Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies on Graft Copolymerization of N-Vinyl-2-pyrrolidone on to Carboxymethylcellulose (Sodium Salt) and Metal Ion Sorption Behavior

Arti Srivastava[a]; Kunj Behari[a]
[a] Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad, India

To cite this Article Srivastava, Arti and Behari, Kunj(2006) 'Studies on Graft Copolymerization of N-Vinyl-2-pyrrolidone on to Carboxymethylcellulose (Sodium Salt) and Metal Ion Sorption Behavior', Journal of Macromolecular Science, Part A, 43: 7, 1065 — 1081

To link to this Article: DOI: 10.1080/10601320600740280

URL: http://dx.doi.org/10.1080/10601320600740280

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1065–1081, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600740280

Studies on Graft Copolymerization of N-Vinyl-2-pyrrolidone on to Carboxymethylcellulose (Sodium Salt) and Metal Ion Sorption Behavior

ARTI SRIVASTAVA AND KUNJ BEHARI

Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad, India

An unreported graft copolymer of N-vinyl-2-pyrrolidone (N-VP) with sodium carboxymethylcellulose has been synthesized under nitrogen atmosphere using peroxymonosulphate/thiourea redox pair at 40°C. The effect of reaction conditions on grafting parameters i.e., grafting ratio, efficiency, conversion, add on, homopolymer and rate of grafting has been studied. Experimental results show that maximum grafting has been obtained at 0.4 g dm^{-3} concentration of sodium carboxymethylcellulose and 10×10^{-2} mol dm^{-3} concentration of N-vinyl-2-pyrrolidone. It has been observed that grafting ratio, add on, conversion, efficiency and rate of grafting increase up to 6.0×10^{-3} mol dm^{-3} of hydrogen ion, 2.84×10^{-3} mol dm^{-3} of thiourea, 5.0×10^{-3} mol dm^{-3} of peroxymonosulphate and 45°C of temperature after that decrease. Grafted and ungrafted gum has been characterized by FTIR spectroscopy and thermogravimetric analysis. Water swelling and metal ion sorption behavior of sodium carboxymethylcellulose and sodium carboxymethycellulose-g-N-vinyl-2-pyrrolidone have been determined. A probable mechanism has been suggested for graft copolymerization. It has been observed that the graft copolymer is thermally more stable than the parent polymer.

Keywords n-vinyl-2-pyrrolidone, carboxymethyl cellulose, graft copolymerization, metal ion sorption, redox pair

Introduction

Among the various methods for modifying polymers, graft copolymerization appears to be highly attractive, and has made a paramount contribution towards improved industrial and biomedical applications (1). The graft copolymerization of cellulose and its derivatives with hydrophilic monomers has received considerable attention during the past decades as a convenient way of introducing ionizable or their polar groups into the cellulose backbone (2). Sodium carboxymethylcellulose is a naturally occurring polysaccharide consisting of substituted anhydroglucose units and also known as cellulose gum. Carboxymethyl group increases the swellability of polysaccharides (3), which gives them unique

Received December 2005; Accepted January 2005.

Address correspondence to Kunj Behari, Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India. E-mail: reach2arti@yahoo.co.uk

applications in various industries e.g. paper (4) and in the pharmaceutical industry (5), etc. Although it possesses various industrial applications, it suffers from a major drawback such as susceptibility to microbial attack, which limits its application and can be improved by grafting of vinyl monomers.

Similarly, N-vinyl-2-pyrrolidone has unique characteristics and the polymers derived from it find many commercial applications (6–9). Furthermore, N-vinyl-2-pyrrolidone is successfully used as a comonomer in the synthesis of hydrogels (10) and its graft copolymer with chitosan is used as a antimicrobial agent (11). Therefore, these properties prompted us to synthesize the graft copolymer of sodium carboxymethylcellulose and N-vinyl-2-pyrrolidone.

Experimental

Materials

Freshly distilled N-vinyl-2-pyrrolidone (Merck) has been used for grafting. Potassium peroxymonosulphate (Sigma), thiourea (E. Merck), sulphuric acid (E. Merck) and carboxymethylcellulose sodium salt (BDH, Pool) have been used as it is. The other chemical reagents are of analytical grade and used without further purification.

Procedure for Grafting

For each experiment, carboxymethylcellulose (sodium salt) solution has been prepared by the slow addition of a weighed amount of sodium carboxymethylcellulose to triple distilled water with rapid stirring in a reactor. A calculated amount of N-vinyl-2-pyrrolidone, thiourea and sulphuric acid solutions have been added into the reactor under a stream of oxygen-free nitrogen gas. The reaction has been initiated by the addition of a known amount of deoxygenated potassium peroxymonosulphate solution after half an hour. After the desired time interval, the reaction has been stopped by allowing air into the reactor. The grafted sample has been precipitated by pouring the reaction mixture into methanol. The precipitate has been separated, dried, and weighed. A pinch of hydroquinone has been added to the filtrate and concentrated by distillation under reduced pressure. The poly(N-vinyl-2-pyrrolidone) has been precipitated by pouring the concentrated filtrate into acetone. The poly (N-vinyl-2-pyrrolidone) thus obtained has been separated, dried, and weighed.

The graft copolymer has been characterized by following grafting parameters (12–14).

$$\text{Grafting ratio } (\%G) = \frac{\text{weight of grafted polymer}}{\text{weight of substrate}} \times 100$$

$$\text{Grafting efficiency } (\%E) = \frac{\text{weight of grafted polymer}}{\text{weight of polymer formed}} \times 100$$

$$\text{Add on } (\%A) = \frac{\text{weight of grafted polymer}}{\text{weight of graft copolymer}} \times 100$$

$$\text{Conversion } (\%C) = \frac{\text{weight of polymer formed}}{\text{weight of monomer charged}} \times 100$$

$$\text{Homopolymer (\%H)} = 100 - \text{\%grafting efficiency}$$

$$\text{Rate of grafting (Rg)} = 1000 \times \frac{\text{weight of grafted polymer}}{\text{volume} \times \text{time} \times \text{mol.wt. of NVP}} moll^{-1}S^{-1}$$

Grafting of N-vinyl-2-pyrrolidone onto carboxymethylcellulose (sodium salt) using a peroxymonosulphate/thiourea redox pair under various conditions has been studied to find optimum conditions for grafting by varying the concentration of N-vinyl-2-pyrrolidone, potassium peroxymonosulphate, thiourea, sodium carboxymethylcellulose, hydrogen ion, reaction time and temperature.

Results and Discussion

The effect of variation of peroxymonosulphate (PMS) concentration on grafting parameters has been investigated from 3.0×10^{-3} to 5.0×10^{-3} mol dm^{-3}, which is depicted in Figures 1 and 2. The increment in grafting parameters might be due to the progressive reduction of PMS by thiourea, which produces primary free radicals ($R^{\bullet} = R_1 S^{\bullet}$ and $SO_4^{\bullet -}$) and these primary free radicals attack on the polymeric backbone to generate active sites on to which monomer addition takes place. The decrement in grafting parameters might be due to the premature termination of a growing grafted chain.

Figure 3 and 4 show the effect of thiourea concentration on grafting parameters. The increment in grafting parameters might be attributed to the increase in number of primary free radicals and decrement in grafting parameters are due to the premature termination of growing grafted chain.

The concentration of hydrogen ion has been varied from 2.0×10^{-3} to 10.0×10^{-3} mol dm^{-3}. It is seen that the grafting parameters increase up to a hydrogen ion concentration of 6.0×10^{-3} mol dm^{-3} and then decrease (Figures 5 and 6). The increment in grafting parameters might be due to more protonation of thiourea on increasing the hydrogen ion concentration and these protonated species react with peroxymonosulphate to give a higher number of primary free radicals

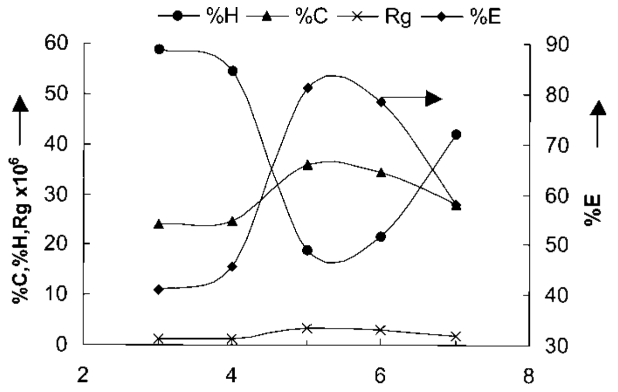


Figure 1. Effect of Potassium peroxymonosulphate concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0×10^{-2} mol dm^{-3}; [TU] = 2.84×10^{-3} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

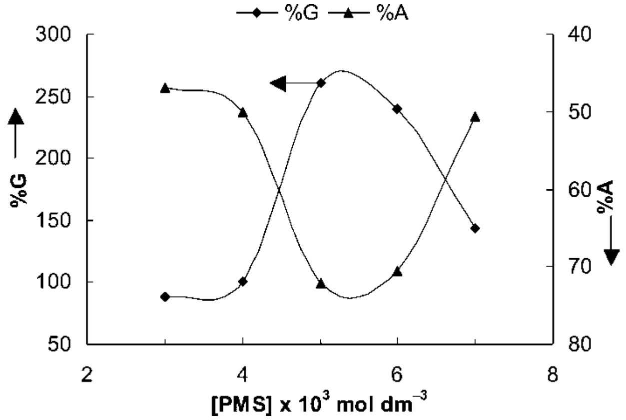


Figure 2. Effect of Potassium peroxymonosulphate concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0 $\times 10^{-2}$ mol dm^{-3}; [TU] = 2.84 $\times$ 10^{-3} mol dm^{-3}; [H^+] = 6.0 $\times 10^{-3}$ mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

therefore increased in the value of grafting ratio, add on, conversion, efficiency and rate of grafting.

Figures 7 and 8 show that grafting ratio, add on, efficiency and rate of grafting increase with increasing the concentration of N-vinyl-2-pyrrolidone from 4.0 $\times$ 10^{-2} to 10.0 $\times$ 10^{-2} mol dm^{-3}, but beyond 10.0 $\times$ 10^{-2} mol dm^{-3} these grafting parameters decrease. Maximum grafting ratio has been observed at 10.0 $\times$ 10^{-2} mol dm^{-3}, which is 402% and at this concentration the percent of homopolymer is 4.28, that means maximum monomer molecules are grafted on the sodiumcarboxymethyl cellulose and it might be attributed to easier accumulation of monomer at the close proximity of

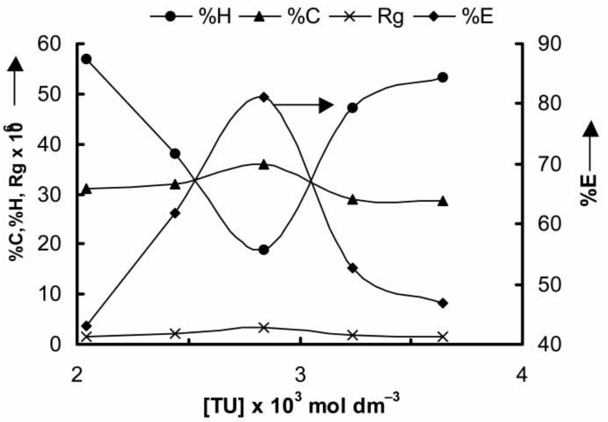


Figure 3. Effect of Thiourea concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0 $\times$ 10^{-2} mol dm^{-3}; [PMS] = 5.0 $\times$ 10^{-3} mol dm^{-3}; [H^+] = 6.0 $\times$ 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

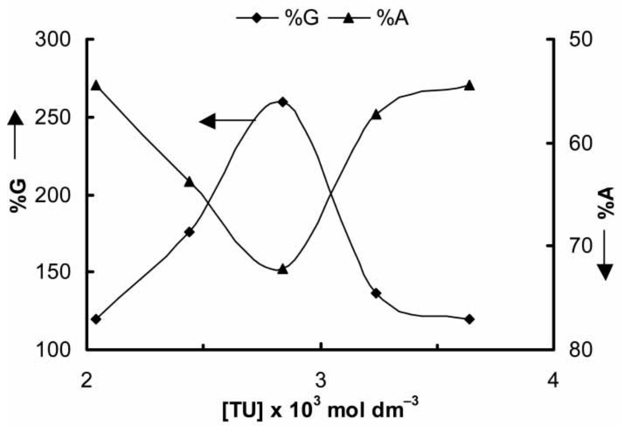


Figure 4. Effect of Thiourea concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; Time =120 min.; Temp. = 40°C.

polymeric backbone. The monomer molecules, which are at the immediate vicinity of the reaction site, become acceptors of carboxymethylcellulose radicals. This results in chain initiation and thereafter they become free radicals donors to the neighboring molecules leading to the lowering termination. The decrease in grafting parameters has been observed beyond 10.0 × 10^{-2} mol dm^{-3} and it is because of a good deal of formation of homopolymer, which increases the viscosity of medium due to the fact that the movement of free radicals is restricted.

The grafting ratio, efficiency and add on have been found to decrease continuously with increasing the concentration of sodium carboxymethylcellulose from 0.4 to 1.8 g dm^{-3} (Figures 9 and 10). This behavior could be explained that as the concentration of sodium carboxymethylcellulose increases, the viscosity of the reaction medium also increases,

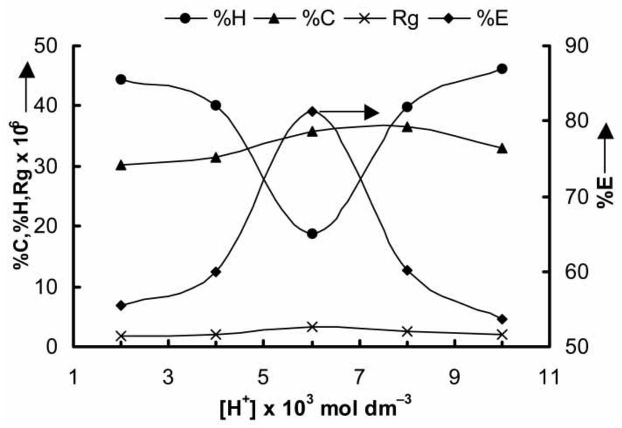


Figure 5. Effect of Hydrogen ion concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

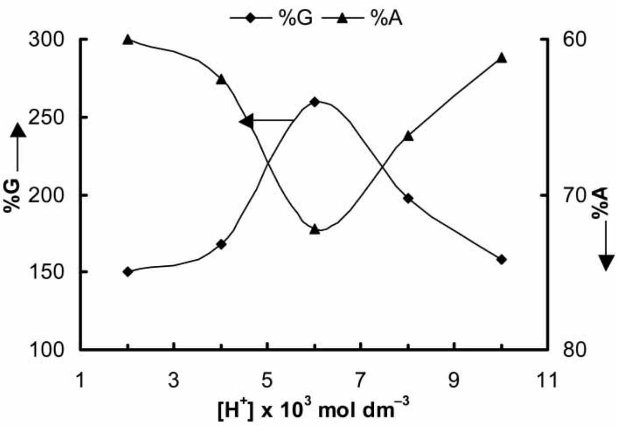


Figure 6. Effect of Hydrogen ion concentration [CMC] = 1.0 g dm^{-3}; [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time =120 min.; Temp. = 40°C.

which hinders the diffusion of primary free radicals thereby decreasing the grafting parameters.

It has been observed that the grafting ratio, add on, conversion and efficiency increase from 60 to 120 min (Figures 11 and 12). With increasing the reaction time, availability of active species takes place due to the fact that propagation of grafting chains occurs at a faster rate, which accounts for a higher grafting parameter. However, with a further increase in time interval, the mutual annihilation of growing grafted chains occurs which is responsible for more homopolymer formation.

Figures 13 and 14 indicate the results that the grafting parameters increase up to 45°C, thereafter it decreases. An increase in temperature seems to cause a high rate of

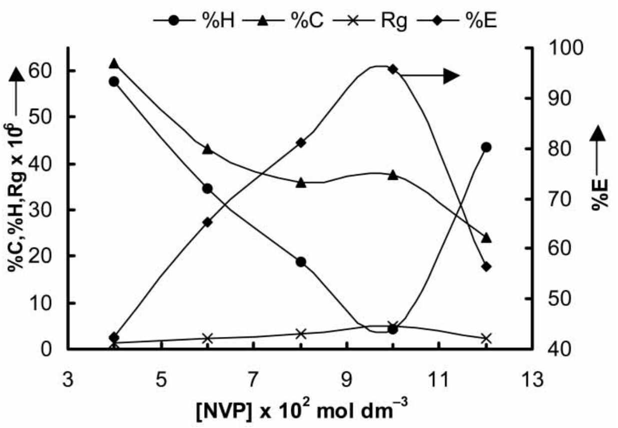


Figure 7. Effect of N-vinyl-2-pyrrolidone concentration [CMC] = 1.0 g dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

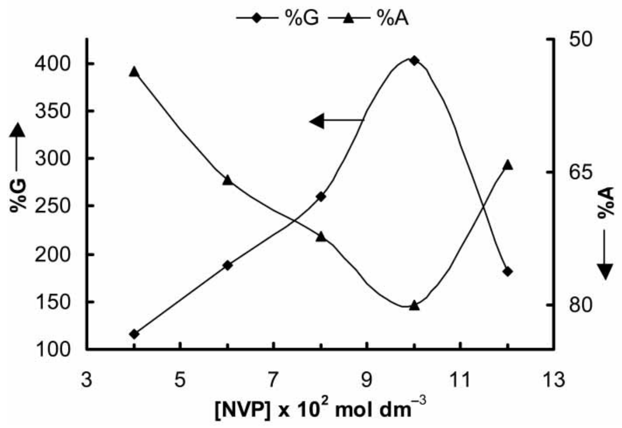


Figure 8. Effect of N-vinyl-2-pyrrolidone concentration [CMC] = 1.0 g dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

formation of free radicals and the mobility of the monomer molecule. But at a higher temperature, i.e., beyond 45°C, grafting parameters have been found to decrease. This is the result of mutual effects: with the increase of T, several effects take place: faster formation of radicals, faster termination of radicals and easier chain transfer to monomer. The first effect is favorable to grafting and the last one is favorable to homopolymer formation.

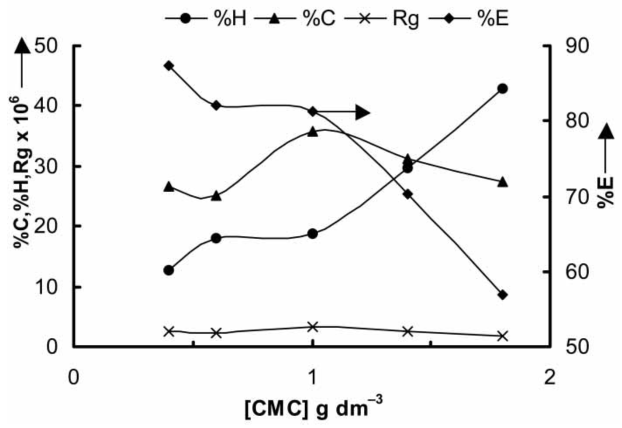


Figure 9. Effect of Carboxymethylcellulose concentration [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.

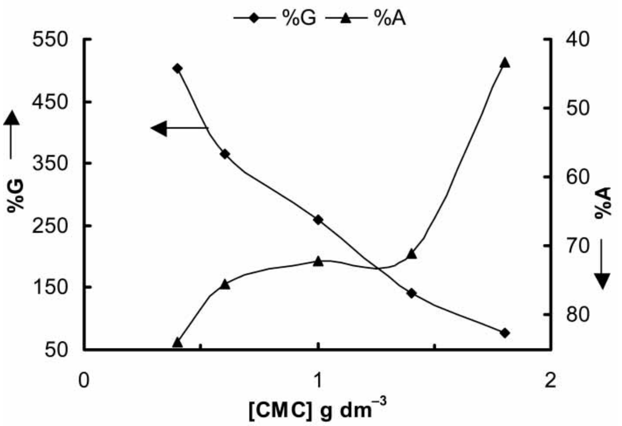


Figure 10. Effect of Carboxymethylcellulose concentration [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time =120 min.; Temp. = 40°C.

Evidence of Grafting

Infrared Spectral Analyses. The FTIR spectra of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-N-vinyl-2-pyrrolidone have been recorded using a Perkin-Elmer-FTIR spectrophotometer Paragon 1000 in the range 500 to 4000 cm^{-1}. On comparing the IR spectra of sodium carboxymethylcellulose and sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone (CMC-g-NVP), some additional bands have appeared in the spectra of CMC-g-NVP, such as a C=O stretching band which appeared at 1690.0 cm^{-1}. This was attributed to the carbonyl group of N-vinyl-2- pyrrolidone, C–N stretching band which appeared at 1428.0 cm^{-1}. The disappearance of the O–H bending vibration in spectra of sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone indicates that the grafting took place on the —OH site of the backbone (Figures 15 and 16).

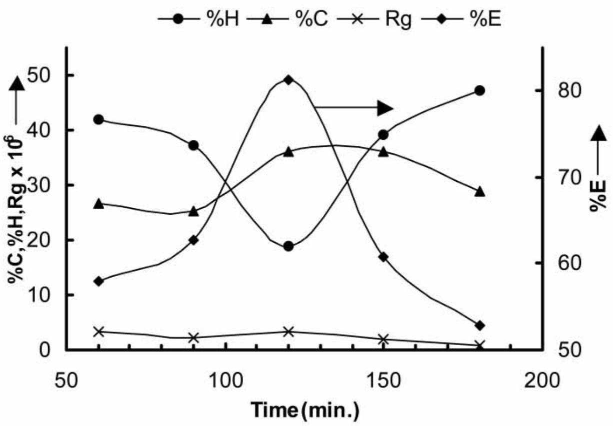


Figure 11. Effect of Time period [NVP] = 8.0 × 10^{-2} mol dm^{-3}; [H$^+$] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; [CMC] = 1.0 g dm^{-3}; Temp. = 40°C.

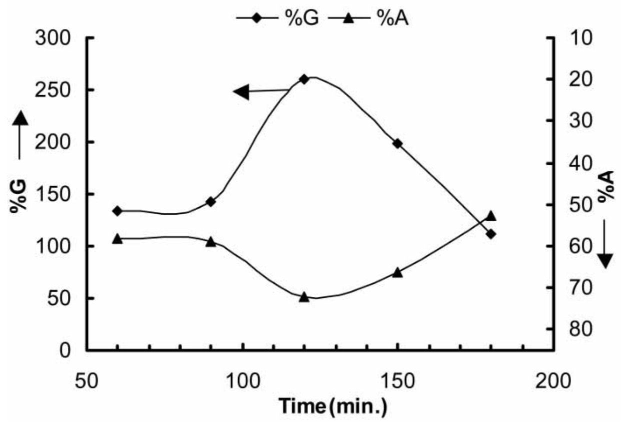


Figure 12. Effect of Time period [NVP] = 8.0×10^{-2} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [PMS] = 5.0×10^{-3} mol dm^{-3}; [TU] = 2.84×10^{-3} mol dm^{-3}; [CMC] = 1.0 g dm^{-3}; Temp. = 40°C.

Mechanism

Initially thiourea reacts with hydrogen ion to give protonated species isothiourea, which further reacts with potassium peroxymonosulphate to form complex. Subsequently complex dissociates, to generate free radicals ($R^{\bullet} = R_1S^{\bullet}$ and $SO_4^{\bullet -}$). The free radicals $R^{\bullet}$ abstract hydrogen atom from sodium carboxymethylcellulose (COH) and producing $CO^{\bullet}$ macroradicals. The N-vinyl-2-pyrrolidone molecules which are in close vicinity of the reaction sites become acceptors of sodium carboxymethyl cellulose radicals resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules. The grafted chains are terminated by coupling to give graft copolymer. The following steps are proposed for the graft copolymerization of N-vinyl-2-pyrrolidone onto sodium carboxymethylcellulose using PMS-thiourea redox pair.

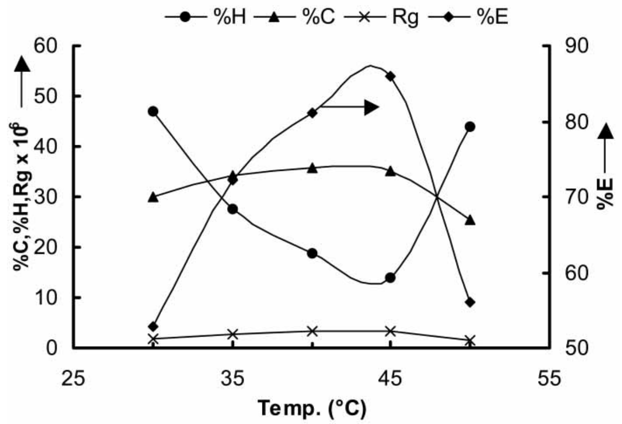


Figure 13. Effect of Temperature [NVP] = 8.0×10^{-2} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [PMS] = 5.0×10^{-3} mol dm^{-3}; [TU] = 2.84×10^{-3} mol dm^{-3}; [CMC] = 1.0 g dm^{-3}; Time = 120 min.

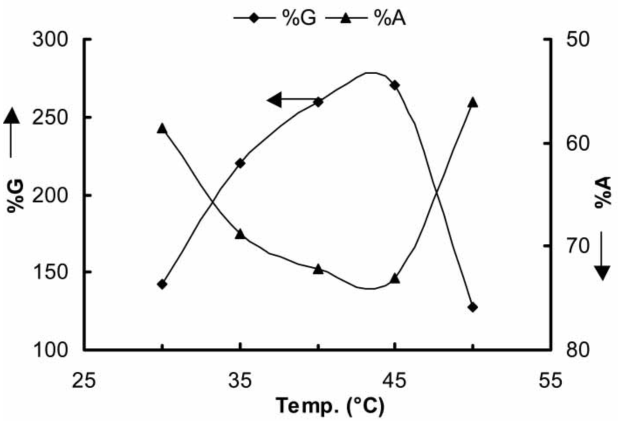
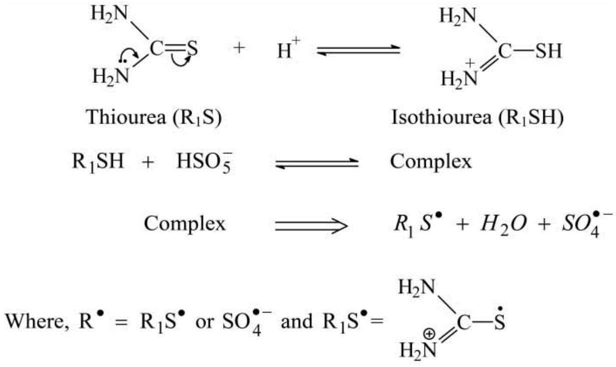


Figure 14. Effect of Temperature [NVP] = 8.0×10^{-2} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [PMS] = 5.0×10^{-3} mol dm^{-3}; [TU] = 2.84×10^{-3} mol dm^{-3}; [CMC] = 1.0 g dm^{-3}; Time = 120 min.

Radical Formation



Amidinosulfenyl free radical

Initiation

$$\mathrm{COH} + \mathrm{R}^{\bullet} \longrightarrow \mathrm{CO}^{\bullet} + \mathrm{RH}$$
$$\mathrm{M} + \mathrm{R}^{\bullet} \longrightarrow \mathrm{RM}^{\bullet}$$

Propagation

$$\mathrm{CO}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{COM}_1^{\bullet}$$
$$\mathrm{COM}_1^{\bullet} + \mathrm{M} \longrightarrow \mathrm{COM}_2^{\bullet}$$

....

....

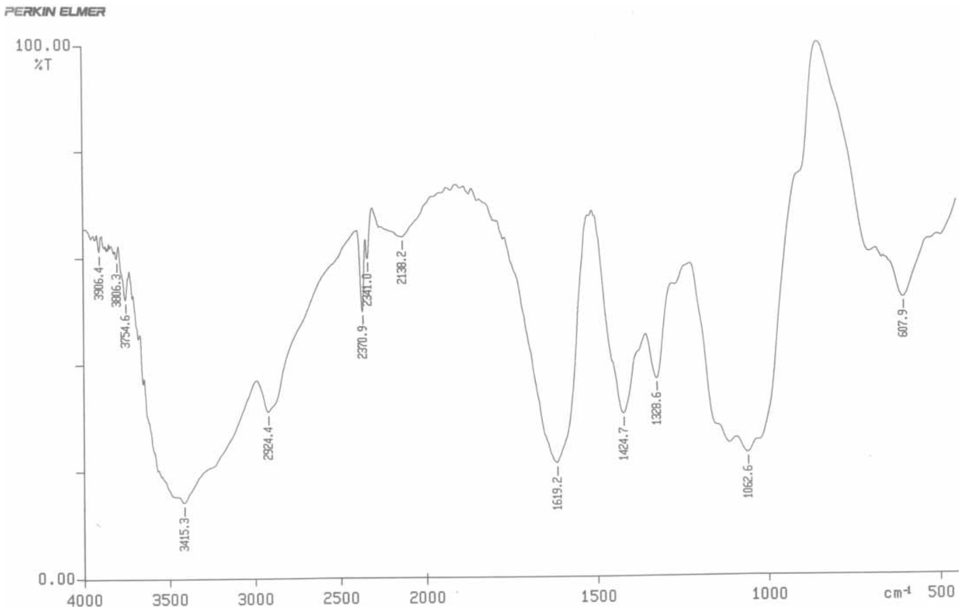


Figure 15. IR spectra of sodium carboxymethyl cellulose.

$$\mathrm{COM}^{\bullet}_{n-1} + \mathrm{M} \longrightarrow \mathrm{COM}^{\bullet}_{n}$$
$$\mathrm{RM}^{\bullet}_{1} + \mathrm{M} \longrightarrow \mathrm{RM}^{\bullet}_{2}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\mathrm{RM}^{\bullet}_{n-1} + \mathrm{M} \longrightarrow \mathrm{RM}^{\bullet}_{n}$$

Termination

$$\mathrm{COM}^{\bullet}_{n} + \mathrm{COM}^{\bullet}_{n} \rightarrow \text{Graft copolymer}$$
$$\mathrm{COM}^{\bullet}_{n} + \mathrm{RM}^{\bullet}_{n} \rightarrow \text{Graft copolymer}$$
$$\mathrm{RM}^{\bullet}_{n} + \mathrm{RM}^{\bullet}_{n} \rightarrow \text{Homopolymer}$$

Where, COH → Sodium carboxymethyl cellulose

M → *N-vinyl*-2-*pyrrolidone*

Thermal Analysis

The thermograms have been recorded on a NETZSCH–Geratebau GmbH thermal analyzer up to 1500°C and with a heating rate of 20°C/min in an atmosphere of Nitrogen.

Sodium Carboxymethylcellulose

The degradation of sodium carboxymethylcellulose started at about 200°C (Figure 17) which takes place in a single step. The rate of weight loss increases with increase in

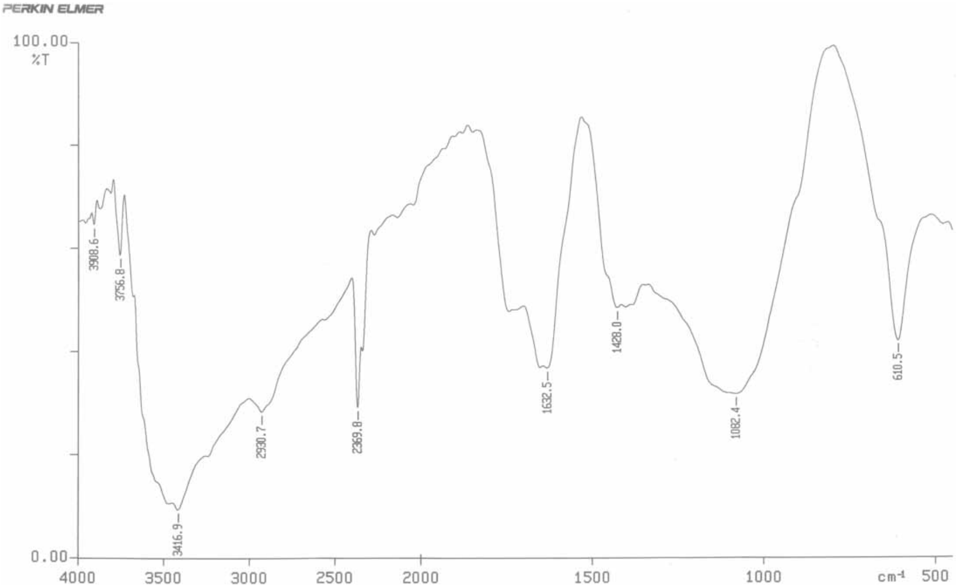


Figure 16. IR spectra of sodium carboxymethyl cellulose-g-N-vinyl-2-pyrrolidone.

temperature from 200°C, and attains a maximum at 286.5°C, and thereafter decreases and attains a constant value. The polymer decomposition temperature (PDT), temperature at which maximum degradation occurs i.e., T_{max}, the final decomposition temperature (FDT) and the Integral procedural decomposition temperature (IPDT) have been found to be 250.0°C, 286.5°C, 443.7°C, and 237.19°C, respectively (Table 1). This T_{max} is also confirmed by an endothermic peak at 297.9°C, and it may be due to the loss of $CH_2COO^-Na^+$ group of sodium carboxymethyl cellulose.

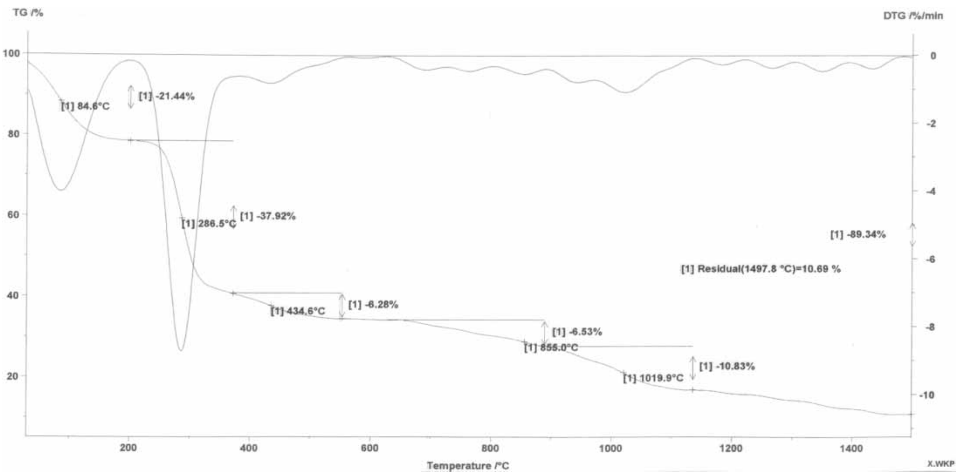


Figure 17. Thermo gravimetric analysis of sodium carboxymethyl cellulose.

Table 1

Thermogravimetric analysis

Sample code	PDT (°C)	IPDT (°C)	FDT (°C)	T_{max} (°C)	DTA Peaks Exopeaks (°C)	DTA Peaks Endopeaks (°C)
C	250	237.19	443.75	286.50	–	297.9
C_P	208	476.25	1331.25	231.50 746.30	–	745.8

Sodium Carboxymethylcellulose-g-N-vinyl-2-pyrrolidone

The graft copolymer began to degrade at about 200°C. The degradation of sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone occurs in two stages, i.e., from 200°C to 231°C and from 593.0°C to 746.3°C, after that, it degrades slowly and attains approximately a constant weight loss (Figure 18). The polymer decomposition temperature (PDT) has been found to be 208°C, which is lower than that of carboxymethylcellulose and it is due to elimination of groups from grafted polymer chain. The maximum weight loss occurs at two temperatures (T_{max}). Thus, there are two T_{max} at which maximum weight loss obtained. The first T_{max} has been found to be 231.5°C and it may be due to the loss of a CH_2COONa group from the parent backbone. The second T_{max} has been found to be 746.3°C, which may be due to the elimination of pyrrolidone ring from pendent polymer chain by breaking of C—N bond. The FDT, and IPDT have been found to be 1331.25°C and 476.25°C, respectively (Table 1). A residual amount of graft copolymer is found to be 25.70% at 1406.6°C. The high value of IPDT, FDT and char yield shows that the graft copolymer has significantly higher thermal stability than

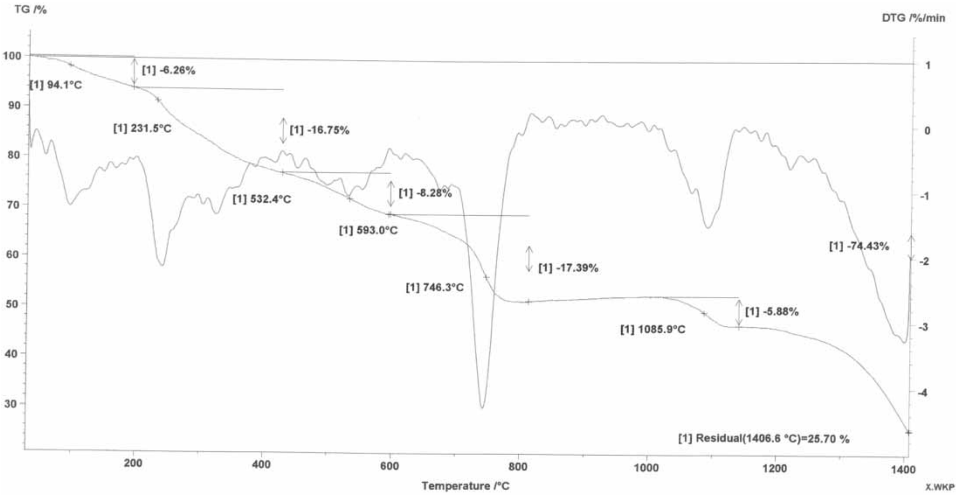


Figure 18. Thermo gravimetric analysis of Sodium carboxymethyl cellulose-g-N-vinyl-2-pyrrolidone Schematic representation of degradation of synthesized graft copolymer.

that of the parent polymer by 888°C. Thus, the incorporation of poly(vinyl-2-pyrrolidone) increases the thermal stability of carboxymethylcellulose significantly.

Sorption Studies

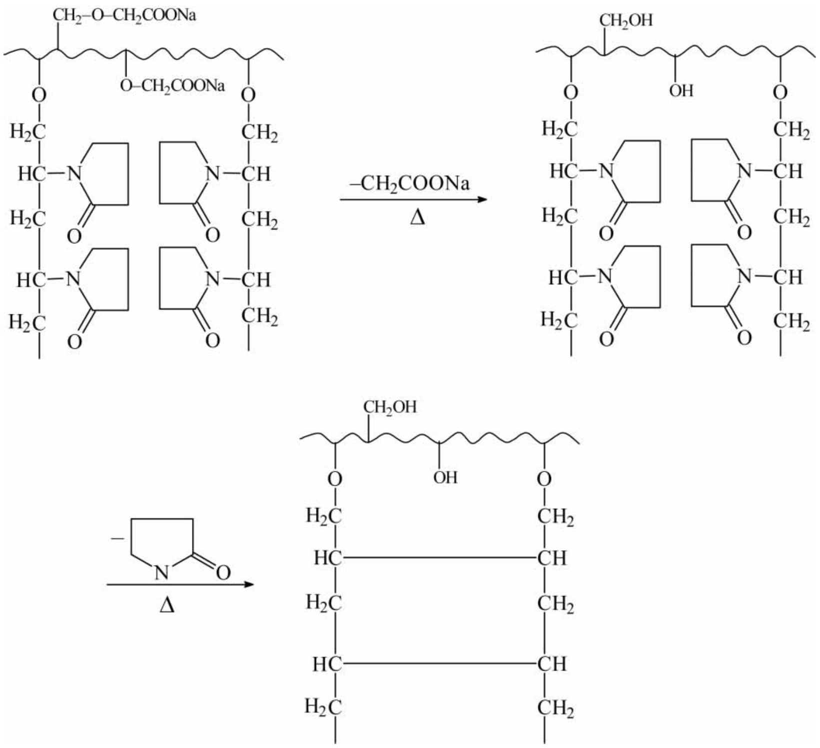
For studying the swelling behavior, the different samples of graft copolymer have been prepared by changing the concentration of N-vinyl-2-pyrrolidone from 4.0×10^{-2} to 12.0×10^{-2} mol dm^{-3}. Swelling studies have been carried out by taking 0.05 gm of the sample in 20 ml of triple distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer (Carboxymethylcellulose-g-N-vinyl-2-pyrrolidone) has been removed by gently pressing between the folds of filter paper; an increase in weight has been recorded. The percent swelling (Ps) has been calculated with the help of following expressions (15) and results are given in Table 2.

$$\mathrm{Ps} = \frac{\mathit{Wt.\ of\ swollen\ polymer} - \mathit{Wt.\ of\ drypolymer}}{\mathit{Weight\ of\ drypolymer}} \times 100$$

Where,

C = Sodium Carboxymethylcellulose.

Cp = Sodium Carboxymethylcellulose-g-N-vinyl-2-pyrrolidone.



Schematic representation of degradation of synthesized graft copolymer

Table 2
Swelling behavior
[Na-CMC] = 1.0 gm dm^{-3}; [PMS) = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; [H^{+}] = 6.0 × 10^{-3} mol dm^{-3}; Time = 120 min; Temp. = 40°C

Sample code	[NVP] × 10^{2} mol dm^{-3}	%G	P_S
C_{P_1}	4.0	116	52
C_{P_2}	6.0	188	84
C_{P_3}	8.0	260	120
C_{P_4}	10.0	402	144
C_{P_5}	12.0	182	70

It has been observed that the percent swelling of graft copolymer increases on increasing the % grafting ratio and maximum 140% swelling has been observed at 402% of grafting. Since N-vinyl-2-pyrrolidone is a hydrophilic monomer, therefore, increases the water retention of graft copolymer. Thus, on increasing the percent grafting ratio percent of hydrophilic character on graft copolymer increases, thereby increasing the swelling capacity of graft copolymer.

Metal Ion Uptake

To study the metal ion sorption behavior of the synthesized graft copolymer, we have taken five metals like Cu, Ni, Zn, Pb, Hg. For this, 0.020 gm of graft copolymer has been taken in 10 ml of metal ion solution of known concentration and kept undisturbed for 24 h. The strength of the unabsorbed metal ions has been determined by standard methods. Different relationships (16) which have been used to determine the sorption behavior of sodium carboxymethylcellulose and sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone are as follows:

$$\text{Percent uptake (Pu)} = \frac{\textit{Amount of metal ion in polymer}}{\textit{Amount of metal ion in feed}} \times 100$$

$$\text{Partition coeffcient (Kd)} = \frac{\textit{Amount of metal ion in polymer}}{\textit{Amount of metal ion left in solution}} \times \frac{\textit{Vol. of solution (ml)}}{\textit{Wt. of dry polymer (gm)}}$$

$$\text{Retention capacity (Qr)} = \frac{\textit{Amount of metal ion in polymer (mEq)}}{\textit{Wt. of dry polymer (gm)}}$$

The effect of percent grafting on sorption behavior of sodium carboxymethyl cellulose and its graft copolymer with N-vinyl-2-pyrrolidone has been studied in terms of percent ion uptake (Pu), partition coefficient (Kd), retention capacity (Qr) and the results are summarized in Table 3. It has been observed that the values of percent ion uptake (Pu), partition coefficient (Kd) and retention capacity (Qr) increase with an increase in % grafting ratio, and which clearly indicates that the percent uptake of metal ion depends on the nature of grafted polymer. This behavior is due to the

Table 3

Sorption Studies of metal ions on sodium carboxymethylcellulose (C) and sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone (C_P)
[CMC] = 1.0 g dm^{-3}; [H^+] = 6.0 × 10^{-3} mol dm^{-3}; [PMS] = 5.0 × 10^{-3} mol dm^{-3}; [TU] = 2.84 × 10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C

Sample code	[NVP] × 10^2 mol dm^{-3}	%G	Percent uptake (Pu)					Partition coefficient (Kd)					Retention Capacity (Qr)				
			Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}
C	–	–	3.6	1.9	1.3	0.9	0.31	18.1	9.6	6.7	4.8	1.5	0.3	0.36	0.17	0.5	0.19
C_{P_1}	4.0	116	14.4	2.5	1.3	1.9	0.91	84.2	11.9	6.9	9.1	4.6	1.5	0.44	0.18	1.1	0.58
C_{P_2}	6.0	188	14.6	2.7	2.9	2.5	1.14	85.8	14.0	15.0	13.1	5.7	1.5	0.52	0.38	1.4	0.72
C_{P_3}	8.0	260	16.8	6.4	4.0	3.4	1.33	101.0	34.7	21.1	17.8	6.7	1.7	1.24	0.53	2.0	0.85
C_{P_4}	10.0	402	18.1	6.8	4.2	3.8	1.42	110.8	36.7	22.1	19.9	7.2	1.9	1.31	0.55	2.2	0.90
C_{P_5}	12.0	182	16.8	3.3	1.5	2.1	0.91	101.2	17.3	7.9	10.8	4.62	1.77	0.64	0.20	1.2	0.58

increased pendent chain of poly (N-vinyl-2-pyrrolidone) onto sodium carboxymethylcellulose. Among five metal ions, Cu^{2+} ion is veryh uptakable, and Hg^{2+} is the least uptakable ion, while other metal ions show better results. The order of absorption of metal ion on graft copolymer has been found in the following manner.

$$Cu^{++} > Ni^{++} > Zn^{++} > Pb^{++} > Hg^{++}$$

Conclusions

It has been found that the synthesized graft copolymer i.e., sodium carboxymethylcellulose-g-N-vinyl-2-pyrrolidone has high thermal stability in comparison to the parent polymer and shows better metal ion sorption behavior in comparison to sodium carboxymethylcellulose. Therefore, synthesized graft copolymer can be used as an absorbent for metal ion sorption.

References

1. Hebeish, A. and Guthric, J.T. (1981) *The Chemistry and Technology of Cellulosic Copolymers*. Springer: New York.
2. Zhang, L.M. and Tan, Ye-B. (2000) *Macromol. Mater. Eng.*, 280–281 (1): 59–65.
3. Trivedi, H.C., Patel, C.P., and Patel, G.M. (1999) *Eur. Polym. J.*, 35: 201–208.
4. Hosokawa, K., Hotta, T., Hanada, N., and Tobata, M. (2003) Additives for wall materials and moisture absorbing wall materials compositions containing the same. In *Chem. Abstr.*, 139, 105168c. Jpn. Kokai Tokkyo Koho, JP, 206,170 (Cl C04B24/38) July 22, 2003.
5. Kim, D.S.; Kim, D.; Lee, J.K.. Anti-adhesion barrier comprising carboxymethyl cellulose and gellan gum. Eur. Pat. 1,323,436 (Cl. A61L15), July 2, 2003. Chem. Abstr., **2003**, 139, 74107a.
6. Schuer, J.P. (2002) Method and apparatus for neutrilizing odors in the air in a non toxic manner. In *Chem. Abstr.*, 13698681t, PCT Int. Appl., WO 02,55,114 (Cl. A61L9/01), July 18, 2002.
7. Gaenger, K.; Florig, E.. Hair styling compositions comprising a combination of three polymers. Eur. Pat. 1,192,931 (Cl. A61K7/06), April 3, 2002. Chem. Abstr. **2002**, 136, 284162d.
8. Kroeppe, R.; Bleckmann, A.. Water in oil emulsions with increased water content as application as cosmetics. Eur Pat. 1,192,929 (Cl. A61 K7/100), April 3, 2002. Chem. Abstr. **2002**, 136, 284182k.
9. Oda, N., Naoki, Kasai, I., and Umeda, K. (2003) Soft touch inner Wears. In *Chem. Abstr.* 13970392s. Jpn. Kokai Tokkyo Koho, JP, 183904 (Cl. A41 B17/00) July 3, 2003.
10. Devine, D.M. and Higginbottom, C. (2004) *Polymer*, 44 (26): 7851–60.
11. Nudga, L.A., Petrova, V.A., Klishevich, N.V., ;, Litvinova, Babenko, A.Y., and Shelegedin, V.N. (2002) *Russian Journal of Applied Chemistry*, 75 (10): 1678–1682.
12. Fanta, G.F. (1973) *Block and Graft Copolymerization*. Ceresa, R.J. (ed.), Wiley Intersciences: New York, 1.
13. Mohanty, E. and Singh, B.C. (1998) *J. Appl. Polym. Sci.*, 69: 2569–2576.
14. Yuan, X., Sheng, J., and Shen, N. (1998) *J. Appl. Polym. Sci.*, 69: 1917–1921.
15. EI-Rehim, Abd, H.A., Hegazy, El-S., and Ali, A.M. (2000) *J. Appl. Polym. Sci.*, 76: 125–132.
16. Rivas, B.L., Maturana, H.A., Molina, M.J., Gomez-Anton, M.R., and Pierala, I.P. (1998) *J. Appl. Polym. Sci.*, 67: 1109–1118.