Application of various viscosity theories to the viscosity data of methyl methacrylate–acrylonitrile random copolymers*

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Values of K_0, Flory constant related to unperturbed dimensions, are evaluated for methyl methacrylate–acrylonitrile random copolymers using Flory–Fox, Kurata–Stockmayer and Inagaki–Ptitsyn methods and compared with the K_0 values obtained by Stockmayer–Fixman method. K_0 values are seen to be less in solvents which have larger a (Mark–Houwink exponent) values. A correlation between K_0 and a is developed to arrive at a more reliable estimate of K_0 for this copolymer system.

INTRODUCTION

The recent studies of the properties of dilute polymer solutions show that 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, and are related, respectively, to the unperturbed average dimensions and the excluded volume effect of a given polymer in a given environment. Various methods[3–6] are available to determine these parameters from the molecular weight dependencies of intrinsic viscosity, which were developed for homopolymers and have been invariably applied to copolymers.

FLORY AND FOX(FF) METHOD

Flory and Fox[7] suggested the following relation:

$$[\eta]^{2/3}/\bar{M}_w^{1/3} = K_0^{2/3} + 0.858\, K_0^{2/3}/\varphi_0\, B(\bar{M}_w/[\eta]) \quad (1)$$

where $[\eta]$ and $\bar{M}_w$ are the intrinsic viscosity and the weight average molecular weight of the polymer, K_0 and B are the Flory constants related to unperturbed dimensions and the polymer–solvent interaction parameter, φ_0 is a universal constant.

According to equation (1), $[\eta]^{2/3}/\bar{M}_w^{1/3}$ is a linear function of $\bar{M}_w[\eta]$, and on extrapolation to zero $\bar{M}_w$, gives a constant intercept $K_0^{2/3}$ on the ordinate irrespective of the type of the solvent used. In practice, equation (1) is found to be inadequate for determining the unperturbed dimensions for most of the polymers, particularly from the data in good solvents; however, in poor solvents, the theory seems to be quite adequate[8].

KURATA–STOCKMAYER (KS) METHOD

Kurata and Stockmayer[3] correlated viscosity–molecular weight data as follows:

$$[\eta]^{2/3}/\bar{M}_w^{1/3} = K_0^{2/3} + 0.363\, \varphi_0 B g(\alpha_\eta) \bar{M}_w^{2/3}/[\eta]^{1/3} \quad (2)$$

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

where α_η is the linear expansion factor, and is given by Flory[1], as:

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \quad (4)$$

where $[\eta]_\theta$ is the intrinsic viscosity at φ condition and is given as[1]:

$$[\eta]_\theta = K_0 \bar{M}_w^{1/2} \quad (5)$$

An iteration method is followed to determine $K_0^{2/3}$. However, recently it has been shown that some viscosity–molecular weight data deviate from the linearity of the KS plot, especially for high molecular weight ranges in good solvents[8].

STOCKMAYER–FIXMAN (SF) METHOD

Stockmayer and Fixman[4] proposed a simpler relation:

$$[\eta]/\bar{M}_w^{1/2} = K_0 + 0.51\, \varphi B \bar{M}_w^{1/2} \quad (6)$$

for the determination of K_0. K_0 values may be obtained by plotting $[\eta]/\bar{M}_w^{1/2}$ against $\bar{M}_w^{1/2}$.The SF plot seems to yield accurate estimates of K_0. For good solvent systems, however, the plots deviate from linearity in the region of large $\bar{M}_w$[8]. Thus, both KS and SF plots lead to overestimates of K_0 for high molecular weight ranges in good solvents.

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Table 1 K_0 values as evaluated by FF, KS, IP and SF methods along with $1/a$ values for MA1. $K_T = 0.37 \times 10^{-3}$

			$K_0 \times 10^3$			
Solvent	Temperature (°C)	1/*a*	FF	KS	IP	SF
MeCN	30	1.34	0.05	0.16	0.12	0.18
MEK	30	1.38	0.11	0.16	0.12	0.18
DMF	30	1.27	0.01	0.11	0.09	0.14
	45	1.31	0.09	0.17	0.17	0.18
	60	1.21	**	0.09	0.07	0.10
γ-BL	30	1.23	**	0.14	0.10	0.15
	45	1.18	**	0.10	0.05	0.13
	60	1.25	**	0.10	0.10	0.16

** Negative intercept

Table 2 K_0 values as evaluated by FF, KS, IP and SF methods, along with $1/a$ values for MA2. $K_T = 0.83 \times 10^{-3}$

			$K_0 \times 10^3$			
Solvent	Temperature (°C)	1/*a*	FF	KS	IP	SF
MeCN	30	1.20	**	0.13	0.09	0.17
	40	1.23	**	0.23	0.17	0.21
	50	1.08	**	0.05	0.02	0.09
MEK	30	1.29	0.04	0.19	0.17	0.20
	45	1.24	**	0.16	0.13	0.17
	60	1.24	**	0.14	0.11	0.15
DMF	30	1.41	0.21	0.32	0.32	0.33
	45	1.33	0.11	0.26	0.24	0.27
	60	1.36	0.13	0.27	0.24	0.28
γ-BL	30, 45	1.32	0.09	0.26	0.23	0.26
	60	1.31	0.09	0.27	0.21	0.26

** Negative intercept

INAGAKI–PTITSYN (IP) METHOD

Inagaki *et al*[5] proposed the following relation:

$$[\eta]^{4/5}/\bar{M}_w^{2/5} = 0.786\ K_0^{4/5} + 0.454\ K_0^{2/3}\varphi_0^{2/3}B^{2/3}\bar{M}_w^{1/3} \quad (7)$$

In this case, the values of K_0 are obtained from the plots of $[\eta]^{4/5}/\bar{M}_w^{2/5}$ against $\bar{M}_w^{1/3}$. The IP plot applies only to high molecular weight polymers in good solvents.

Reddy *et al.*[9] used these methods to evaluate the K_0 and B values for the styrene–acrylonitrile copolymers and found that the K_0 values obtained by FF method were low, while the values obtained from SF, IP and KS methods agreed within the limits of experimental error. The specific solvent effect on K_0 was found to be negligible. Studies on the dilute solution properties of methyl methacrylate–acrylonitrile random copolymers[10–15] have indicated that K_0 values, obtained by SF method, depend both on the solvent as well as the temperature for all the copolymer compositions studied. Further, K_0 values were lower in a solvent with large values of a – the Mark–Houwink (MH) exponent. It is also anticipated that the incorporation of acrylonitrile (AN) into methyl methacrylate (MMA) might have introduced some stiffness into the chain. Therefore, it is likely that for such a stiff and polar system, these methods need modification to arrive at a more reliable estimate of K_0. Therefore, the objective of the present communication is (i) to evaluate the K_0 values by FF, KS and IP methods and to compare them with the K_0 values obtained by SF method and (ii) to look for a correlation between K_0 and a.

EXPERIMENTAL

MMA–AN random copolymers of four different compositions (0.289 mol fraction (mf) of AN designated as MA 1; 0.415 mf AN:MA2; 0.566 mf of AN:MA3; 0.657 mf of AN:MA4) were prepared by solution polymerization method and were fractionated. The details of their preparation and fractionation are given elsewhere[16]. Weight-average molecular weight ($\bar{M}_w$) of the copolymer fractions were determined in acetonitrile. Intrinsic viscosity, $[\eta]$ of the copolymer fractions were determined in acetonitrile. (MeCN) and 2-butanone (MEK) at 30°C and in *N,N'*-dimethyl formamide (DMF) and γ-butyrolactone (γ-BL) at 30, 45 and 60°C. Details of the light scattering and viscosity measurements have been given earlier[10–13].

RESULTS AND DISCUSSION

The intrinsic viscosity data of MA1–MA4 are treated by FF, KS and IP methods and the K_0 values are obtained by these methods (*Tables 1–4*). K_0 values, as obtained by SF method[10–14], are also listed along with these values.

From *Tables 1–4*, it is obvious that except for MA3–MEK system, FF method yields a very low value of K_0, KS and SF methods yield very close K_0 values, and IP method gives a slightly lower value than that obtained by KS and SF method. In the case of MA3–MEK system, whereas the K_0 values obtained by FF, KS and SF methods are identical, that obtained by IP method is higher.

It is also seen that *Tables 1, 2* and *4* show some K_0 values which are denoted by **. These are such values where K_0 values could not be calculated from the intercepts of FF, KS and IP plots, viz $K_0^{1/2}$, $K_0^{2/3}$ and 0.768 $K_0^{4/5}$, as the intercepts obtained in those cases were

Table 3 K_0 values as evaluated by FF, KS, IP and SF methods along with $1/a$ values for MA3

			$K_0 \times 10^3$			
Solvent	Temperature (°C)	1/*a*	FF	KS	IP	SF
MeCN	30	1.28	0.07	0.30	0.27	0.35
MEK	30	1.68	0.40	0.40	0.50	0.40
DMF	30	1.31	0.20	0.44	0.37	0.46
	45	1.27	0.10	0.33	0.26	0.38
	60	1.28	0.02	0.33	0.23	0.34
γ-BL	30	1.30	0.04	0.36	0.38	0.49
	45	1.23	0.03	0.35	0.29	0.41
	60	1.29	0.05	0.39	0.31	0.41

Table 4 K_0 values as evaluated by FF, KS, IP and SF methods along with $1/a$ values for MA4. $K_T = 0.92 \times 10^{-3}$

			$K_0 \times 10^3$			
Solvent	Temperature (°C)	1/*a*	FF	KS	IP	SF
MeCN	30	1.19	**	0.17	0.13	0.20
DMF	30	1.08	**	0.07	**	0.11
	45	1.01	**	0.04	**	0.04
	60	1.04	**	0.03	**	0.08
γ-BL	30	0.93	**	**	**	0.05
	45	0.95	**	**	**	−0.03
	60	0.93	**	**	**	−0.11

** Negative intercept

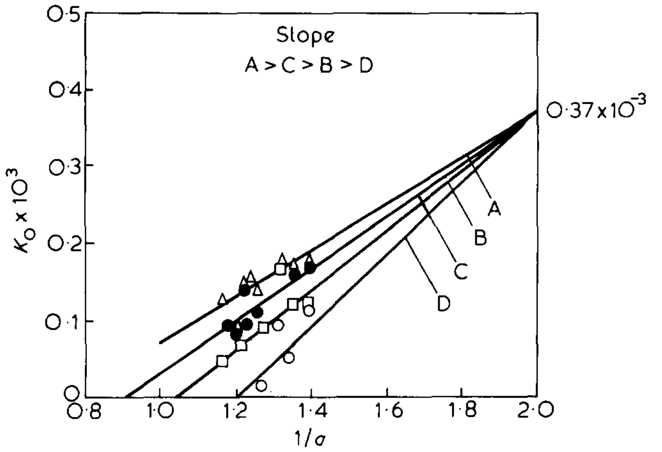

Figure 1 The unperturbed dimension K_0 plotted against the reciprocal of the Mark–Houwink parameter 1/a for MA1. A, △, SF; B, □, IP; C, ●, KS; D, ○, FF

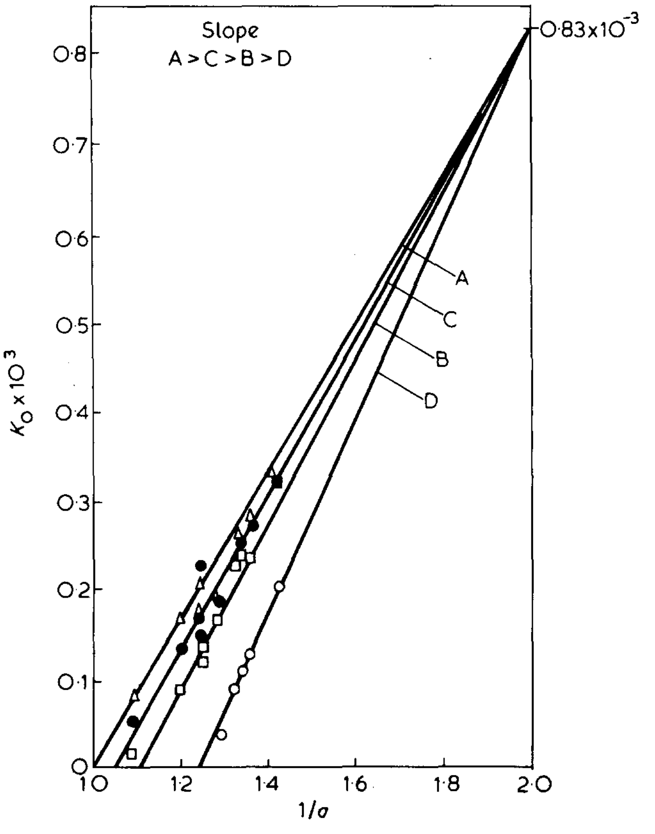

Figure 2 The unperturbed dimension K_0 plotted against the reciprocal of the Mark–Houwink parameter 1/a for MA2. A, △, SF; B, □, IP; C, ●, KS; D, ○, FF

negative and they had to be raised to the powers of 3/2, 3/2 and 5/4 (after dividing the intercept by 0.786) respectively, in order to arrive at the K_0 values. It is obvious, K_0 could not be determined from such negative intercepts.

Table 4 shows negative K_0 values as obtained by SF method for MA4–γ–BL system. It is difficult to visualize the significance of such negative values from the existing theories.

The K_0 values are dependent on the solvent, contrary to the present belief that it should be practically independent of the nature of the solvent. Such deviations have been noticed by earlier workers for polystyrene[17], polytetrahydrofuran[18] and for a copolymer of MMA–AN of 0.48 mf of AN, by Shimura[19].

The short range interactions within the chain depend mainly on the geometric parameters such as the bond lengths and bond angles, staric interactions and torsional potentials which hinder the rotation about the bonds. In

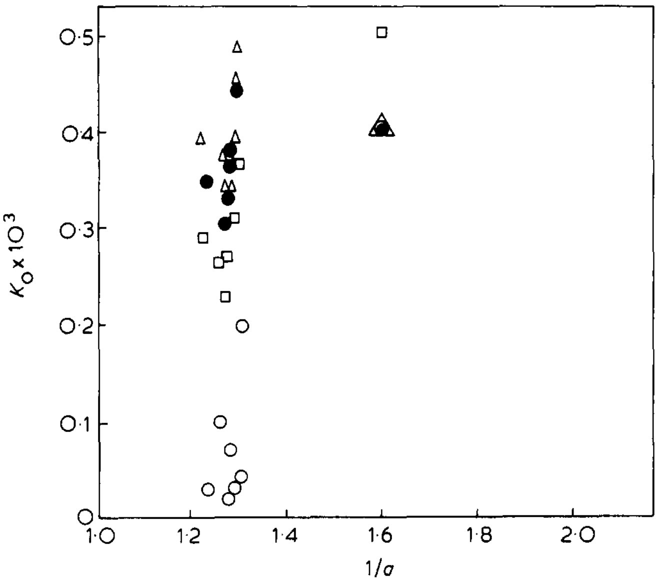

Figure 3 The unperturbed dimension K_0 plotted against the reciprocal of the Mark–Houwink parameter 1/a for MA3. △, SF; □, IP; ●, KS; ○, FF

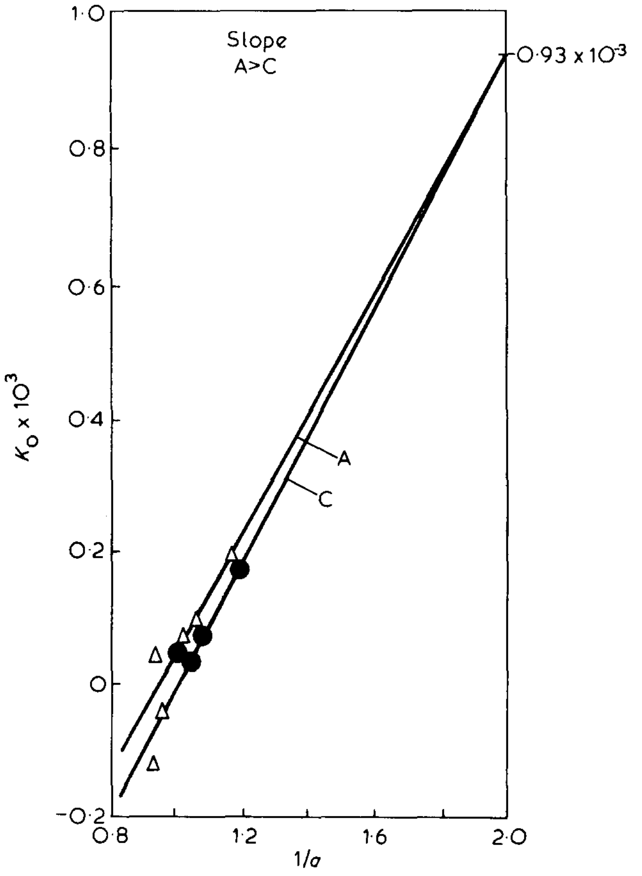

Figure 4 The unperturbed dimension K_0 plotted against the reciprocal of the Mark–Houwink parameter 1/a for MA4. A, △, SF; C, ●, KS

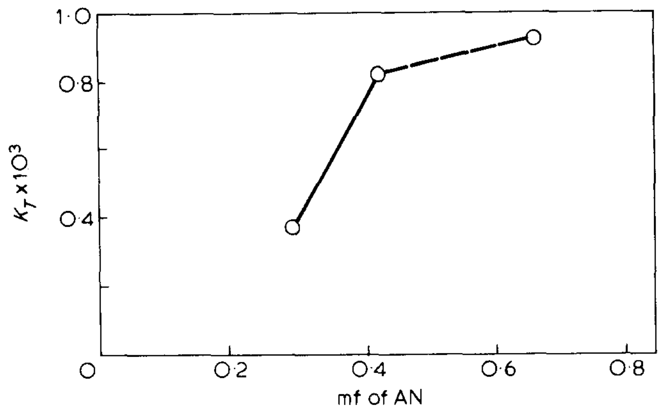

Figure 5 K_T vs. composition (mf of AN) where $K_T = (K_0)_{a=0.5}$

the absence of the excluded volume effects, interactions between atoms and groups which are near neighbours in the chain will determine the end-to-end dimensions. Rao *et al.*[20,21] pointed out that for stiff cellulosic chains, the small change in the bond angles which are brought in either by specific solvent effects or by substituents, lead to the large changes in the unperturbed dimensions. This might be the reason for the observed differences of the unperturbed dimensions in different solvents. They also noticed that the substituents have little effect on the unperturbed dimensions of cellulosic chains. As the present copolymers behave like some cellulose derivatives in solution[10–15], it is possible to advance this argument for the present copolymer system and in that case, the large variations in the K_0 could be due to the specific solvent effects alone.

It has been observed that K_0 values are lower in a solvent with large values of a – the Mark Houwink exponent[10–14]. Therefore, it was thought that a plot between K_0 *versus* $1/a$ should be linear.

Figures 1–4 show K_0 vs. $1/a$ plots for all the copolymer systems. Except in the case of MA3, a linear relationship exists between these two variables. In the case of MA3, it is seen that for a very narrow range of $1/a$, K_0 variations are relatively larger, though MA3–MEK system ($a = 0.60$) has been able to provide an equivalent value of K_0 from all the methods except the IP method, suggesting that the K_0 values of 0.40×10^{-3} could be taken as a fairly accurate estimate. In *Figures 1*, *2* and *4* all the plots provide a common intercept on the K_0 axis, corresponding to $a = 0.5$, which is nothing but the θ-condition. In that case, $(K_0)^{a=0.5}$ values are the true estimates of K_0 (may be designated as K_T) which are independent of solvent and temperature. The slopes of these plots are in the order SF > KS > IP > FF. However, it is difficult to visualize the significance of these slopes at this stage.

Figure 5 shows the variation of these K_T values with the composition of the copolymers. The dotted part of *Figure 5* is due to the failure of this method to provide $(K_0)_{a=0.5}$ for MA3.

An independent method, like conformational characteristics, for this copolymer system should be studied[22] to enable a comparison with these K_T values and raise the confidence in this method. Further, the present correlation between K_0 and $1/a$, needs to be established for a very large number of experimental data on the polymers and copolymers, where such a phenomenon occurs.

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