#### ORIGINAL PAPER

# Synthesis and characterizing a novel polymeric flocculant based on amylopectin-*graft*-polyacrylamide*graft*-polyacrylic acid [(AP-g-PAM)-g-PAA]

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**Abstract** The article highlights the development of a new generation of polymeric flocculant by grafting binary monomer mixture of acrylamide and acrylic acid onto a natural polymer—amylopectin [(AP-*g*-PAM)-*g*-PAA]. Primary graft copolymerization of acrylamide onto AP and binary graft copolymerization of acrylic acid onto AP-*g*-PAM was accomplished in 84 and 91 % grafting efficiency (% GE) using potassium persulphate as initiator. The influence of initiator concentration onto % GE was investigated. The developed binary graft copolymer was characterized using various materials characterization techniques like viscometry, elemental analysis, FTIR spectroscopy, <sup>13</sup>C NMR spectroscopy, molecular weight and radius of gyration by Zimm plot using SLS analysis. Flocculation studies reveal that the synthesized binary grafted product is an efficient flocculant, which is because of its higher molecular weight and radius of gyration.

Keywords Amylopectin · Binary grafting · Flocculation · Radius of gyration

# Introduction

Polysaccharides are naturally occurring polymers, which are polyhydroxy compounds composed of several monosaccharide units linked through oxygen to give complex composition. India is a rich center of polysaccharides and has great potential for the sustainable utilization of these natural resources by converting plant wealth through biotechnology. Chemical modification of polysaccharides is useful for alter their chemical and physical properties. Because of their superior properties, the modified polysaccharides can be used as a replacement to the more expensive

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materials. In general, the properties of natural polysaccharides are altered to a remarkable degree by the introduction of very small amounts of substituent groups of either neutral or ionic types. The beauty of water-soluble polysaccharides [1] lies in the diversity of their applications. It would be virtually impossible for human beings to pass a day without encountering any of these polymers, be it in the food we eat, the toiletries and cosmetics we use, the beverages we drink, the medicines we take, and many more. Water-soluble polymers are available in a wide variety of forms.

An important member of water-soluble polymers derived from natural process is starch, the most abundant storage polysaccharide [2]. In its crude form, starch is a mixture of two polymers [3] of anhydroglucose units, amylose and amylopectin (AP). Amylose is minor fraction variation up to 25 % depending upon source and AP constitutes major fraction with variation up to 95 %. AP is a branched polymer (Fig. 1) of  $\alpha$ -D-glucopyranosyl residues [4] linked together mainly by  $1 \rightarrow 4$  linkages with  $1 \rightarrow 6$  bonds at the branch points. It is of high molecular weight between 50,000 and  $10^7$  g mol<sup>-1</sup>. AP is soluble in water whereas amylose is only sparingly soluble [5].

Modifications of natural polysaccharides may be done either by derivatization [6–9] of functional groups or by grafting [10–14]. These modified polysaccharides possess better mechanical properties and applicability than unmodified polysaccharides. The graft copolymerization provides a unique technique for modifying polymers to meet desired end user requirements. The graft copolymers of polysaccharides are of additional interest because of their potential use as viscosifiers in enhanced oil recovery operations, as flocculants for wastewater treatment. An important advantage of graft copolymerization is that the polymeric substrate or backbone polymer and grafted polymer chains are held together by



Fig. 1 Structure of AP

chemical bonding allowing the two polymers to be intimately associated rather than as mere physical mixtures. The method of graft copolymerization has been utilized as a special technique in the recent decades for synthesizing new class of polymeric materials by modifying the physical and chemical properties of synthetic and natural polymers [15–19]. Grafting of vinyl monomers from their binary mixtures is a significant technique, as it introduces dual properties in the backbone polymer and also influences the extent of grafting of a monomer by synergistic effect which exhibits lesser tendency for grafting individually [20–25]. Binary graft copolymerization has been successfully used to alter significantly the solution properties of both non-grafted polymers and primary grafted polymers. The viscosity, gelling characteristics, solution rheology, e.g., degree of pseudoplasticity, ion compatibility, etc., can be drastically changed through binary graft copolymerization reaction. Enhanced functionality can also be imparted to substrates which will allow them to be more effective in flocculation, dispersion, and other applications such as retention aids in paper, dry strength additives, etc.

Both polyacrylamide and polyacrylic acid are efficient flocculant for the treatment of wastewater. However, they are not biodegradable and shear resistant. Natural polymers, mainly polysaccharides (like AP) are shear stable, biodegradable, and less efficient as flocculant. The biodegradability of natural polymers reduces their shelf life and needs to be suitably controlled. By grafting binary mixture of acrylamide and acrylic acid onto AP backbone, it is possible to develop an efficient flocculant which would be shear stable, controlled biodegradable, and flexible in nature (because of the presence of flexible polyacrylamide and polyacrylic acid chains onto rigid AP backbone). Here in, we report the first example of a novel polymeric material based on binary grafting of polyacrylamide and polyacrylic acid onto AP. The focus of this study is to synthesize and well characterize the binary graft copolymer and targeting its application in flocculation for treatment of a synthetic effluent (Fe ore suspension).

#### Experimental

#### Materials

AP was purchased from Fluka Biochemica, Switzerland. Acrylamide, acrylic acid, and potassium persulphate (KPS) were obtained from Merck, India. Analar grade acetone and hydroquinone were supplied by S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification.

Fe ore (Zeta potential: -5.07 mV at neutral pH; particle size: 87.7 nm) was a gift sample from Tata Steel Co., Jamshedpur, India.

Synthesis of binary graft copolymer [AP-g-PAM]-g-PAA

The binary grafting reaction was carried out in a three-necked round-bottom flask. The flask was fitted with an electrically operated magnetic stirrer (TARSONS, MODEL: SPINOT DIGITAL), maintained at temperature  $70 \pm 1$  °C. One gram of

Polymer	Amount of amylopectin (mol)	Amount of initiator $(mol \times 10^{-5})$	Amount of acrylamide (mol)	Amount of acrylic acid (mol)	% GE	Intrinsic viscosity (dL g <sup>-1</sup> )
AP-g-PAM 1	0.0061	1.85	0.140	_	72	7.11
AP-g-PAM 2	0.0061	3.70	0.140	-	84	7.55
AP-g-PAM 3	0.0061	5.55	0.140	-	79	6.74
(AP-g-PAM)-g-PAA 1	0.0061	1.85	-	0.138	75	17.24
(AP-g-PAM)-g-PAA 2	0.0061	3.70	-	0.138	91	20.70
(AP-g-PAM)-g-PAA 3	0.0061	5.55	-	0.138	88	18.5
AP	-	_	_	_	-	0.95

 Table 1
 Synthesis details of AP-g-PAM and [(AP-g-PAM)-g-PAA]

 $\% \text{ GE (Primary grafting)} = \frac{\text{Wt. of graft copolymer - wt. of polysaccharide}}{\text{Wt. of monomer}} \times 100$   $\% \text{ GE (Binary grafting)} = \frac{\text{Wt. of binary copolymer - wt. of primary graft copolymer}}{\text{Wt. of monomer}} \times 100$ 

AP was slowly dissolved in 100 mL of distilled water with constant stirring (300 rpm) at a temperature of 70 °C for about 15 min. Required quantity of acrylamide (Table 1) was dissolved in 20 mL of distilled water and mixed with the AP solution. Afterwards, 5 mL of KPS solution of desired concentration listed in Table 1 was added and the grafting reaction was continued for another 1 h at same temperature and stirring speed (i.e., 300 rpm). The whole reaction was carried out in presence of nitrogen atmosphere. At the end, the reaction was terminated by adding hydroquinone solution (0.0001 g hydroquinone in 2.5 mL water). The resultant graft copolymer was precipitated by adding 400 mL of acetone, dried in a hot air oven at 60 °C for 6 h, pulverized and sieved through a 125-µm sieve.

The optimized grade of polyacrylamide grafted AP (AP-g-PAM) was dissolved in 100 mL of distilled water, followed by addition of acrylic acid solution (desired quantity as listed in Table 1). Afterward, the initiator (KPS) was added and the binary grafting reaction was performed in the same way as discussed in previous paragraph. The binary grafting of polyacrylamide and polyacrylic acid onto AP backbone will follow the mechanistic pathway as shown in Scheme 1.

# Extraction of homopolymers

The small amount of homopolymer (PAM or PAA) may be present along with graft copolymers. If any homopolymer (PAM/PAA) formed during polymerization reaction, has been extracted from the graft copolymer/binary graft copolymer by solvent extraction method using a mixture of formamide and acetic acid (1:1 by volume) [26]. The detailed procedure of homopolymer (PAM or PAA) extraction is as follows:

Two grams of graft copolymer/binary graft copolymer was taken in a 250-mL beaker. Hundred milliliters of the prepared solvent (1:1 formamide: acetic acid) was



Scheme 1 Schematic representation for the synthesis of [(AP-g-PAM)-g-PAA]

added to it. The reactants were kept at 50 °C for 12 h. Afterwards, the mixture was filtered using Buchner funnel. The residue was washed with same solvent mixture for ten times and in every time the filtrate was checked with acetone whether there was a precipitation of PAM/PAA or not. After which, the polymer was again washed with methanol and kept it for 24 h to remove the solvent. The pure graft copolymer was then dried in a hot air oven at 60 °C for 4 h.

# Characterization

Viscosity measurements of polymer solutions were carried out with the help of Ubbelohde viscometer in aqueous solution at 25 °C. The C, H, N analysis was performed using an Elemental Analyzer (Perkin Elmer, Series-II, CHNS/O analyzer-2400). Molecular weight and radius of gyration were determined by Zimm plot using SLS analysis. FTIR spectra were recorded in solid state using KBr pellets with a FTIR spectrophotometer (Model IR-Perkin Elmer, Spectrum 2000) between 400 and 4,000 cm<sup>-1</sup>. <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz on a Bruker Advance II-500 NMR spectrometer.

# Flocculation studies

# Investigation of flocculation characteristics in Fe ore suspension using jar test method

Flocculation tests of Fe ore suspensions were carried out on standard flocculation jar apparatus (supplied by Gon Engineering Works, Dhanbad, India). The jar test apparatus consists of 6 stirrer blades connected to a variable speed motor through a gear system. In 1-L beakers, 400 mL of 0.25 wt% iron ore suspension was taken. The beakers were placed on the flocculator dipping the stirrer blades in the suspension. Under a slow stirring condition, the polymer solution was added to each beaker to make predetermined polymer concentration (0.25-3 ppm; calculated with respect to the total weight of the solution). Immediately after the addition of polymer solution, the suspensions were stirred at a constant speed of 75 rpm for 2 min, followed by low stirring at 25 rpm for 5 min. The flocs were then allowed to settle down for 15 min. Clean supernatant liquid was drawn from the top layer (up to depth of 1 cm) and its turbidity was measured using a digital nephelo turbidity meter (supplied by Systronics, Ahmedabad, India) to express the turbidity in nephelo turbidity unit (NTU). The relationship between polymer concentration and residual turbidity of the supernatant liquid are plotted in Fig. <u>6</u>a, b.

# Investigation of flocculation characteristics in Fe ore suspension using settling test method

The flocculation characteristics of AP, AP-g-PAMs and [(AP-g-PAM)-g-PAA]s were investigated in a synthetic effluent (i.e., Fe ore suspensions) using column settling method. This test employs a 100-mL stoppered graduated cylinder (Height—40 cm; Inner dia—2.5 cm) and stopwatch. First of all, the slurry sample was taken in the cylinder and then polymer solution was added into it. The cylinder was inverted ten times for thorough mixing. Then, the cylinder was set upright and the height of interface between supernatant water and settling solid bed was measured over time.

# **Results and discussions**

# Synthesis of [(AP-g-PAM)-g-PAA]

[(AP-g-PAM)-g-PAA] was synthesized by conventional method, using KPS as free radical initiator, in nitrogen atmosphere. Table 1 shows various grades of primary and binary graft copolymers synthesized using conventional process by varying the initiator concentration and found [(AP-g-PAM)-g-PAA] 2 is the best (optimized) grade with respect to its higher intrinsic viscosity, higher radius of gyration, and better flocculation characteristics. A plausible explanation for mechanism of binary graft copolymerization is based on the assumption that KPS generates free radical sites on AP, and AP-g-PAM backbone. These active free radicals in the presence of acrylic monomers generate single/binary graft copolymers (Scheme 1).

# Effect of initiator concentration

The average number of grafting sites per polymer backbone depends on the ratio of KPS concentration to AP, or AP-g-PAM. A relatively low concentration of initiator will initiate few grafting sites, resulting in longer PAM/PAA chains against shorter PAM/PAA chains with higher concentration of KPS. So by grafting synthetic polymers onto AP/AP-g-PAM, two possibilities are there—one can either have a small number of long grafted chains (i.e., higher % GE) or a large number of short grafted chains (i.e., lower % GE) in the single/binary graft copolymer. In the former case, the compact shape of the graft copolymer would be changed, because of the presence of longer polyacrylamide/polyacrylic acid chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity as well as higher radius of gyration (Table 1). On the other hand, a large number of short polyacrylamide chains will not alter the original compact shape to a great extent and hence lower would be hydrodynamic volume (i.e., intrinsic viscosity).

# Characterization

#### Estimation and interpretation of intrinsic viscosity

From the relative viscosity of various polymer solutions of known strength, inherent viscosity and reduced viscosity were evaluated and plotted against concentration. The intrinsic viscosity (Table 1; Fig. 2) for the polymer system at a given temperature (25 °C) was measured by the intercept of the plot of  $\eta_{\rm sp}/c$  versus *c* and ln  $\eta_{\rm rel}/c$  versus *c*, when the linear experimental plot is extrapolated to zero concentration, or more precisely, to infinite dilution condition [27, 28].

The inherent viscosity and reduced viscosity were calculated by using the following relations:

**Fig. 2** Intrinsic viscosity of **a** AP, **b** AP-*g*-PAM 2, and **c** [(AP-*g*-PAM)-*g*-PAA] 2



$$\eta_{\rm rel} = t/t_0 \tag{1}$$

$$\eta_{\rm sp} = \eta_{\rm rel} - 1 \tag{2}$$

$$\eta_{\rm red} = \eta_{\rm sp}/C \tag{3}$$

$$\eta_{\rm inh} = (\ln \eta_{\rm rel})/C \tag{4}$$

It has been observed from Table 1 that the intrinsic viscosity of all the three grades of AP-g-PAM is higher than that of AP. This is because of the presence of grafted PAM chains onto the polysaccharide backbone. After binary grafting, the viscosity has enhanced drastically. This is because of huge steric repulsions between grafted polyacrylamide and polyacrylic acid chains. However, among various grades of binary graft copolymers, the polymer having highest % GE, i.e., longer grafted chains is having highest intrinsic viscosity.

Polymer	% C	% H	% N	% O	% S
AP	38.20	7.98	0.10	53.62	0.00
Polyacrylamide	50.80	7.69	19.76	21.7	0.00
AP-g-PAM 1	34.62	7.02	7.56	50.72	0.00
AP-g-PAM 2	33.64	6.40	8.23	51.71	0.00
AP-g-PAM 3	33.80	7.52	8.11	50.51	0.00
(AP-g-PAM)-g-PAA 1	30.05	6.01	7.90	55.98	0.00
(AP-g-PAM)-g-PAA 2	28.71	5.88	8.04	57.34	0.00
(AP-g-PAM)-g-PAA 3	29.03	6.81	7.94	56.20	0.00

Table 2 C, H, N analysis result

#### C, H, N analysis result

C, H, N analysis (Table 2) results reveal that there is considerable percentage of nitrogen in case of primary grafted products (i.e., AP-*g*-PAM) in comparison to AP, which is because of the presence of grafted PAM chains. However, by comparing primary and binary graft copolymer, there is substantial increase in % of oxygen in case of binary grafted product. This clearly indicates that polyacrylic acid has been grafted onto AP-*g*-PAM backbone, i.e., binary grafting took place.

#### Molecular weight and radius of gyration

It is obvious from Table 3 that all the grades of AP-g-PAM are having higher molecular weight as well as radius of gyration. This is because of primary grafting of polyacrylamide chains onto AP backbone. However, binary grafted products are having higher molecular weight than AP-g-PAM, which is due to the presence of PAA and PAM chains onto AP backbone. Among binary grafted products, [(AP-g-PAM)-g-PAA] 2 (Fig. 3) is having highest molecular weight as well as radius of gyration. This is because of its higher % GE.

#### FTIR spectra

The grafting of PAM and PAA onto AP was confirmed by FTIR spectroscopy. Figure 4a shows the spectrum of AP which exhibited signal at 3,394 cm<sup>-1</sup> due to the stretching vibrations of O–H. Also, it shows stretching vibration at 2,930 cm<sup>-1</sup> for C–H groups. The bands at 985 and 910 cm<sup>-1</sup> are attributed to  $CH_2$ –O– $CH_2$  stretching vibrations.

In case of AP-g-PAM (Fig. 4b), there are few additional bands present in comparison to AP. The band at  $1,665 \text{ cm}^{-1}$  is attributed to C=O stretching vibration. One peak at  $1,451 \text{ cm}^{-1}$  is for C–N stretching vibrations. The presence of these additional peaks confirms successful grafting of PAM chains onto AP backbone.

By comparing AP-g-PAM 2 and [(AP-g-PAM)-g-PAA] 2 (Fig. 4c), there is one additional band present in binary grafted product at  $1,727 \text{ cm}^{-1}$ , which is assigned

Table 3	Result of molecular	
weight a	nd radius of gyration	

Polymer	Molecular weight (g mol <sup>-1</sup> )	Radius of gyration (nm)
AP	$1.76 \times 10^{6}$	58.60
AP-g-PAM 1	$4.44 \times 10^{6}$	72.40
AP-g-PAM 2	$5.47 \times 10^{6}$	81.30
AP-g-PAM 3	$5.01 \times 10^{6}$	79.00
(AP-g-PAM)-g-PAA 1	$7.80 \times 10^{6}$	95.60
(AP-g-PAM)-g-PAA 2	$8.94 \times 10^{6}$	112.04
(AP-g-PAM)-g-PAA 3	$8.43 \times 10^{6}$	106.50



Fig. 3 Zimm plot of [(AP-g-PAM)-g-PAA] 2

to –COOH group. The presence of this additional band is a strong proof of grafting of PAA onto AP-g-PAM backbone.

# <sup>13</sup>C NMR spectra

The solid state <sup>13</sup>C NMR spectrum of AP (Fig. 5a) reveals three distinct peaks. The absorption peak at  $\delta = 102.2$  ppm is for anomeric carbon atom and the peak at  $\delta = 72.6$  ppm can be assigned for carbon atoms connected by –OH groups (i.e., the carbon atoms in the six-membered ring except anomeric carbon atom). Third peak at  $\delta = 61.4$  ppm is attributed for the carbon atom of CH<sub>2</sub>OH group.



Fig. 4 FTIR spectra of (a) AP, (b) AP-g-PAM 2, and (c) [(AP-g-PAM)-g-PAA] 2



Fig. 5 <sup>13</sup>C NMR spectra of a AP, b acrylic acid, c AP-g-PAM 2, and d [(AP-g-PAM)-g-PAA] 2

The literature report [18] shows that <sup>13</sup>C NMR spectrum of acrylamide has three major peaks. The peak at  $\delta = 177.3$  ppm is attributed to the amide carbonyl carbon. Peaks at  $\delta = 130.5$  and  $\delta = 138.2$  ppm are assigned for two *sp*<sup>2</sup> hybridized carbon atoms (i.e., CH<sub>2</sub>=CH–).

The <sup>13</sup>C NMR spectrum of primary grafted product (AP-g-PAM 2) (Fig. 5c) contains two additional peaks in compare to AP. The presence of a peak at  $\delta = 180.4$  ppm is because of carbonyl groups, along with an additional peak at  $\delta = 46.0$  ppm, is attributed to  $sp^3$  hybridized carbon (i.e., -CH<sub>2</sub>-CH<sub>2</sub>-); which is absent in the spectra of acrylamide as well as AP. This confirms that grafting of polyacrylamide chains onto AP backbone took place.

Further, <sup>13</sup>C NMR spectrum of [(AP-*g*-PAM)-*g*-PAA] 2 (Fig. 5d) is having one additional peak at 170.9 ppm. This is for the carbon of carboxylic acid group, which clearly confirms that binary grafting do takes place. Further, the intensity of the methylene carbon is higher compared to AP-*g*-PAM 2, which is accounted for the  $(-CH_2-CH_{-})_n$  of polyacrylamide as well as polyacrylic acid. It is also to be noted that there is no homopolymer present neither in primary grafted product nor in binary grafted product (as homopolymer has been extracted using solvent extraction method) and therefore, the NMR studies give the clear evidence of covalent attachment of the PAM/PAA chains onto the AP backbone.

### Flocculation characteristics

#### Jar test in Fe ore suspensions

The flocculation characteristics of various grades of primary graft copolymers and that of AP (Fig. 6a) was compared in 0.25 wt% iron ore suspension. In each case, the turbidity of the supernatant liquid after flocculation was plotted against polymer concentration. It is obvious from Fig. 6a that the flocculation efficacies of all primary graft copolymers are better than AP. This is because of the presence of polyacrylamide chains onto AP backbone. As on grafting, the radius of gyration as well as molecular weight of the polymer enhanced (Table 3), which enhanced its flocculation efficiency. However, among various graft copolymers, the polymer having highest % GE as well as highest radius of gyration is the best flocculant. Figure 6b explains the flocculation properties of best performing primary graft copolymer and binary graft copolymers. Here, it is obvious that [(AP-g-PAM)-g-PAA] 2 surpasses the flocculation efficacy of others. The higher molecular weight and radius of gyration was likely the reason why it outperformed others. As it has already been established qualitatively and quantitatively that with increase in molecular weight and radius of gyration of a flocculant, the approachability of the contaminant particles toward the polymeric flocculant is enhanced and thereby increasing the flocculation efficacy [29, 30].

# Settling test in Fe ore suspensions

The flocculation efficiencies of AP and various grades of AP-g-PAMs were tested in 5 wt% Fe ore suspension. The results of the flocculation studies in Fe ore

**Fig. 6** Jar test result in 0.25 wt% Fe ore suspension



**Fig. 7** Settling characteristics of Fe ore suspension using various flocculants

Table 4     Result of settling       velocity	Polymer	Settling velocity $(\text{cm s}^{-1})$	
	Without flocculant	0.0036	
	AP	0.29	
	AP-g-PAM 1	0.96	
	AP-g-PAM 2	1.33	
	AP-g-PAM 3	1.18	
	(AP-g-PAM)-g-PAA 1	1.43	
	(AP-g-PAM)-g-PAA 2	1.82	
Bold represents the optimized	(AP-g-PAM)-g-PAA 3	1.38	

suspension are shown in Fig. 7. The faster the iron ore particles are flocculated and settle, steeper will be the curves for interphase height versus time.

It is obvious from the results that by adding the flocculants, the flocculation efficiency increases. The performance of AP-*g*-PAM 2 is better than other graft copolymers followed by AP (Fig. 7a). The better flocculation efficacy of grafted AP over AP is because of its higher molecular weight, and higher radius of gyration.

Afterward, the best performing graft copolymer was compared with the binary grafted products (Fig. 7b). Here, it has been found that all the binary grafted products are showing better flocculation efficacy compared to primary grafted product. The reason behind the fact is that, after binary grafting of polyacrylic acid onto AP-*g*-PAM, there is huge steric repulsions between the grafted chains, which will enhanced the hydrodynamic volume (i.e., intrinsic viscosity) as well as radius of gyration. As a result, the approachability of the contaminants toward the binary graft copolymer enhanced and thereby increasing the flocculation efficiency.

From the settling curves (Fig. 7), it is observed that the fall of interface is linear for a considerable height before it becomes non-linear. This means that the rate of fall of the interface is constant initially, after which it gradually declines. Initial settling rate is calculated from the slope of the linear portion of the settling curves. In this study, it has been observed that satisfactory linearity was maintained for about 20 cm fall of the interface height in case of Fe ore suspension. The settling velocities of Fe ore with addition of different flocculants are reported in Table 4. It is evident from the result that [(AP-g-PAM)-g-PAA] 2 is having highest settling velocity and hence is the best flocculant.

#### Conclusion

[(AP-g-PAM)-g-PAA] was developed by a two-step method using KPS as initiator. Various physicochemical characterizations confirm that binary grafting of polyacrylamide and polyacrylic acid onto AP backbone took place. Further, the synthesized material finds potential application as an efficient flocculant for the treatment of synthetic wastewater. It has also to be mentioned that higher is the radius of gyration, better would be the flocculation efficacy. **Acknowledgments** Authors earnestly acknowledge the financial support from Indian School of Mines, Dhanbad to carry out the reported investigation.

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