

## VISCOSITIES OF DILUTE POLYMER SOLUTIONS: SIGNIFICANCE OF THE MARK-HOUWINK CONSTANTS

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Constants  $K_m$  and  $a$  of the Mark-Houwink equation,  $[\eta]=K_m.M^a$ ; are related to the polymer dimension in solution. These two parameters, therefore, can be used to evaluate the dimension of polymers. Two methods of estimating the Flory  $K$  from values of  $K_m$  and  $a$  for polystyrene, polymethylmethacrylate, bisphenol A polycarbonate and amylose are verified. These methods of evaluation of  $K$  seem to apply for flexible polymers and suggest that  $K$  is independent of solvent power.

Of the parameters of dilute solution viscosities of polymers, the one with any significance in terms of macro-molecular dimension is the intrinsic viscosity denoted by  $[\eta]$ . The relation between  $[\eta]$  and molecular weight  $M$  is given by the Mark-Houwink equation,

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

where  $K_m$  and  $a$  are constants for a given polymer-solvent system. Equation 1, though empirical, has similarity in form with the equation of Flory-Fox<sup>1</sup> deduced from the excluded volume consideration,<sup>2</sup>

$$[\eta]=K.M^{\frac{1}{2}}.\alpha^3 \quad (2)$$

$$\text{where } K=\Phi(\bar{r}_0^2/M)^{3/2} \quad (3)$$

and  $\bar{r}_0^2$  is the mean square end-to-end distance of the molecule in the unperturbed state,  $\alpha$ , the extension factor representing expansion over the unperturbed state and  $\Phi$ , the universal constant. The intrinsic viscosity  $[\eta]$  being dependent on temperature<sup>3</sup> except in athermal solvents;  $K_m$  and  $a$  appear to vary with temperature.<sup>3</sup> However, this paper concerns with the relation of  $K_m$  and  $a$  with the molecular dimension and hence with  $K$  and not with their temperature coefficients.

Excluded volume treatment of Flory<sup>2</sup> predicts that  $\alpha$  varies with  $M^{\circ}=1$  in a solvent in which the interaction between polymer and solvent is absent and the exponent of  $M$  increases with increase in solvent power reaching the maximum of  $M^{\circ \cdot 1}$ .  $[\eta]$ , therefore, in a very good solvent becomes proportional to  $M^{\circ \cdot 8}$  whereas for cellulose derivatives<sup>4</sup> the exponent of  $M$  approaches unity. Flory's relationship<sup>1</sup> represents a very close approximation to the solution viscosities of flexible polymers. The behaviour of cellulose derivatives and stiff chain polymers in general can be accounted for by the theory of Kurata *et al.*<sup>5</sup> which makes an allowance for  $\alpha$  becoming proportional to  $M^{1/6}$  in a very good solvent. The Mark-Houwink equation empirically represents the viscosity behaviour of both flexible and stiff chain

polymers in solutions. Values of  $a$  between 0.5 and 0.8 indicating approximately isotropic coil expansion represent flexible polymers and values exceeding 0.8 suggest predominance of draining effect.

In absence of the interaction between a polymer and a solvent the extension factor,  $\alpha$  becomes unity and such a solvent representing  $\alpha=1$ , is termed a theta solvent for the polymer in the system. In this condition of theta, equations 1 and 2 can be equated with the result

$$K=K_m \quad (4)$$

$$\text{and } a=0.5 \quad (5)$$

With increase in the solvent power, the polymer-solvent interaction comes into consideration and deviations from conditions given in equations 4 and 5 occur. Whatever be the magnitude of deviation, it is apparent that  $K_m$  and  $a$  are related to the molecular dimension. Voek<sup>6</sup> has suggested the following relationship between  $a$  and  $\alpha$ ,

$$a=(4\alpha^2-3)/(5\alpha^2-3) \quad (6)$$

which does not suggest variation of  $a$  with solvent and of  $\alpha$  with molecular weight and, therefore, is unreliable. However, it is possible to evaluate  $K$  from  $K_m$  and  $a$ . It is also evident that such methods of determining  $K$  may not be applicable to stiff chain polymers<sup>4</sup> which do not fulfil the requirements of Flory's excluded volume treatment and consequently of equation 2.

Determination of  $K_m$  and  $a$  are simple and made from the graphical representation of equation 1 in the logarithmic form.

$$\log[\eta]=\log K_m+a \log M \quad (7)$$

Reasonably homogeneous fractions are needed and the log-log plots of  $[\eta]$  against  $M$  as is evident from equation 7 are linear (Fig. 1).  $K_m$  and  $a$  are obtained from the intercept and the slope respectively. Values of  $K_m$  and  $a$  for polystyrene,<sup>7-11</sup> polymethylmethacrylate,<sup>12-17</sup> bisphenol A polycarbonate<sup>18</sup> and amylose<sup>19,20</sup> in different solvents are given in Table 1.



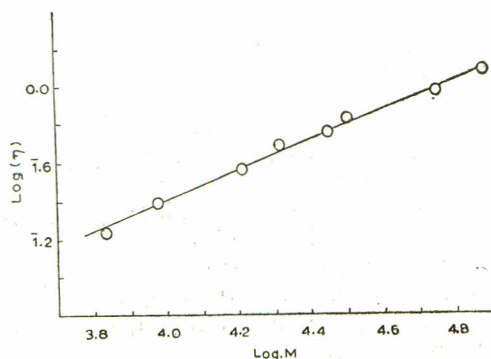


Fig. 1.—Plot of  $\log [\eta]$  against  $\log M$  for bisphenol A polycarbonate in chloroform.

TABLE I.—VALUE OF  $K_m$  AND  $a$  AT 25°C.

Polymer	Solvent	$K_m \times 10^5$	$a$	Ref
Polystyrene	Chloroform	7.16	0.76	7
	Benzene	9.52	0.74	8
	Toluene	10.00	0.72	9
	Ethylbenzene	17.60	0.68	10
	Dichloroethane	21.00	0.66	11
	Methylethyl ketone	39.00	0.58	11
Polymethylmethacrylate	Chloroform	3.40	0.83	12
	Benzene	6.15	0.76	13
	Nitromethane	5.70	0.74	14
	Methylethyl ketone	7.10	0.72	15
	Toluene	8.12	0.71	16
	Ethylene dichloride	17.00	0.68	17
Bisphenol A polycarbonate	Chloroform	11.20	0.82	18
	Methylene chloride	13.00	0.18	18
	Ethylene chloride	14.20	0.78	18
	Dioxane	30.90	0.71	18
	Tetrahydrofuran	49.00	0.67	18
	Cyclohexanone	77.60	0.62	18
Amylose	Aqueous			
	KOH (0.5M)	8.50	0.76	19
	Ethylene diamine	15.50	0.70	20
	Dimethyl sulfoxide	30.60	0.64	19

It follows from the Table I that the greater the value of  $a$ , the lower is the value of  $K_m$ . As  $a$  is related to  $\alpha$ ,  $a$  should give the measure of solvent power and such agreements have also been reported.<sup>21</sup>  $K_m$  increases with decrease in the solvent power and in the limiting case of theta condition  $K_m$  becomes equal to  $K$ . It seems logical that extrapolation of  $K_m$  in terms of the solvent power would enable evaluation of  $K$ .

Several relationships<sup>22,23</sup> expressing  $K$  as functions of  $K_m$  and  $a$  have been proposed, the simpler one is due to Kamide and Moore,<sup>23</sup>

$$-\log K_m + \log [2\{(a-\frac{1}{2})^{-1} - 2\}^{-1} + 1] = (a-\frac{1}{2}) \log M_0 - \log K \quad (8)$$

where  $M_0$  is the geometric mean of the molecular weight range to which  $K_m$  and  $a$  refer. A plot of the left-hand side of equation 8 against  $(a-\frac{1}{2})$  should be linear and  $K$  could be determined from

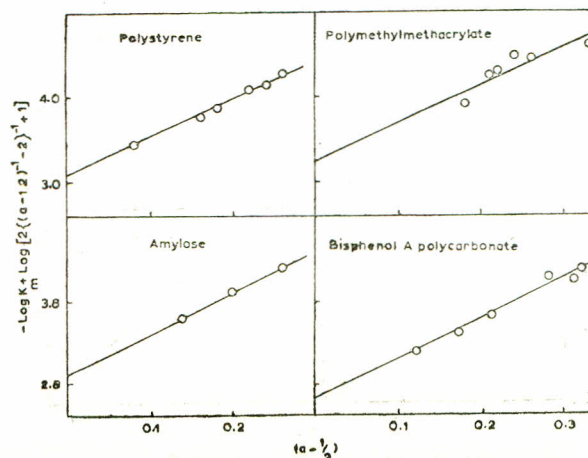


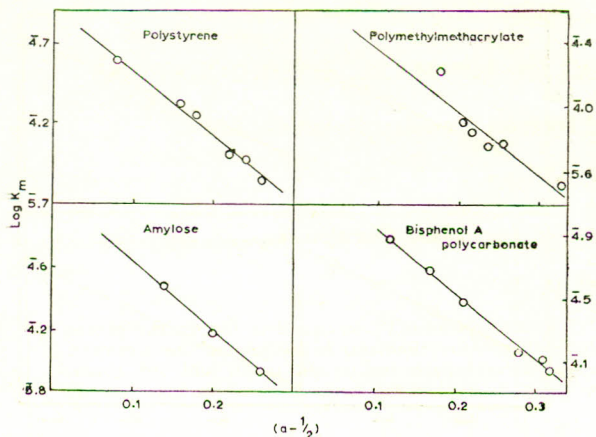
Fig. 2.—Plots, left-hand side of eq. 8 against  $(a-\frac{1}{2})$ .

the intercept. For nonpolar and not very polar polymers  $K$  is independent of solvents<sup>24</sup> and, therefore, this method of estimation of  $K$  appears reasonable. For stiff chain polymers, the solvent dependence of  $K$ , the draining effect and the non-Gaussian nature of polymer chains complicate the procedure. Plots of the left-hand side of equation 8 against  $(a-\frac{1}{2})$  for polystyrene, polymethylmethacrylate, bisphenol A polycarbonate and amylose are shown in Fig. 2 and  $K$  values calculated from the intercepts are given in Table 2.

Another method suggested by Barrales-Reinda and Pepper<sup>25</sup> needs plotting  $\log K_m$  against  $a$  for a number of solvents and  $K$  is obtained from the ordinate at  $a=0.5$ . From equation 7 it appears reasonable that such a plot should be linear and this method has been found to apply for polyacenaphthalene.<sup>25</sup> Plots for polystyrene, polymethylmethacrylate, bisphenol A polycarbonate and amylose are shown in Fig. 3 and  $K$  values determined thereby are included in Table 2.  $K$  values obtained from the methods based on equations 7 and 8 are in good agreement with the values estimated from viscosity measurements in theta solvents.<sup>8,18,19,26</sup> These values are also included in Table 2.

Figures 2 and 3 show that the plots except for polymethylmethacrylate are straightforward. The uncertainty in the case of polymethylmethacrylate arises from the non-availability of results around  $a=0.6$ . However, polymers considered here cover a good range of polarity and, therefore, both these methods could be said to be applicable for estimation of  $K$  for flexible polymers. These are simpler methods compared to the methods based on Fixman type relationships,<sup>2,5,27,28</sup> which often need correction of uncertain magnitude for different range of molecular weights.<sup>29</sup> Further limitation<sup>30</sup> results from the inapplicability of these treatments to lower molecular weights



Fig. 3.—Plots,  $\log K_m$  against  $(a - \frac{1}{2})$ .TABLE 2.—VALUES OF  $K$  FROM EQUATIONS 7 AND 8 AND FROM THETA SOLVENT.

Polymer	$K \times 10^4$ from			Ref
	Eq.7	Eq.8	Theta solvent	
Polystyrene	8.50	8.30	8.20	8
Polymethylmethacrylate	5.75	6.16	5.92	26
Bisphenol A polycarbonate	22.90	22.90	21.40	18
Amylose	12.00	11.20	11.50	19

( $M < 2 \times 10^4$ ) of polymers. Estimation of  $K$  from equations 7 and 8 seems to be free from these drawbacks. Moreover, these methods indicate that  $K$  is independent of solvents and a similar conclusion has been reported for bisphenol A polycarbonate.<sup>18,31</sup>

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