E.K. at 23°C are utilised. Poor linearity is obtained in case of Flory eq. while in case of K-S-R and Ptitsyn plots fairly good linearity is obtained and the linearity in case of Palit's plot is good with a slope of 1.86×10^{-2} . The K-S-R and Ptitsyn plots pass through the origin while Flory plot is found to give an abscissa intercept at about 68000 M.

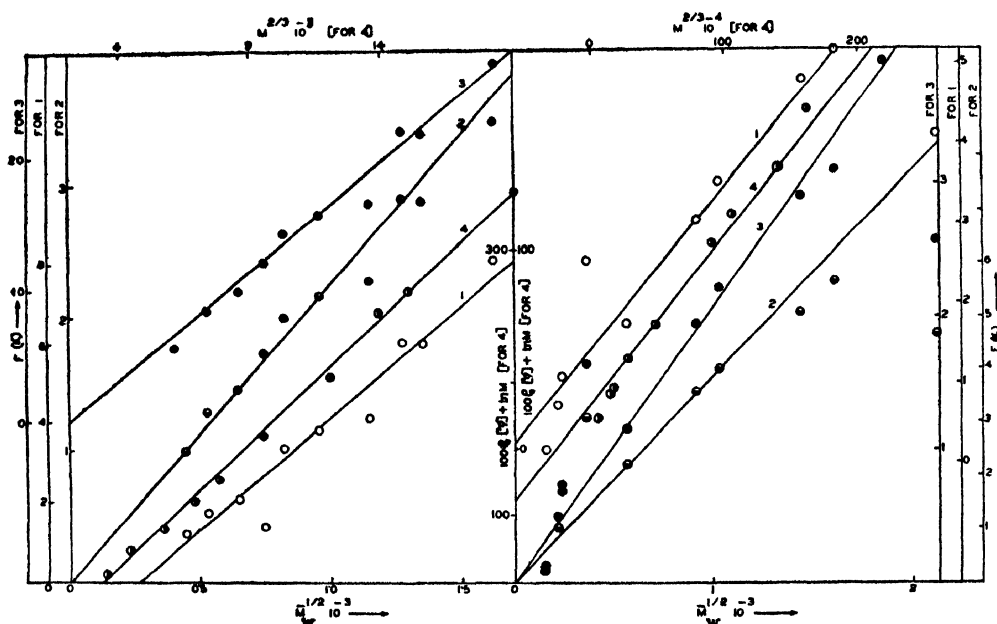


Fig. 16. Polyethyl Methacrylate in M.E.K. at 23°C .

Fig. 17. Polyvinyl Carbazole in Benzene at 25°C .

8. *Polyvinyl Carbazole* (Fig. 17) : The M_{LS} and $[\eta]$ data of Ueberreiter *et al.* (1963) in benzene at 25°C are utilised. Very poor linearity is obtained in case of Flory plot and it gives an ordinate intercept. The K-S-R and Ptitsyn plots are poorly linear but they pass through the origin. Good linearity is obtained in case of Palit plot up to 2.07×10^6 M after which it exhibits curvature and it has a least square slope of 1.26×10^{-2} .

9. *Polyvinyl Acetate* (Fig. 18) : The M_{LS} and $[\eta]$ data of Varadaiah (1956) in benzene are utilised. In case of all the first three eqs. the plots are too much scattered to give any linearity. Ordinate intercepts are obtained by least square

method. Evidently none of the three equations is valid. Data may not be very reliable. However, the Palit plot is fairly satisfactory with a slope of 2.13×10^{-2} .

10. *Polyacrylonitrile*: The data of Bisschops (1955) are utilised. When $[\eta]$ and M_{SD} values are utilised, the Flory eq. in D.M.F. at 25°C (Fig. 19) is found

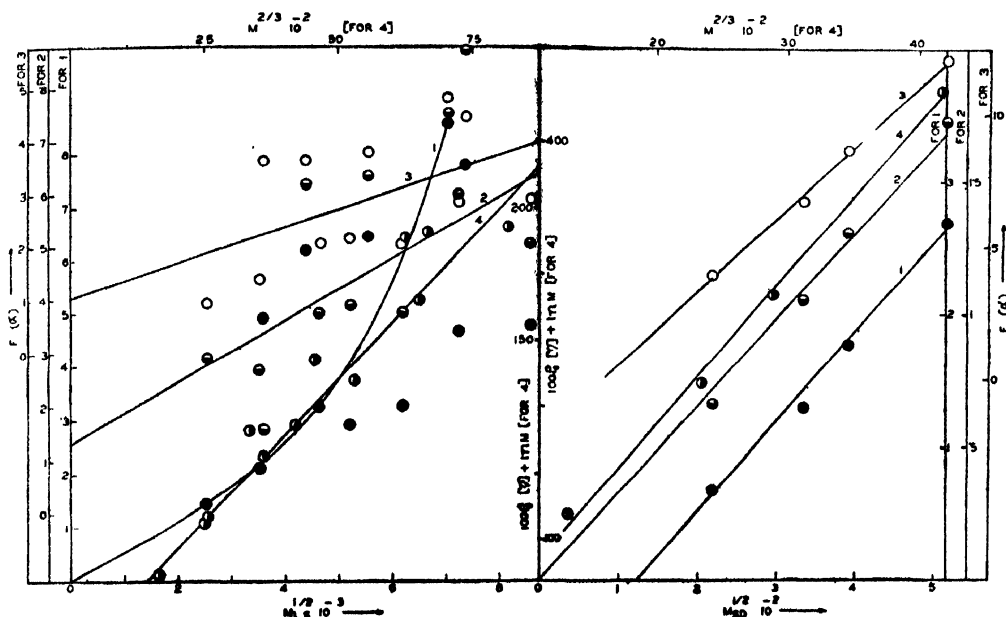


Fig. 18. Polyvinyl Acetate in Benzene at 30°C.

Fig. 19. Polyacrylonitrile in D.M.F. at 25°C.

to give good linearity with an abscissa intercept at about 15200 M. At 65°C upward curvature is noted. Very poor linearity is obtained in case of K-S-R eq., but it passes through the origin at all temperatures. The Ptitsyn plot at 25°C is excellently linear but it gives an abscissa intercept corresponding to about 5600 M. Fairly good linearity is obtained in case of Palit's eq. with a slope of 11.38×10^{-2} .

When $[\eta]$ and \bar{M}_W values of the same fractions are utilised the K-S-R plot is linear passing through the origin, while the Flory and Ptitsyn plots—though linear have got abscissa intercepts at about 16000 and 1200 Ms.

11. *Poly-N-N-Dimethyl Acrylamide*: The M_{LS} and $[\eta]$ data of Trossarelli *et al* (1962) are utilised. In methanol at 25°C (Fig. 20), the Flory plot is poorly linear with an abscissa intercept at about 6000 M. The K-S-R and Ptitsyn plots are poorly linear but they pass through the origin. Palit plot is good linear with a slope of 2.05×10^{-2} .

In water at 25°C (Fig. 21), fairly good linearity is obtained in case of Flory plot with an abscissa intercept at about 24000 and 8100 Ms at 25° and 40°C res-

pectively. Good linearity is obtained in case of K-S-R- plot and it passes through the origin. Fairly good linearity is obtained in case of Ptitsyn plot and it passes through the origin. Palit's plot is fairly good linear with a slope of 1.93×10^{-2} .

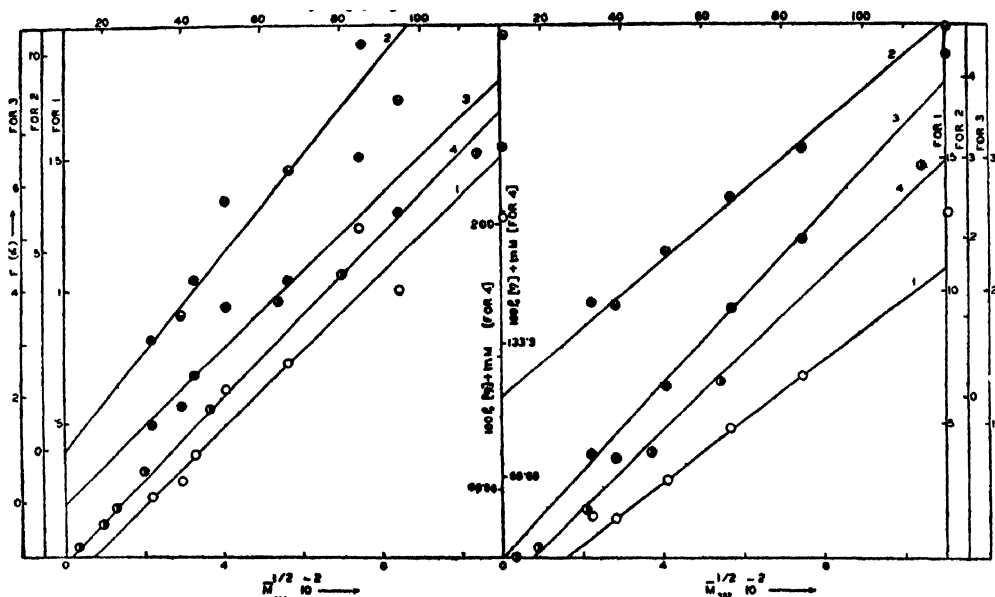


Fig. 20. Poly-N-N-Dimethylacrylamide in Methanol at 25°C.

Fig. 21. Poly-N-N-Dimethylacrylamide in Water at 25°C.

12. *Polyacrylamide* (Fig. 22): The $M_{END\ GROUP}$ and $[\eta]$ data of Collinson *et al* (1957) in water at 25°C are utilised. Fairly good linearity is obtained in case of Flory, K-S-R and Ptitsyn plots with abscissa intercepts at about 5300, 900 and 4600Ms respectively. Very good linear Palit plot is obtained with a slope of 6.75×10^{-2} .

13. *Cis-Tactic Polybutadiene* (Fig. 23); The \bar{M}_n and $[\eta]$ data of Danusso (1961) in toluene at 30°C are utilised. Fairly good linearity is obtained in all the first three cases. The K-S-R plot passes through the origin, while the Flory and Ptitsyn plots have abscissa intercepts at about 4600 and 600Ms respectively. Good linearity is obtained in case of Palit plot with a slope of 6.51×10^{-2} .

14. *Polyvinyl Chloride* (Fig. 24): The \bar{M}_n and $[\eta]$ data of Ciampa *et al* (1956) in cyclohexanone at 25°C are utilised. Fairly good linearity is obtained in Flory plot with an abscissa intercept at about 8700 M. Poor linearity passing through the origin is obtained in K-S-R plot. Very poor linearity is obtained in Ptitsyn plot with an abscissa intercept at about 3000 M. Poor linearity with a slope of 9.05×10^{-2} is obtained in case of Palit plot. Data may not be very reliable,

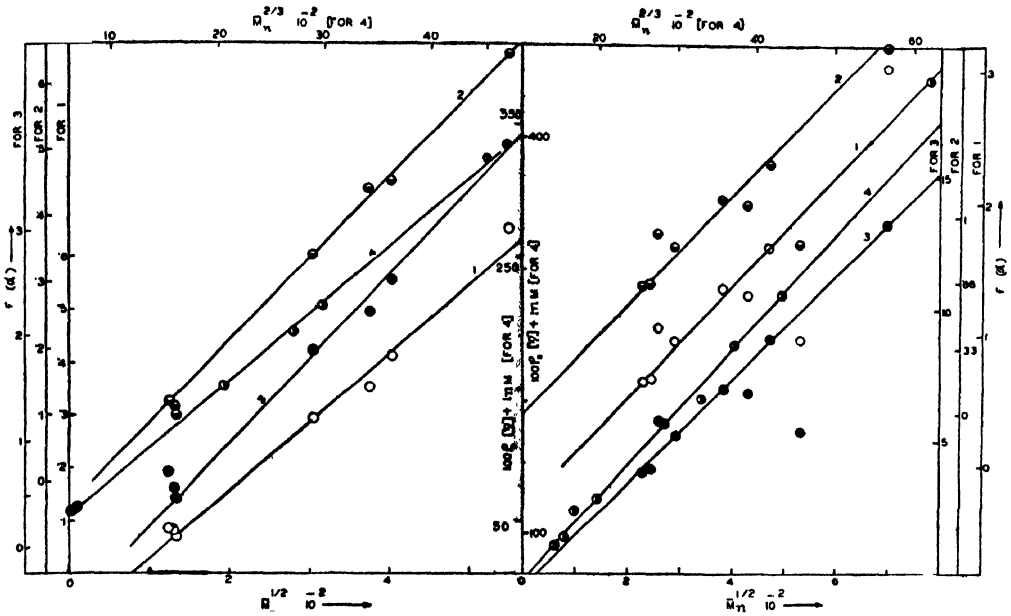


Fig. 22. Polyacrylamide in Water at 25°C.

Fig. 23. Cis-Tactic Polybutadiene in Toluene at 30°C.

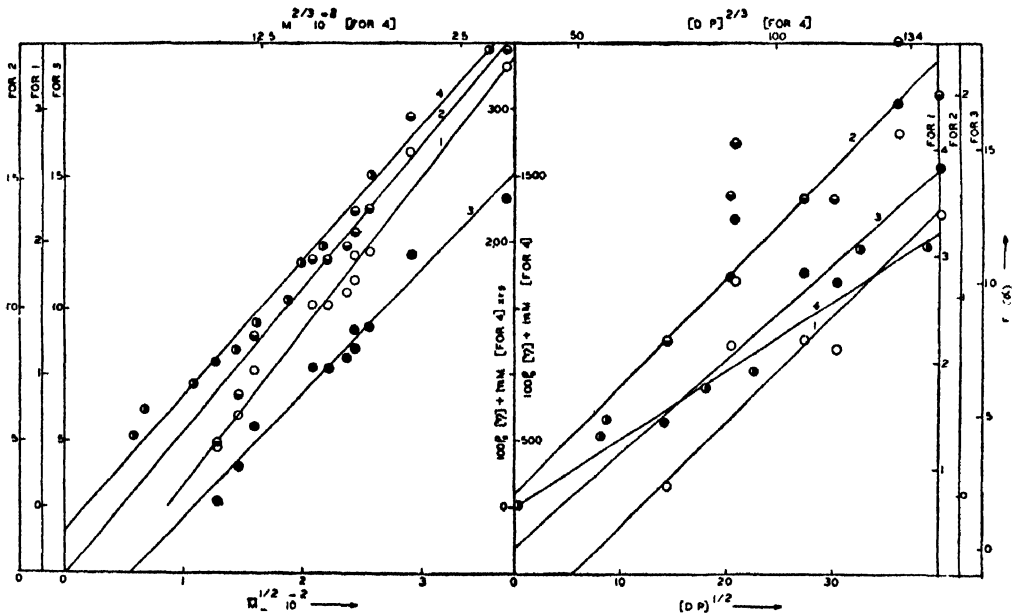


Fig. 24. Polyvinyl Chloride in Cyclohexanone at 25°C.

Fig. 25. Na-Carboxy Methyl Cellulose in aqueous solution at $I_E = 0.1M$ at 26°C.

B. SEMISYNTHETICS FROM CELLULOSE

1. *Na-Carboxy Methyl Cellulose* (Fig. 25): The M_{SD} and $[\eta]$ data of Sitaraniyah *et al* (1962) in aqueous solution at $I_E = 0.1M$ at 26°C are utilised.

Linearity is poor in case of Flory plot while in case of K-S-R- and Pitsyn plots the linearity is very poor. The Flory plot has an abscissa intercept at about 29 D.P. while K-S-R- and Pitsyn plots pass through the origin. Palit plot is poor but is least poor, in comparison to the rest, having slope of 9.75×10^{-2} .

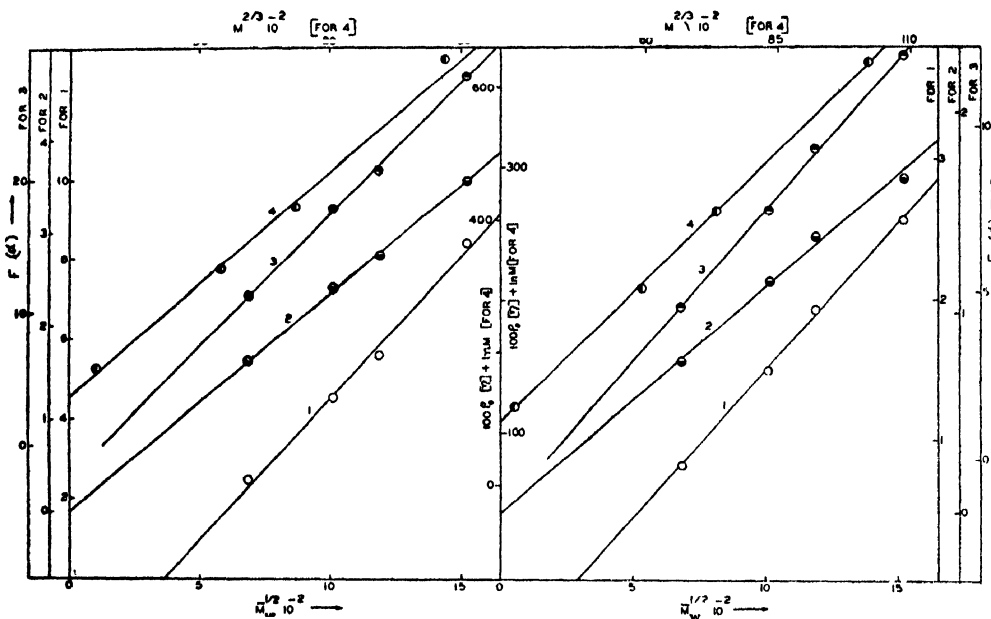


Fig. 26. Amylose Acetate in Chloroform at 30°C.

Fig. 27. Amylose Acetate in Nitromethane at 30°C.

2. *Amylose-Acetate* : The \bar{M}_w and $[\eta]$ data of Patel *et al* (1965) in chloroform and nitromethane at 25°C are utilised. K is evaluated by procedure 2. In Chloroform (Fig. 26) fairly good linear Flory plot is obtained with an abscissa intercept at about 133200 M. Good linear K-S-R- plot is obtained and it passes through the origin. Excellent linear plot is obtained in case of Pitsyn eq. and it has an abscissa intercept at about 16900 M. Fairly good linear Palit plot is obtained with a slope of 6.8×10^{-2} .

With nitromethane (Fig. 27), as solvent good linear Flory and Pitsyn plots are obtained with abscissa intercepts at about 84100 and 18900 Ms respectively. Fairly good linear K-S-R plot is obtained and it passes through the origin. Excellent linear plot is obtained in case of Palit eq. with a slope of 3.87×10^{-2} .

C. CONDENSATION POLYMERS

Polydimethyl Siloxane (Fig. 28) : The \bar{M}_v and $[\eta]$ data of Flory *et al* (1962) in M.E.K. at 30°C are utilised. The first three plots are too much scattered to give any linearity—the hand drawn curves appear to meet at a common point

on the abscissa corresponding to about 32400M. The least square straight lines give ordinate intercepts. Palit plot is slightly curved.

D. POLYETHER

Polyethylene Oxide (Fig. 29) : The $[\eta]_0$ and $[\eta]$ data of Rossi *et al* (1962) in benzene at 25°C are utilised. The Molecular weight determination on the fractions were made by the method of chemical titration in pyridine solution with well reproducible results. Fairly good linear plot is obtained in case of K-S-R- and Ptitsyn eqs. with abscissa intercepts at about 59 and 128 Ms. Good linearity is obtained with Flory plot with an abscissa intercept at about 196 M. Very good linearity is obtained in Palit's plot with a slope of 6×10^{-2} .

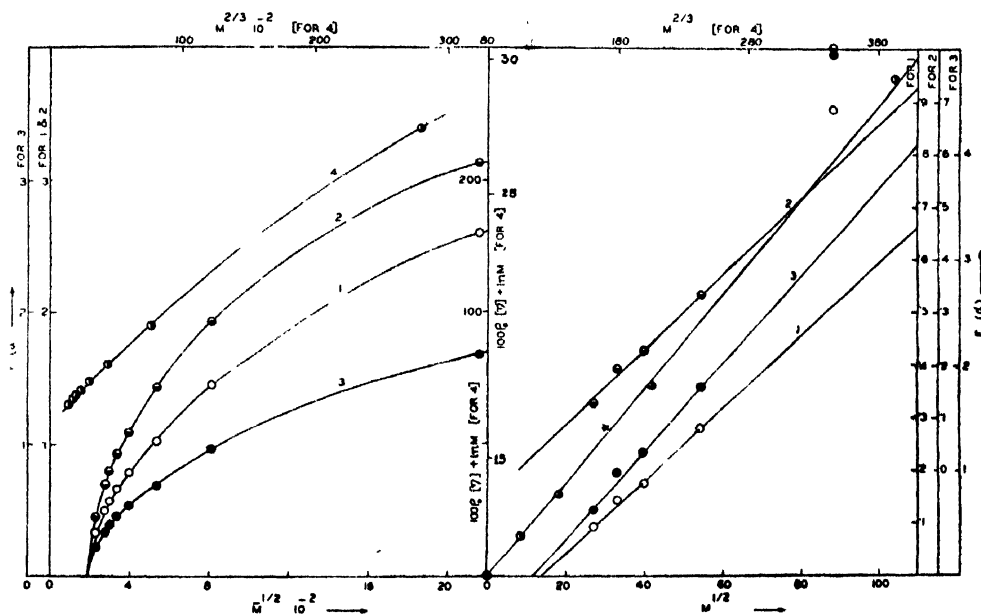


Fig. 28. Poly Dimethyl Siloxane in M.E.K. at 30°C.

Fig. 29. Polyethylene Oxide in Benzene at 25°C.

E. POLYESTER

Bisphenol A Polycarbonate : The \bar{M}_n and $[\eta]$ data of Sitaramaiah (1965) at 25°C are utilised. The Flory relation is found to be applicable only over 6000M. In tetrahydrofuran (Fig. 30), excellent linear plot is obtained in case of Flory eq. Fairly good linear plot passing through the origin is obtained in case of K-S-R- eq. Good linear plot passing through the origin is obtained in the case of Ptitsyn eq. Good linear Palit plot with a slope of 6.35×10^{-2} is obtained.

In ethylene dichloride (Fig. 31), poor linear Flory plot is obtained. Very poor linear plot is obtained in case of K-S-R eq., but it passes through the origin.

Fairly good linear plot with an abscissa intercept at about 225M is obtained in case of Ptitsyn eq. Poorly linear Palit plot with a slope of 6.51×10^{-2} is obtained.

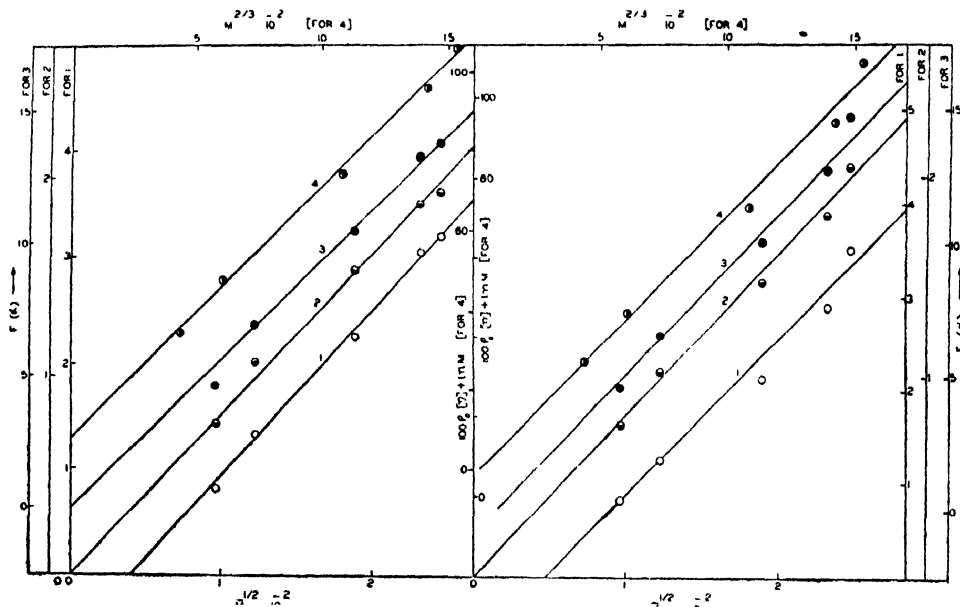


Fig. 30. Bisphenol A Polycarbonate in Tetrahydrofuran at 25°C.

Fig. 31. Bisphenol A Polycarbonate in Ethylene Dichloride at 25°C.

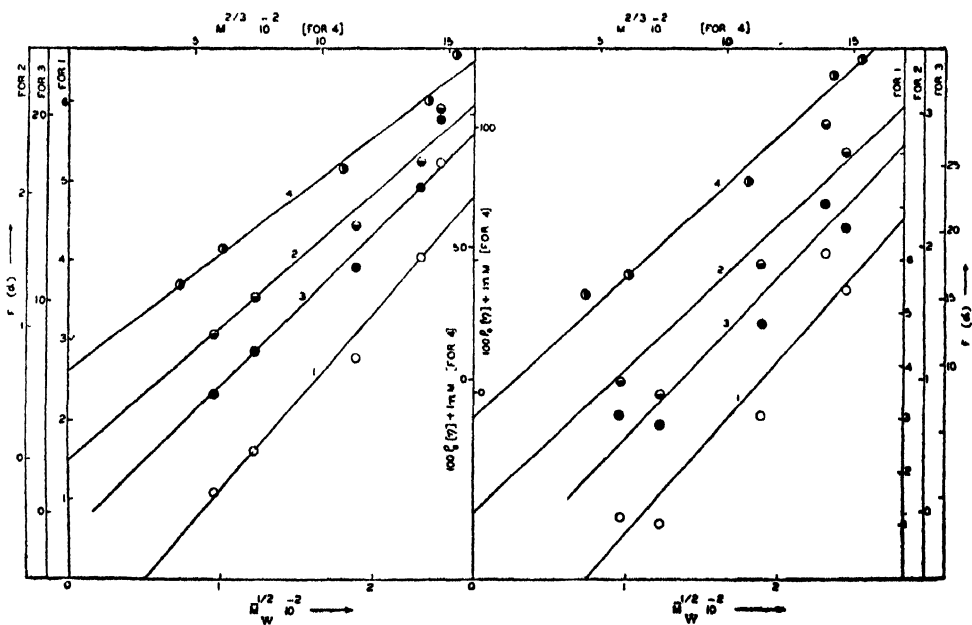


Fig. 32. Bisphenol A Polycarbonate in Chloroform at 25°C.

Fig. 33. Bisphenol A Polycarbonate in Tetrachloroethane at 25°C.

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In chloroform (Fig. 32) fairly good linear plots are obtained in case of Flory and Ptitsyn eqs. the latter having an abscissa intercept at about 275 M. Poorly linear K-S-R plot—passing through origin is obtained. Good linear Palit plot with a slope of 7.29×10^{-2} is obtained.

In Tetrachloroethane (Fig. 33) very poor linearity is obtained in all the first three eqs. The K-S-R plot passes through the origin whereas the Ptitsyn plot gives an abscissa intercept at 3600M. Poor linearity is obtained in case of Palit's eq. with a slope of 8.84×10^{-2} .

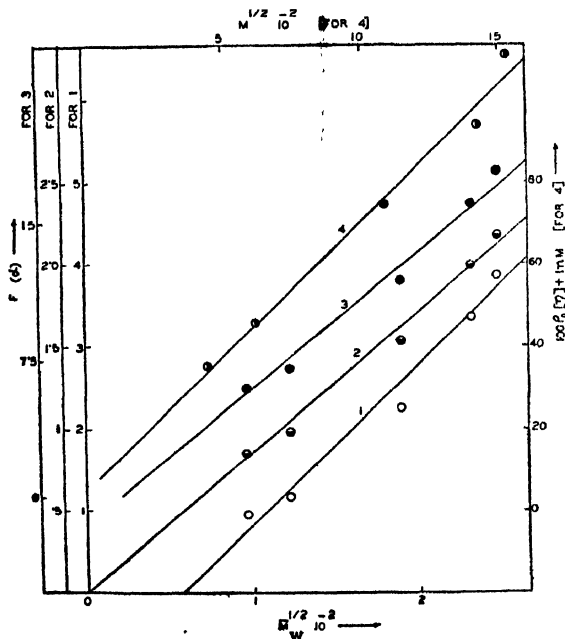


Fig. 34. Bisphenol A Polycarbonate in Methylene Chloride at 25°C.

In methylene chloride (Fig. 34) poorly linear plot is obtained in all the first three cases. K-S-R plot is found to pass through the origin. Ptitsyn plot has an abscissa intercept at about 400 M. Fairly good linear Palit plot is obtained with a slope of 6.58×10^{-2} .

F. POLYPEPTIDES

Poly-γ-Benzoyl-L-Glutamate The M_{LS} and $[\eta]$ data of Doty *et al* (1956) in dichloroacetic acid and D.M.F. at 25°C are utilised. In dichloroacetic acid (Fig. 35) very good linearity is obtained in case of Flory plot though it has an abscissa intercept at about 5000 M. Fairly good linear plot passing through the origin is obtained in case of K-S-R eq. Good linear plot is observed in case of Ptitsyn eq. though it gives a large ordinate intercept. Fairly good linear Palit plot with a slope of 4.05×10^{-2} is obtained.

In D.M.F. (Fig. 36) all the first three plots are much scattered. When least square method is applied the Flory and Ptitsyn eqs. are found to give abscissa

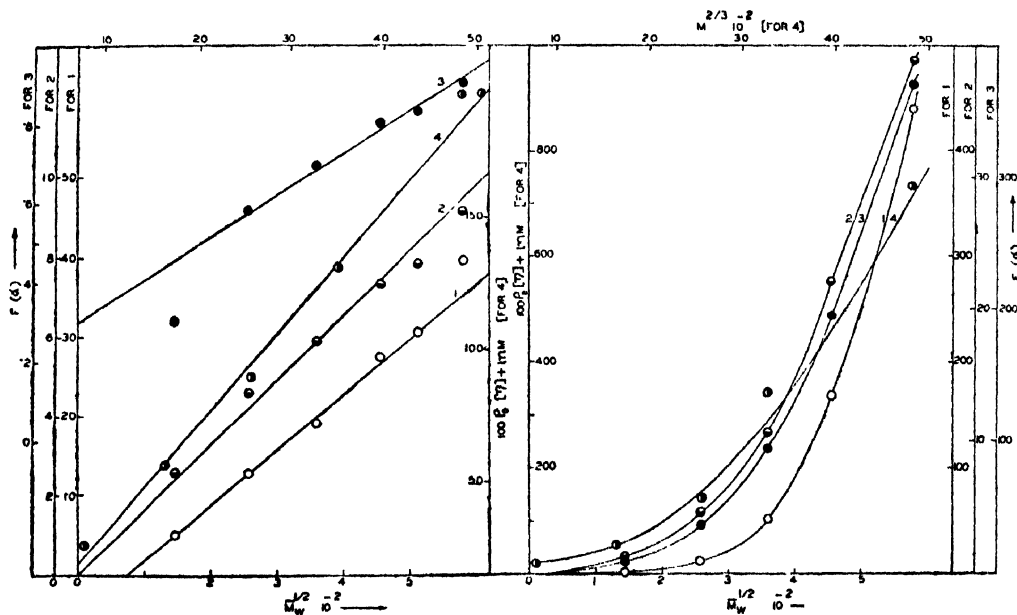


Fig. 35. Poly- γ -Benzoyl-L-Glutamate in Dichloroacetic acid at 25°C.

Fig. 36. Poly γ -Benzoyl-L-Glutamate in D.M.F. at 25°C.

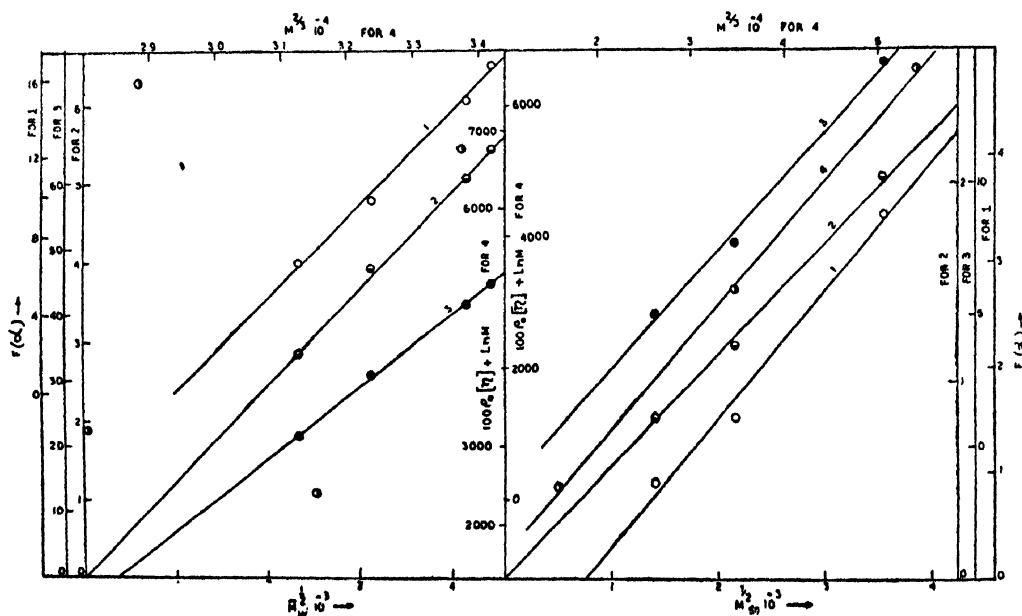


Fig. 37. D.N.A. in Water at 20°C.

Fig. 38. Renatured D.N.A. in water at 20°C.

TABLE III
Tabular Summary of Results

Polymer	Solvent	Temp. °C	LINEARITY AND ABSCISSA INTERCEPTS IN TERMS OF M					GENERAL REMARKS	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Pitsyn plot Eq. 3	Palit plot Eq. 4, $K_1, 10^2$	Best Linear eq.	Eq. that passes through the origin.	
Poly-p-Chloro-Styrene	Chlorobenzene	30	good 99000	fairly good 2500	very good 28000	good 1.79	3		
	Toluene	"	good 60000	poor 0	fairly good 13000	very good 1.1	4	2	
	M.E.K.	"	good 57000	very poor 0	good 10000	very good 1.97	4	2	
Poly-p-Methyl Styrene	Toluene	"	fairly good 9000	poor *	fairly good 0	very good 2.91	4	3	
	Cyclohexane	"	good 63000	good 0	good 9000	very good 2	4	2	
	M.E.K.	"	poor 53000	good 0	good 14000	very good 1.35	4	2	
Poly-m-Methyl Styrene	Benzene	"	good 15000	poor 0	poor 0	good 2.75	1 and 4	2 and 3	
	Cyclohexane	"	fairly good 5000	scattered 0	fairly good 0	good 1.83	4	2 and 3	
	Ethyl Acetate	"	poor 8100	poor 0	poor 0	fairly good 1.35	4	2 and 3	

TABLE III—(contd).

Polymer	Solvent	Temp. °C	LINEARITY AND ABSCISSA INTERCEPTS IN TERMS OF \bar{M}				GENERAL REMARKS	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Ptitsyn plot Eq. 3	Palit plot Eq. 4, $K_1 \cdot 10^2$	Best Linear eq.	Eq. that passes through the origin
Poly- α -Methyl Styrene	Toluene	25	highly-scattered	fairly good 0	poor 0	very good 1.88	4	2 and 3
Polystyrene	M.E.K. (Ref. 12)	34.5	poor 40000	highly scattered 12100	highly scattered 25600	very good 1.45	4	
	Toluene (Ref. 12)	"	very poor 44100	good 4220	very good 12100	good 2.56	3	
	M.E.K. (Ref. 13)	"	highly scattered 6400	very poor 0	scattered 1600	fairly good 1.47	4	2
Poly-methyl Methacrylate	Toluene	25	highly scattered small*	highly scattered large*	poor 0	fairly good 1.94	4	3
	M.E.K.	"	fairly good 96000	poor 0	poor 0	very good 1.62	4	2 and 3
Polyethyl Methacrylate	M.E.K.	23	poor 68000	fairly good 0	fairly good 0	good 1.86	4	2 and 3
Polyvinyl Carbazole	Benzene	25	very poor *	poor 0	poor 0	good 1.26	4	2 and 3
Polyvinyl Acetate	Benzene	30	highly scattered *	highly scattered *	highly scattered *	fairly good 2.13	4	
Polyacrylonitrile	D.M.F.	25	good 15200	very poor 0	very good 5600	fairly good 11.38	3	2

TABLE III (contd.)

Polymer	Solvent	Temp. °C	LINEARITY AND ABSCISSA INTERCEPTS IN TERMS OF η					GENERAL REMARKS	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Ptitsyn plot Eq. 2	Palit plot Eq. 4, $K_1 \cdot 10$	Best Linear eq.	Eq. that passes through the origin.	
Poly-N-N-Dimethyl Acrylamide	Methanol	25	poor 6000	poor 0	poor 0	good 2.05	4	2 and 3	
	Water	"	fairly good 24000	good 0	fairly good 0	fairly good 1.93	2	2 and 3	
Polyacrylamide	Water	"	fairly good 5300	fairly good 900	fairly good 4600	very good 6.75	4		
	Toluene	30	fairly good 4600	fairly good 0	fairly good 600	good 6.51	4	2	
Polyvinyl Chloride	Cyclohexanone	25	fairly good 8700	poor 0	very poor 3000	poor 9.05	1	2	
Na-Carboxy Methyl Cellulose	Water $I_2=0.1M.$	26	poor 29 D.P.	very poor 0	very poor 0	least poor 9.75	4	2 and 3	
	Chloroform	30	fairly good 133200	good 0	very good 16900	fairly good 6.8	3	2	
Poly Dimethyl Siloxane M.E.K.	Nitromethane	"	good 84000	fairly good 0	good 18900	very good 3.87	4	2	
	M.E.K.	"	* highly curved	* highly curved	* highly curved	slightly curved	4		
Polyethylene Oxide	Benzene	25	good 196	fairly good 59	fairly good 128	very good 6	4		

TABLE III (contd.)

Polymer	Solvent	Temp. °C	LINEARITY AND ABSCISSA INTERCEPTS IN TERMS OF M					GENERAL REMARKS	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Pitsyn plot Eq. 3	Pzilit plot Eq. 4, K ₁ .10	Best Linear eq.	Eq. that passes through the origin.	
Bisphenol A Polycarbonate	Tetrahydrofuran	25	very good 6000	fairly good 0	good 0	good 6.35	1	2 and 3	
	Ethylene Dichloride	"	poor 6000	very poor 0	fairly good 225	poor 6.51	3	2	
	Chloroform	"	fairly good 6000	poor 0	fairly good 275	good 7.29	4	2	
	Tetrachloroethane	"	very poor 6000	very poor 0	very poor 3600	poor 8.84	4	2	
	Methylene Chloride	"	poor 6000	poor 0	poor 400	fairly good 6.58	4	2	
Poly-γ-Benzoyl L-Glutamate	Dichloro Acetic Acid	"	very good 5000	fairly good 0	good large*	fairly good 4.05	1	2	
	D.M.F.	"	highly curved 48000	highly curved 0	highly curved 33000	curved	4	2	
D.N.A.	Water	20	good 1000000	good 0	very good 360000	highly scattered	3	2	
Renatured D.N.A.	Water	"	poor 640000	fairly good 0	fairly good 133000	good 16.47	4	2	

* Stands for ordinate intercept

D.P. Stands for degree of polymerization.

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intercepts at about 48000 and 33000 Ms respectively while the K-S-R eq is found to pass through the origin. The hand drawn curves can be made to pass through the origin. Palit plot is markedly curved but is least curved in comparison to the rest.

G. POLYNUCLEOTIDES

1. *D.N.A.* (Fig. 37) : The \bar{M}_w and $[\eta]$ data of Butler *et al* (1959) in water at 20°C are utilised. Good linear plot is obtained in case of Flory eq. with an abscissa intercept at about 1000000 M. Excellent linear Ptitsyn plot with an abscissa intercept at about 360000 M is obtained. Good linear plot is obtained in case of K-S-R eq. and it passes through the origin. Palit eq. is found to be not at all valid.

2. *Renatured D.N.A.* (Fig. 38) : The $M_{S\eta}$ and $[\eta]$ data of Doty *et al* (1965) in water at 20°C are utilised. Poor linearity is observed in case of Flory plot and it has an abscissa intercept at about 640000 M. Fairly good linearity is observed in case of K-S-R and Ptitsyn plots; the former passes through the origin while the latter gives an intercept at about 133000 M. Good linear plot with a slope of 16.47×10^{-2} is obtained in case of Palit's equation.

DISCUSSION

From Table III it will be observed that as regards linearity, out of 38 different polymer-solvent systems studied, Palit's plot is found to be best in 27 cases, Ptitsyn's eq. is found to be best in 6 cases, K-S-R eq. is best in 1 case and Flory eq. is best in 3 cases—there being a single case where it is difficult to ascertain whether Palit eq. or Flory eq. is best suited. From these statistics, it is evident that in so far as satisfaction of linearity is concerned, Palit's eq. is the best.

As regards the criteria of passing through the origin, the K-S-R and Ptitsyn eqs. are satisfied in 29 and 13 cases respectively, while the Flory eq. is not satisfied in a solitary case—it always gives either an abscissa intercept (in majority of cases) or an ordinate intercept (in a few cases). In cases where abscissa intercepts are given by all the three eqs., the intercept is always found to be the least in case of K-S-R eq. and it is always greatest in the case of Flory eq. So the K-S-R eq., based on an equivalent ellipsoid model, is best suited to interpret the molecular expansion of most of the polymers discussed. In cases where only K-R-S plot passes through the origin, the Ptitsyn eq. always gives smaller intercepts. So the Ptitsyn eq. is better suited to various polymer-solvent systems in comparison to Flory eq.

CONCLUSION

The general conclusion is that the Flory eq. suffers from a serious limitation—it is valid generally in the high molecular weight range. The K-S-R and Ptitsyn expressions are well suited to interpret the molecular expansion of most of the

polymers discussed. Palit's eq. excellently correlates intrinsic viscosity and molecular weight of polymers.

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