

Characterization of Polyacrylamide-Grafted Sodium Alginate: A Novel Polymeric Flocculant

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Received 9 November 1999; accepted 29 August 2000

ABSTRACT: The synthesis of sodium alginate-*g*-polyacrylamide was carried out by a ceric-ion-induced solution polymerization technique. Six grades of graft copolymers were synthesized by the variation of catalyst and monomer concentrations. These graft copolymers were characterized by intrinsic viscosity measurements, ¹³C-NMR spectroscopy, infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, and X-ray diffraction. From the characterizations, it could be concluded that there was a substantial amount of grafting with a minimum formation of homopolymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3296–3308, 2001

Key words: characterization; flocculation; graft copolymers; polyacrylamide; sodium alginate

INTRODUCTION

Pure water is an essential requirement for the survival of human beings and for any modern industry, whether it is steel, copper, food, paper, petroleum, or a chemical- or mineral-processing industry. To meet the requirements of potable, industrial, and agricultural water, the immediate need is to treat waste water, particularly the sewage sludges and slimes from municipal and industrial effluents. These effluents are highly undesirable and unsafe. The removal of organic and inorganic contaminants from these effluents is a must before they can be reused. The removal of contaminants from effluents involves the process of coagulation and flocculation.

Flocculation is a process¹ that involves the formation of aggregates and the settling of colloidal particles from stable suspensions caused by the addition of soluble chemicals known as *flocu-*

lants in minute quantities. Commercial flocculants are of two types: organic and inorganic. Of the two, organic flocculants are more effective because they are required only in minute quantities, they produce less sludge, and they do not need any pH adjustments. Organic flocculants may be natural or synthetic. Starch, alginic acid, and guar gum are among the natural polymers used in flocculation. Among the synthetic flocculants commonly used are polymers such as polyacrylamide and poly(ethylene oxide) in the non-ionic category, poly(diallyldimethylammonium chloride) in the cationic category, and poly(styrenic sulfonic acid) in the anionic category. Natural polymers have the advantages of low cost and biodegradability. The biodegradability of natural polymers as such also acts as a drawback in that it reduces the storage life and the flocculation performance. Moreover, because of the variation in the composition of natural polymers from source to source, their performance varies widely. On the other hand, synthetic polymers are highly efficient and can be tailored to the needs of a particular application. However, their biggest disadvantage is their shear degradability.

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Contract grant sponsor: CSIR (New Delhi).

Journal of Applied Polymer Science, Vol. 81, 3296–3308 (2001)
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Recently, a new class of flocculating agents based on graft copolymers²⁻⁴ of natural polysaccharides and synthetic polymers has been reported. They essentially combine the best properties of both components. Thus, the graft copolymers are biodegradable to some extent because of the presence of natural polysaccharide backbones. The graft copolymers have also been found to be reasonably shear stable⁵ because of the attachment of flexible synthetic polymers onto their rigid polysaccharide backbones. The study of flocculation characteristics of the graft copolymers of polyacrylamide and various polysaccharides such as guar gum, starch, and xanthan⁶⁻⁸ has proven that each of the graft copolymers is a better flocculating agent than polyacrylamide. Based on the previously mentioned studies, a model was proposed by Singh² that the better efficiency of graft copolymers compared to the linear polyacrylamide was probably caused by better approachability of the branched chains to the colloidal particles.

In a previous study,⁹ we carried out the synthesis, flocculation characterizations, and some of the characterization of the polyacrylamide-grafted sodium alginate. It was also determined that among the various grades of the grafted product, the graft copolymers with longer polyacrylamide chains showed better flocculation performance. Because the molecular attributes of grafted copolymers play an important role in the flocculation phenomenon, proper characterization is essential. This article reports on the detailed characterization of polyacrylamide-grafted sodium alginate.

EXPERIMENTAL

Materials

Sodium alginate was procured from Aldrich Chemical Co. (USA) Acrylamide was procured from E. Merck (Germany). Ceric ammonium nitrate (CAN) was procured from Loba Chemie (Bombay, India). Acetone and hydroquinone were supplied by s.d. Fine Chemicals Bombay (India). Sodium nitrate was supplied by E. Merck (Bombay, India). All the chemicals were used as received without further purification.

Synthesis

All the graft copolymers were synthesized by the ceric-ion-induced solution polymerization method.

The reaction conditions were established according to the literature and also from our previous experience.^{2,6,9} Grafting was carried out in an atmosphere of nitrogen because it is well known that oxygen inhibits the polymerization of vinyl monomers. A reaction temperature of 27°C was selected based on our previous experience. Sodium alginate (2.5 g) was dissolved in 100 mL of distilled water at room temperature with constant stirring and the bubbling of a slow stream of nitrogen for about 15 min. Acrylamide (required amount) was dissolved in 75 mL of distilled water and mixed with the sodium alginate solution. Oxygen-free nitrogen was purged through the solution for 20 min. At this stage 25 mL of CAN solution was added to the reaction mixture; then the solution was further purged with nitrogen for 10 min. The temperature was maintained at 27°C throughout the reaction. The reaction was allowed to continue for 24 h, after which it was terminated by the addition of a saturated solution of hydroquinone. At the end of the reaction, the resulting polymer was placed in a 1-L beaker, where it was made into a homogeneous slurry with the addition of distilled water. The viscous polymer was then precipitated by the addition of excess acetone. The precipitated polymer was kept in acetone for about 6 h to remove unreacted acrylamide (if any). It was then transferred to a vacuum oven and dried at 70°C for about 24 h. Afterward, it was pulverized and then sieved. In a similar way, several grades of graft copolymers were synthesized by the variation of monomer and catalyst concentrations. The synthesis parameters of the graft copolymers are summarized in Table I. The grafted products of sodium alginate and polyacrylamide are referred to as SAGs.

Purification of the Graft Copolymer by Solvent Extraction

Scheme 1 was followed to purify the graft copolymer. The extraction of occluded polyacrylamide was carried out by solvent extraction with a mixture of formamide and acetic acid (1:1 by volume). The detailed procedure was as follows: Graft copolymer (3 g) was placed in a 250-mL beaker. Then, 100 mL of the solvent was added, and it was kept at 40°C for 12 h. Next, the mixture was filtered with a Buchner funnel. The residue was washed with same solvent mixture ten times, and each time, the filtrate was checked with acetone to see whether or not there was a precipitation of polyacrylamide. After washing, the polymer was

Table I Synthetic Details of the Graft Copolymers

Polymer	Polysaccharide (g)	Acrylamide (mol)	Amount of CAN (mol $\times 10^{-4}$)	% Conversion ^a	Intrinsic Viscosity (dL/gm)	$\bar{M}_w \times 10^6$	$\bar{M}_n \times 10^6$
SAG-I	2.5	0.12	1.003	83.76	6.75	1.93	1.19
SAG-II	2.5	0.12	2.006	84.58	6.63	1.89	1.15
SAG-III	2.5	0.12	3.009	85.88	6.00	1.67	0.99
SAG-IV	2.5	0.12	5.015	92.35	5.15	1.37	0.78
SAG-V	2.5	0.24	2.006	93.45	7.82	2.32	1.48
SAG-VI	2.5	0.30	2.006	95.56	8.20	2.47	1.59

^a Percent conversion was calculated from the following equation: % conversion = [(weight of grafted product - weight of polysaccharide)/weight of acrylamide] $\times 100$.

again washed with methanol to remove the solvent and then kept in methanol for 24 h. Afterward, it was dried in a vacuum oven.

Characterization

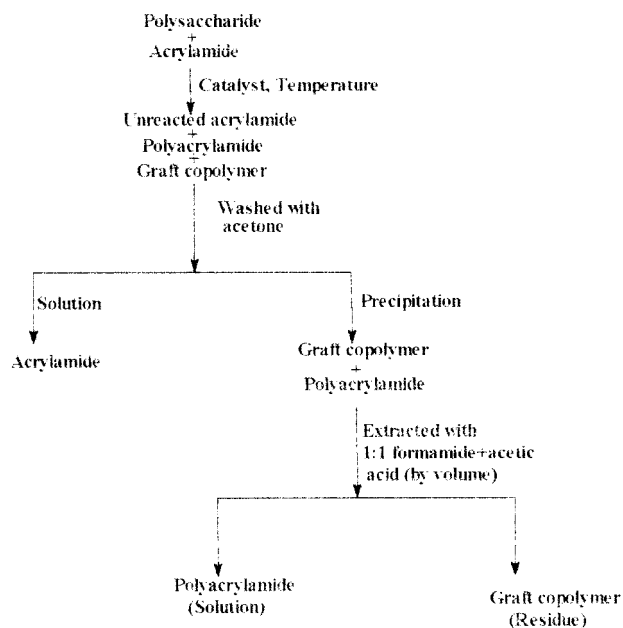
Viscosity Measurement

Viscosity measurements of polymer solutions were carried out with a Ubbelohde viscometer (constant = 0.00527) at 26°C. The viscosities were measured in 1M NaNO₃ solution. The flow time was measured for 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 (as shown in Fig. 1). Here, c is the polymer concentration in grams per deciliter and η_{sp} and η_{inh} are the specific and inherent viscosities, respectively. The intrinsic viscosities of all the graft copolymers are also reported in Table I.

Infrared (IR) Spectroscopy

One of the previous grades (SAG-II) was subjected to IR spectral analysis. A PerkinElmer-883 IR spectrophotometer (United Kingdom) was used, and the potassium bromide (KBr) pellet method followed for IR study. The IR spectra of sodium alginate and sodium alginate-*g*-polyacrylamide are shown in Figures 2(a) and 2(b).



Scheme 1 Purification of the graft copolymer.

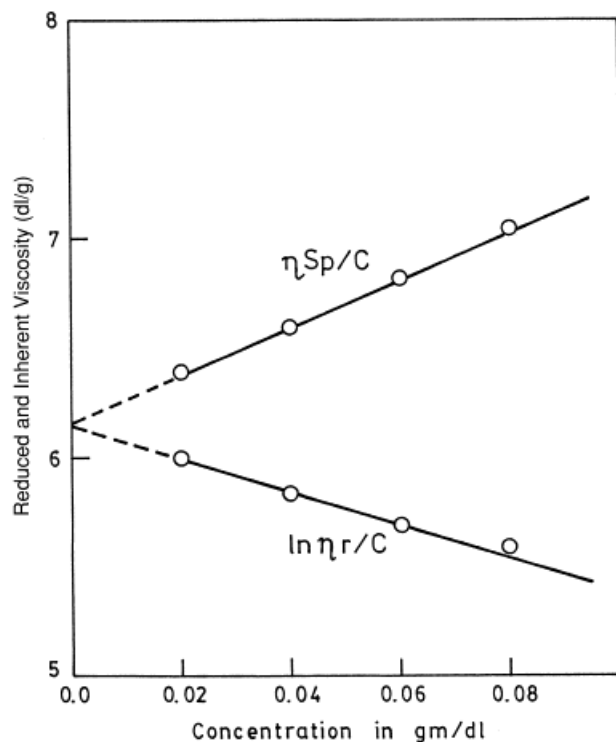


Figure 1 Intrinsic viscosity measurements for SAG-IV.

¹³C-NMR Spectroscopy

¹³C-NMR spectroscopy of sodium alginate, acrylamide, and all the graft copolymers was carried out by the solid-state method with a DSX-300 solid-state spectrometer. The spectra are shown in Figures 3(a), 3(b), 3(c), and 3(d).

Elemental Analysis

Elemental analysis of all the graft copolymers was done with a Carlo Erba 1108 elemental analyzer. The estimation of only three elements, that is, carbon, hydrogen, and nitrogen, was done. The results are shown in Table II.

X-Ray Diffraction (XRD) Analysis

Sodium alginate, polyacrylamide, and all the graft copolymers were used for XRD analysis. The powder polymer sample was packed into a hole of 2 mm in diameter in a small container made of perspex [poly(methyl methacrylate)] about 1.5 mm thick. This piece was mounted on the specimen holder with pressure-sensitive tape so that the X-ray beam passed through the hole. A PW 1840 diffractometer and a PW 1729 X-ray generator (Philips, Holland) were used for this study to

produce CuK α radiation. The results are shown in Figures 4(a), 4(b), and 4(c).

Scanning Electron Microscopy (SEM) Analysis

Scanning electron micrographs for acrylamide, sodium alginate, and all six graft copolymers are shown in Figure 5. The small granules left after the pulverized graft copolymers were sieved, were subjected to SEM study. The samples were gold-coated, and a magnification of 200–300 times was obtained. Similarly, acrylamide and sodium alginate were subjected as such to SEM study. A Cam Scan Series-2 (Cambridge Scanning Company, United Kingdom) was used for SEM study.

Thermogravimetric Analysis (TGA)

TGA of all the samples was carried out with a Stanton Redcroft (STA 625, UK) thermal analyzer. TGA of the samples was performed up to a temperature of 600°C, with a starting point at room temperature in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10°C/min. The curves are shown in Figures 6 and 7.

RESULTS AND DISCUSSION

Synthesis and Intrinsic Viscosity

Table I shows the synthetic details of the graft copolymers based on sodium alginate. A series of six graft copolymers were synthesized with sodium alginate. For the first four graft copolymers (I–IV), the catalyst concentration was varied with the concentration of acrylamide and sodium alginate fixed. For the second set of two graft copolymers (V–VI), only acrylamide concentration was varied with the other 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. When a simplistic approach is followed, a low concentration of catalyst should initiate a few grafting sites, which results in longer polyacrylamide chains, compared to a high concentration of catalyst, which will initiate a larger number of grafting sites, thus making the average polyacrylamide chains shorter for the same acrylamide concentration. This was reflected in the graft copolymers in the series.

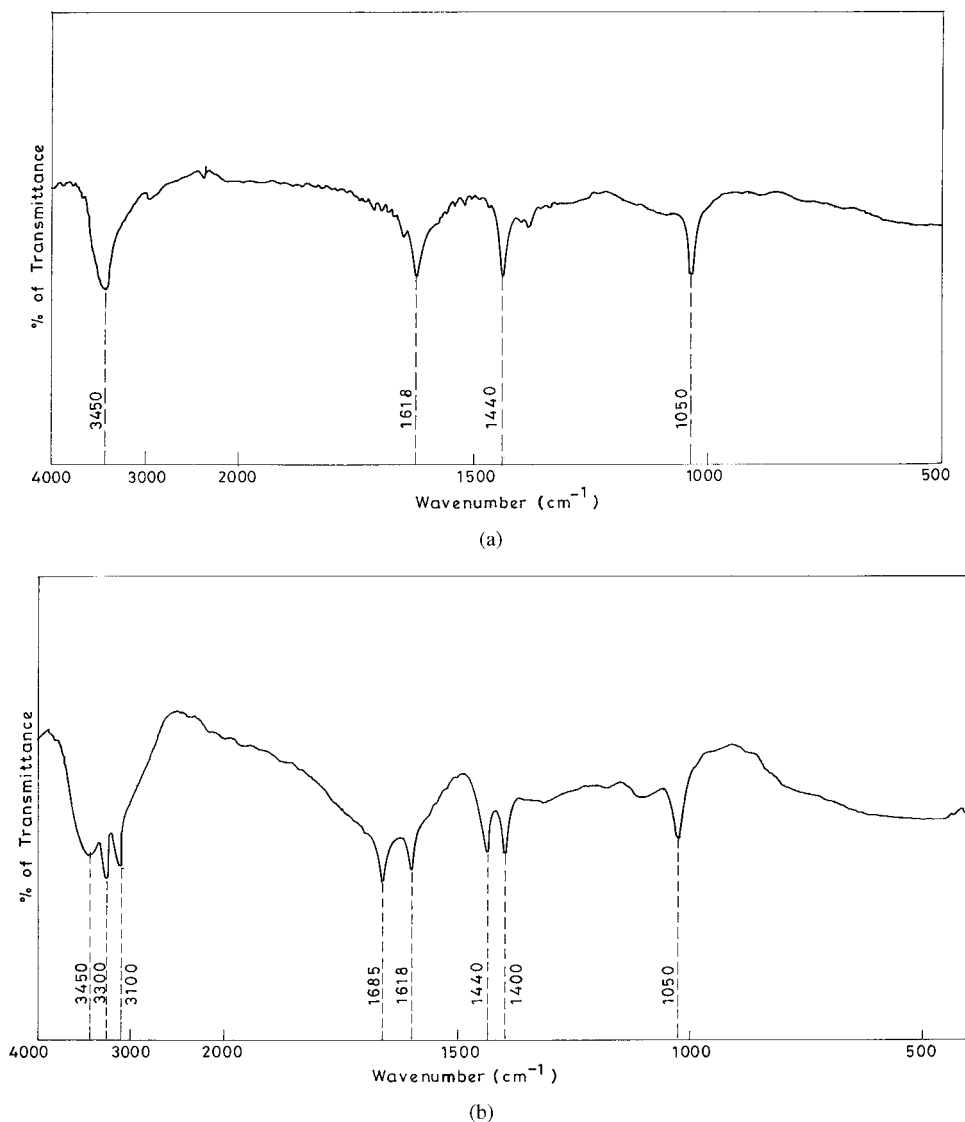


Figure 2 IR spectra of (a) sodium alginate and (b) SAG-IV.

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, the nature of the solvent, and the temperature of the medium. When the others factors are kept constant, for two polymers of approximately similar molecular weight, a branched polymer will have a lower hydrodynamic volume and, hence, a lower intrinsic viscosity compared to its linear counterpart. Further, along a series of branched polymers, the longer the branches are, the higher the intrinsic viscosity will be and vice versa. This has been observed in practice. Thus, SAG-I with 1.003×10^{-4} mol of CAN had an intrinsic viscosity of 6.75 compared to SAG-VI with 5.015×10^{-4} mol

of CAN, which had an intrinsic viscosity of 5.15. Similarly, a variation of the monomer concentration, with the catalyst concentration fixed, in the second series of two graft copolymers produced variation in the intrinsic viscosities.

Calculation of the Approximate Molecular Weight

The molecular weight of polymer samples can be estimated from the intrinsic viscosity $[\eta]$ values. The Mark-Houwink equation, $[\eta] = KM^\alpha$ is generally employed for the estimation of the molecular weight of linear polymers, where K and α are constants for a given polymer/solvent/temperature system. For polyacrylamide, the values of K and α are given as follows:¹⁰

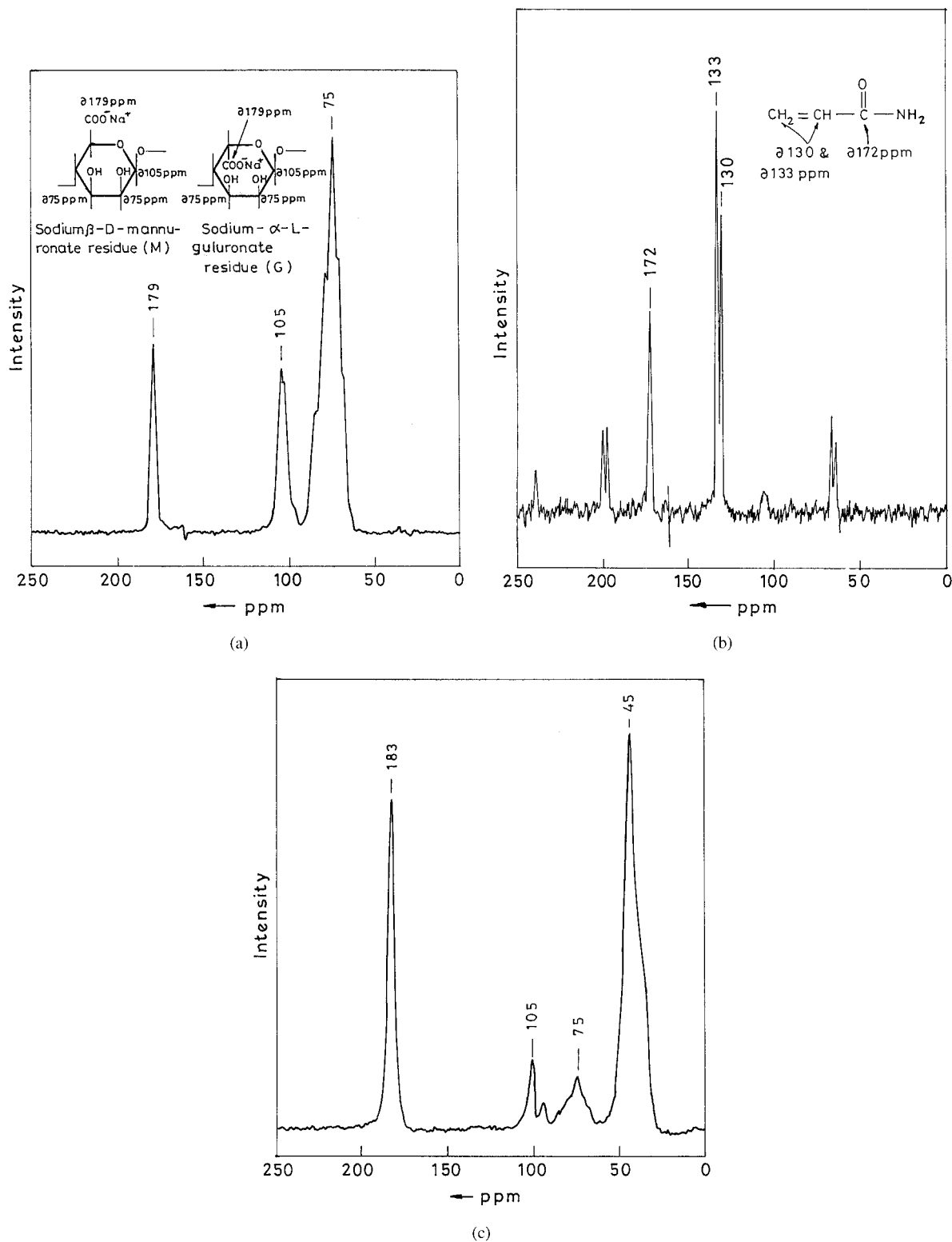


Figure 3 ^{13}C -NMR spectra of (a) sodium alginate, (b) acrylamide, (c) SAG-IV, and (d) three graft copolymers.

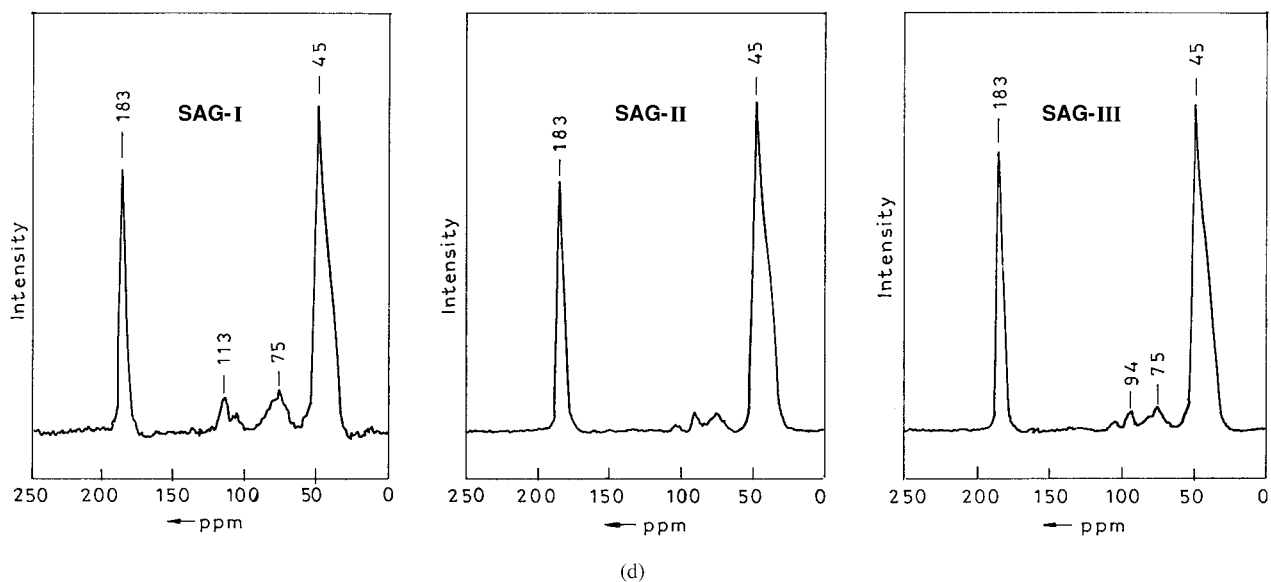


Figure 3 (Continued)

$$[\eta] = 6.8 \times 10^{-4}(\bar{M}_n)^{0.66} \quad (1)$$

$$[\eta] = 6.31 \times 10^{-5}(\bar{M}_w)^{0.80} \quad (2)$$

where M_n is the number-average molecular weight and M_w is the weight-average molecular weight. Graft copolymers are synthesized by the opening of the rings of polysaccharide mers on the backbone and the grafting of polyacrylamide onto the free radicals so generated. The opening imparts slight flexibility to the backbone. Moreover, the percentage of polysaccharide is small in comparison with the polyacrylamide. Hence, for grafted polysaccharides, several workers¹⁰⁻¹² have used the Mark-Houwink equation to estimate approximate molecular weight that is applicable for linear polymers. The same was done in this case. The approximate molecular weights of the graft copolymers are given in Table I.

Table II Elemental Analysis of the Grafted Sodium Alginate-Polyacrylamide

Polymer	% N	% C	% H
SAG-I	12.6	39.8	6.2
SAG-II	13.6	40.8	6.4
SAG-III	14.2	42.6	6.8
SAG-IV	12.7	38.2	6.1
SAG-V	15.9	44.5	7.2
SAG-VI	16.00	44.6	7.5

IR Spectra

Evidence of grafting was provided by IR spectroscopy. From the IR spectra of sodium alginate [Fig. 2(a)], it was obvious that sodium alginate showed a broad peak at 3450 cm^{-1} for —OH groups and two peaks, one at 1618 cm^{-1} and the other at 1440 cm^{-1} , for the —COO⁻ groups. One sharp peak at 1050 cm^{-1} was for the —C—O groups. However, in the graft copolymers [Fig. 2(b)], apart from the previous peaks, four additional peaks were present. Two peaks at 3300 cm^{-1} and 3100 cm^{-1} were for the NH₂ groups (one for symmetrical and the other for antisymmetrical stretching of two —N—H bonds). The peak at 1685 cm^{-1} was caused by the amide carbonyl group, and the peak at 1400 cm^{-1} was for the —C—N group. When the removal of acrylamide and polyacrylamide are assumed, the presence of peaks at 3300 , 3100 , 1685 , and 1400 cm^{-1} in the graft copolymer is strong evidence for grafting.

Table III Thermal Analysis of SAG-III

Transition	Start (°C)	Onset (°C)	Midpoint (°C)	End (°C)	Stop (°C)	Weight (%)
I	30.2	40	51.5	66.6	91.6	7.7
II	177.3	227.1	238.9	250.9	274.7	17.9
III	275.3	299	318.7	357.8	427.6	30.3
IV	428.2	460.5	483	527.26	560.3	33.7

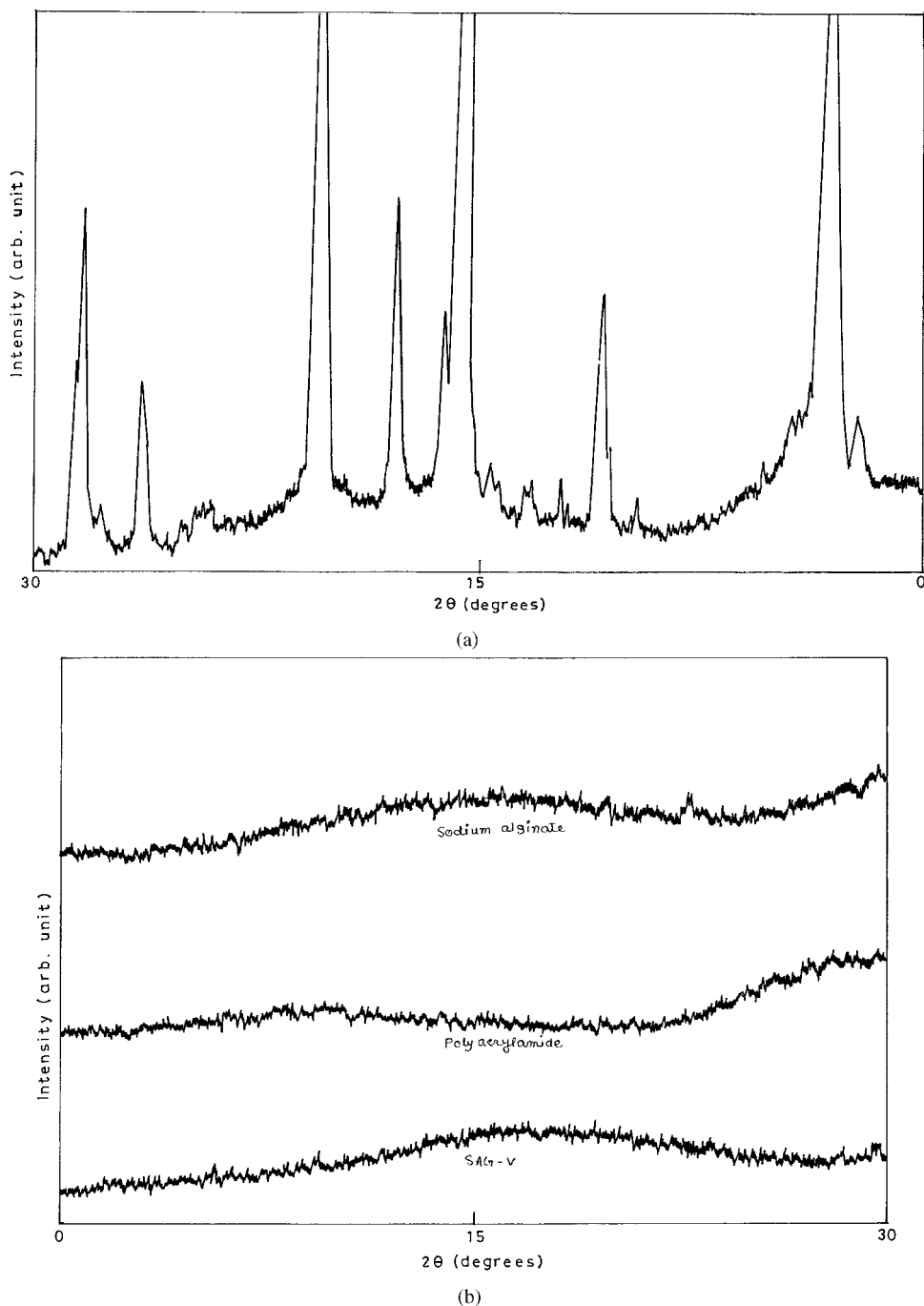


Figure 4 XRD studies of (a) acrylamide, (b) sodium alginate, polyacrylamide, and SAG-V, and (c) six graft copolymers.

¹³C-NMR Spectra

It is obvious from Figure 3(a) that sodium alginate had three distinct peaks in the ¹³C-NMR spectrum. The absorption peak at $\delta = 179$ ppm was for the carboxyl carbon atom of $-\text{COO}^- \text{Na}^+$ group, that of $\delta = 105$ ppm was for anomeric

carbon atom (i.e., C_1), and the peak at $\delta = 75$ ppm was for carbon atoms connected by $-\text{OH}$ groups (i.e., the carbon atoms in the six-member ring except the anomeric carbon atom). Sodium alginate is the sodium salt of alginic acid, which is a polymer of D-mannuronic acid (M) and L-Gulu-

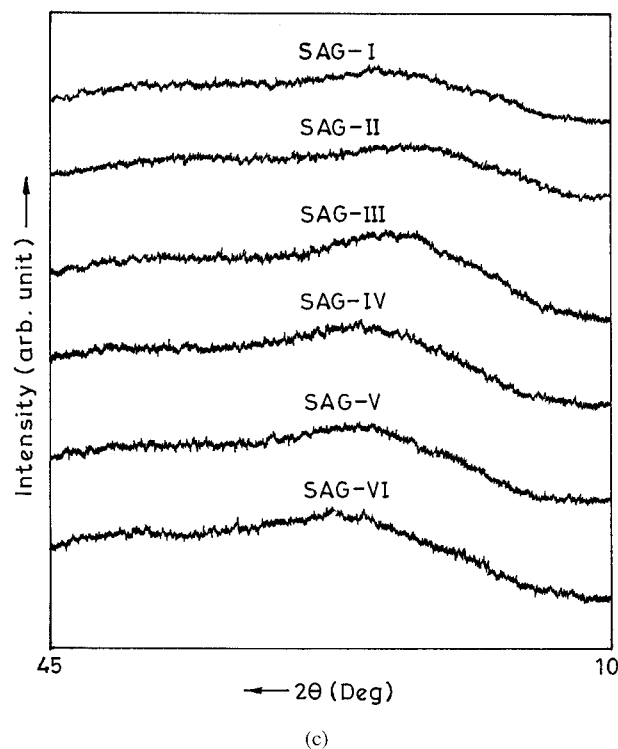


Figure 4 (Continued)

ronic acid (G), linked $\rightarrow 4$ - β -D-ManA-(1 and $\rightarrow 4$)- α -L-GulA-(1).¹³ These two monomers may be linked in blocks (e.g., -M-M-M-M-G-G-G-G-) or mixed (e.g., -M-G-G-M-M-G-). The detailed arrangement of the two acids is dependent on the source.¹³ The structure of sodium alginate, along with the ¹³C-NMR values, is represented in Figure 3(b).

Figure 3(b) shows the ¹³C-NMR spectrum of acrylamide. Acrylamide had three major peaks in the ¹³C-NMR spectrum. The peak at $\delta = 172$ ppm was for amide carbonyl carbon. Peaks at $\delta = 130$ and $\delta = 133$ ppm were for two sp^2 hybridized carbon atoms (i.e., $CH_2=CH-$). These are shown in Figure 3(b).

The ¹³C-NMR spectrum of one of the graft copolymers (SAG-IV) is shown in Figure 3(c). The graft copolymer had four characteristic peaks at $\delta = 183$, 105, 75, and 45 ppm. The peak at $\delta = 183$ ppm was for the carboxyl carbon of $-COO^-Na^+$, which was present in the sodium alginate spectrum at $\delta = 179$ ppm. The peak at $\delta = 105$ ppm was for the anomeric carbon atom, which was also present in the sodium alginate spectrum. The peak at $\delta = 75$ ppm was for the carbons with the secondary hydroxyl groups, and the peak at $\delta = 45$ ppm was for $-CH_2-CH_2-$ groups those were formed during the polymerization reaction.

As seen in ¹³C-NMR spectra of the graft copolymers and acrylamide, acrylamide had two peaks at $\delta = 130$ and 133 ppm of two sp^2 hybridized carbon atoms, which were absent in the graft copolymer. Moreover, one additional peak was present in for the graft copolymer at $\delta = 45$ ppm, which was for sp^3 hybridized carbon atoms (i.e., $-CH_2-CH_2-$ units in the graft copolymer). Neither the sodium alginate nor the acrylamide spectrum had this peak. So, the absence of peaks at $\delta = 130$ and 133 ppm and the presence of a peak at $\delta = 45$ ppm was clear evidence of the grafted polyacrylamide chains into the backbone of sodium alginate. Similar observations were also obtained from the ¹³C-NMR spectra of all the graft copolymers as shown in Figure 3(d).

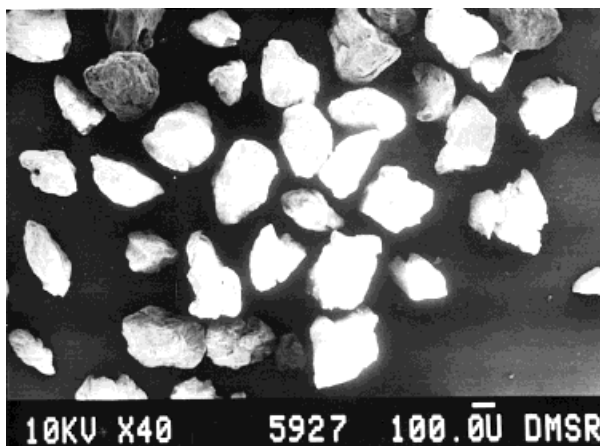
Again, the peak intensity at $\delta = 105$ ppm, which was for the carbons with secondary hydroxyl groups in the sodium alginate, was less in all the graft copolymers. This could be explained by the lesser number of carbon atoms connected by the secondary hydroxyl groups. Because Ce^{+4} oxidizes the 1,2-glycolic linkage of the polysaccharide to form free radicals that are responsible for the grafting reaction, the number of carbon atoms with secondary hydroxyl groups became less in the graft copolymers. This was also evidence for the grafting.

Elemental Analysis

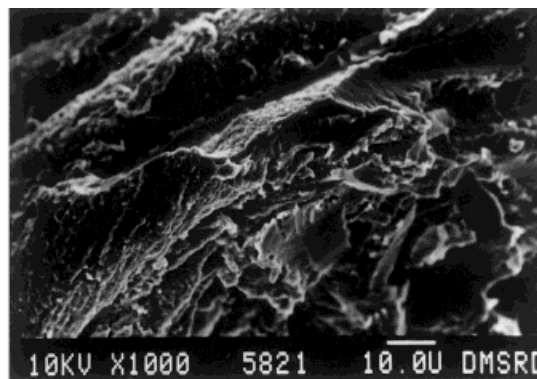
The results of the elemental analysis of sodium alginate and all the graft copolymers are given in Table II. Sodium alginate did not show any presence of nitrogen. There was a considerable percentage of nitrogen in the graft copolymers, which could be accounted for by the presence of grafted polyacrylamide chains. In the series of graft copolymers based on sodium alginate, the variation in the nitrogen content, although small, was significant in the case of SAG-III, SAG-V, and SAG-VI compared to the other graft copolymers. The higher percentage of nitrogen may have been caused by the increased polyacrylamide content in the graft copolymer. Among other graft copolymers, SAG-IV had the smallest percentage of nitrogen, which was again lowest polyacrylamide content compared to the other graft copolymers in the series.

X-Ray Diffractometry

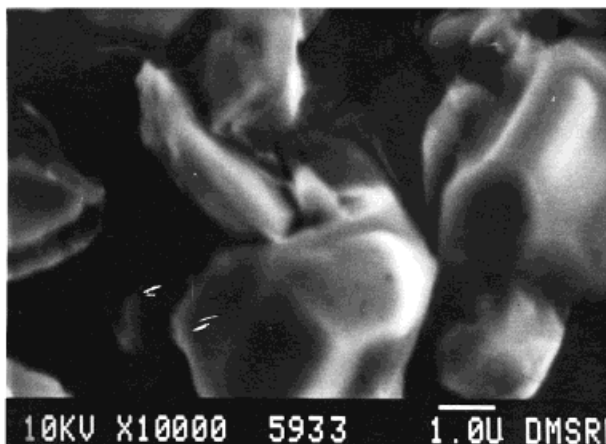
XRD analysis showed that sodium alginate [Fig. 4(b)] exhibited a very small crystallinity. How-



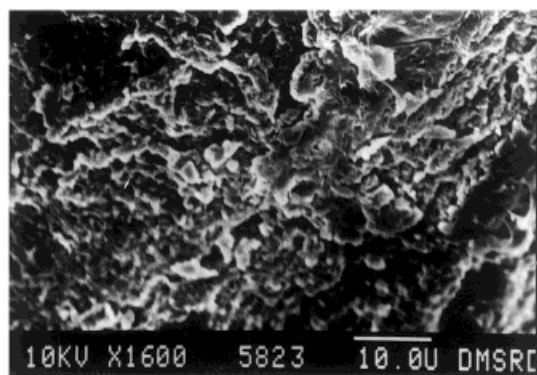
(a)



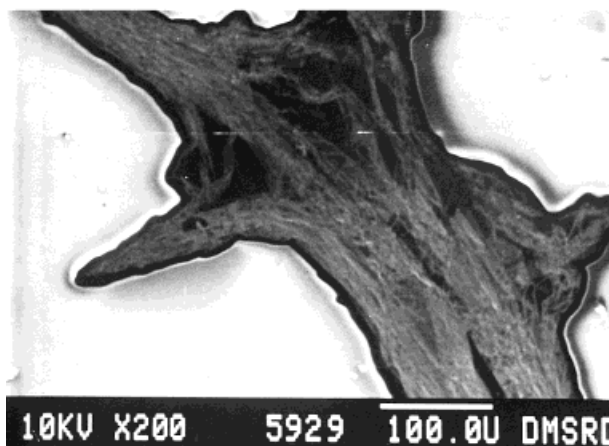
SAG-I



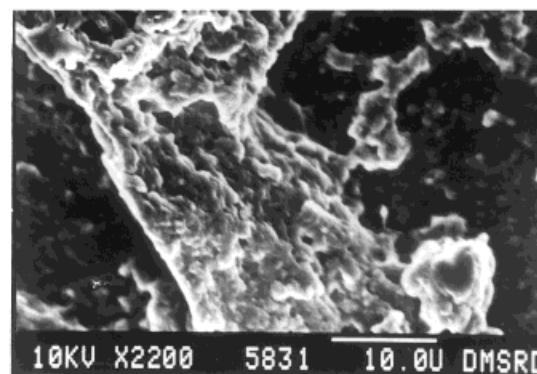
(b)



SAG-II

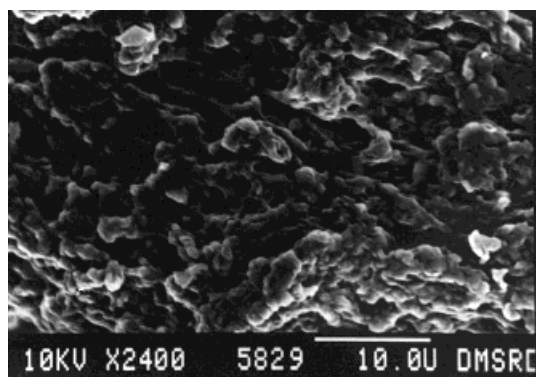


(c)

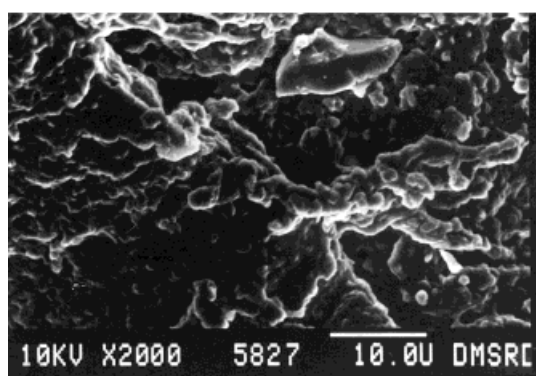


SAG-III

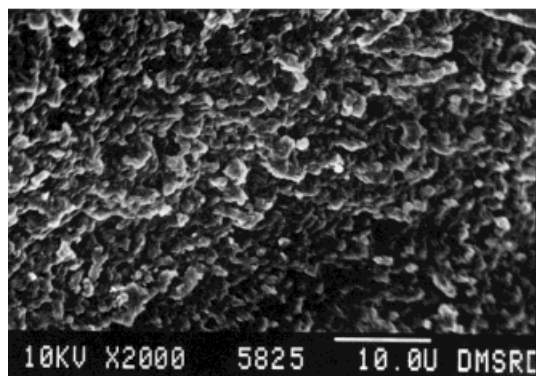
Figure 5 SEM analysis of (a) sodium alginate, (b) polyacrylamide, (c) SAG-VI, and (d) all six graft copolymers.



SAG-IV



SAG-V



SAG-VI

Figure 5 (Continued)

ever, the grafted products [Fig. 4(c)] did not have any peak that indicated crystallinity. Also, any sharp peak caused by acrylamide monomer [Fig. 4(a)] was also absent in the grafted products. This was indicative of an absence of acrylamide monomer.

Scanning Electron Micrographs

Figures 5(a) and 5(b) show the scanning electron micrographs of sodium alginate, polyacrylamide, acrylamide, and the series of six sodium-alginate-based graft copolymers, respectively. A careful examination of the micrographs reveals a large difference in the morphological appearance of the polymers. Polyacrylamide has a granular structure, which changed drastically when it was grafted into sodium alginate. This observation also supported the grafting of acrylamide onto sodium alginate.

Thermal Analysis (TGA, DTG, and DSC)

Figure 6 shows the TGA/DTG curve of SAG-III. It is obvious from the curve that it had four regions: I at 40–99.5°C, II at 227.1–274.7°C, III at 299–427.6°C, and IV at 460.5–560.3°C. The corresponding peaks where the degradation occurred were observed at 51.8, 239.3, 318.6, and 483°C in the DTG curve of SAG-III as shown in Table III. The initial weight loss of the polymer may have been caused by the presence of moisture in the sample. In the second region, the percent weight loss was caused by the loss of CO₂ from the polysaccharide backbone of the graft copolymer. As there were COO⁻ groups in the sodium alginate, it would decarboxylate in this temperature range. In the third zone, the weight loss was caused by the elimination of NH₃ from the polyacrylamide chains of the graft copolymer. This peak was absent in the TGA/differential scanning calorimetry (DSC) curve (Fig. 7) of sodium alginate. In the temperature range between 460.5 and 560.3°C, the weight loss might have been caused by the loss of abundant hydroxyl groups on the polysaccharide in the form of water. Sodium alginate also followed the same degradation pattern to that of SAG-III, except for the peak at 318.6°C. Sodium alginate was not completely degraded in this temperature range. It maintained a weight percent of about 35% at 560°C. The graft copolymer SAG-III was also not completely degraded in this temperature range. A residue of about 4% was retained up to 600°C.

CONCLUSIONS

The aim of this study was to prove the occurrence of grafting by various techniques. Variation of the synthetic parameters resulted in a series of graft

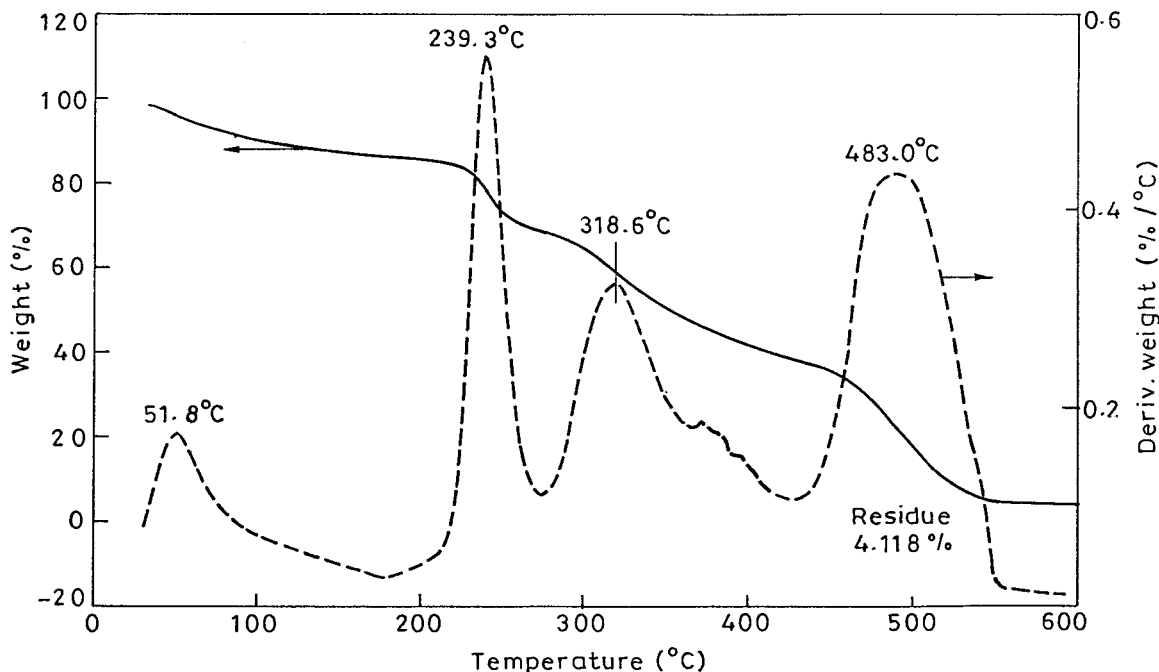


Figure 6 TGA/DTG curve of SAG-III.

copolymers with variation in the number and length of polyacrylamide chains, which resulted in different intrinsic viscosities and different molecular weights. The study of IR spectra of the

graft copolymers after extraction of the homopolymer provided strong proof of grafting. ^{13}C -NMR spectra also supported the formation of the graft copolymers. TGA results showed different ther-

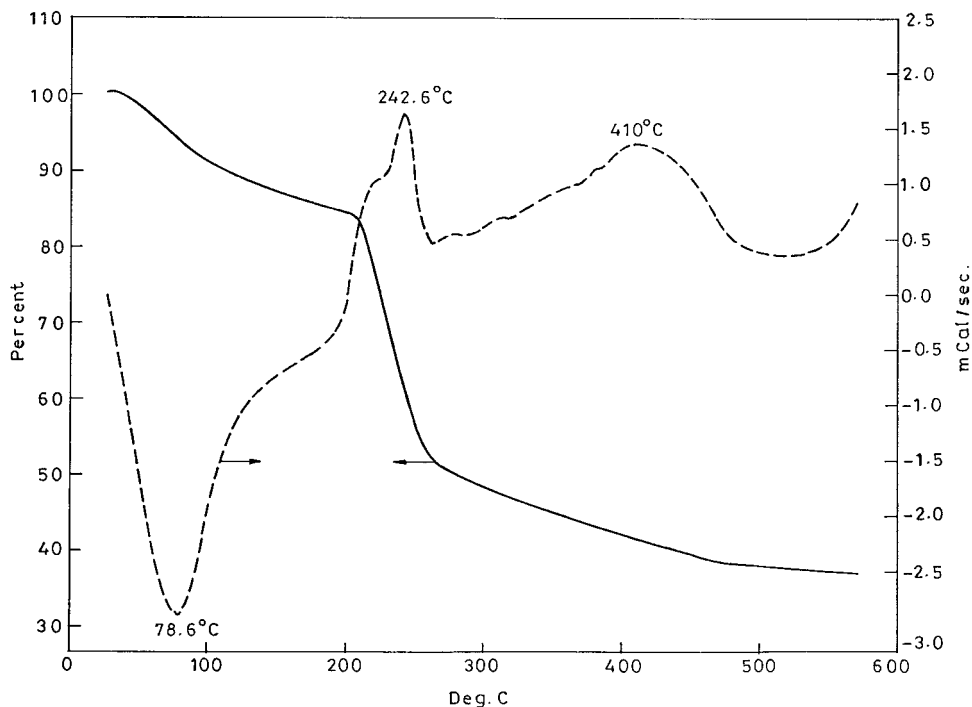


Figure 7 TGA/DSC curve of sodium alginate.

mal decomposition patterns for the virgin polysaccharide and the graft copolymers. XRD patterns showed the presence of crystallinity in the acrylamide, which disappeared after grafting because of the disruption in the original crystalline structure as a result of the formation of polyacrylamide side branches in the graft copolymers. The morphological variation of graft copolymers, polysaccharide, and acrylamide also supported the previous conclusion.

The authors thank Professor P. L. Majumdar, Calcutta University, for his valuable discussions, and CSIR New Delhi for financial support.

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