# SEMI-IPNs OF POLYACRYLAMIDE WITH METHYLCELLULOSE IN AQUEOUS MEDIUM

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## Abstract

*The polymerization and gelation of a dilute aqueous solution of acrylamide is studied in the presence of methylcellulose (MC) at a high temperature. This phenomenon is unprecedented as the well-known gel effect is observed at a much higher concentration. Methylcellulose forms gels (inverse gelation) at the polymerization temperature ($64^oC$) of acrylamide and this helps in inducing the gelation of polyacrylamide by increasing the viscosity of the reaction medium. At a lower temperature, the MC gels revert back to sol state, leading to a lowering of viscosity. This allows in forming a semi-IPN of polyacrylamide-MC gel. The gel particles of polyacrylamide were observed under the optical microscope. An increase in the size of polyacrylamide gel particles was also observed with an increase in the concentration of acrylamide in the semi-IPN.*

***Key Words****:  gel effect, polyacrylamide, dilute solution; induced gelation*

## I.    INTRODUCTION

The reversible gelation of aqueous methylcellulose (MC) solution was first investigated by Heymann (1935). According to Heymann, the gelation is due to the dehydration of hydrated MC molecules. Several mechanisms of thermogelation of aqueous methylcellulose solution were proposed. The major discussion concerns the nature of the zones in MC, responsible for the gelation. Sarkar (1995) postulated that the gelation was due to hydrophobic or micellar interaction. Haque and Morris reported the presence of crystalline zones of methylcellulose in the gels. Koto et al.(1978)  remarked that the cross linking loci of methylcellulose gel consist of crystalline sequences of trimethyl glucopyranose units, which was confirmed by Khomutov et al (1993). Methylcellulose (MC) solution consists of dissolved bundles of partly methylated chains, which are cross linked, both by residual cellulose crystallites and by the hydrophobic interactions of densely substituted regions in the cellulose backbone. These hydrophobic regions become solvated by a cage like water structure around the polymer chain in the temperature range of $30^oC$ to $55^oC$, but this cage like solvation shell melts at a higher temperature. If the solvation shell melts, the methylcellulose starts to form a gel, driven by hydrophobic interactions of densely substituted strands (Haque et.al (1993); Sarkar et.al (1995); Hirrien et.al. (1996); Hirrien et.al. (1998); Takahashi et.al (2000); L Li. et.al (2001)). For the first time, the present manuscript reports induced gelation of acrylamide in the presence of methylcellulose (MC) gels at $64^oC$, resulting in the formation of semi-IPN of polyacrylamide in aqueous methylcellulose solution.

## II.    EXPERIMENTAL

### 2.1 Materials and Sample preparation.

Methyl cellulose, Acrylamide and Potassium persulphate Laboratory reagent in powdered form were supplied by Central Drug House (P) Ltd., New Delhi (India).

Viscosity of 2 % methylcellulose aqueous solution at 20 $^{o}$C as supplied by the manufacturer is about 4000 cps. The viscosity average molecular weight of MC is 149,000 and its methoxy value is 26-30%. Solution of methylcellulose was prepared in double distil water, by slow addition of methylcellulose in warm water (42 $^{o}$C) with continuous stirring. The prepared solution is cooled to obtain clear solution. Acrylamide in water was polymerized at 64 $^{o}$C [11] using potassium persulphate (1%) as initiator and N, N' Methylenebisacrylamide (0.5%) as crosslinker in the presence of MC for 30 min (as per semi-IPN composition in Table 1).

**Table 1: Composition of semi-IPNs**

| Sr. No. | Methylcellulose (Wt %)* | Acrylamide (Wt %) |
|---------|--------------------------|--------------------|
| 1. | 90 | 10 |
| 2. | 70 | 30 |
| 3. | 50 | 50 |
| 4. | 30 | 70 |

The morphology of methylcellulose films is examined using a Scanning Electron Microscope JSM 6100 (JEOL), equipped with a digital image processor. Specimens are mounted on aluminium sample stubs and sputter coated with gold prior to examination in the SEM at a voltage of 25 kV whereas, morphology of the aqueous MC-films obtained by drying at 60 $^{o}$C in a hot air oven for 6 hr is studied with the help of an optical microscope (QX5 digital blue) at same magnifications.

## 2.1 Release studies of GA through MC-PAAm matrix

GA release through porous and non-porous MC-PAAm films is studied in 20 ml of deionised water/ethanol mixture (50:50 v/v) at different temperatures (10, 25 and 45 $^{o}$C). The release experiments are performed with 0.1 gm sample having 1 mm thickness and 0.1, 0.3, 0.5, 0.7 and 1.0 wt % GA. The samples are withdrawn at different time intervals and tested in Agilent 8453 diode array UV-Visible spectrophotometer for measurement of concentration of GA by assigning the UV spectra at 235 nm.

## III.    RESULTS AND DISCUSSIONS

When a dilute aqueous solution of acrylamide (AAm) is polymerized at 64 $^{o}$C, no gel effect was observed. On the other hand, gelation was observed during the polymerization of AAm at higher concentration. At very high monomer conversions, the reaction medium becomes highly viscous and the macroradicals are no longer to move via translational diffusion. Instead, the addition of new monomer units to the chain end results in a change in the position of the radical chain end. This process has been termed as reaction diffusion. The rate of free radical polymerization is given by

$$R_p = K_p \left( \frac{fk_d}{k_t} \right)^{0.5} [M][I]^{0.5} \quad \text{..................................... (1)}$$

Where $K_d$ is the rate constant of initiator decomposition, $K_t$ is the bimolecular termination rate constant, $K_p$ is the propagation rate constant, f is fraction of free-radical produced, [M] is monomer concentration and [I] is initiator concentration [12]. For a fixed monomer and initiator concentration, the rate of polymerization is dependent on the kinetic parameter, $\left( \frac{K_p}{K_t} \right)^{1/2}$ for a n isothermal polymerization, $K_p$ is constant and thus, the rate of polymerization is totally dependent on $K_t$. In bimolecular termination reaction, the radicals need to come closer through diffusion. With the progress of polymerization, the viscosity of the reaction medium also increases. This obstructs the diffusion of macroradicals due to the bulkiness. The result is a reduction in the rate of termination. From equation (1), the reduction in termination rate constant (for constant initiator and monomer concentration) results in an increase in the rate of polymerization, leading to gelation. Although, the phenomenon of gelation was explained but there is no report on gelation by increasing the viscosity of the reaction medium. Theoretically, the induced reduction in the rate of termination is due to higher viscosity of the reaction medium, predicts the lower $K_t$ value. Thus, essentially the rate of polymerization will increase leading to gelation. For the first time, the present manuscript reports induced gelation of acrylamide in the presence of methylcellulose (MC) gels at 64 °C. When MC solution is heated, the water structure around MC molecules breaks down with an increase in entropy, allowing the hydrophobic groups to interact and causing gelation. MC solution consists of dissolved bundles of partially methylated chains, which are crosslinked, both by residual cellulose crystallites and by the hydrophobic interactions of densely substituted region in the cellulose backbone. These hydrophobic regions become solvated by a cage like water structure around the polymer chain in the temperature range of 30 to 55 °C.
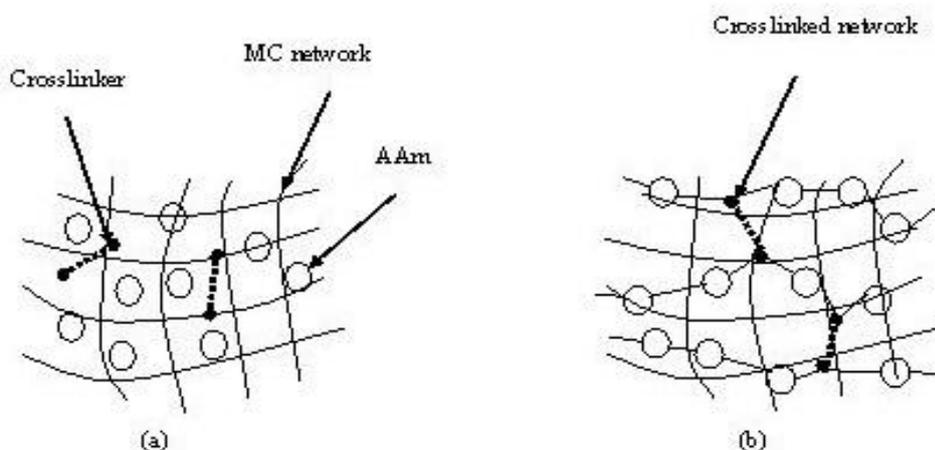


**Scheme 1:** Representation of acrylamide gels in the presence of MC. (a) MC gel at 64 °C along with acrylamide and crosslinker and no initiator. (b) Formation of polyacrylamide gels in presence of crosslinker and initiator at 64 °C in MC network.

The phenomenon of inverse gelation for MC in aqueous solution observed at higher temperature is capitalized for increasing the viscosity of the acrylamide solution. As the temperature of the aqueous solution is increased, the aggregation of the MC starts. This aggregation becomes denser at 64 $^o$C (scheme 1(a)). At this stage, the initiator ($K_2S_2O_8$) molecules start to disintegrate to free radicals leading to initiation of the polymerization process and subsequently a crosslinked network of polyacrylamide is formed (scheme 1(b)). Therefore, by increasing the viscosity of the reaction system, $K_t$ (as in equation 1) can be lowered. Hence, the rate of polymerization is increased. The term induced gel effect is used because thermo-gelation of MC plays an important role in inducing the polymerization and gelation of polyacrylamide.
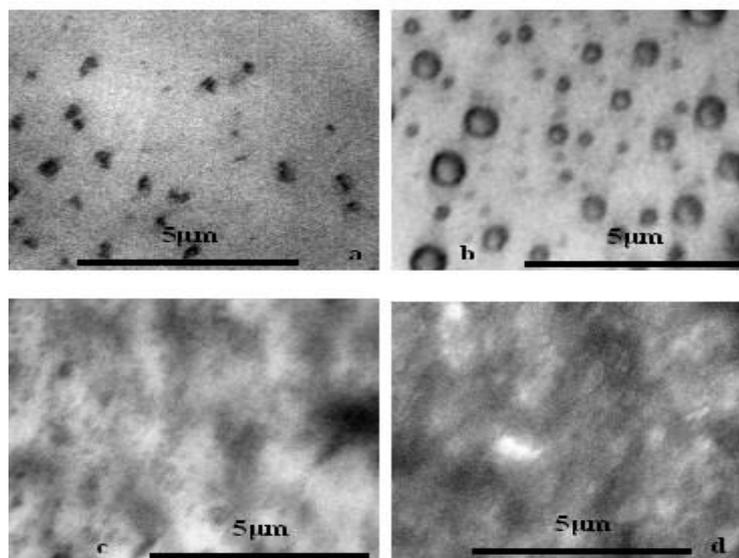


**Figure 1: Optical micrograph of different composition of MC-PAAm films**
**a)   10/90 wt. ratio of MC/PAAm**
**b) 70/30 wt. ratio of MC/PAAm**
**c) 50/50 wt. ratio of MC/PAAm d) 30/70 wt. ratio of MC/PAAm**

The films containing various amounts of acrylamide in the semi-IPNs of polyacrylamide in MC (for fixed concentration of MC i.e. 1%) are prepared by casting the solution. The morphology of these films is studied by optical microscope (Figure 1). The fixed (1 %) concentration of MC is used due to its gelation at around 64$^o$C and this is the temperature at which polymerization of acrylamide initiates. In our experiments, the concentration of AAm is varied from 1.11 to 2.3 wt %. The higher concentration of AAm is avoided, because for higher concentration of AAm, the *Trommsdorff or gel effect* was already reported [11]. From Figure 1, it is interesting to note that the microgels are present in the films and their size increases with an increase in the concentration of monomer.
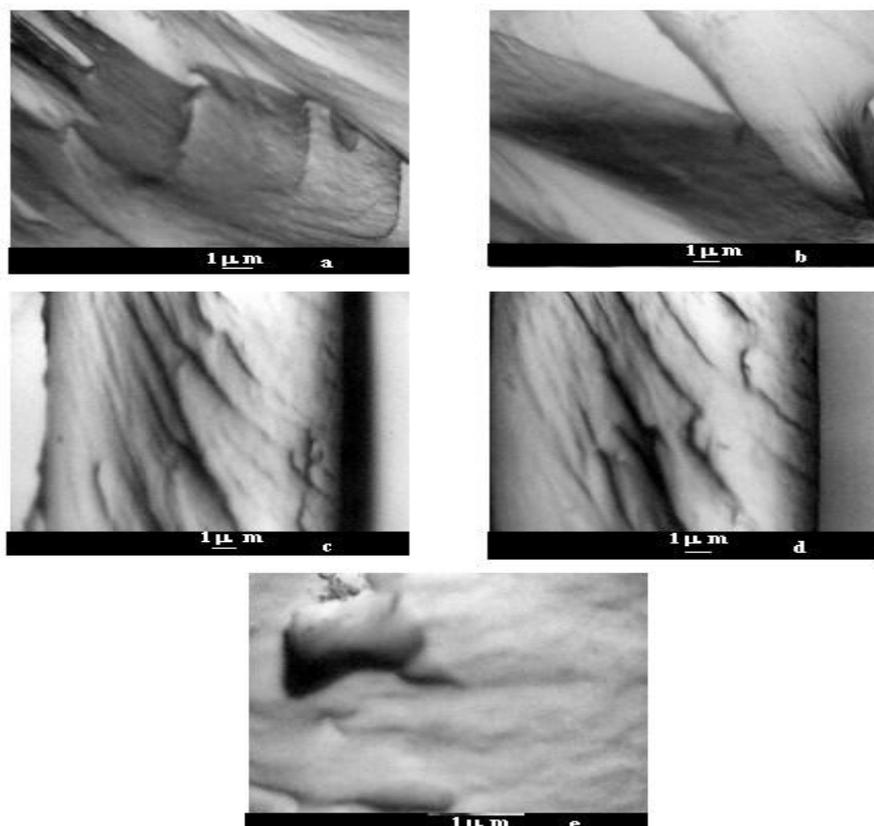
**Figure 2: SEM of different composition of MC-PAAm $N_2$ cracked films**
**a) 10/90 wt. ratio of MC/PAAm          b ) 70/30 wt. ratio of MC/PAAm**
**c) 50/50 wt. ratio of MC/PAAm          d) 30/70 wt. ratio of MC/PAAm**
**e) 90/10 Error! Not a valid link.**

## 3.1 Scanning Electron Microscope Studies

The morphology of MC-PAAM films, having different composition is studied at 1 μ is represented in Figure 2. It is observed from Figure 2 that there is single phase of MC-PAAM films. However, the percentage of both the polymer is increased to maximum (90-10 and 10-90) then also the phase separation in not observed.

## 3.2 Growth Hormone Release Studies

To study the release profile of gibberellic acid (GA), a plant growth regulator through non-porous MC-PAAm films, the release experiments are performed at 25 °C with 0.1 g of sample having 1 mm thickness and containing 0.1, 0.3, 0.5, 0.7 and 1 wt % of GA, respectively. The dissolution profile of GA from MC-PAAm IPN films at various time intervals in 20 ml of deionised water/ethanol mixture (50:50 v/v) is plotted in Figure 3. The nature of release profiles is similar for all samples with different concentrations of GA. The growth hormone (GA) release is moderate for initial 5 hrs and a steady state release of GA is observed for the next 7 hrs of release.
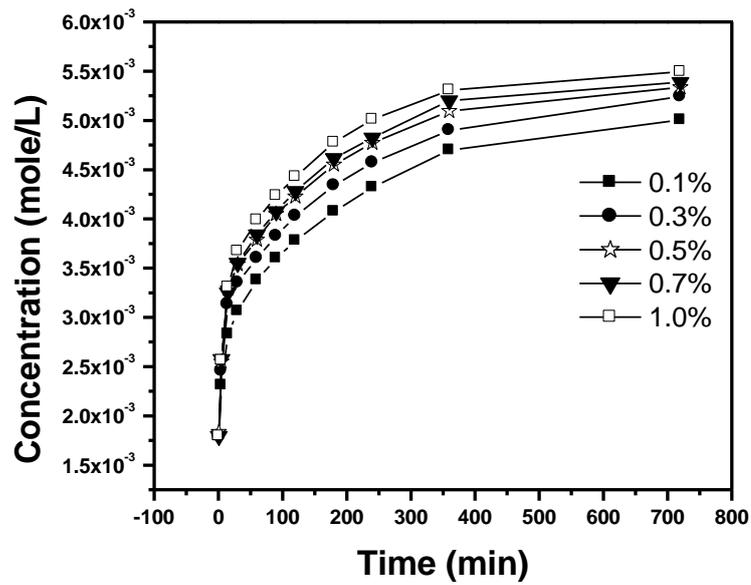
**Figure 3: Release profile of GA (0.1, 0.3, 0.5, 0.7 and 1 wt %) through non porous MC films**

Figure 4 illustrates the release profile of GA (0.1, 0.3, 0.5, 0.7 and 1 wt %) through mesoporous MC-PAAm films at room temperature (25 °C) in 20 ml of deionised water/ethanol mixture (50:50 v/v). It is observed from Figure 4 that the release profile of GA can be divided into two stages. The burst release is observed for initial 6 hrs, followed by a constant release. The burst release occurs during the swelling of MC-PAAm film. Whereas, the constant release after 7 hrs occurs through the pores present in the MC matrix. Hence, the order of release of GA from mesoporous MC-PAAm films is independent of the concentration of GA after 7 hours.
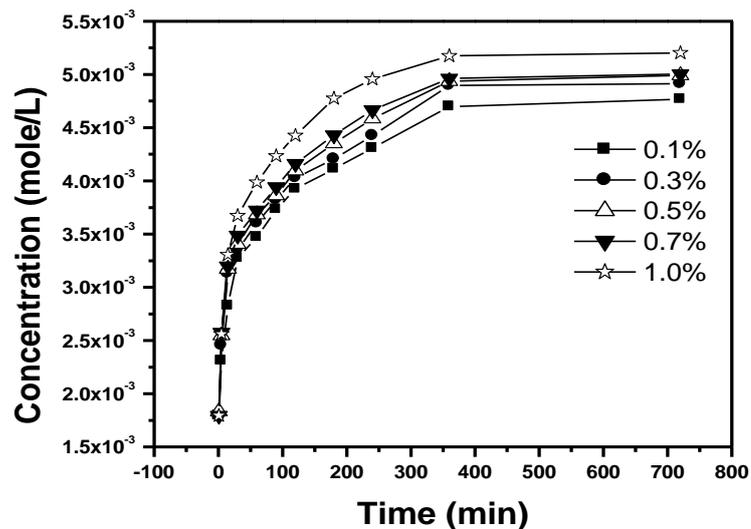


**Figure 4: Release profile of GA (0.1, 0.3, 0.5, 0.7 and 1 wt %) through mesoporous MC films at various temperatures. (a) 10 (b) 25 and (c) 45 °C.**

In our previous studies on release profile of urea from porous and non porous MC film, the release of urea is observed to be high in porous MC films. In case of release of GA through porous and non porous MC films, the release of GA is marginally less for porous than that for non porous MC films. It may be due to bulky size of GA and swelling of MC films in 50:50 ratios (v/v) of water/ethanol. The swelling of MC is higher in pure water than that in water and ethanol mixture. However, the release of GA also depends on its solubility in water and ethanol mixture. In comparison, the solubility of urea is found to be much higher than that of GA in water. This leads to the higher release of urea in porous MC films.
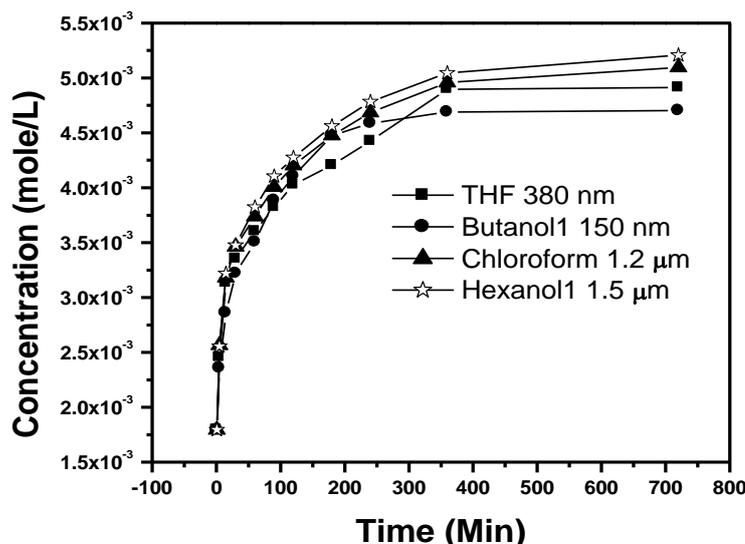


**Figure 5: Release behavior of 0.3 wt % GA through different pore sizes of MC film.**

The release profile of GA through mesoporous MC-PAAm films (pores are generated by leaching of butanol-1-wax, THF-wax, hexanol-1-wax and chloroform-wax) containg 0.3 % GA is represented in Figure 5. The pore size follows the following order, minimum pore size for butanol-1-wax system and maximum for hexanol-1-wax system Table 3.

butanol-1-wax < THF-wax < chloroform-wax < hexanol-1-wax

It is observed from Figure 5, that the release of GA increases with an increase in the pore size of the MC matrix. It is interesting to note that the release profile of GA through different porous MC films is almost similar

## IV.    CONCLUSION

The process of gelation during the polymerization a dilute solution of acrylamide is induced by the presence of methylcellulose. This phenomenon is unprecedented as the well-known gel effect observed at much higher concentration. Methylcellulose, which forms gels (inverse gelation) at the polymerization temperature ($64^{o}C$) of acrylamide, helps in inducing the gelation of polyacrylamide by increasing the viscosity of the reaction medium. At lower temperature, the MC gels revert back to sol state, leading to a lowering of viscosity and a formation of semi-IPN of polyacrylamide in MC. The semi-IPN formed by the gelation of polyacrylamide in methylcellulose was observed under optical microscope. The presence of

polyacrylamide gel particles in the films of semi-IPN was observed. An increase in the size of polyacrylamide gel particles was also observed with an increase in the concentration of acrylamide in the semi-IPN.

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