Viscometric Studies of Graft Copolymers of Methylcellulose and Polyacrylamide

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Abstract. Viscometric studies of graft copolymers (methyl cellulose *g* polyacrylamide) were made at four temperatures. The values of intrinsic viscosity of the graft copolymers were found to be much less than the linear methyl cellulose which was used as a backbone polymer. Intrinsic viscosity also decreased with the increase in the number and length of the branches.

Huggin's slope constant k' was found to be much higher than the linear methyl cellulose. k' values also increased with increase in the number of the branches as well as the length of the branches and are temperature dependent. These observations clearly indicate the branched nature of the copolymer.

I. Introduction

Intrinsic viscosity is related to molecular mass by the following equation :

$$[\eta] = KM^a$$

where M is molecular mass of a dissolved polymer. K and a are constants characterizing a given polymer solvent system.

In the case of the graft copolymers, however, the intrinsic viscosity-molecular weight relationship is not applicable due to branching. It was found[1] that graft copolymer had a lower intrinsic viscosity than the corresponding homopolymers in the same solvent at the same molecular weight. But O' Driscoll *et al*[2] accepted intrinsic viscosity as a measure of molecular weight. Zimm and Stockmayer[3] showed that intrinsic viscosity decreases with increase in branching of the molecular chain for any

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given molecular weight of the solute. Many other authors also worked on the significance of intrinsic viscosity of graft copolymers[4-12]. For polyvinyl alcohol *g* polystyrene, Sharma and Varma[13] found that [η] first increases and then decreases due to incompatible polymer chains which contract the overall structure.

2. Experimental

2. *Materials*

Methyl cellulose (MC) (British Cellenease Ltd.) with 22 per cent methoxy content and viscosity of 20 *cP* in 2 per cent solution was used without further purification. Acrylamide (E. Merck) Potassium persulphate (E. Merck) was used as initiator.

2.2 *Procedure*

Two sets of copolymers were synthesized by the method reported in our previous paper[14]. One set (MC-g-11.5% PAM, MC-g-19.5% PAM, MC-g-28.0% PAM and MC-g-41.0% PAM) was initiated with 3.70×10^{-4} mol/l of pottassium persulphate. The other set (MC-g-10.0% PAM, MC-g-22.4% PAM, MC-g-27.5% PAM and MC-g-39.0% PAM) was initiated with 18.50×10^{-4} mol/l of initiator . Care was taken to obtain nearly same percentage of grafting in both sets by changing the monomer/polymer ratio but keeping the time of reaction same. The polymerization was performed at 30°C.

A Ubbelohde dilution viscometer was used for all viscometric studies. Values of intrinsic viscosity, [η], were obtained by extrapolating η Sp/C values to zero concentration. Experiments were performed at four different temperatures. Kinematic correction was not applied as the efflux time for the solvent was sufficiently high (> 120 sec).

3. Results and Discussion

Results of the present work are presented in Table 1 [η] of untreated methyl cellulose at 30°C was 1.72 dl/g.

The values of intrinsic viscosity of the graft copolymers are less than that of the untreated linear methyl cellulose. This is to be expected because of the branched structure of the copolymer.

The highest values of [η] are found for the samples with 10.0 and 11.4 per cent grafting. This clearly indicates that less is the percentage of polyacrylamide in a copolymer higher is the intrinsic viscosity. At a comparatively low temperature, water is good solvent for methyl cellulose, or in other words the water-methyl cellulose

Table 1. Intrinsic viscosity of different copolymers at different temperatures

Initiator : 3.70 × 10 mol/l of $K_2S_2O_8$ (dl/g)   Initiator : 18.5 × 10 mol/l of $K_2S_2O_8$ (dl/g)

Tempera- ture °C Percent grafting	20	30	40	50	Tempera- ture °C Percent grafting	20	30	40	50
11.5	1.58	1.20	1.50	1.22	10.0	1.00	0.95	1.00	0.92
19.5	1.21	0.92	1.19	1.20	22.4	0.85	0.83	0.95	0.85
28.0	0.89	0.80	0.95	1.10	27.5	0.76	0.65	0.72	0.80
41.0	0.75	0.72	8.89	1.00	39.0	0.58	0.55	0.68	0.75

interaction is stronger than polymer-polymer or solvent-solvent interaction. This tendency decreases with increase of percentage of polyacrylamide in the copolymer. The polymer-solvent interaction gives a larger coil which is reflected in the higher values of $[\eta]$ at low percentage of grafting and at lower temperature.

This view is supported by the values of $[\eta]$ determined for the same samples of copolymers at 20,30,40 and 50°C. The results are graphically depicted in Figs 1-4.

From Table 1 it is also evident that $[\eta]$ increases with rise in temperature when the percentage of polyacrylamide is more in the graft copolymer. This can be explained by the fact that as the temperature is increased water becomes a better solvent for
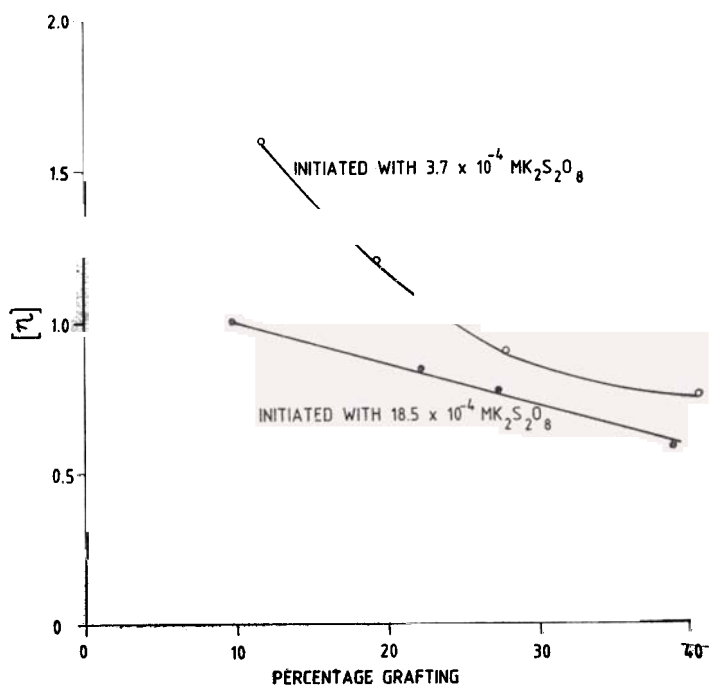
Figure 1. Intrinsic viscosity versus percentage of grafting at 20 ± 0.1°C.

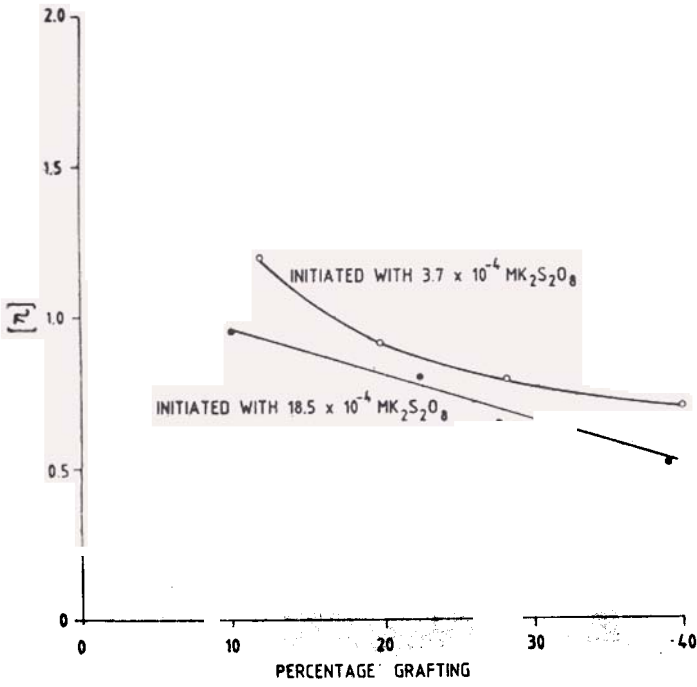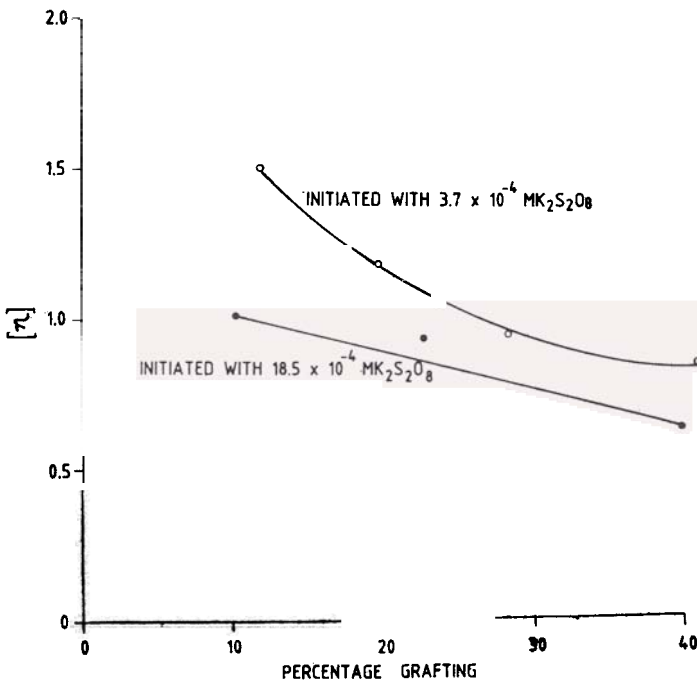**Figure 2.** Intrinsic viscosity versus percentage of grafting at $30 \pm 0.1°C$.

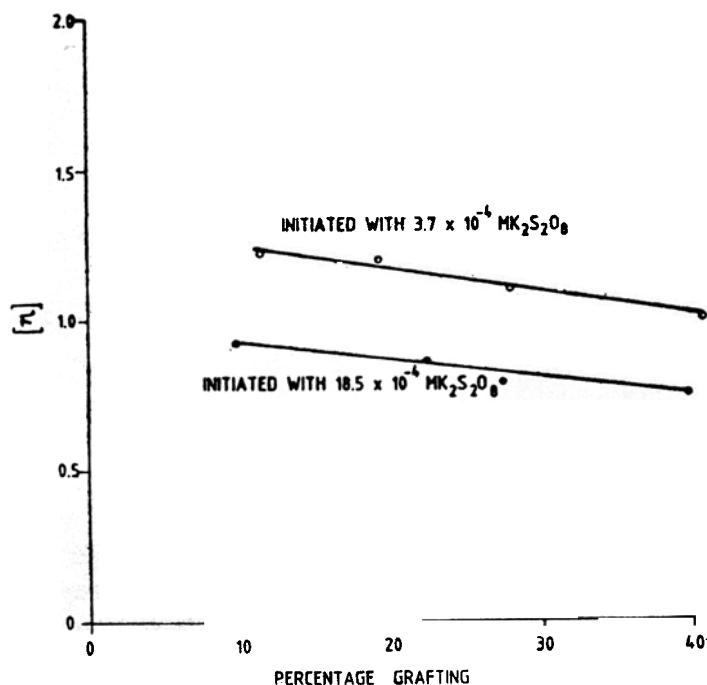**Figure 3.** Intrinsic viscosity versus percentage of grafting at $40 \pm 0.1°C$.

Figure 4. Intrinsic viscosity versus percentage of grafting at $50 \pm 0.1°C$.

polyacrylamide. At higher temperature PAM-water interaction is more than the polymer-polymer or solvent-solvent interaction thus giving rise to an uncoiled structure. The uncoiled structure has a higher intrinsic viscosity.

Table 1 also shows that the copolymers initiated with 18.50×10^{-4} mol/l of potassium persulphate give lower values of $[\eta]$ than the copolymers initiated with 3.70×10^{-4} mol/l. This is also evident from Figs. 1-4.

The higher concentration of the initiator creates more free radical sites on the backbone and at the same time shorter graft chain length; whereas the lower concentration of initiator creates less number of active sites on the backbone and hence longer chain lengths, if the percentage of grafting is kept nearly constant. Two facts are clear from the above observations. Firstly, that keeping the concentration of initiator constant, when the percentage of grafting is increased, i.e. keeping the number of branches constant, when the length of the branches increases, the intrinsic viscosity decreases. Secondly, at a fixed percentage of grafting, increase of concentration of initiator produces more number of branches and hence shorter chain lengths) which leads to decrease in intrinsic viscosity.

4. Huggin's constant k'

Huggin's constant, k', for the grafted copolymers were also calculated from the viscometric data using the following equation :

$$\frac{\eta\, sp}{C} = [\eta] + k' \,[\eta]^2\, C$$

where k' is approximately constant for a given system but is structure-sensitive. It also depends on the solvent, its value in a good solvent system is smaller than that in a poor solvent. k' is also dependent on the chain length of the copolymer[15].

Table 2 gives the values of Huggin's slope constant k' calculated from the viscometric data obtained at 20,30,40 and 50°C.

Table 2. Huggin's constant of the graft copolymers

[S₂O₈] 3.70 × 10⁻⁴ mol/l					[S₂O₈] 18.50×10⁴ mol/l				
Temperature °C / Percent grafting	20	30	40	50	Temperature °C / Percent grafting	20	30	40	50
11.5	0.92	1.46	2.60	1.30	10.0	3.40	2.20	1.40	2.90
19.5	2.70	2.30	1.40	1.40	22.4	4.70	2.50	1.70	3.60
28.0	4.10	5.70	2.80	3.00	27.5	6.40	5.80	8.10	3.70
41.0	8.70	7.30	5.30	1.90	39.0	90.0	8.60	5.40	4.10

It is also found that k' values for the graft copolymers are much higher than the linear methyl cellulose backbone which was determined to be 0.27 at 30°C. This clearly indicates that the copolymers are branched. Many evidences indicating a correlation between the presence of branching in a polymer and unusually large values of k' have been reported[16-18] Simha[19] had shown on theoretical grounds that the k' should be higher for branched species. Speiser and Whittenberg[20] found that for amylopectin, the branched form of starch, k' was much higher than for amylose, the linear form, Walker and Winkler[21] also observed similar effect of branching on k' values.

Highest values of k' are obtained when percentage of grafting is maximum. Moreover, when the amount of polyacrylamide introduced in the copolymer is kept nearly constant and the initiator concentration is increased, that is the number of branches increased, the Huggin's constant k' shows a higher value. Two effects of branching are evident from the observations given in Table 2. k' increases with increase in the length of the branches and as the number of branches increase, k' also increases,

Temperature also profoundly affects the slope constant k', As temperature is increased, it is found that k' for the graft copolymers decreases, This effect is more pronounced when the percentage of grafting is more. The observed data should be attributed to the fact that with rise in temperature water becomes a better solvent for polyacrylamide which results in lower values of k'.

Acknowledgements

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