

Synthesis, Characterization and Application of Novel Polyacrylamide-grafted Barley

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ABSTRACT: Polyacrylamide-grafted barley (BAR-g-PAM) was synthesized by ceric ion-based conventional method. The grafting of polyacrylamide chains on the polysaccharide backbone was confirmed through various physicochemical techniques such as intrinsic viscosity measurement, ^{13}C -NMR spectra, FTIR spectroscopy, elemental analysis, scanning electron microscopy morphology, thermogravimetric analysis study, number-average molecular weight, and aqueous solubility. Furthermore, flocculation efficacy of the graft copolymers was studied in coal fine suspension through “jar test” procedure, toward its possible application as a novel flocculant for treatment of coal washery effluent. BAR-g-PAM is reported as a novel flocculant that can be used for bulk treatment of coal washery effluents. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41046.

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INTRODUCTION

Barley (*Hordeum vulgare* L.) is a well-known natural dietary fiber and a complex carbohydrate. In barley, the total carbohydrate content is 80.2% and remaining components are protein and fats.¹ The known component of dietary fiber in barley is β -glucans, which is insoluble in water. β -Glucans is a polysaccharide of D-glucose monomers linked by β -glycosidic bonds.² The significant amount of carbohydrate in barley is starch, which consists of 25–30% amylose while the major component is extensively branched amylopectin.³ Amylose is a linear polymer made up of D-glucose units and amylopectin is highly branched polymer of glucose made up with α (1→4) glycosidic bonds by glucose unit.⁴ Barley ranks fourth after maize, rice, and wheat as a cultivated product. It is a part of natural healthy food.^{5,6} The easy availability, low cost, and widespread usage since times immemorial make it a popular and natural choice to prepare beverages, as food, and animal feed.^{7,8} Apart from these uses, we have tried this material to be used as a flocculant for water treatment. This choice of material is based on its low cost, food-grade nature hence safe for metabolism, as well as possibility to be developed as a popular flocculant that can be used safely for bulk water treatment in any part of the world.

Water treatment is an integral part of any industrial treatment before final discharge of effluents or for recycling purposes also.

Coal mining and processing is no exception to it.^{9–12} The removal of coal fines from coal washery effluent is carried out by using the coagulants (e.g., alum) but owing to their large dosage, nonbiodegradability, and long settling time required,¹³ there is a need to replace them by better counterparts like flocculants.

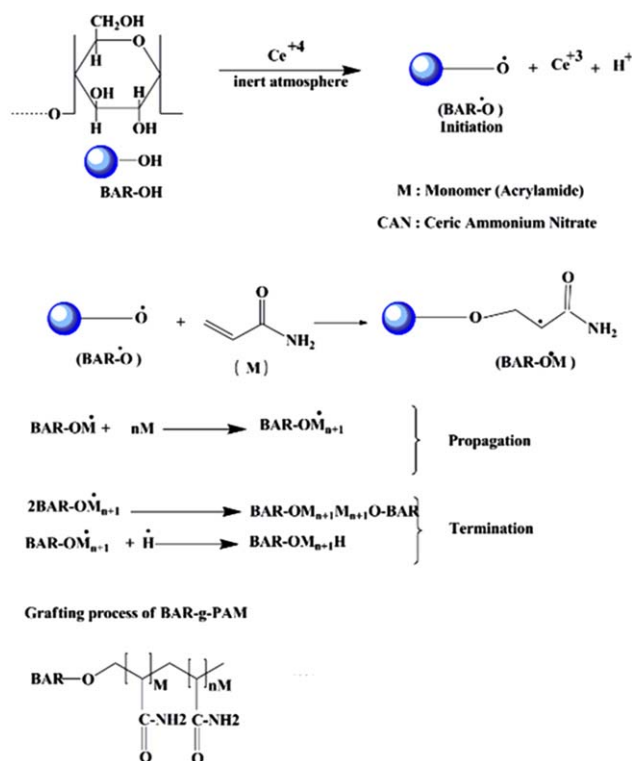
Flocculants are very effective for the separation of the colloidal particles even in minute dosage¹⁴ and are environmentally benign. They may be natural (e.g., polysaccharides) or synthetic (e.g., polyacrylamide). Natural flocculants need high dosage and have shorter shelf life. However, they form flocs with high shear stability. Synthetic flocculants require less dosage owing to their relatively high molecular weight and large surface area. However, synthetic flocculants result in fragile flocs with the colloidal particles. Also, for the removal of suspended solids from the coal washery effluent, wastewater, and river water, flocculation aided by synthetic and semisynthetic flocculants continues to be a very effective strategy.^{13,15–19}

Polyacrylamide is a polymer of acrylamide monomer. It is soluble in polar solvents and is nontoxic in nature. Polyacrylamide has also been reported to be used as a flocculant for waste water treatment.^{20–22}

Grafting of natural polysaccharides and synthetic polymers results in formation of highly branched hybrid polymeric materials with advantages of both the classes as flocculants.²³

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Schematic representation of mechanism for synthesis of BAR-g-PAM using “conventional method.” [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Among the widely available polysaccharides, barley occupies a prominent place. Yet, reports of chemical modification of this agricultural product are scarce. Nothing has been reported yet regarding grafting of barley to the best of our knowledge.

In this investigation, we have reported the grafting of polyacrylamide (PAM) chains on the backbone of barley in the reaction mixture, thus resulting in synthesis of polyacrylamide-grafted barley (BAR-g-PAM). The synthesis has been carried out by conventional method^{24,25} using ceric ammonium nitrate (CAN) to initiate the grafting reaction. The synthesized grafted product has been characterized by various physicochemical techniques followed by its assessment as flocculant in coal fine suspension for its possible usage as a flocculant for the treatment of coal washery effluent.

Table I. Synthesis Details of BAR-g-PAM

Polymer grade	Wt. of barley (g)	Wt. of acryl amide (g)	Wt. of CAN (g)	% Grafting (%G)	% Grafting efficiency (%GE)	Intrinsic viscosity (dL/g)	Number-average molecular weight (kDa)
Barley	–	–	–	–	–	1.83	176.6
BAR-g-PAM 1	1	10	0.1	922.3	92.23	6.88	3255
BAR-g-PAM 2	1	10	0.2	993.6	99.36	8.53	4080
BAR-g-PAM 3	1	10	0.3	824.4	82.44	6.01	2481.66
BAR-g-PAM 4	1	5	0.2	398.4	79.68	5.9	1625
BAR-g-PAM 5	1	15	0.2	1410.2	93.46	10.6	7778

MATERIALS AND METHODS

Materials

Barley was procured from Reckitt Benckiser, New Delhi, India, and acrylamide was supplied by CDH, New Delhi, India. CAN was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received without further purification.

Synthesis

Synthesis of Graft Copolymer by “Conventional Method” (Using CAN as a Free Radical Initiator) (BAR-g-PAM). Grafting reaction was carried out by ceric ion-induced redox initiation method.²⁶ The details of the synthesis and reaction conditions are as follows:

One gram of barley was dissolved in 40 ml distilled water with constant stirring and purging with nitrogen gas. Desired amount of acrylamide was dissolved in 10 ml distilled water and added to the above solution and mixed well. The oxygen-free nitrogen gas was purged through the solution mixture followed by addition of catalytic amount of CAN of desired concentration and the nitrogen purging was continued. Consequently, the reaction vessel was left undisturbed, stoppered, and left for 24 h. The reaction temperature was maintained at room temperature throughout. Subsequently, the gel-like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and dried in hot air oven, pulverized, sieved, and purified (as explained in the next section). The reaction followed the mechanistic pathway as shown in Scheme 1. Various grades were obtained by varying the reaction parameters. The percentage grafting (%G) and percentage grafting efficiency (%GE)²⁷ of this conventionally synthesized BAR-g-PAM were evaluated as

$$\%G = \frac{\text{Wt. of graft copolymer} - \text{Wt. of polysaccharide}}{\text{Wt. of polysaccharide}} \times 100$$

$$\%GE = \frac{\text{Wt. of graft copolymer} - \text{Wt. of polysaccharide}}{\text{Wt. of monomer}} \times 100.$$

The synthesis details of various grades of the graft copolymer are shown in Table I.

Purification of the Graft Copolymer by Solvent Extraction Method. Any occluded polyacrylamide formed by competing homopolymer formation reaction was removed from the graft copolymer synthesized as above, by extraction with acetone for 24 h.^{28–31} The mechanism of synthesis of the graft copolymer is summarized in Scheme 1.

Characterization

Intrinsic Viscosity Measurement. Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm) at 25°C. The viscosities were measured in aqueous solutions. The pH of the solution was neutral. The time of flow for solutions was measured at four different concentrations (0.1, 0.05, 0.025, and 0.0125%). From the time of flow of polymer solutions (t) and that of the solvent (t_0 , for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity (η_{sp}), relative viscosity (η_{rel}), reduced viscosity (η_{red}), and inherent viscosity (η_{inh}) were mathematically calculated as:

$$\begin{aligned}\eta_{sp} &= \eta_{rel} - 1 \\ \eta_{red} &= \eta_{sp} / C \\ \eta_{inh} &= \ln \eta_{rel} / C,\end{aligned}$$

where C represents polymer concentration in g/dL.

The reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were simultaneously plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (i.e., η_{red} versus C and $\ln \eta_{inh}$ versus C) to zero concentration.³² The intrinsic viscosity thus evaluated for various grades of the graft copolymer is reported in Table I. The relation between intrinsic viscosity and percentage grafting is graphically depicted in Supporting Information Figure F1.

Elemental Analysis. The elemental analysis of barley and BAR-g-PAM 5 (best grade of the grafted barley synthesized) was undertaken with an Elemental Analyzer (Make—M/s Elementar, Germany; Model—Vario EL III). The estimation of four elements, i.e., carbon, hydrogen, nitrogen, and oxygen, was undertaken. The results are summarized in Supporting Information Table S1.

FTIR Spectroscopy. The FTIR spectra of barley [Figure 1(a)] and BAR-g-PAM 5 [Figure 1(b)] were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} . The important FTIR peaks of barley and BAR-g-PAM 5 are reported in Supporting Information Table S3.

Scanning Electron Microscopy. Surface morphology of barley [Figure 2(a)] and BAR-g-PAM 5 [Figure 2(b)] was analyzed by scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

TGA Studies. The thermogravimetric analysis (TGA) of barley, polyacrylamide, and the BAR-g-PAM 5 was carried out with TGA instrument (Model: DTG-60; Shimadzu, Japan). The study was performed in an inert atmosphere (nitrogen) from 25 to 800°C. The heating rate was uniform in all cases at 5°/min. The combined TGA curve of barley, polyacrylamide, and BAR-g-PAM 5 is shown in Figure 3.

Determination of Number-Average Molecular Weight. The number-average molecular weights of barley and various grades

of BAR-g-PAM was determined in aqueous medium by Osmometer (A+ Adv. Instruments, Model 3320, Osmometer).

¹³C-NMR Spectroscopy. The ¹³C-NMR spectra of barley, polyacrylamide, and BAR-g-PAM(5) in solid state was measured at 500 MHz on a Advance Bruker 500MHz spectrometer.

Solubility in Aqueous Solution. The solubility of barley and the synthesized grades of BAR-g-PAM was determined in aqueous medium at room temperature by standard gravimetric procedure. The aqueous medium used was of neutral pH. The aqueous solubility for barley and various grades of BAR-g-PAM has been correlated with their respective percentage grafting in Supporting Information Figure F1.

Determination of Particle Size. The particle size of coal fine was determined in aqueous by light scattering measurement using Malvern Inst., UK; Nano ZS. Measurement angle is 173°.

Flocculation Study in Coal Fine Suspension

Flocculation studies were carried out in 1% coal-fine suspension (particle size range: 295.3–3091 nm) by standard “jar test” procedure.

Flocculation experiments of all synthesized grades of BAR-g-PAM, barley (starting material), polyacrylamide (commercial flocculant), and alum (coagulant) were carried out in jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 mL) of the 1% coal-fine suspension in six 1-L borosil beakers. Calculated amount of the flocculant was added in concentrated solution form (except blank) to achieve the desired flocculant dosage (from 0 to 1.25 ppm in increments of 0.25 ppm). The solutions were identically stirred in “jar test” apparatus, at 150 rpm for 30 s, 60 rpm for 5 min, followed by 5 min of settling time. Afterward, supernatant liquid was collected from each jar and optical density was measured by using spectrophotometer (DR/2400, Hach®) at λ_{max} 520 nm. The flocculation efficacy thus studied for barley and all the synthesized grades of BAR-g-PAM has been compared graphically in Figure 4.

RESULTS AND DISCUSSION

Synthesis

Synthesis of BAR-g-PAM by Conventional Method. BAR-g-PAM has been synthesized by conventional method.^{16,17,25} It refers to the synthesis of graft copolymer initiated by chemical-free radical initiator, CAN in this case.

Various grades of BAR-g-PAM were synthesized by varying the CAN and monomer (acrylamide) concentration. The synthesis details are tabulated in Table I. The optimized grade has been determined through its higher percentage grafting, intrinsic viscosity, and number-average molecular weight. The approach of synthesis involved optimization with respect to CAN, keeping the acrylamide concentration constant (i.e., BAR-g-PAM 1, BAR-g-PAM 2, and BAR-g-PAM 3), followed by optimization with respect to acrylamide, keeping the CAN concentration as optimized before (i.e., BAR-g-PAM 2, BAR-g-PAM 4, and BAR-g-PAM 5). From Table I, it is obvious that the grafting is optimized at acrylamide concentration of 15 g and CAN concentration of 0.2 g in the reaction mixture (~50 mL).

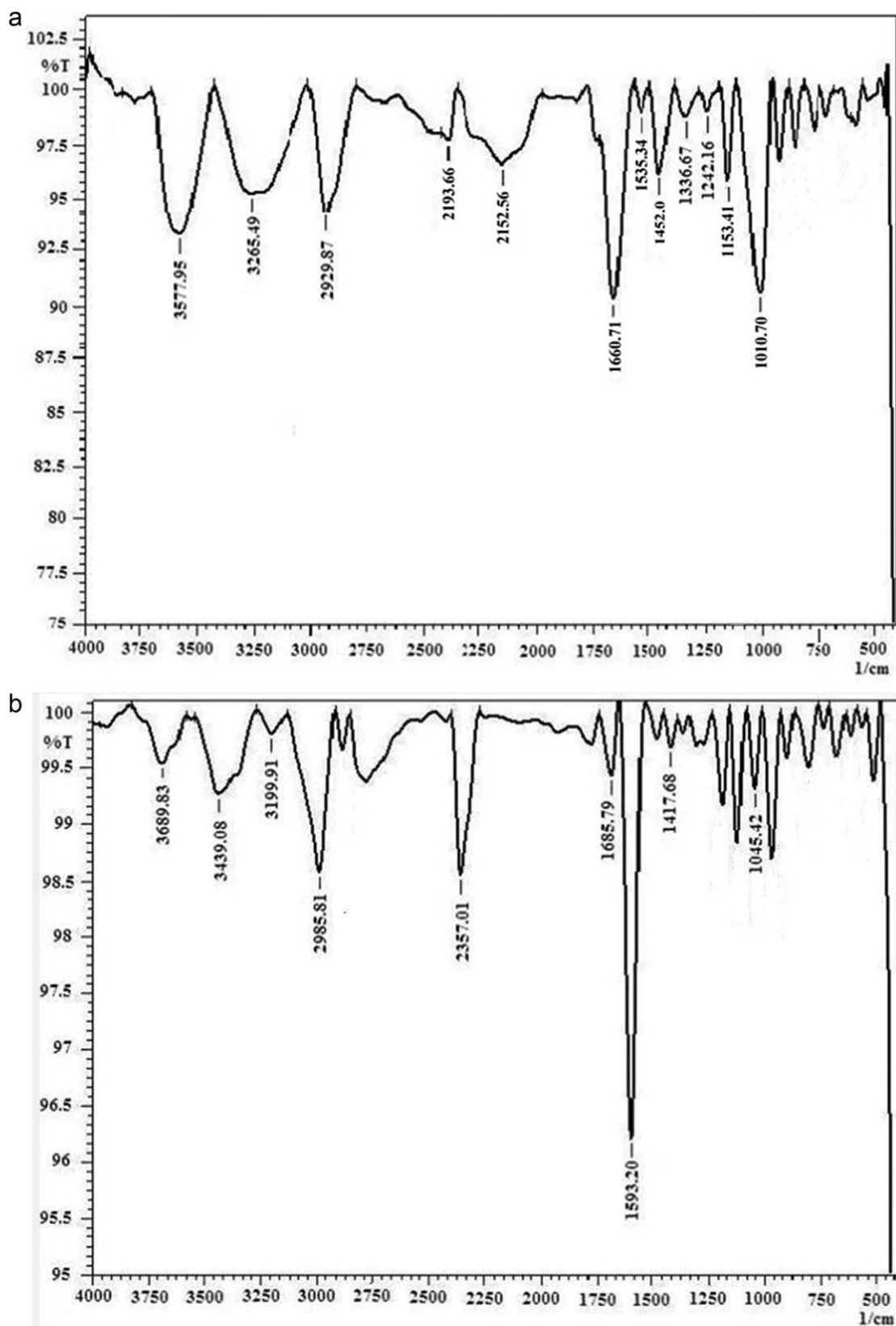


Figure 1. (a) FTIR spectrum of barley. (b) FTIR spectrum of BAR-g-PAM 5.

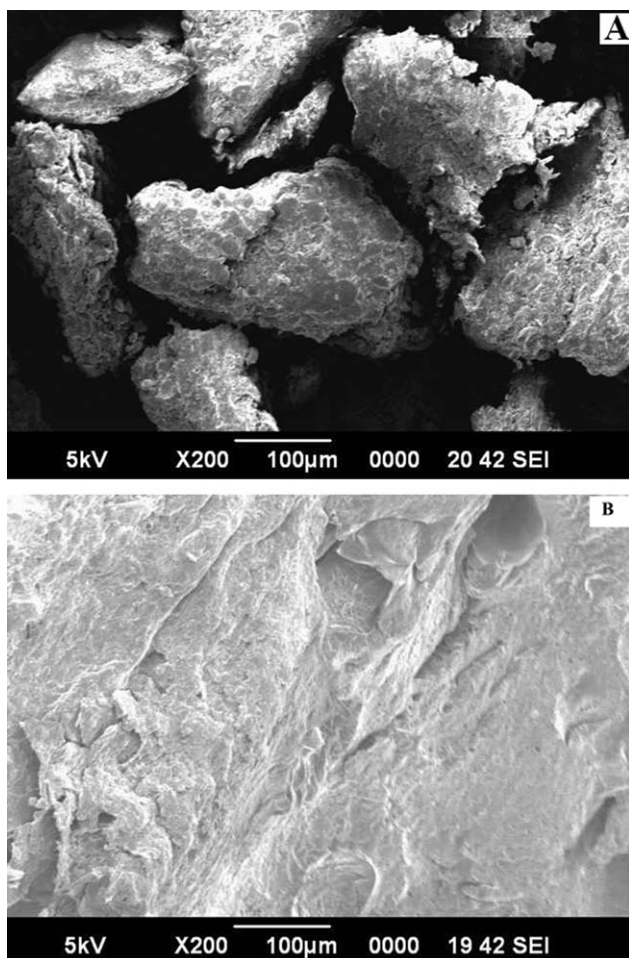


Figure 2. (a) SEM morphology of barley ($\times 200$ magnification). (b) SEM morphology of BAR-g-PAM 5 ($\times 200$ magnification).

The mechanism by which Ce (IV) ion generates free radical sites on the backbone of barley proceeds via direct oxidation in the reaction mixture.³¹ These active free radical sites are occupied by acrylic monomers to generate graft copolymers. Based

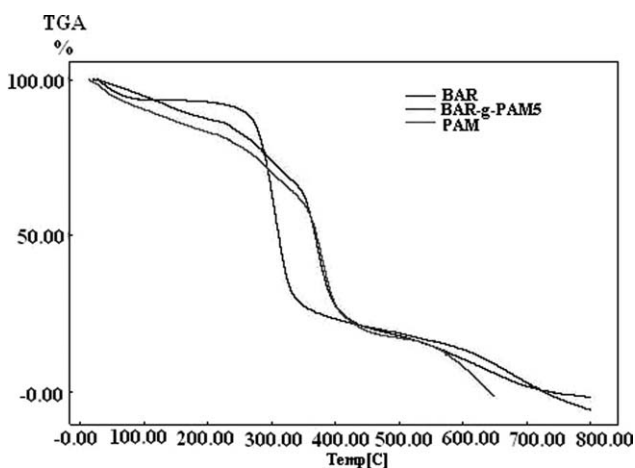


Figure 3. The combined TGA curve of barley, polyacrylamide, and BAR-g-PAM 5.

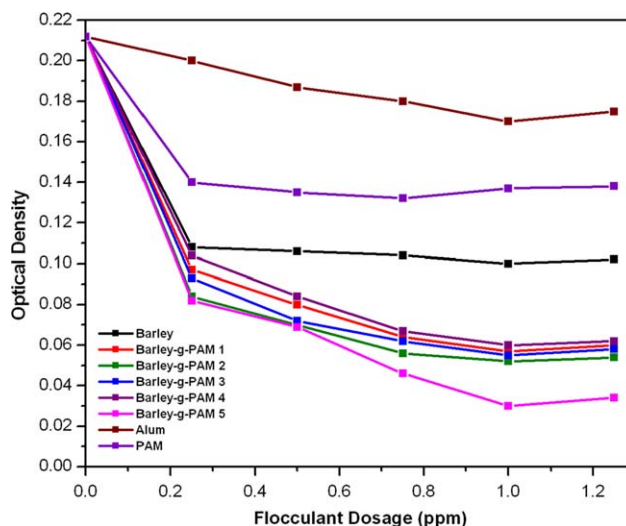


Figure 4. Flocculation profile in coal-fine suspension. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the above explanation, following mechanism is proposed in Scheme 1.

Effect of CAN initiator concentration. It is obvious that a low concentration of catalyst initiates a few grafting sites and a high concentration of catalyst initiates a larger number of grafting sites. Consequently, a low concentration of a catalyst results in formation of a longer polyacrylamide chain owing to insufficient grafting sites, whereas sufficient grafting sites become available when catalyst is used in comparatively higher concentration.²⁴ In this case, percentage grafting is increased when catalyst amount was varied from 0.1 to 0.2 g. It decreased subsequently, when catalyst concentration was taken as 0.3 g. Therefore, while polyacrylamide is grafting on barley backbone, it may proceed in two ways: (1) a small number of long polyacrylamide chains are formed and (2) a large number of short polyacrylamide chains are formed. In the first case, the rigid shape of barley would be changed owing to the presence of long polyacrylamide chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity. On the other hand, a large number of short polyacrylamide chains will not change the rigid structure of barley, thus resulting in lower hydrodynamic volume, leading to its lower intrinsic viscosity.

Effect of monomer (acrylamide) concentration. With the increase in concentration of acrylamide, percentage grafting increased continuously. This is due to the fact that an increase in monomer concentration leads to the accumulation of monomer molecules in close proximity to the barley backbone leading to more profound grafting reaction.

Characterization

Estimation and Interpretation of Intrinsic Viscosity. The intrinsic viscosity was evaluated for barley and for all the synthesized grades of BAR-g-PAM, as shown in Table I.

Intrinsic viscosity is practically the hydrodynamic volume of the macromolecule in the solvent. As evident from Table I, intrinsic viscosities of all the grades of BAR-g-PAM are greater than those

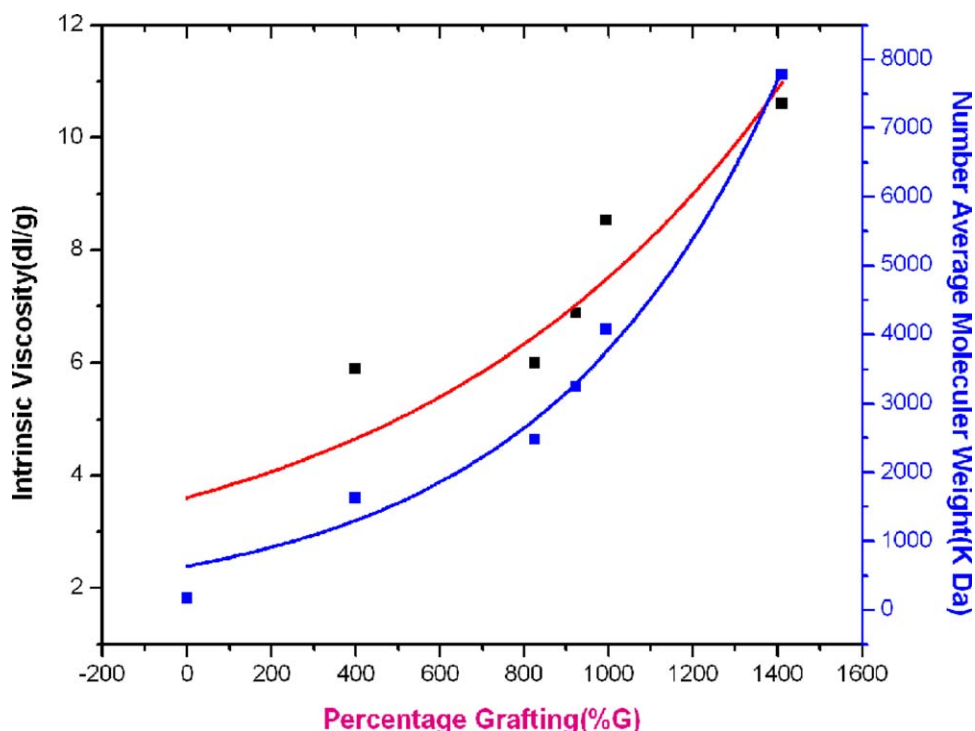


Figure 5. Co-relation graph of intrinsic viscosity, percentage grafting, and number-average molecular weight of barley and different grades of BAR-g-PAM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of barley. Intrinsic viscosity of the best grade of BAR-g-PAM (i.e., grade 5) is greater than that of all the synthesized grades of BAR-g-PAM. This is due to the increase in hydrodynamic volume resulting from grafting of the polyacrylamide chains on the main polymer backbone (barley). The grafted polyacrylamide chains increase hydrodynamic volume by the following two ways:

- By contributing their own hydrodynamic volume.
- Through steric hindrance to intramolecular bonding resulting in uncoiling of the polysaccharide chain.

Further, the increase in intrinsic viscosity due to increase in percentage grafting is in good agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM^\alpha$, where K and α are constants, both related to stiffness of the polymer chains), applying which we can explain the increase in intrinsic viscosity as a result of increase in molecular weight due to the grafted polyacrylamide chains. The value of $K(5.89)$ and $\alpha(0.46)$ constants are determined from the $\log \eta$ (dL/g) vs. $\log M$ (kDa) plot in Supporting Information Figure F2.

The correlation between percentage grafting (%G), intrinsic viscosity (η), and number-average molecular weight is plotted in Figure 5.

Elemental Analysis. The results of elemental analysis for barley, polyacrylamide, and the best grade of BAR-g-PAM 5 are given in Supporting Information Table S1. Barley has very low percentage of nitrogen (1.314%) when compared with BAR-g-PAM 5 (15.92%). The higher percentage of nitrogen of BAR-g-PAM is contributed by the grafted polyacrylamide chains. The higher

percentage of nitrogen of BAR-g-PAM than the starting material (barley) is a confirmation for grafting of polyacrylamide chains on barley.

FTIR Spectroscopy. As evident from Figure 1(a), barley (BAR) has a $1^\circ\text{O}-\text{H}$ stretching peak at 3265.49 cm^{-1} and $2^\circ\text{O}-\text{H}$ stretching peak at 3577.95 cm^{-1} , C–H stretching peak at 2929.87 cm^{-1} , and C–O–C stretching peak at 1010.70 cm^{-1} . One C=O symmetric stretching peak is at 1660.71 cm^{-1} due to the presence of some amount of protein in barley.³³

The broad peak between 3300 and 3200 cm^{-1} indicates that the $1^\circ\text{O}-\text{H}$ stretching peak of barley carbohydrate and N–H stretching peak of protein overlap. Sharp N–H bending peak is not apparent due to the very low protein percentage. As evident, amide-related peaks are not prominent in barley.

In case of BAR-g-PAM 5 [Figure 1(b)], there is an additional peak at 3199.91 cm^{-1} due to the “N–H” stretching vibration and another sharp peak at 1593.20 cm^{-1} due to the “N–H” bending vibration. The peak at 1417.68 cm^{-1} is due to the C–N stretching vibration. Existence of these peaks establishes the prominence of amide group in the grafted product, which confirms the grafting of polyacrylamide chains on the backbone of barley.

Further, it is noteworthy that owing to grafting, intensity of the $1^\circ\text{O}-\text{H}$ and $2^\circ\text{O}-\text{H}$ stretching peak decreases with respect to other peaks (e.g., C–H stretching peak) in BAR-g-PAM(5). This signifies that $1^\circ\text{O}-\text{H}$ and $2^\circ\text{O}-\text{H}$ are the sites on barley moiety where free radicals are being created and subsequently grafting takes place. The significant FTIR peaks of barley and BAR-g-PAM 5 are reported in Supporting Information Table S2.

SEM Analysis. It is evident from the SEM micrographs of barley [Figure 2(a)] and best grade of BAR-g-PAM (i.e., grade 5) [Figure 2(b)] that profound morphological changes, in form of transition from granular to fibrillar structure, have taken place because of grafting of polyacrylamide chains onto the polysaccharide backbone (of barley).

Thermal Gravimetric Analysis. The TGA curves of barley (Figure 3) essentially involved three distinct zones of weight loss. The initial weight loss is at 30–240°C. This is due to the traces of moisture present. The second zone (240–400°C) and the third zone of weight loss (400–800°C) were due to degradation of the barley backbone.

In the case of polyacrylamide (Figure 3), it involves three distinct zones of weight loss. The initial weight loss is at (30–350°C) due to the traces of moisture present. The second and third weight loss zone corresponding to (350–450°C) and (450–640°C) are due to the degradation of the polyacrylamide.

In case of BAR-g-PAM 5 (Figure 3), a fourth zone of weight loss (430–800°C) overlaps the third zone of weight loss of barley backbone. This fourth zone of weight loss is due to polyacrylamide chains grafted on barley moiety.

Number-Average Molecular Weight of the Polymers. The number-average molecular weight is calculated using the following equation

$$\frac{\pi}{C_{\text{dry}}} = \frac{\Phi \times n}{M_n} \times 10^3,$$

where M_n is the number-average molecular weight, C_{dry} is the concentration of the dry sample in the solution, Φ is the osmotic coefficient, which accounts for the nonideal behavior of the solution (here, assuming that the sample behaves ideally), n is the number of components into which a molecule dissociates, and π is the osmosis per kilogram solvent.³⁴

As evident from Table I, higher the percentage grafting, higher is the number-average molecular weight. This is due to the greater number of acrylamide monomers grafted. The correlation between the three parameters, i.e., percentage grafting (%G), intrinsic viscosity, and number-average molecular weight, is depicted in Figure 5.

¹³C-NMR Spectroscopy. The results obtained from the solid state of barley [Figure 6(a)] show four distinct peaks at $\delta = 102.751$, 81.739 , 72.196 , and 61.919 , which can be assigned to anomeric carbon (i.e., C-1 in six-membered ring), carbon atom connected to —OH groups (i.e., C-2, C-3, and C-4 in six-membered ring, carbon atom of —CH₂OH group, and for the C-5 carbon atom at six-membered ring).

As per the literature reports, the ¹³C-NMR spectra of acrylamide shows three major peaks at $\delta = 177.3$ ppm for the amide carbon atom and at $\delta = 130$, 138.2 for two sp² hybridized carbon atoms.³⁵

The ¹³C-NMR spectra of polyacrylamide show two distinct peaks as shown in Figure 6(b). The peak at $\delta = 41.618$ is for the sp³ hybridized carbon atom of polyacrylamide and the peak at $\delta = 179.542$ corresponds to the amide carbon atom of

polyacrylamide because due to polymerization the hybridization of carbon atom of acrylamide is changed from sp² to sp³ due to absence of two peaks at $\delta = 130.5$ and 138.2 .

The solid-state ¹³C-NMR spectra of BAR-g-PAM 5 is shown in Figure 6(c). The two additional peaks appear at $\delta = 179.542$ and 41.618 in comparison to the solid-state ¹³C peaks of pure barley. The additional peak at $\delta = 179.542$ signifies that the presence of amide carbonyl carbon atom which is present in the pure acrylamide ¹³C-NMR spectrum. Another additional peak at $\delta = 41.618$ signifies the presence of sp³ hybridized carbon atom which is formed during the polymerization reaction.³⁶ The δ value is slightly shifted toward higher value (i.e., C-1 to C-5 carbon atom in six-membered ring and C-6 carbon atom of —CH₂OH) for BAR-g-PAM due to the grafting.

Solubility in Aqueous Solution. The solubility details of barley and different grades of BAR-g-PAM in aqueous solution (polar solvent) are reported in Supporting Information Table S3. All the grades of grafted barley have shown better solubility than barley in aqueous solution. As barley is an amphiphilic polysaccharide it shows partial solubility in both types of solvents, i.e., polar (e.g., aqueous solution). Grafting of polar monomers (i.e., acrylamide) on the backbone of barley improved its solubility in water, by the virtue of the incorporated polar groups. Consequently, higher the percentage grafting of the barley, higher is its solubility in aqueous solution, i.e., the best grade (the grade with highest percentage grafting) has highest solubility.

The correlation between percentage grafting and solubility for grafted barley is depicted in Supporting Information Figure F1.

Flocculation Study and Dosage Optimization in Coal-Fine Suspension

The flocculation study in 1% coal-fine suspension in “jar test” apparatus, for dosage from 0 (control) to 1.25 ppm in increments of 0.25 ppm is shown in Figure 4.

All the grades of grafted barley have shown better flocculation efficacy than the polysaccharide (barley), polyacrylamide (commercial flocculent), and alum (coagulant). Further, higher the percentage grafting, higher is its flocculation efficacy. This is due to the higher hydrodynamic volume (i.e., intrinsic viscosity) with higher percentage grafting, as reported in Table I. The higher hydrodynamic volume of the macromolecule leads to higher flocculation efficacy.³⁷ The much higher flocculation efficacy of the grafted product than the original polysaccharide confirms the Singh’s easy approachability model.^{38,39}

In general, if the surface area of the polymer increases, the probability of the attachment of the colloid suspended particles also increases. Here, as a result of grafting of polyacrylamide on barley, the surface area increases and is more than either barley or polyacrylamide. This is because of the branched structure of BAR-g-PAM where polyacrylamide chains are attached on the barley backbone and result in its high surface area and ability to remove colloidal impurities forming flocs. So, the flocculation efficacy of BAR-g-PAM will be greater than that of polyacrylamide and barley. This behaviour of the flocculation curve is in fine agreement with bridging mechanism.⁴⁰ It states that a single polymer chain bridges between two or more particles.

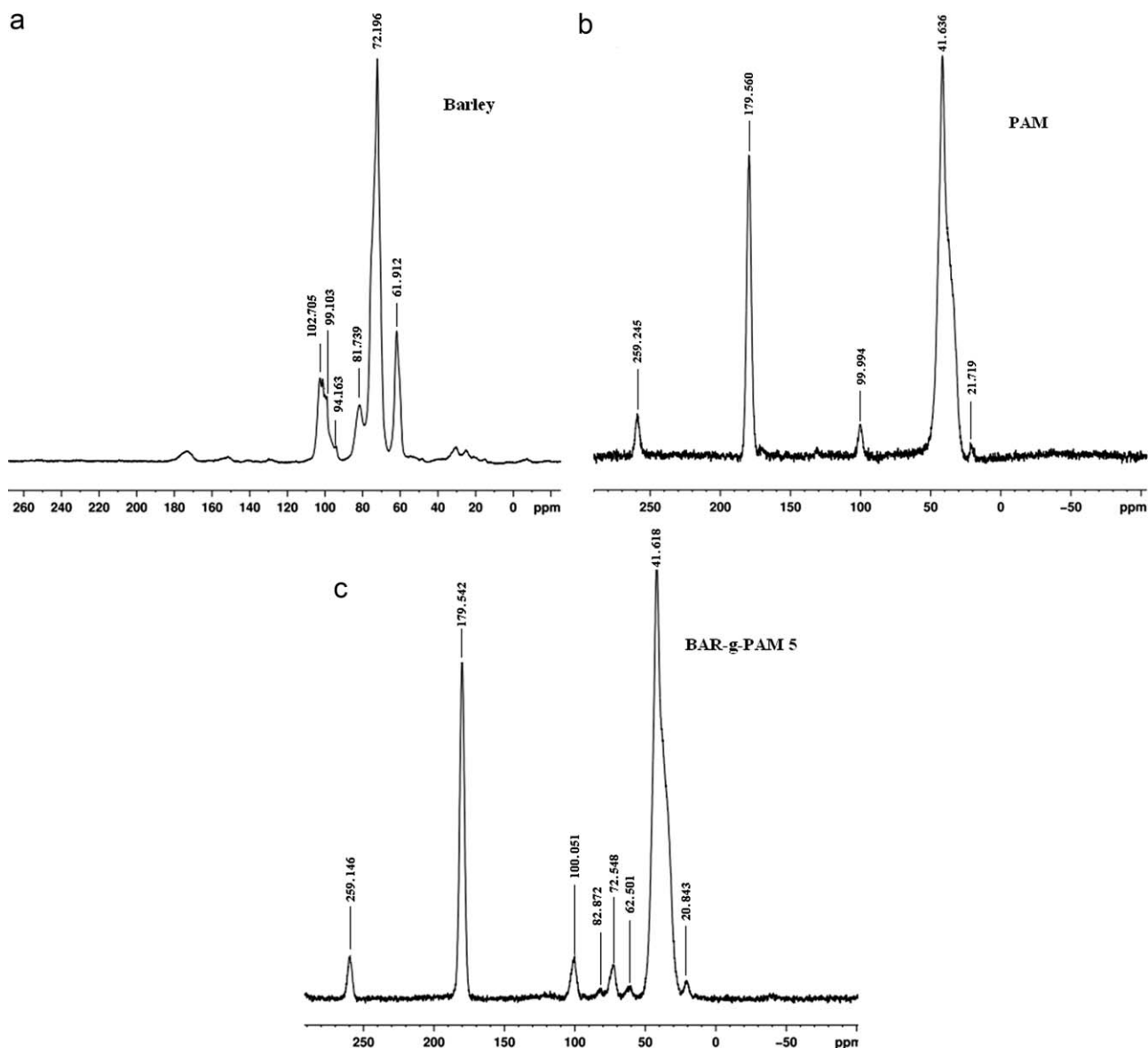


Figure 6. (a) ^{13}C -NMR spectra of barley. (b) ^{13}C -NMR spectra of polyacrylamide. (c) ^{13}C -NMR spectra of BAR-g-PAM 5.

When long-chain polymers are added to a colloidal suspension, they get adsorbed on two or more particle surfaces and thus form a bridge between them.^{41,42} There should be sufficient unoccupied space on the particle surface so as to form polymer bridging. This phenomenon is observed up to a particular dosage of polymer beyond which flocculation diminishes, the process being known as steric stabilization. Hence, at lower dosages of polymer, inadequate bridging occurs between the particles. Similarly, at higher dosages of polymer, there is insufficient particle surface for attachment of the polymer segments leading to destabilization. Floccs formed by bridging mechanism are found to be large and stronger than those produced by addition of salts. However, under high shear rates, these floccs are broken and may not reform once again. Hence, at this optimal dosage, flocculation efficacy is maximum (i.e., the optical density of the supernatant collected is minimum), beyond which the

flocculation decreases (i.e., optical density of the collected supernatant increases).

The optimal dosage of BAR-g-PAM 5 as flocculant in 1% coal-fine suspension is at 1 ppm. This translates to the fact that 1 mg of the grafted barley is capable of treatment of 1 L of coal washery effluent.

CONCLUSION

BAR-g-PAM is successfully synthesized by the conventional method. Further, it has been assessed for its potential application in water treatment. The results show high flocculation efficacy of BAR-g-PAM, particularly BAR-g-PAM 5, in coal-fine suspension which makes it a superior flocculant. It has been compared with the parent material barley, polyacrylamide, and contemporary coagulant alum, and it has been found to show

highest efficiency as a flocculant among all the materials for coal washery effluent treatment.

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