

# Synthesis, Characterization, and Application of Amylopectin-graft-poly(AM-co-AMPS)

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**ABSTRACT:** A series of graft copolymers poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) [Ap-g-p(AM-co-AMPS)] have been synthesized by graft copolymerization of amylopectin (Ap) with acrylamide (AM) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The copolymerization has been carried out by solution polymerization technique and using ceric ammonium nitrate (CAN) as initiator. The characterization of graft copolymer has been carried out by elemental analysis fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and scanning electron microscopy (SEM). The effects of reaction conditions on graft copolymerization and the use of the copolymer as flocculating agent in kaolin suspension have been investi-

gated. Experiments have shown that graft copolymer with higher grafting level, higher intrinsic viscosity, and higher anionic degree can be obtained by changing the method of addition of monomers and by controlling the ratio of AMPS and AM. The flocculation performances have been investigated through jar test method, and it has been observed that the graft copolymer with molar ratio of 2 : 1 of AM and AMPS shows best performance in flocculating kaolin suspension. Metal ion sorption study with  $\text{Cu}^{2+}$  has shown that the graft copolymer absorbs  $\text{Cu}^{2+}$  efficiently. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** polymer synthesis; graft copolymer; amylopectin; acrylamide; 2-acrylamido-2-methylpropanesulfonic acid

## INTRODUCTION

Polymers containing ionic groups are interesting both from a fundamental and from an applied point of view. Anionic polymers of acrylamide (AM) and other vinyl monomers are currently commercialized and widely applied in numerous fields such as petroleum industry and environmental protection. The preparation of copolymers of AM with sodium acrylate in inverse emulsion has been reported earlier.<sup>1</sup> Poly(*N*-vinylpyrrolidone) groups are grafted onto poly(3-hydroxybutyrate-co-3-hydroxyvalerate) backbone to obtain modified properties of graft copolymer.<sup>2–4</sup> The synthesis and characterization of *N*-vinylformamide with sodium 3-acrylamido-3-methyl butanoate, sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and sodium acrylate has also been reported.<sup>5</sup> However, drawbacks of these products are a high-cost and poor dissolution properties.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) has previously been copolymerized with a range of different AM monomers.<sup>6,7</sup> A series of random and graft copolymers of AM with NaAMPS, diacetone AM, and sodium acrylate has been studied.<sup>8</sup> There has been investigation on the thermal characteristics

of copolymers of AMPS with AM prepared by radical copolymerization.<sup>9</sup> Hydrogel based on AM and AMPS has been synthesized and characterized.<sup>10</sup>

Starch consists of two types of polymers of anhydroglucose units, i.e., amylose, the low molecular weight linear fraction and amylopectin (Ap), the high molecular branched fraction.<sup>11,12</sup> Ap has been grafted with AM using a ceric ion-induced redox initiation technique.<sup>13</sup> Starch has been grafted with AM and AMPS and applied as flocculant.<sup>11,14</sup> Cerium-induced graft copolymerization of acylamide and sodium 2-acrylamido-2-methylpropanesulfonate onto dextran has also been reported.<sup>15</sup>

Graft copolymerization of vinyl monomers onto polysaccharide substrates is widely used for property modification of polysaccharides.<sup>16,17</sup> Biodegradable drag-reducing agents and flocculants based on polyacrylamide-grafted polysaccharides have been widely explored.<sup>18,19</sup>

In this article, synthesis of Ap-graft-poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) [Ap-g-p(AM-co-AMPS)] is studied by using ceric-induced initiation. The article discusses the preparation method and effect of reaction conditions on properties of the product. The application of the graft copolymer as a flocculating agent in kaolin suspension is also investigated. In addition, the metal ion sorption behavior of graft copolymer was studied for metal ion ( $\text{Cu}^{2+}$ ). It is observed that the graft copolymer absorbs a good amount of metal ion.

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**TABLE I**  
**Elemental Analysis**

S. no.	Polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	Ap	39.2	5.9	0.1
2	Ap-g-p(AM-co-AMPS) 1	42.22	6.79	8.21
3	Ap-g-p(AM-co-AMPS) 2	42.6	6.93	9.90
4	Ap-g-p(AM-co-AMPS) 3	42.39	7.71	10.21
5	Ap-g-p(AM-co-AMPS) 4	43.3	7.82	10.99
6	Ap-g-p(AM-co-AMPS) 5	43.59	7.90	9.88
7	Ap-g-p(AM-co-AMPS) 6	43.80	7.60	9.52

## EXPERIMENTAL

### Materials

AM is obtained from S.D. Fine Chemicals, Mumbai, India. Ap, AMPS, acetone of laboratory grade, and hydroquinone are procured from Himedia, Mumbai, India. Ceric ammonium nitrate (CAN) is obtained from Loba Chemie, Mumbai, India. NaOH is obtained from S.D. Fine Chemicals, Mumbai, India. Kaolin has been gifted by Rajmahal Quartz and sand (Kolkata, India). Commercial flocculants N 9901 and N 9903 have been gifted by Nalco Chemicals, Kolkata, India. All the chemicals are used without further purification.

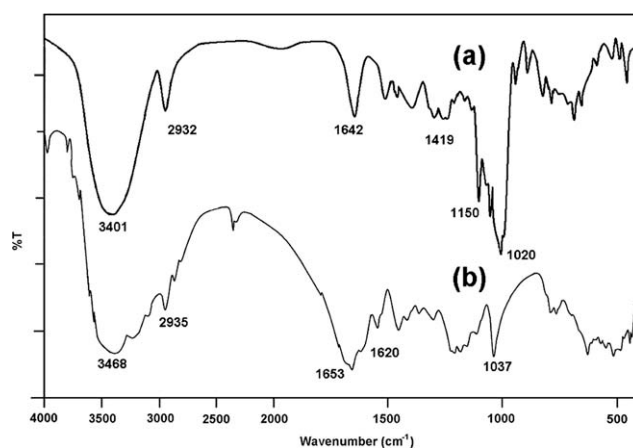
### Preparation of the graft copolymer

The reaction is carried in a four-necked round-bottom flask equipped with stirrer, thermometer, nitrogen gas inlet, and condenser. The flask is heated in a thermostatic water bath (SONAR, India). About 100 mL of 0.125 mol AGU L<sup>-1</sup> of Ap solution is taken into the flask and heated for 30 min at 60°C. After the slurry turned to a transparent solution, the flask contents are cooled to 50°C. AM, AMPS, and CAN are added, and the reaction is allowed to continue for 3 h at 50°C.

### Analysis of the graft copolymer

The solution with prepared Ap-g-p(AM-co-AMPS) is precipitated with acetone and washed twice with acetone to remove the unreacted monomer. The product is dried at 40°C. The homopolymers and the AM-AMPS copolymers are removed from the precipitated graft copolymers by soxhlet extraction with a 60 : 40(v/v) mixture of ethylene glycol and acetic acid.<sup>20</sup> The graft copolymer is then washed with ethanol and is dried in a vacuum oven at 40°C to a constant weight. The product is then analyzed by elemental analysis FTIR and <sup>1</sup>H-NMR and SEM.

The elemental analysis of Ap and all the graft copolymers is performed using (CHNS) analyzer CE- 440 Elemental analyzer, Mexico. The estimated analysis of three different elements carbon, hydrogen and nitrogen is undertaken. The results are



**Figure 1** FTIR spectrum of (a) Ap and (b) Ap-g-p(AM-co-AMPS).

shown in Table 1. The FTIR spectrum (Fig. 1) is recorded in solid state using KBr pellet. A Thermo Nicolet FTIR Spectrophotometer (Model-JASCO FTIR-5300) is used to record the spectra in the range of 4000–400 cm<sup>-1</sup> wave numbers. The NMR analysis (Fig. 2) is performed with JEOL AL300 FT-NMR. The spectrum is recorded in the range of 0–10 ppm, and the solvent used is DMSO. For SEM study of the polymer samples, HRSEM SUPRA 40, Zeiss (Germany) is used. For this study, Ap is used in the powder form, whereas the graft copolymer is studied in small granular form. Figure 3(a,b) shows the SEM of Ap and graft copolymer, respectively.

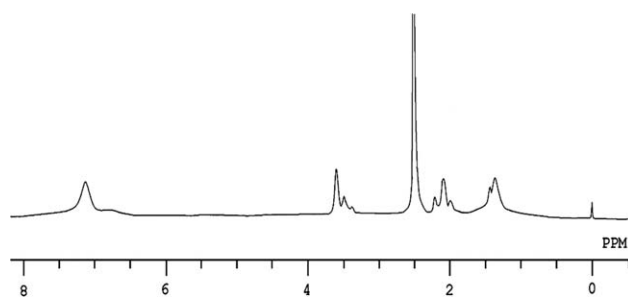
### The graft level of the graft copolymer

The percentage of grafting (PG), conversion of the monomer (C), and the grafting efficiency (GE) are calculated by following equations.<sup>21</sup>

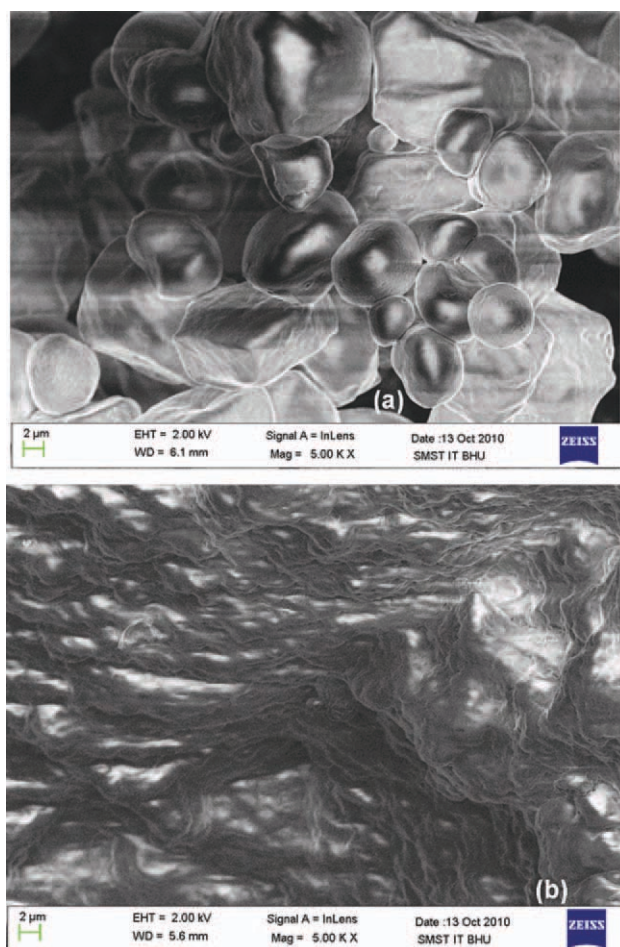
$$PG = \frac{W_G}{W_{Ap}} \times 100\% \quad (1)$$

$$C = \frac{W_{GC} + W_H}{W_M} \times 100\% \quad (2)$$

$$GE = \frac{W_{GC}}{W_M} \times 100\% \quad (3)$$



**Figure 2** NMR spectrum of Ap-g-p(AM-co-AMPS).



**Figure 3** Scanning electron micrographs of (a) Ap and (b) Ap-g-p(AM-co-AMPS). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$W_G$  = weight of the graft copolymer;  $W_{AP}$  = weight of Ap;  $W_{GC}$  = weight of grafted chains;  $W_M$  = weight of reacted monomers;  $W_H$  = weight of homopolymers.

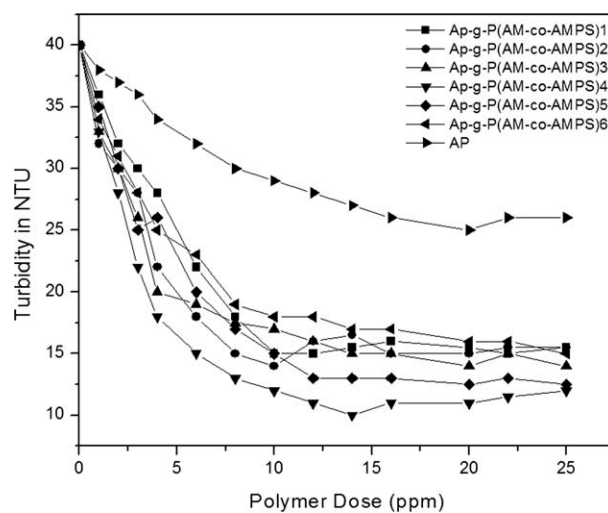
#### The intrinsic viscosity of the graft copolymer

The intrinsic viscosity of the graft copolymer is determined with an Ubbelohde viscometer (CS/S: 0.00386) at  $30 \pm 0.1^\circ\text{C}$  using the standard method to evaluate intrinsic viscosity.<sup>22</sup>

#### Anionic degree of the graft copolymer

Measurements of anionic degree (AD): a dry product sample (0.03–0.05 g) is dissolved in distilled water and titrated with a standardized solution of sodium hydroxide ( $0.01 \text{ mol L}^{-1}$ ). The following formula is used to calculate the AD of the product:

$$\text{AD (wt \%)} = \frac{207CV}{1000W} \times 100\% \quad (4)$$



**Figure 4** Comparison of flocculation characteristics of various grades of Ap-g-p(AM-co-AMPS).

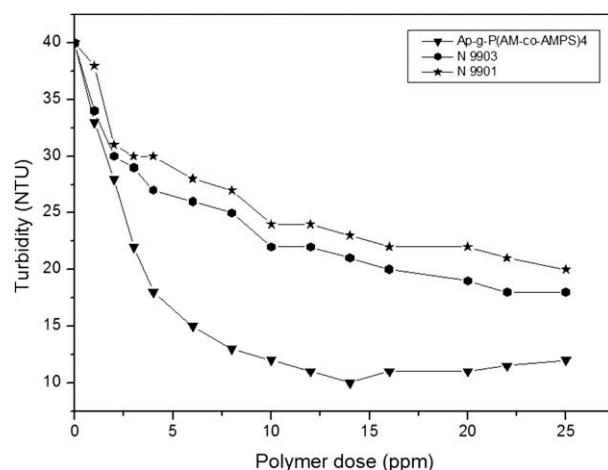
where  $C$  ( $\text{mol L}^{-1}$ ) is the molar concentration of sodium hydroxide.  $V$  (mL) is the volume of consumed sodium hydroxide for the sample,  $W$  (g) is the weight of the sample, and 207 is the molecular weight of AMPS.

#### Flocculation by jar test

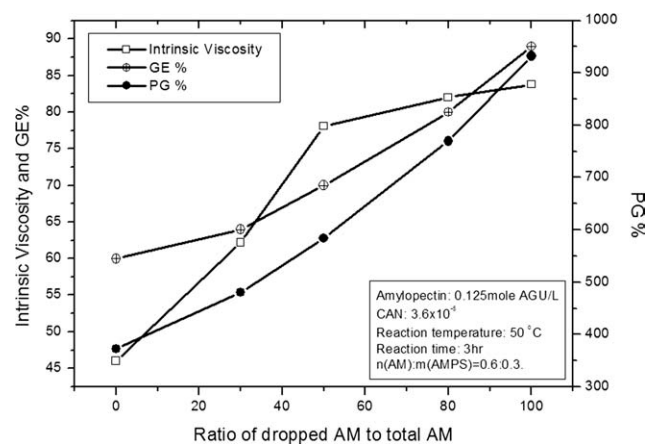
The flocculator used is supplied by SONAR, India. Turbidity measurements are carried out using Digital Naphelo Turbidity meter supplied by Bellstone Hi Tech International, Delhi, India.

The flocculation performance of various grades is compared in 1.0% kaolin suspension. The results are shown in Figure 4. Figure 5 is a comparison of flocculation efficiency with two commercial flocculants N 9901 and N 9903 which are anionic in nature. A standard jar test procedure is followed.

The suspension is put in each of six 1-L beakers, and the flocculant is added in solution form.



**Figure 5** Comparison of flocculation performance of Ap-g-p(AM-co-AMPS) 4 with commercial flocculants.



**Figure 6** Effect of the monomer addition method on grafting.

Immediately after the addition of the flocculant, the suspension is stirred at a uniform speed of 175 rpm for 2 min. This is followed by slow stirring of 125 rpm for 5 min. afterward settling time of 10 min is allowed. At the end of the settling period, the turbidity of supernatant liquid is measured using Digital Nephelo turbidity meter. The dose of flocculant is varied from 0 to 25 ppm. The turbidity of the supernatant liquid after flocculation is plotted against polymer concentration.

### Cu<sup>2+</sup> absorption study

The metal ion sorption studies were carried out with various grades of graft copolymer by taking 0.02 g (20 mg) in 10 mL of a metal ion solution of known concentration and keeping it undisturbed for 24 h. The strength of unabsorbed metal ions was determined by standard methods.<sup>23</sup> Percent uptake (Pu) and retention capacity (Qr) are calculated using the following expressions.<sup>24</sup>

$$Pu = \frac{A_{Mip}}{A_{Mif}} \times 100 \quad (5)$$

$$Qr = \frac{A_{Mip}}{A_{Dp}} \quad (6)$$

$A_{Mip}$  = amount of metal ion in polymer (mequiv);  
 $A_{Mif}$  = amount of metal ion in reaction feed;  $A_{Dp}$  = amount of dry polymer (g).

## RESULTS AND DISCUSSION

### Characterization of grafting

The results of elemental analysis of Ap and its graft copolymers are given in Table 1. Ap does not show any significant presence of nitrogen. In case of graft copolymers, it is found that there is considerable per-

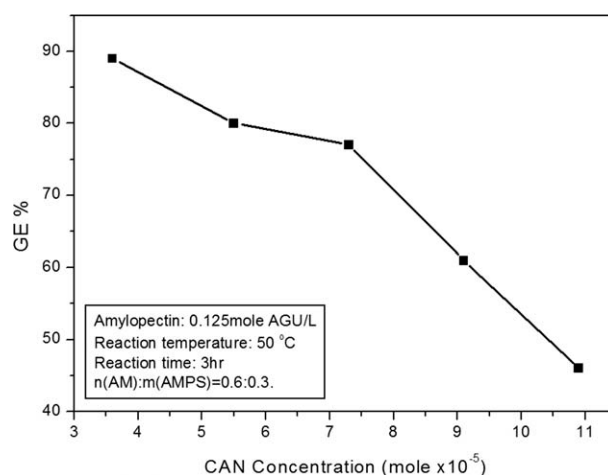
centage of nitrogen proving the grafting of PAMPS and PAM chains on the polysaccharides backbone. It is observed that the graft copolymer with molar ratio 2 : 1 Ap-g-p(AM-co-AMPS) 4 has the highest nitrogen content. Figure 1(a,b) shows the spectra of Ap and graft copolymer, respectively. In Figure 1(a), the absorption peak at 3401 cm<sup>-1</sup> is attributed to -OH stretching vibration of Ap. Absorption peak at 2932 cm<sup>-1</sup> is attributed to CH stretching vibration. In Figure 1(b), the FTIR spectrum shows the characteristic absorption peak at 3468 cm<sup>-1</sup> is attributed to -OH stretching vibration of Ap, that the characteristic absorption peak at 1653 and 1620 cm<sup>-1</sup> results from C=O stretching vibration and NH bending vibration of the -CONH<sub>2</sub> group, and that the characteristic absorption peak at 1037 cm<sup>-1</sup> is due to S=O stretching vibration of -SO<sub>3</sub><sup>-</sup> in AMPS. These results prove that Ap has been grafted with AM and AMPS.

In Figure 2, the resonances at 1.5 and 2.1 ppm are attributed, respectively, to the protons of methylene group and methine group of polyacrylamide chain. The resonances at 3.6 and 1.4 ppm are attributed, respectively, to the protons of methylene and methyl groups of -C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub> in the poly(AMPS) molecule. Resonance at 7.4 ppm is attributed to NH protons. The results prove that PAM-polyacrylamide and AMPS is found in the graft copolymer.

Figure 3(a,b) shows the scanning electron micrographs of Ap and graft copolymer. Surface morphology of Ap before grafting shows a granular structure, which has been changed to fibrillar form after grafting. Thus, comparison of these figures reveals the changes due to grafting.

### Effect of the addition method

In graft copolymerization of Ap with AM and AMPS, using a batch process may lead to a high ratio of AM-AMPS in the copolymer chains in the



**Figure 7** Effect of CAN concentration on grafting.

**TABLE II**  
Effect of the Mixed Monomer Concentration on Grafting

S. no	Polymer	AM (mol L <sup>-1</sup> )	AMPS (mol L <sup>-1</sup> )	PG (%)	C (%)	GE (%)	[η] (dL g <sup>-1</sup> )	Anionic degree (%)
1	Ap-g-p(AM-co-AMPS) 1	0.28	0.15	546	82	78	67.7	24
2	Ap-g-p(AM-co-AMPS) 2	0.42	0.24	664	85	83	74.2	27
3	Ap-g-p(AM-co-AMPS) 3	0.5	0.26	774	88	86	79.1	30
4	Ap-g-p(AM-co-AMPS) 4	0.6	0.3	932	91	89	83.8	33
5	Ap-g-p(AM-co-AMPS) 5	0.64	0.31	880	80	80	81.8	34
6	Ap-g-p(AM-co-AMPS) 6	0.70	0.34	864	73	72	76.5	37

Amylopectin: 0.125 mol AGU L<sup>-1</sup>; CAN: 3.6 (mol × 10<sup>-5</sup>); reaction temperature: 50°C; reaction time: 3 h.

initial stages. The composition drift is severe, and the uneven charge distribution in the copolymer can adversely effect its applications. Consequently, the graft copolymer is synthesized in a modified batch process.<sup>14</sup> First, all AMPS and a part of AM are added, and then remainder of AM is dropped into the system at a rate of 1.0 mL min<sup>-1</sup> after the reaction is initiated. The intrinsic viscosity increases with increase in amount of AM and is shown in Figure 6. Experiments show that in this method anionic monomer is consumed successively with prolongation of reaction time, and the charge of the polymer is well distributed. When the AM monomer of high activity is continuously added, the graft copolymerization is carried out more easily, and therefore, the amount of AM homopolymers may decrease. Thus, by controlling the addition rate of AM, a constant composition of the chains of Ap-graft-poly(AM-co-AMPS) could be obtained.

#### Effect of the initiator concentration on grafting

Keeping all other reaction variables same, the effect of amount of initiator on grafting reaction is examined. The relationship between GE of the product and the amount of initiator used is understood from Figure 7. The GE is found to decrease with increase in CAN concentration. This can be explained by the fact that the increase of amount of initiator causes the increase of homopolymerization reaction.

#### Effect of the concentration and the ratio of two monomers on grafting

The concentration and the ratio of two monomers are important parameters affecting the properties of the copolymer. These parameters are related to the grafting level and the anionic degree of the copolymer. Various grades Ap-g-p(AM-co-AMPS) 1 to Ap-g-p(AM-co-AMPS) 6 are synthesized by varying the molar ratio of two monomers. The effects are shown in Table II. Keeping the appropriate ratio of AM to AMPS, the grafting percentage, the GE increase with the increase in total concentration of monomers, which changes in the range of 0.43–1.04 mol L<sup>-1</sup>. When the mixed monomer concentration increases over 0.9 mol L<sup>-1</sup>, the grafting percentage and the GE decrease with the increase in total concentration of the monomers. This can be ascribed to the following fact that increasing the monomer concentration is beneficial to the diffusion of monomer molecules to radical site on the backbone, thus leading to an increase in PG and GE. Also beyond a limiting value of monomer concentration, grafting is not favorable. The reasons might be that radical transfer from Ap macroradical to monomer molecules leads to increase in the homopolymer and copolymer p(AM-co-AMPS) concentration and decrease in the concentration of graft copolymer. Hence, PG and GE decrease.

Estimate of anionic degree of all the grafted grades is also done in Table II. With higher concentration of AMPS higher anionic degree is observed.

**TABLE III**  
Metal Ion (Cu<sup>2+</sup>) Sorption Studies

S. no.	Polymer	% Grafting	Percent uptake (Pu)	Retention capacity (Qr) (mequiv g <sup>-1</sup> )
1	Ap		2.8	0.2
2	Ap-g-p(AM-co-AMPS) 1	546	7.1	0.7
3	Ap-g-p(AM-co-AMPS) 2	664	8.2	0.9
4	Ap-g-p(AM-co-AMPS) 3	774	9.1	1.2
5	Ap-g-p(AM-co-AMPS) 4	932	10	1.4
6	Ap-g-p(AM-co-AMPS) 5	880	8.1	0.8
7	Ap-g-p(AM-co-AMPS) 6	864	6.3	0.6

### Flocculation test

The flocculation performance of the polysaccharide and various grades of graft copolymer Ap-g-p(AM-co-AMPS) 1 to Ap-g-p(AM-co-AMPS) 6 with different monomer ratio are compared by jar test in kaolin suspension as shown in Figure 4. It is observed that the graft copolymers show better flocculation performance than the polysaccharide and the grade with molar ratio 2 : 1 Ap-g-p(AM-co-AMPS) 4 is showing best flocculation performance. The reason for better flocculating power of the graft copolymers over the linear polymers like polysaccharides is for effective bridging.<sup>18</sup> Figure 5 is a comparison between commercial flocculants N 9901 and N 9903, and the best performing flocculant obtained from the previous comparison among various grades. It is observed that Ap-g-p(AM-co-AMPS) 4 outperforms commercial flocculants.

### Metal ion sorption study

Results of metal ion ( $\text{Cu}^{2+}$ ) absorption studies are summarized in Table III. It is observed that the percent ion uptake and retention capacity increase with increase in value of percentage of grafting and maximum is observed in case of Ap-g-p(AM-co-AMPS) 4 which may be due to increased pendent poly(AMPS) chain onto Ap.

### CONCLUSIONS

The graft copolymerization of Ap with AM and AMPS has been carried out by solution polymerization technique in nitrogen atmosphere and using CAN as initiator. By controlling the addition rate of AM, a constant composition of the chains of Ap-graft-poly(AM-co-AMPS) could be obtained. Appropriate molar ratio of 2 : 1 of two monomers AM and AMPS has lead to graft copolymer with maximum intrinsic viscosity. Study of FTIR and NMR spectra has provided strong proof of grafting. SEM study has revealed a major difference in structure. The flocculation performance of graft copolymer in kaolin suspension has been estimated. It has been observed that the graft copolymer Ap-g-p(AM-co-

AMPS) 4 having maximum intrinsic viscosity and highest nitrogen content has outperformed other graft copolymer grades as well as the parent polysaccharide. The graft copolymer has also shown better flocculation efficiency than various commercial flocculants.  $\text{Cu}^{2+}$  absorption studies with various grades of graft copolymer have shown that Ap-g-p(AM-co-AMPS) 4 with maximum GE exhibits better results.

### References

1. Kurenkoy, V. F.; Verihzinkova, A. S.; Myagchenkov, V. A. *Euro Polym J* 1984, 20, 357.
2. Wang, W.; Zhang, Y.; Zhu, M.; Chen, Y. *J Appl Polym Sci* 2008, 109, 1699.
3. Wang, W.; Zhang, Y.; Chen, Y. *Iran Polym J* 2007, 16, 195.
4. Wang, W.; Zhang, Y.; Chen, Y. *Polymer (Korea)* 2007, 31, 385.
5. Kathmann, E. E.; White, L. A.; McCormick, C. L. *Macromolecules* 1996, 29, 5268.
6. Yamamoto, H.; Tomatsu, I.; Hashidzume, A.; Morishima, Y. *Macromolecules* 2000, 33, 7852.
7. Karlsson, L. E.; Jannasch, P.; Wesslen, B. *Macromol Chem Phys* 2002, 203.
8. McCormick, C. L. *J Macromol Sci Part A* 1985, 22, 955.
9. Aggour, Y. A. *Polym Degrad Stab* 1993, 44, 71.
10. Durmaz, S.; Okay, O. *Polymer* 2000, 41, 3693.
11. Pareta, R.; Edirisinghe, M. J. *Carbohydr Polym* 2006, 63, 425.
12. Araújo, M. A.; Cunha, A. M. *Biomaterials* 2004, 25, 2687.
13. Rath, S. K.; Singh, R. P. *Colloids Surf A* 1998, 139, 129.
14. Song, H.; Zhang, S. F.; Ma, X. C.; Wang, D. Z.; Yang, J. Z. *Carbohydr Polym* 2007, 69, 189.
15. McCormick, C. L.; Park, L. S. *J Polym Sci* 1984, 22, 49.
16. Adhikary, P.; Tiwari, K. N.; Singh, R. P. *J Appl Polym Sci* 2007, 103, 773.
17. Krishnamoorthi, S.; Mal, D.; Singh, R. P. *Carbohydr Polym* 2007, 69, 371.
18. Singh, R. P.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Tripathy, T.; Panda, J.; Kanan, K.; Jain, S. K.; Lan, N. T. *Polym Eng Sci* 2000, 40, 46.
19. Adhikary, P.; Krishnamoorthi, S.; Singh, R. P. *J Appl Polym Sci* 2011, 120, 2621.
20. Cao, Y. F.; Yang, J. Z.; Liu, Z. L. *J Chem Indus Eng* 2004, 55, 325.
21. Gao, J. P.; Yu, J. G.; Wang, W. *J Appl Polym Sci* 1998, 68, 1965.
22. Krishnamoorthi, S.; Adhikary, P.; Mal, D.; Singh, R. P. *J Appl Polym Sci* 2010, 118, 3539.
23. Basset, J.; Denny, R. C.; Jeffery, G. H.; Mendham, J. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed.; William Clowes & Sons: Becales and London, 1978; p 324.23.
24. Rivas, B. L.; Maturana, H. A.; Molina, M. J.; Gomez-Anton, M. R.; Pierola, I. F. *J Appl Polym Sci* 1998, 67, 1109.