

Grafted Polysaccharides Based on Acrylamide and *N,N*-Dimethylacrylamide: Preparation and Investigation of Their Flocculation Performances

Haradhan Kolya, Tridib Tripathy

Postgraduate Division of Chemistry, Midnapore College, West Bengal 721101, India

Correspondence to: T. Tripathy (E-mail: tridib_tripathy@yahoo.co.in)

ABSTRACT: The graft copolymerization of *N,N*-dimethylacrylamide (DMA) and acrylamide (AM) were carried out onto different polysaccharide backbones separately. The graft copolymers were synthesized by ceric ion induced redox polymerization technique. Three polysaccharides were used, namely hydroxyethyl starch (HES), hydroxyethyl cellulose (HEC) and Amylopectin (AP), for the grafting reactions. Among the three polysaccharides, HEC has linear structure, while HES and AP have a branch one. The graft copolymers were characterized by intrinsic viscosity measurements, FTIR spectroscopy, NMR (both ^1H and ^{13}C) spectroscopy, and thermal analysis. Flocculation performances of the graft copolymers were evaluated in 1 wt % kaolin and in 0.25 wt % iron ore suspensions. A detailed comparative study of the flocculation properties of the synthetic graft copolymers was also made. It showed that graft copolymers based on DMA were better flocculants than those based on AM. Among the synthetic graft copolymers, HES-*g*-Poly (DMA) performed best when compared with the other synthetic graft copolymers as well as to the commercial flocculants in the same suspensions. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: grafting; flocculation; *N,N*-dimethylacrylamide; hydroxyethyl starch; hydroxyethyl cellulose

Received 13 July 2011; accepted 28 February 2012; published online

DOI: 10.1002/app.37603

INTRODUCTION

The process of the flocculation^{1,2} is the aggregation of small particles in a liquid suspension into larger masses called flocs. Inorganic flocculants commonly referred to as coagulants, were used before but they are less effective.³ However, organic polymeric flocculants are much more effective and are extensively used for the treatment of industrial effluents and mineral processing.^{4,5} Polymeric flocculants are convenient for use and do not affect the pH of the medium. They are used in very small quantities, and the flocs formed during flocculation are bigger and stronger.³ Anionic, cationic, and nonionic synthetic as well as natural polymers were widely used. It is well known that the polyacrylamide (PAM) and its copolymers are good flocculants for the mineral beneficiation process and the treatment of mineral industries. However, the serious drawback of PAM lies in the fact that it is shear degradable. Among the flocculating agents, a class of graft copolymers has been developed recently by grafting synthetic polymers onto natural polysaccharides.^{6–11} This class of graft copolymers is reasonably shear stable due to the presence of shear stable polysaccharide backbone.¹² The flocculation performance of this type of graft copolymers is

enhanced compared with PAM itself because of the approach¹³ of the flexible PAM chains onto rigid polysaccharide backbones to the contaminant particles in the industrial effluent or solid suspension. Hence, it is possible to develop efficient and shear stable flocculants¹⁴ by grafting PAM chains onto polysaccharides.

Poly(*N,N*-dimethylacrylamide) (PDMA) is highly water soluble, biocompatible,¹⁵ and its copolymer was used in oil recovery.¹⁶ Graft copolymer based on DMA and polysaccharide^{17,18} and the flocculation performance of *k*-carrageenan-*g-N,N*-dimethylacrylamide in coal suspension have been reported recently.¹⁸ But no attempt has been made to investigate the flocculation performance of graft copolymers based on DMA and polysaccharides in detail. Between acrylamide (AM) and DMA, the latter has two methyl groups at the 'N' atom, which increases the electron density and hence polarity of the amide functionality as the methyl group has electron donating effect. Again in polymeric chain of the AM the $-\text{NH}_2$ groups take part in intramolecular hydrogen bonding with the $\text{C}=\text{O}$ groups of the neighboring amide groups, which reduce the water solubility of the PAM graft

© 2012 Wiley Periodicals, Inc.

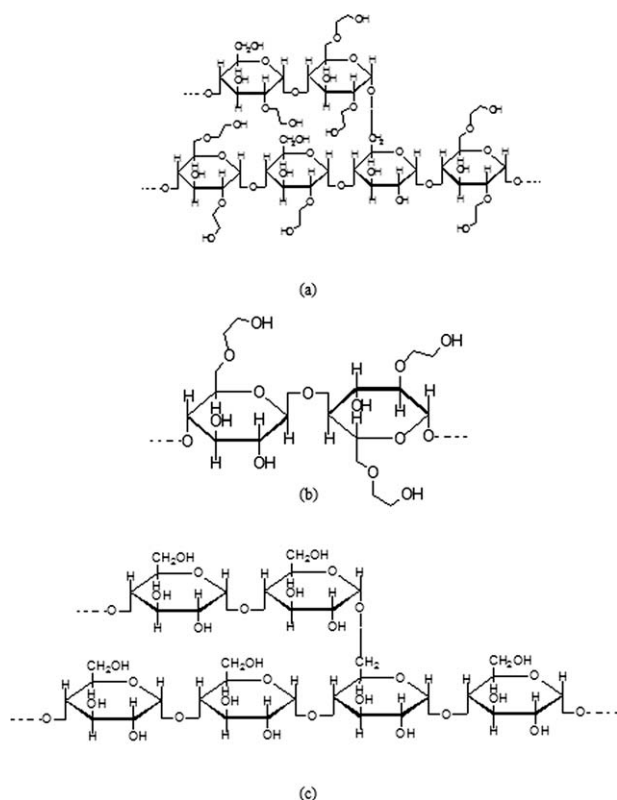


Figure 1. Structures of polysaccharides (a) HES, (b) HEC, and (c) AP.

copolymers to some extent. However, no such intramolecular hydrogen bonding is possible in the PDMA, which makes easy water soluble.¹⁹

We chose to carry out a study to investigate the effect of methyl groups at the 'N' atom of the amide groups on the flocculation performance of the graft copolymers based on polysaccharides and DMA in detail. Three polysaccharides were chosen for the grafting reaction with DMA namely hydroxyethyl starch (HES), hydroxyethyl cellulose (HEC), and amylopectin (AP).

Among the three polysaccharides, HES and AP have branch structure and HEC has the linear structure. HES is a derivative of AP, containing only branched chains of glycoside molecules, lack of a linear component.²⁰ Their structures were given in Figure 1.

EXPERIMENTAL

Materials

HES, HEC, AP, and DMA were procured from Aldrich chemical company, USA. The degree of substitution of HES is 0.1 and that of HEC is 0.3. DMA was purified by vacuum distillation and the middle fraction was used for the study. Ceric ammonium nitrate (CAN), PAM (M.W. = 5×10^6), Acetone were obtained from Loba Chemie (Bombay, India). AM and sodium nitrate were supplied by E. Merck (Bombay, India). Iron ore slime was obtained from TISCO mine, (Bihar, India). Kaolin clay was obtained from Famous Minerals and Chemical (Mumbai, India). The average particle size of kaolin clay is 79.6 nm, and the suspension zeta potential is -3.9 mV at pH 7.6. The

average particle size of iron ore slime is 104.6 nm and the suspension zeta potential is -31.72 mV at pH 7.2. Magnafloc 1011 was obtained from BASF India (Mumbai, India). Telfloc-2230 was obtained as a gift from Balaji Paper & Newsprint (Manikpara, W.B, India). The commercial flocculants are PAM based linear homopolymers and their structures are totally classified by their manufacturer. Doubly distilled water was used for the synthesis. PDMA (M.W. is the order of 10^6) was procured from Scientific Polymer Product, USA.

Synthesis of the Graft Copolymer

The graft copolymers of polysaccharides and DMA were synthesized by the use of ceric ion induced redox initiation method.²¹ The typical experimental details for one graft copolymer involving HES and DMA are as follows; 1.5 g of HES was dissolved in 100 mL of distilled water at 100°C with constant stirring and bubbling of nitrogen for about 15 min. Ten milliliters (0.109 moles) of DMA was added to the HES solution. Then nitrogen gas was purged through the solution for 20 min and at this stage 40 mL of the required CAN solution was added to the reaction mixture followed by further purging with nitrogen for 15 min. The reaction was allowed to continue for 24 h after which it was terminated by adding saturated solution of hydroquinone. At the end of the reaction, the polymer was precipitated by adding excess quantities of acetone. The homopolymer PDMA was removed by Soxhlet extraction using methanol as a solvent. The precipitated polymer was then dried under vacuum. Afterwards it was pulverized and sieved. The PAM grafted polysaccharides were also synthesized by ceric ion induced redox initiation method under the similar condition as stated above. The detailed synthetic process was given in our previous article.⁷ The synthetic details of all the graft copolymers are given in Tables I and II.

Isolation of Grafted PDMA and PAM Chains

The grafted PDMA chains were isolated by hydrolyzing the graft copolymers in 70% (v/v) H_2SO_4 ²² for 12 h at boiling point. The mixture was poured into excess acetone and hexane mixture (1 : 1 by volume). The PDMA thus precipitated was redissolved in water and precipitated again in acetone and hexane mixture. The PDMA was dried in vacuum. The grafted PAM chains were also isolated from the polysaccharides backbone by treatment with 70% (v/v) aqueous sulfuric acid for 24 h at the temperature of 25°C . The mixture was poured into excess acetone and the PAM precipitated was redissolved in water and reprecipitated in acetone. Then it was dried in vacuum. The graft copolymers, the isolated PDMA and PAM were used for the IR study.

Characterization of the Graft Copolymers

Viscosity Measurement. Viscosity measurement of polymer solutions was carried out using an Ubbelohde viscometer (constant = 0.00527) at 27°C . The viscosities were measured in aqueous 1M NaNO_3 solution. The flow time was measured for the solutions at five different concentrations. The intrinsic viscosity was calculated by plotting η_{sp} versus c and η_{inh} versus c ; and then taking the common intercept at $c = 0$ of the best fitted straight lines through the two sets of points.²³ Here, c is the polymer

Table I. Synthetic Details of the Graft Copolymers Based on DMA

Polymer	Polysaccharide (g)	DMA (mol)	Amount of CAN (mol × 10 ⁻⁴)	Percentage of conversion ^a	Grafting ratio ^b (% G)	Intrinsic viscosity (dL/g)
AP-g-PDMA	1.5	0.109	4.564	83.86	703.33	7.1
HES-g-PDMA	1.5	0.109	4.564	84.21	706.66	7.4
HEC-g-PDMA	1.5	0.109	4.564	83.76	702.66	7.3

^aPercentage conversion is calculated from the relation, % conversion = [(wt of graft copolymer – wt of polysaccharide)/amount of DMA] × 100, ^bGrafting ratio (% G) is calculated from the relation % G = (wt of grafted polymer/wt of polysaccharide) × 100.

concentration in g/dL; η_{sp} and η_{inh} are the specific and inherent viscosity calculated from the following equations.

$$\eta_{rel} = t/t_0$$

where η_{rel} is the relative viscosity, t is the time of flow of the solution and t_0 is the time of flow of solvent (here water) at the same temperature $\eta_{sp} = (t - t_0)/t_0$ $\eta_{inh} = \ln \eta_{rel}/c$. The values of intrinsic viscosities of all the graft copolymers are given in Tables I and II.

FTIR-Spectroscopy. The homopolymer PDMA was removed from all the PDMA graft copolymers by Soxhlet extraction using methanol as solvent. The homopolymer PAM was also removed by the same procedure using a mixture of formamide and acetic acid (1 : 1 by volume)²⁴ from the PAM graft copolymers. Then the graft copolymers, PDMA and PAM were subjected to IR spectral analysis. A Perkin-Elmer-883 Infrared spectrophotometer (UK) was used and the potassium bromide (KBr) pellet method was followed for IR spectrum. The spectra are shown in Figures 2 and 3. The IR spectra of the isolated PDMA chains from the PDMA graft copolymer and the isolated PAM from the PAM graft copolymers are also shown in Figures 2 and 3.

NMR-Spectroscopy. Both ¹H-NMR and ¹³C-NMR spectral analysis of all the graft copolymers based on DMA and AM were carried out with a 500 MH NMR instrument (JEOL, Tokyo, Japan) in D₂O solvent at 25°C. The spectra are shown in Figures 4 and 5.

Thermal Analysis

The thermal analysis (TGA) of all the graft copolymers based on DMA and AM along with the homopolymers PDMA and PAM was carried out with Stanton Red Croft (STA625) thermal analyzer. TG analysis of the samples was performed up to a

temperature of 700°C starting from 10°C in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10° min⁻¹ the TGA curves are shown in Figures 6 and 7.

Flocculation Study

Flocculation Jar Test⁴ was carried out in standard flocculation Jar apparatus supplied by Scientific Engineering Corporations (New Delhi, India). Turbidity measurements were carried out with a Digital Nephelo Turbidity meter (Model-331, cell width 275 × 175 × 125 mm, light source 6 V Tungsten lamp) procured from EI Products (Haryana, India). Both the flocculation and turbidity measurement were carried out at 27°C. The detailed flocculation procedure was given in our previous article.⁷ A 1.0 wt % kaolin clay and 0.25 wt % iron ore slime were used for flocculation studies. The dose of flocculant varied in the range of 1–10 ppm for iron ore slime and 1–8 ppm for kaolin clay suspension.

RESULTS AND DISCUSSION

Synthesis and Intrinsic Viscosity of the Graft Copolymers

The synthetic details of the graft copolymers are shown in Tables I and II. Six graft copolymers were synthesized namely HES-g-PDMA, HEC-g-PDMA, and AP-g-PDMA using DMA as the monomer and HES-g-PAM, HEC-g-PAM, and AP-g-PAM using AM as the monomer keeping all the reaction parameters constant. The mechanism of ceric ion action involves the formation of a chelate complex that decomposes to generate free-radical sites on the polysaccharide backbone. These active free-radical sites in the presence of acrylic monomers generate graft copolymers. The reaction parameters were fixed according to our previous experience.⁷

It is known that the intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn is a function of the polymer molecular weight, its structure, nature

Table II. Synthetic Details of the Graft Copolymers Based on AM

Polymer	Polysaccharide (g)	AM (mol)	Amount of CAN (mol × 10 ⁻⁴)	Percentage of conversion ^a	Grafting ratio ^b (% G)	Intrinsic Viscosity (dL/g)
AP-g-PAM	1.5	0.140	4.564	84.88	665.86	7.6
HES-g-PAM	1.5	0.140	4.564	84.11	660.73	7.8
HEC-g-PAM	1.5	0.140	4.564	83.81	658.73	7.2

^aPercentage conversion is calculated from the relation, % conversion = [(wt of graft copolymer – wt of polysaccharide)/amount of AM] × 100, ^bGrafting ratio (% G) is calculated from the relation % G = (wt of grafted polymer/wt of polysaccharide) × 100.

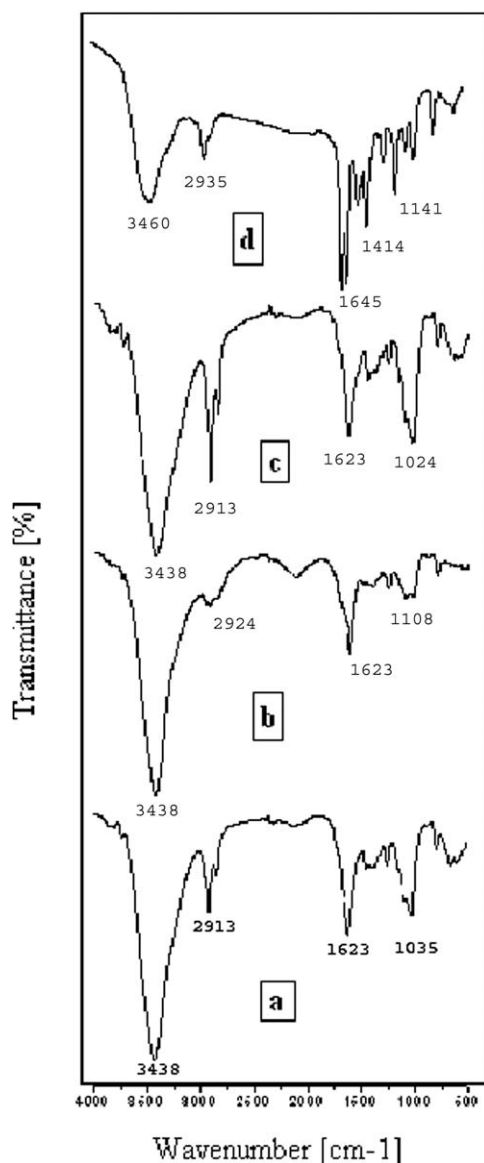


Figure 2. FTIR Spectra of (a) HES-g-PDMA, (b) HEC-g-PDMA, (c) AP-g-PDMA, and (d) PDMA.

of the solvent, and the temperature of the medium. Keeping the other factors constant, two polymers of approximately similar intrinsic viscosity will have approximately similar molecular weight.²⁵

FTIR Spectroscopy

The grafting is supported by IR spectroscopy. The IR spectra of HES-g-PDMA, HEC-g-PDMA, AP-g-PDMA, and PDMA are shown in Figure 2. The IR spectrum of PDMA [Figure 2(d)] shows a peak at 1645 cm^{-1} for amide $\text{C}=\text{O}$ group, the peak at 1414 cm^{-1} is for C—N group, a peak at 2935 cm^{-1} is for aliphatic C—H group. The peak at 3460 cm^{-1} is due to the presence of absorbed moisture. The graft copolymer HES-g-PDMA [Figure 2(c)] shows characteristic absorption on 1623 cm^{-1} for amide $\text{C}=\text{O}$ group, 1457 cm^{-1} is for the C—N group and 3438

cm^{-1} for the —OH groups of the polysaccharide backbone present in the graft copolymers. Since the DMA and PDMA were removed, the presence of peaks at 3438, 1623, and 1457 cm^{-1} in the graft copolymer is a strong evidence for grafting. Similar results are also obtained in the other graft copolymers HEC-g-PDMA and AP-g-PDMA with slight variation of the peak values [Figure 2(b,c)].

In Figure 3, the IR spectrum of HES-g-PAM, HEC-g-PAM, AP-g-PAM, and PAM are shown. Here, the peaks that remain in PAM molecule [Figure 3(d)] at 3355 and 3185 cm^{-1} for —NH₂ group, 1670 cm^{-1} for amide $\text{C}=\text{O}$ group, 1421 cm^{-1} for C—N group are also present in the graft copolymer HES-g-PAM at 2924, 1655, and 1445 cm^{-1} [Figure 2(a)]. Since the AM and PAM were removed, the presence of peaks at 2924, 1655, and 1445 cm^{-1} in the graft copolymer is a strong evidence for the grafting. Similar results are also obtained in the other PAM grafted polysaccharides namely HEC-g-PAM and AP-g-PAM

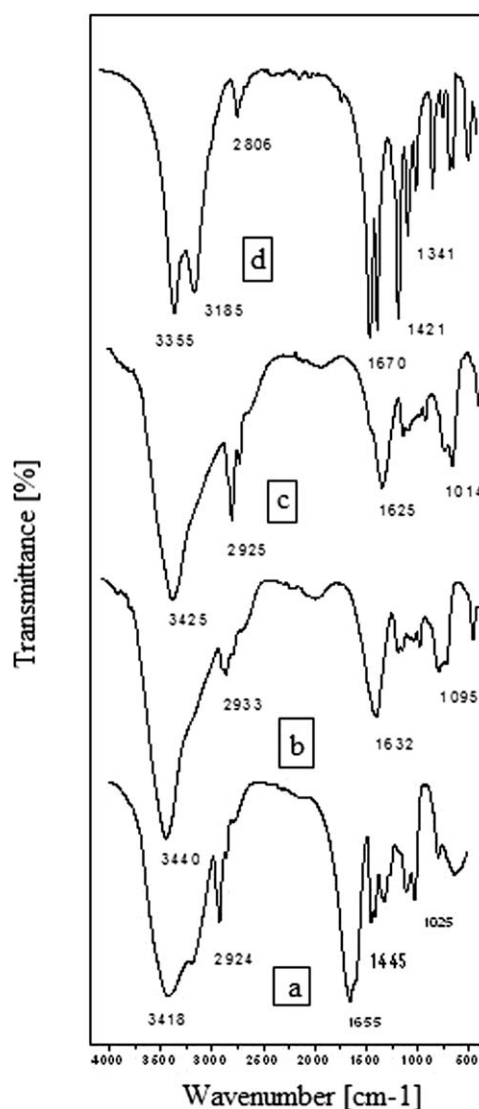


Figure 3. FTIR Spectra of (a) HES-g-PAM, (b) HEC-g-PAM, (c) AP-g-PAM, and (d) PAM.

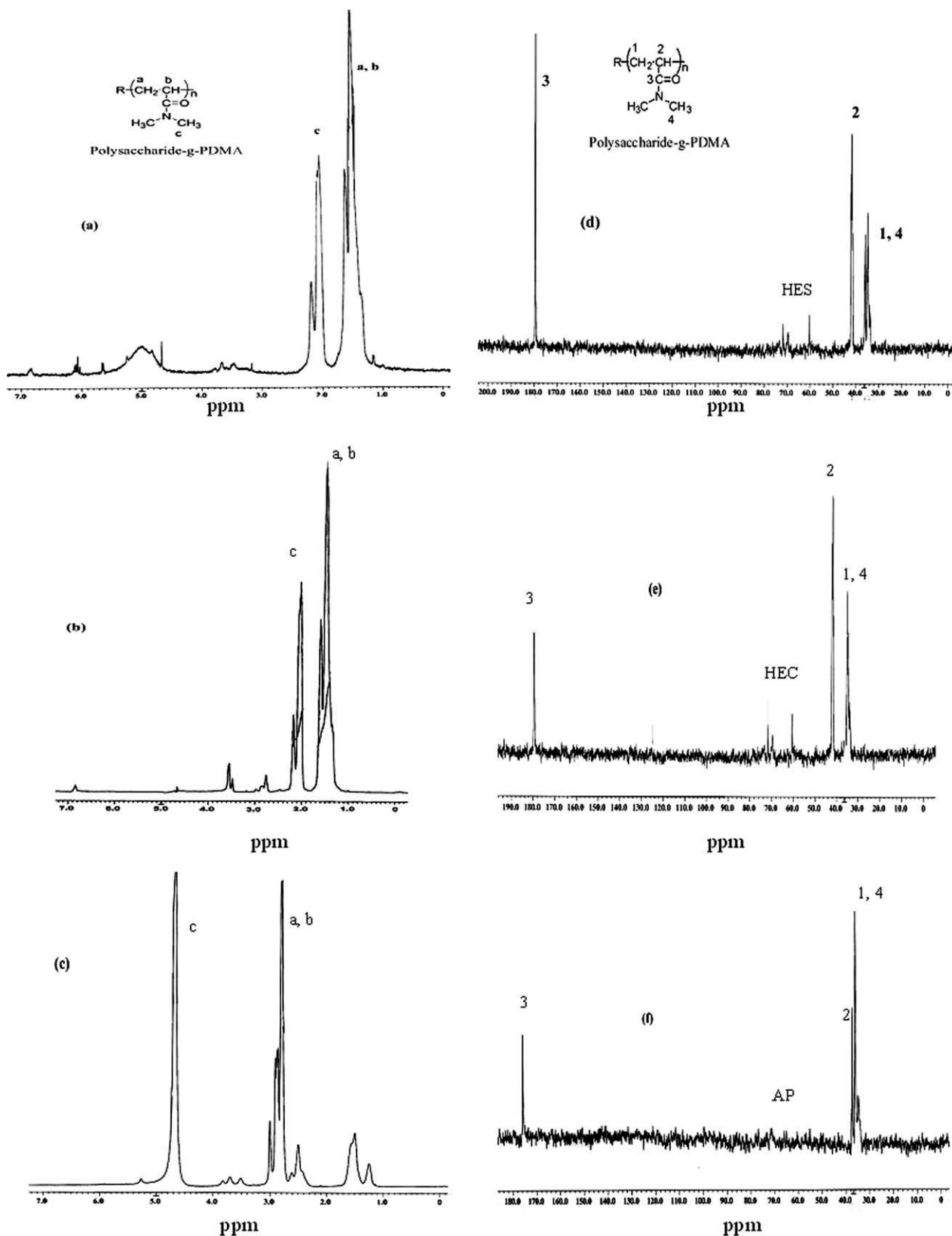


Figure 4. ^1H -NMR and ^{13}C -NMR spectrum of (a, d) HES-g-PDMA, (b, e) HEC-g-PDMA, and (c, f) AP-g-PDMA.

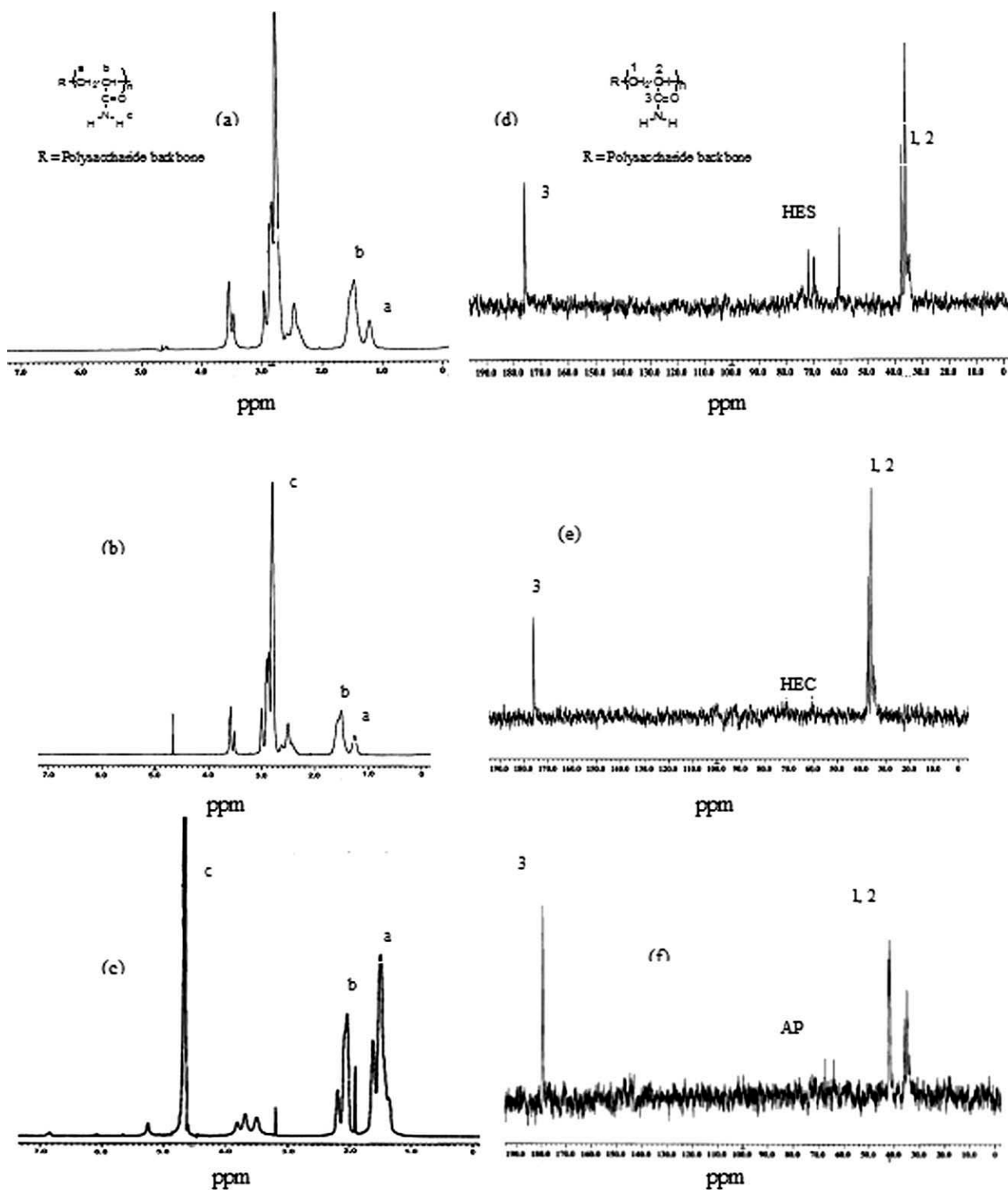


Figure 5. ^1H -NMR and ^{13}C -NMR spectrum of (a, d) HES-g-PAM, (b, e) HEC-g-PAM, and (c, f) AP-g-PAM.

with slight variation of the peak values as shown in Figure 3(b,c), respectively.

NMR-Spectroscopy

Figure 4(a) shows the ^1H -NMR spectrum for the HES-g-PDMA in D_2O at 25°C . The bands at 2.0–2.8 ppm are attributed to the

methyl proton and those observed at 1.3–1.8 ppm are due to the $-\text{CH}_2-$ and $-\text{CH}-$ protons. Figure 4(d) shows a ^{13}C -NMR spectrum for HES-g-PDMA in D_2O at 25°C . The characteristic peak for PDMA moieties is observed at 35 ppm, which is due to the CH_3- group. The peak at 60–75 ppm are due to the

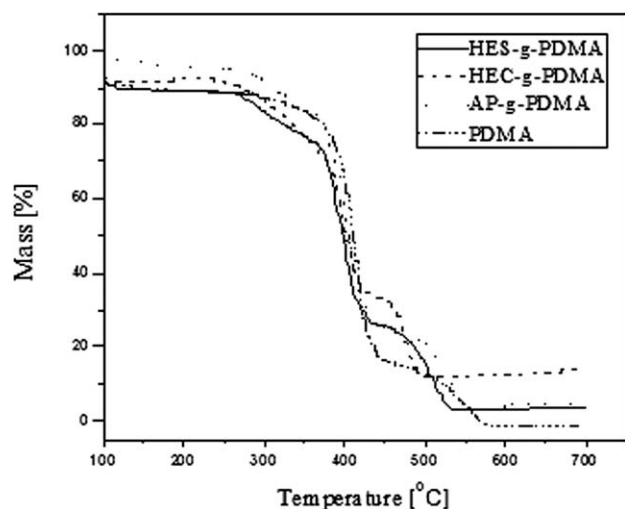


Figure 6. TGA curves of HES-g-PDMA, HEC-g-PDMA, AP-g-PDMA, and PDMA.

carbon for HES backbone and the peak appears at 180 ppm is due to the carbon of the carboxylic group. Similar results are obtained in the other graft copolymers HEC-S-PDMA [Figure 4(b,e)] and AP-g-PDMA [Figure 4(c,f)] with slight variation of peak values.

In Figure 5(a) the $^1\text{H-NMR}$ spectrum of HES-g-PAM is shown. The peaks observed at 2.3–3.0 ppm are due to the NH_2 group. The peak at 1.2 ppm is due to the $-\text{CH}_2-$ proton and at 1.7 ppm is due to the $-\text{CH}$ proton. $^{13}\text{C-NMR}$ spectrum of HES-g-PAM is shown in Figure 5(d). Here, the peak at 176 ppm is due to the $\text{C}=\text{O}$ group of amide, at 30–40 ppm is due the $-\text{CH}_2-$ and $-\text{CH}$ carbon and 60–80 ppm is due to the carbon for the HES back bone. Similar results are obtained in case of other graft copolymers namely HEC-g-PAM and AP-g-PAM with

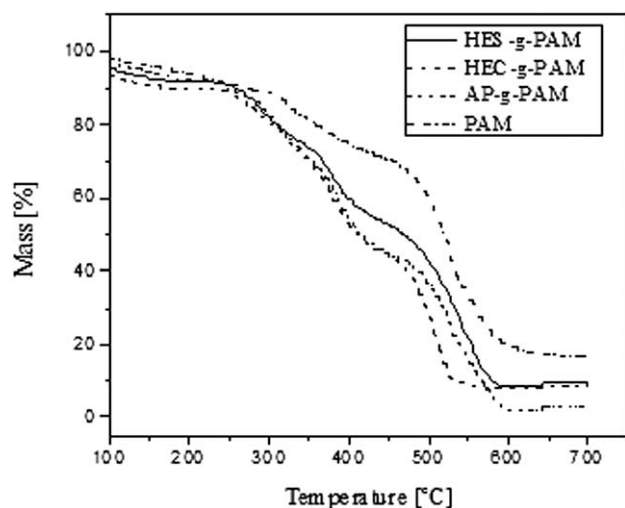


Figure 7. TGA curves of HES-g-PAM, HEC-g-PAM, AP-g-PAM, and PAM.

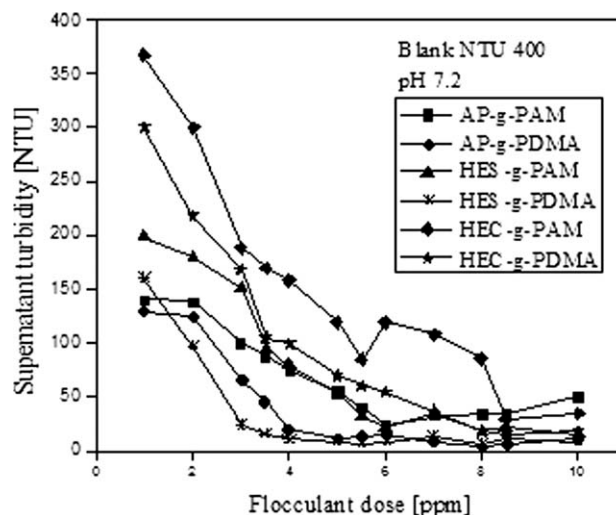


Figure 8. Comparison of flocculation characteristics of AP-g-PAM and AP-g-PDMA; HES-g-PAM and HES-g-PDMA and HEC-g-PAM and HEC-g-PDMA in 0.25 wt % iron ore slime suspension.

slight variation at peak values as shown in Figure 5(b,c,e,f), respectively.

Thermal Analysis

The TGA curves of HES-g-PDMA, HEC-g-PDMA, AP-g-PDMA, and PDMA are shown in Figure 6. In all the three graft copolymers, four distinct zones are observed where the weight is being lost. The weight loss at $\sim 220^\circ\text{C}$ is due to the elimination of water by the degradation of polysaccharide backbones. No degradation occurs in case of PDMA at this temperature range. Decarbonylation (elimination of CO) occurs at $\sim 340\text{--}350^\circ\text{C}$. The decomposition at $\sim 440^\circ\text{C}$ is due to the loss of Me_2NH group from the PDMA chains. In the last zone the weight loss might be due the loss of abundant hydroxyl groups in the polysaccharide in the form of water.²⁶ Similar results are also obtained from the TGA curves of HES-g-PAM, HEC-g-PAM, AP-g-PAM, and PAM, as shown in Figure 7. Except PAM, four degradation zones are observed in all the three graft copolymers. The weight loss in the third zone at $\sim 420\text{--}430^\circ\text{C}$ is due to the loss of NH_3 from PAM chains. From the TG results, it can be concluded that PDMA and PAM chains are successfully grafted onto the polysaccharide backbones.

Flocculation Study

The flocculation efficiencies of the synthesized graft copolymers were tested in 1.0 wt % of kaolin clay and 0.25 wt % of iron ore slime suspensions. The results are shown in Figures 8–13. In each case, the turbidity of supernatant liquid after flocculation was plotted against the polymer concentration. The flocculation properties of AP-g-PDMA was compared with AP-g-PAM; HES-g-PDMA was compared with HES-g-PAM and HEC-g-PDMA was compared with HEC-g-PAM in iron ore and kaolin clay suspension as depicted in Figure 8 for iron ore and Figure 9 for kaolin clay suspension, respectively. In the above two cases, graft copolymers based on DMA showed better performance than those based on AM. In all cases, the performance of a particular flocculants was expressed in terms of turbidity. The lower the

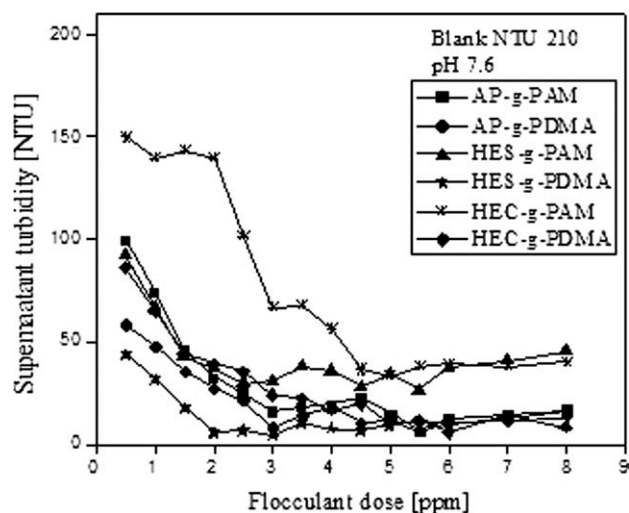


Figure 9. Comparison of flocculation characteristics of AP-g-PAM and AP-g-PDMA; HES-g-PAM and HES-g-PDMA and HEC-g-PAM and HEC-g-PDMA in 1.0 wt % kaolin clay suspension.

turbidity, the better the performance will be. The reason for the better flocculation performance of PDMA grafted polysaccharides will be as follows.

The major mechanisms of flocculation of polyelectrolytes are surface charged neutralization and bridging. Surface charged neutralization occurs, if the charge of flocculant is opposite in sign to that of the suspended particles. For neutral flocculants, the major mechanism of flocculation is the polymer bridging. When very long chain polymer molecules are absorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may also dangle. These loops and ends may come into contact with, and attach to other particles. This is the bridging mode of flocculation. Essentially, a polymer bridging occurs because segments of a polymer chain get absorbed in various

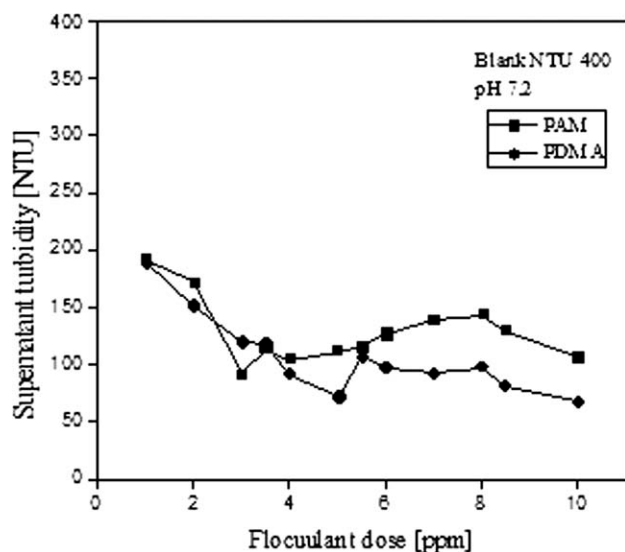


Figure 10. Comparison of flocculation characteristics of PAM and PDMA in 0.25 wt % iron ore slime suspension.

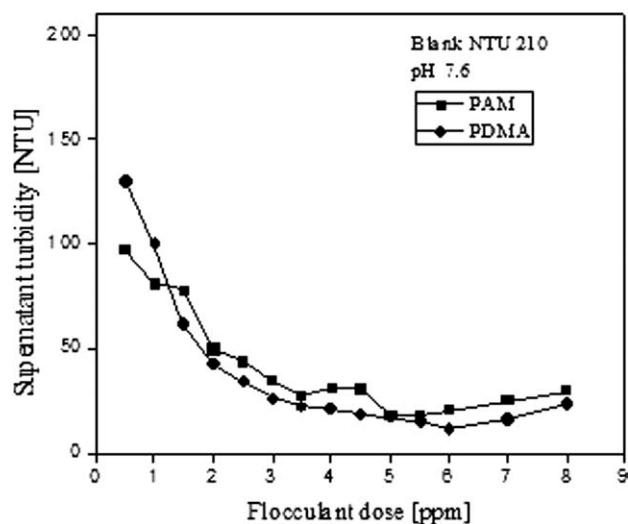


Figure 11. Comparison of flocculation characteristics of PAM and PDMA 1.0 wt % kaolin clay suspension.

particles, thus bringing the particles together. For effective bridging to occur, there must be a sufficient polymeric chain length, which extends far enough from the particle surface to attach to other particles and the flexibility of the polymeric chains.

In water medium, in the PAM chains, strong intramolecular hydrogen bonding between the $-\text{CO}$ and $-\text{NH}_2$ groups occurs, which makes the chain stiffen and helical.²⁷ Thus, the approachability of the grafted PAM chains to the contaminant particle becomes less. But in case of PDMA chains, the intramolecular hydrogen bonding does not occur. The absence of hydrogen bonding increases the flexibility of the grafted PDMA chains. So, in the PDMA grafted polysaccharides due to the better flexibility of the dangling grafted PDMA chains, the approachability of the grafted chains to the colloidal particles becomes easier than that of the grafted PAM chains. Hence, for PDMA grafted

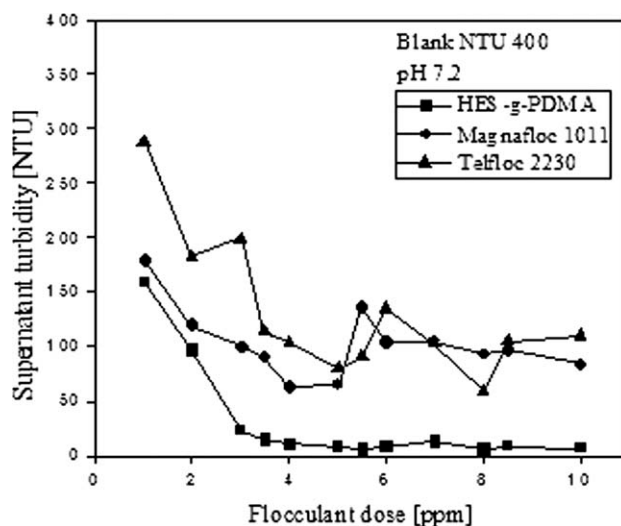


Figure 12. Comparison of flocculation characteristics of HES-g-PDMA, Magnafloc 1011 and Telfloc 2230 in 0.25 wt % iron ore slime suspension.

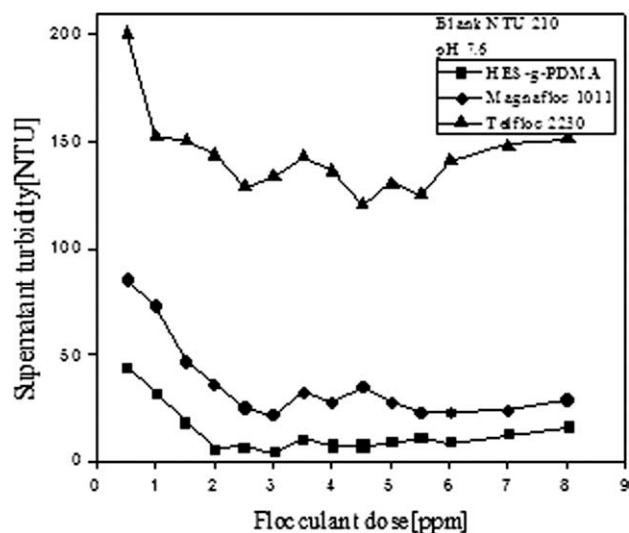
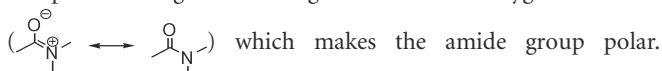


Figure 13. Comparison of flocculation characteristics of HES-g-PDMA, Magnafloc 1011 and Telfloc 2230 in 1.0 wt % kaolin clay suspension.

polysaccharides bridging will be better and easier than that of PAM grafted polysaccharides.

Again, in the amide functionality ($\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\text{N}\langle$) the electron delocalization of the lone pair of nitrogen into the adjacent carbonyl group places a partial positive charge on the nitrogen atom and a partial negative charge on the oxygen atom²⁸



Hence, the colloidal particles are attracted by the amide groups in a polymer chain irrespective of surface charges (Zeta potential) of the suspended colloidal particles. The polarity of $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\text{NMe}_2$ group (present in DMA molecule) is higher than that of the $\text{—}\text{CONH}_2$ group (present in AM molecule) due to the presence of electron donating methyl ($\text{—}\text{Me}$) groups at the nitrogen atom of the former, which helps the absorption of the colloidal particles into the grafted PDMA chains resulting strong bridging. For this effective intense bridging capabilities of the PDMA chains, PDMA grafted polysaccharides showed better flocculation performance over PAM grafted polysaccharides. This finding is further supported by the following fact. When the flocculation performance of the homopolymer PAM and PDMA were compared in both the iron ore and kaolin suspension it was observed that the performance of PDMA is better than the PAM. The results are shown in Figures 10 and 11, respectively.

The flocculation performances of the three synthesized graft copolymers were compared in iron ore and kaolin clay suspension also. From the Figures 8 and 9, it is obvious that the flocculation performance follows the order HES-g-PDMA > AP-g-PDMA > HEC-g-PDMA in both the cases. Between HES and AP, the former contains polar hydroxy ethyl groups (Figure 1), which further help the bridging mechanism because of which HES-g-PDMA shows better performance than AP-g-PDMA. Between HEC-g-PDMA and HES-g-PDMA, the latter shows bet-

ter result although both have hydroxy ethyl groups. Because of the branch structure of HES, it shows better performance in flocculation than the linear polysaccharide HEC. This is in accordance with the previous study.⁸

In Figures 12 and 13, the flocculation performance of the best performing graft copolymer HES-g-PDMA was compared with two commercially available flocculants Telfloc-2230 and Magnafloc-1011 in iron ore slime and kaolin clay suspensions respectively. From the figures, it is obvious that HES-g-PDMA showed better performance than the two commercial flocculants. The commercial flocculants are PAM based linear polymer; hence, their performance is inferior to the graft copolymers. The results were in accordance with previous studies^{6–10,13,14} where it was explained that the graft copolymers show better flocculation performance over linear polymers in various synthetic suspensions.

CONCLUSIONS

From the above investigations, the following conclusions can be drawn. Polysaccharides-g-PDMA and polysaccharides-g-PAM were synthesized by ceric ion induced redox polymerization technique in aqueous solution. Studies of IR, NMR spectra, and TGA of the graft copolymers after extracting the homopolymers provide strong proof of grafting. The flocculation efficiencies of the graft copolymers of polysaccharides and PDMA are better than the graft copolymers of polysaccharides and PAM. The graft copolymer, HES-g-PDMA showed better performance than the other PDMA grafted polysaccharides as well as some commercial flocculants. Hence, by grafting PDMA chains onto different polysaccharide backbone effective flocculating agents can be developed for the treatment of wastewater.

REFERENCES

- Rose, G. R., Sr.; John, M. R. In *Flocculation*. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F., Ed.; Wiley: New York, **1987**; Vol. 7, p 211.
- Hudson, H. E., Jr. *AWWA* **1957**, 49, 1721.
- Halverson, F.; Panzer, H. P. In *Encyclopedia of Chemical Technology*, 3rd ed.; Mark, H. F., Othmer, D. F., Overberger, C. G., Seaberg, G. I., Eds.; Wiley: New York, **1980**; Vol. 10.
- Bratby, J. *Coagulation and Flocculation*; Uplands Press: Croydon, UK, **1980**; Chapter 8.
- Gregory, J. *The Effect of Polymers on Dispersion Properties*; Tadros, Th.F., Ed.; Academic Press: London, **1987**; Chapter 8.
- Tripathy, T.; Singh, R. P. *J. Appl. Polym. Sci.* **2001**, 81, 3296.
- Tripathy, T.; Pandey, S. R.; Karmakar, N. C.; Bhagat, R. P.; Singh, R. P. *Eur. Polym. J.* **1999**, 35, 2057.
- Rath, S. K.; Singh, R. P. *J. Appl. Polym. Sci.* **1997**, 66, 1721.
- Karmakar, G. P.; Singh, R. P. *Colloids Surf. A* **1998**, 113, 119.
- Tripathy, T.; Karmakar, N. C.; Singh, R. P. *Int. J. Polym. Mater.* **2000**, 46, 81.

11. Pal, S.; Mal, D.; Singh, R. P. *J. Appl. Polym. Sci.* **2007**, *105*, 3240.
12. Wunderlich, T.; Stelter, M.; Tripathy, T.; Nayak, B. R.; Brenn, G.; Yarin, A. L.; Singh, R. P. *J. Appl. Polym. Sci.* **2000**, *77*, 3200.
13. Singh, R. P. In *Advanced Turbulent Drag Reducing and Flocculating Materials Based on Polysaccharides*; Prasad, P. N., Mark, E., Fai, T. J., Ed.; Plenum Press: New York, **1995**; p 227.
14. Singh, R. P.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Tripathy, T.; Pandey, S. R.; Kannan, K.; Jain, S. K.; Lan, N. T. *Polym. Eng. Sci.* **2000**, *40*, 46.
15. Kataoka, K.; Miyazaki, H.; Okano, T.; Sakurai, Y. *Macromolecules* **1994**, *27*, 1061.
16. McCormick, C. L.; Chen, G. S. *J. Polym. Sci. Part A: Polym. Chem.* **1984**, *22*, 3633.
17. Tripathy, J.; Mishra, D. K.; Yadav, M.; Behari, K. *Carbohydr. Polym.* **2010**, *79*, 40.
18. Mishra, D. K.; Tripathy, J.; Behari, K. *Carbohydr. Polym.* **2008**, *71*, 524.
19. Shriner, R. L.; Hermann, C. K. F.; Morrill, T. C.; Curtin, D. Y.; Fuson, R. C. *The Systematic Identification of Organic Compounds*; Wiley: New York, **2004**; p 119.
20. Cerny, L. C.; Graham, R. C.; James, H. J. R. *J. Appl. Polym. Sci.* **1941**, *11*, 1967.
21. Mino, G.; Kaizerman, S. *J. Polym. Sci.* **1958**, *31*, 242.
22. Yan, L.-F.; Taow, J. *Biomed. Sci. Eng.* **2008**, *1*, 37.
23. Collins, E. A.; Bares, J.; Billmeyer, F.W., Jr. *Experiments in Polymer Science*; Wiley: New York, **1973**; p 394.
24. Fanta, G. F. In *Synthesis of Graft and Block Copolymer of Starch*; Ceresa, R. J., Ed.; Wiley: New York, **1973**; Vol. 1, p 11.
25. Wales, M.; Marshall, P. A.; Weissberg, S. G. *J. Polym. Sci.* **1952**, *X2*, 229.
26. Tripathy, T.; Singh, R. P. *J. Appl. Polym. Sci.* **2001**, *81*, 3296.
27. Kulicke, W. M.; Kniewske, R.; Klein, J. *Prog. Polym. Sci.* **1982**, *8*, 373.
28. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: UK, **2001**; p 293.