

Research Article

Ag(I) Catalyzed Grafting of Acrylonitrile onto Gum Arabic by Ce(IV) in H₂SO₄ Medium: A Kinetic Study

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Grafting of Acrylonitrile (AN) onto water-soluble polymer Gum arabic (GA) was carried out using ceric ammonium sulfate [Ce(IV)] as initiator in the presence and absence of Ag(I) in H₂SO₄ medium at 313 K. The rate of oxidation (R_{oxi}), rate of grafting (R_g), and grafting efficiency (GE) were determined for catalyzed and uncatalyzed grafting and suitable mechanism was proposed to explain the observed results. No homopolymerization in the absence of GA indicates that the polymer obtained is purely a graft copolymer. A probable mechanism involving the formation of Ag(I)-GA adduct followed by its oxidation with Ce(IV) to give Ag(II)-GA adduct, and its decomposition to give initiating radicals is proposed to explain the observed results. The graft polymer was characterized using Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), X-ray diffraction, and scanning electron microscopy (SEM) considering GA as reference.

1. Introduction

The water-soluble polymers are of immense importance in industry [1]. Their use is limited due to their biodegradability. Chemical modification of conventional polymers can provide a potential route for significantly altering their physical and chemical properties. Such a modification can be made through graft copolymerization technique. Various initiators are used for grafting technique [2] and the graft copolymerization occurs through the abstraction of hydrogen atom from the backbone polymer containing a hydroxyl group or an amino group [3].

The Ce(IV) is known to be one of the versatile water-soluble initiators for grafting of vinyl monomers onto natural and synthetic polymers. Graft polymerization of vinyl acetate onto starch [4], graft copolymerization of acrylonitrile onto cassava starch [5], synthesis of potato starch—g-polyacrylonitrile [6], grafting of acrylonitrile onto cellulose [7], grafting of acrylamide onto cellulose [8], graft copolymerization of acrylonitrile onto polyvinyl alcohol [9], kinetic study of grafting of acrylonitrile onto polyvinyl alcohol [10], synthesis of xanthum-g-vinyl formamide [11], graft copolymers of carboxymethylcellulose with acrylonitrile [12], vinyl

pyrrolidone [13], acrylamide [14], and characterization [15], grafting of acrylonitrile onto sodium alginate [16], and synthesis of Agar/alginate-g-polyacrylonitrile [17] have been reported. In all these cases graft copolymers were formed along with homopolymer which is very difficult to separate. In view of this we thought it is worthwhile to search for effective initiator systems to prepare exclusive graft copolymers without contamination of homopolymer. We have carried out the grafting of acrylonitrile onto water-soluble polymer GA with Ce(IV) in presence and absence of Ag(I) in order to get exclusively pure graft copolymers with greater efficiency and without contamination of homopolymer.

2. Experimental Section

2.1. Materials. All the chemicals used were of the BDH AR grade. The monomer acrylonitrile was purified by distilling at low pressure under N₂ atmosphere after washing with 5% NaOH, 3% H₃PO₄, and water. Gum arabic (Merck) was used after purification. Ceric ammonium sulfate, ferrous ammonium sulfate, and silver nitrate (Aldrich) were used without further purification.

2.2. Synthesis of GA-g-Acrylonitrile. The grafting reactions were conducted in dark under N₂ atmosphere to prevent any photochemical reaction and to avoid inhibition by atmospheric oxygen. 100 mL of stock solution of 1% GA was prepared in distilled water. A calculated amount of AN, Ag(I) (in catalyzed grafting) was added to a 25 mL flask thermostated at 40±°C containing polymer solution. After sometime definite amount of Ce(IV) is added and this was assumed as zero time. The reaction was terminated by addition of calculated amount of ferrous ammonium sulfate at appropriate time. The precipitate of copolymer was isolated by filtration and dried in vacuum maintained at 50°C for 48 hrs. Time-average kinetics were followed and assumed as steady-state kinetics. The rate of grafting (R_g), rate of oxidation (R_{oxi}), and grafting efficiency were calculated as follows:

$$R_g = -\frac{d[\text{monomer}]}{dt} = \frac{1000 \times W_1}{V_2 \times t \times M},$$

$$R_{oxi} = -\frac{d[\text{Ce(IV)}]}{dt} = \frac{V_2 \times c}{t}, \quad (1)$$

$$\% \text{ GE} = \frac{W_1 - W_2}{W_3} \times 100$$

W_1 , W_2 , and W_3 are weights of copolymer, polymer, and monomer, respectively. V_1 and V_2 are the volumes of reaction mixture and Ce(IV), respectively, while "M" is the molecular weight of monomer, "t" is the reaction time, and "c" is the concentration of Ce(IV) solution.

In the oxidation reactions, the concentration of the total Ce(IV) in the reaction mixtures was estimated volumetrically by ferrous ammonium sulfate, using ferrous ophenanthroline (ferroin) as an indicator.

Infrared spectra were recorded in the form of KBr pellets in the wave number range 4000–400 cm⁻¹ using JASCO IR 5300 spectrometer.

The powder X-ray diffractograms were recorded on Siemens D-5000 powder X-ray diffractometer using Cu K α radiation of wavelength 1.5406 Å.

SEM images were recorded on the HITACHI SU 1500 variable pressure scanning electron microscope (VP-SEM).

DSC of powder samples was carried out on Mettler Toledo DSC-851e model in nitrogen atmosphere in the temperature region 35–500°C at the rate of °C min⁻¹.

3. Results and Discussion

3.1. Rate of Ce(IV) Disappearance. Oxidation of GA was carried out with Ce(IV) in the presence and absence of Ag(I) at 313 K in H₂SO₄ medium. The rate of oxidation of GA by Ce(IV) was determined in the presence and absence of Ag(I) and the orders in [GA] were found to be 0.69 and 0.90, respectively (Figure 1). The orders in Ce(IV) were found to be unity in the presence and absence of [Ag(I)]. The rate of oxidation was studied by varying [Ag(I)] in the range of 5 × 10⁻² to 25 × 10⁻² M and the order in Ag(I) was 0.80 (Figure 1). The increase in R_{oxi} with an increase in Ag(I) is due to the formation of Ag(I)-GA polymer adduct and which is oxidized by Ce(IV) to form radicals at a faster rate in comparison to the rate in absence of Ag(I).

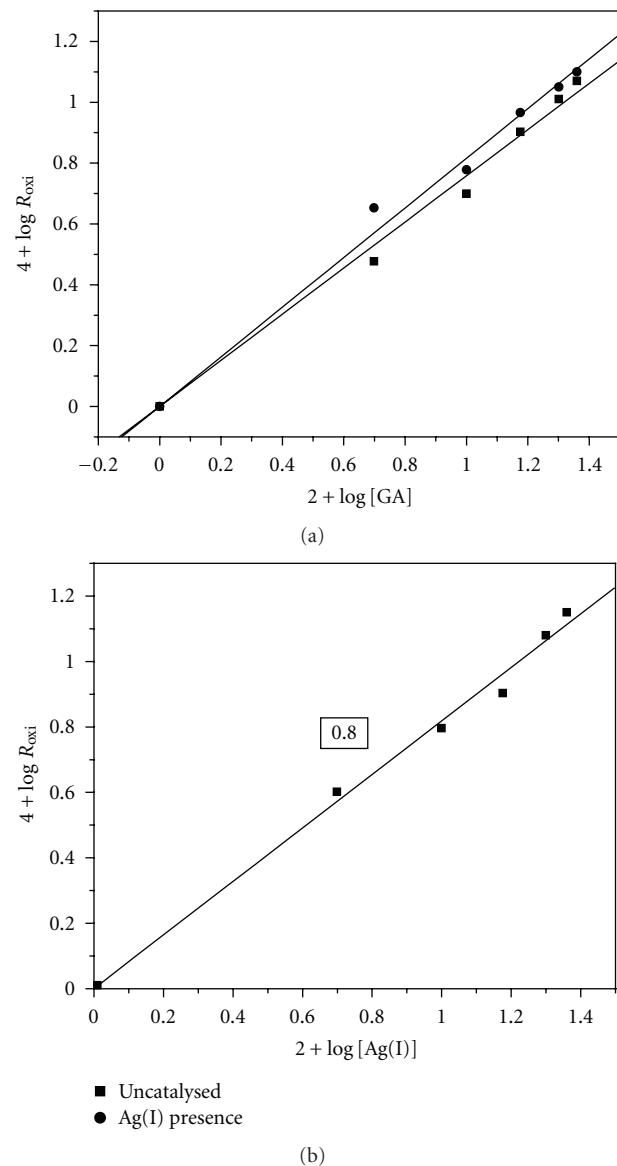
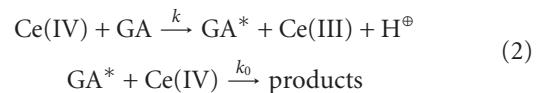


FIGURE 1: (a) Effect of [GA] on rate of oxidation. Plot of $4 + \log R_{oxi}$ versus $2 + \log [\text{GA}]$. $[\text{Ag(I)}] = 1.00 \times 10^{-2}$ M, $[\text{Ce(IV)}] = 5.00 \times 10^{-3}$ M, $[\text{H}_2\text{SO}_4] = 0.1$ M, $[\text{AN}] = 4.00 \times 10^{-2}$ M, and Temp = 313°K. (b) Effect of [Ag(I)] on rate of oxidation. Plot of $4 + \log R_{oxi}$ versus $2 + \log [\text{Ag(I)}]$. $[\text{GA}] = 10 \times 10^{-2}$ %(w/v), $[\text{Ce(IV)}] = 5.00 \times 10^{-3}$ M, $[\text{H}_2\text{SO}_4] = 0.1$ M, $[\text{AN}] = 4.00 \times 10^{-2}$ M, and Temp = 313 K.

The mechanism for oxidation of GA by Ce(IV) in the absence and presence of Ag(I) proposed is as follows:

Mechanism of Oxidation in Absence of Ag [I]:



The rate law is given as

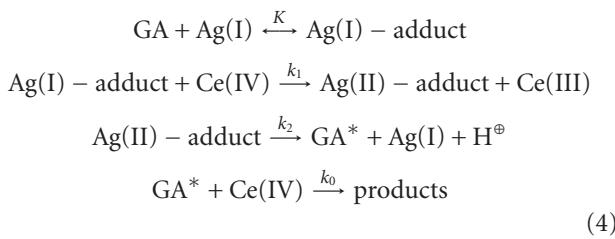
$$\frac{d[\text{Ce(IV)}]}{dt} = k[\text{Ce(IV)}][\text{GA}]. \quad (3)$$

TABLE 1: Comparison of rate of oxidation and rate of grafting.

System	$R_{\text{oxi}} \times 10^3$	$R_g \times 10^5$
GA + Ce(IV)	5.00	—
GA + Ce(IV) + Ag(I)	5.50	—
AN + Ce(IV)	4.50	Nil
AN + Ce(IV) + Ag(I)	5.25	Nil
GA + AN + Ce(IV)	5.50	5.80
GA + AN + Ce(IV) + Ag(I)	6.00	10.5

[Ag(I)] = 1.00×10^{-2} M, [Ce(IV)] = 5.00×10^{-3} M, $[\text{H}_2\text{SO}_4] = 0.1$ M, [AN] = 4.00×10^{-2} M, [GA] = 10×10^{-2} % (w/v), Temp = 313 K.

Mechanism of Oxidation in the Presence of Ag(I):



The rate law is given as

$$\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_1 K [\text{GA}] [\text{Ag(I)}] [\text{Ce(IV)}]}{\{1 + K[\text{GA}] + K[\text{Ag(I)}]\}}. \tag{5}$$

The oxidation rates for different systems observed under the identical experimental conditions are given in Table 1.

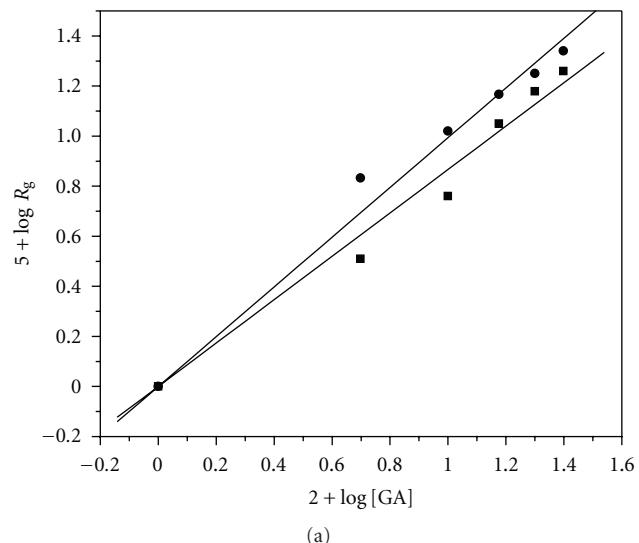
These observations from Table 1 suggest the following.

- (1) The rate of oxidation of GA is found to be more in the presence of Ag(I).
- (2) The rate of oxidation of acrylonitrile is comparatively less but no homopolymer of acrylonitrile is formed either in the presence or absence of Ag(I) with Ce(IV) in reaction conditions.
- (3) In the presence of Ag(I), the rate of oxidation of acrylonitrile-GA is slightly higher but R_g was significantly higher.

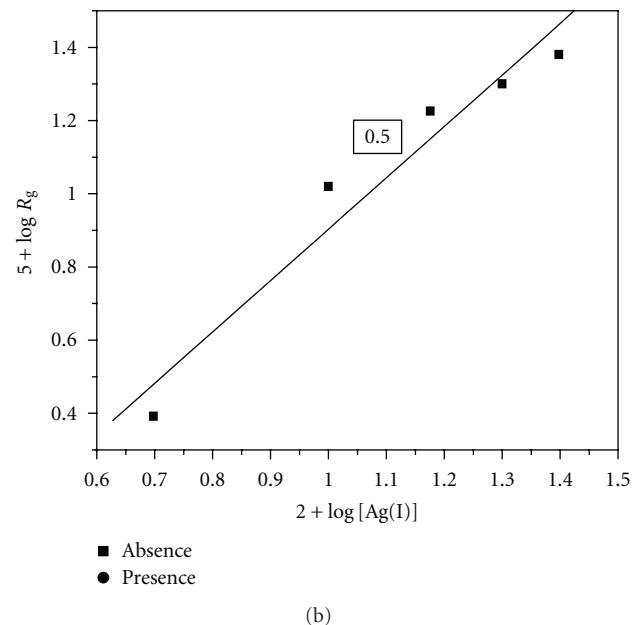
The observations indicate that the polymer obtained under experimental conditions is purely a graft copolymer. Ag(I) exclusively catalyzes the graft copolymerization.

3.2. Rate of Monomer Disappearance in the Absence of Ag(I). Grafting of AN onto GA was carried by Ce(IV) at 313 K in H_2SO_4 medium. In the absence of GA, polymerization was negligible under otherwise similar experimental conditions. In the presence of GA however the polymerization was noticed without any induction period indicating that the polymer obtained is purely a graft copolymer without any contamination of homopolymer.

3.2.1. Effect of [Ce(IV)] on Grafting. Rate of graft copolymerization and grafting efficiency decreased with the increase in [Ce(IV)] (Table 2). The decrease in R_g is due to participation of Ce(IV) in initiation and termination steps.



(a)



(b)

FIGURE 2: (a) Effect of [GA] on rate of grafting (R_g). Plot of $5 + \log R_g$ versus $2 + \log [GA]$ in presence and absence of Ag(I). $[(\text{Ce(IV)})] = 5.00 \times 10^{-3}$ M, [AN] = 4.00×10^{-2} M, Temp = 313 K, $[\text{H}_2\text{SO}_4] = 0.1$ M, $[\text{Ag(I)}] = 1.00 \times 10^{-2}$ M. (b) Effect of [Ag(I)] on Rate of grafting (R_g). Plot of $5 + \log R_g$ versus $2 + \log [\text{Ag(I)}]$. $[\text{GA}] = 10 \times 10^{-2}$ % (w/v), [AN] = 4.00×10^{-2} M, Temp = 313 K, $[\text{H}_2\text{SO}_4] = 0.1$ M, $[(\text{Ce(IV)})] = 5.00 \times 10^{-3}$ M.

3.2.2. Effect of [AN] on Grafting. The rate of graft copolymerization increased significantly with the increase in [AN] and the order in [AN] was found to be 2.0 in the concentration range of 0.32×10^{-2} – 0.64×10^{-2} M (Table 2). The increase in R_g with the increase in [AN] could be due to the availability of more amount of monomer to grafting sites. It is evident that order in [monomer] of 1.00–2.00 can be explained by linear termination of grafted polymer.

3.2.3. Effect of [GA] on Grafting. Increasing the percentage of polymer (w/v), the rate of grafting as well as grafting

TABLE 2: Effect of [Ce(IV)], [AN] on R_g and Grafting Efficiency (GE) in presence and absence of Ag(I). $[H_2SO_4] = 0.1\text{ M}$, Temp = 313 K.

$[Ce(IV)] \times 10^3$	$[Ag(I)] \times 10^2$	$[GA] \times 10^2\text{ (w/v)}$	$[AN] \times 10^2$	$R_g \times 10^5$	GE
5.00	1.00	1.00	0.32	7.30	21.8
5.00	1.00	1.00	0.40	10.5	22.5
5.00	1.00	1.00	0.48	12.6	25.0
5.00	1.00	1.00	0.56	15.7	26.7
5.00	1.00	1.00	0.64	19.9	29.6
5.00	1.00	1.00	0.40	10.5	25.3
7.50	1.00	1.00	0.40	15.7	37.5
10.0	1.00	1.00	0.40	13.1	31.3
12.5	1.00	1.00	0.40	9.42	22.7
5.00	0.00	1.00	0.32	2.62	7.80
5.00	0.00	1.00	0.40	5.03	12.0
5.00	0.00	1.00	0.48	7.75	15.4
5.00	0.00	1.00	0.56	10.2	17.4
5.00	0.00	1.00	0.64	13.3	19.8
5.00	0.00	1.00	0.40	5.87	14.0
7.50	0.00	1.00	0.40	9.96	24.0
10.0	0.00	1.00	0.40	7.65	18.2
12.5	0.00	1.00	0.40	5.87	14.0

efficiency was increased (Table 2), and the order in [GA] was 1.0 (Figure 2). The unity order in [reductant] can be explained by linear termination of grafted polymer radicals.

3.3. Rate of Monomer Disappearance in the Presence of Ag(I). Grafting of AN onto GA was carried in the presence of Ag(I) by Ce(IV) in H_2SO_4 medium at 313 K under identical conditions as above. The grafting efficiency and R_g were high in the presence of Ag(I) compared to that in the Ag(I) absence.

3.3.1. Effect of $[Ag(I)]$ on Grafting. The rate of graft copolymerization and grafting efficiency increased significantly with the increase in $[Ag(I)]$ in the range of 5.0×10^{-2} – 25.0×10^{-2} . The order in Ag(I) was found to be 0.50 as evident from the slope of plot $5 + \log R_g$ versus $2 + \log [Ag(I)]$ (Figure 2). The catalytic activity of Ag(I) is probably due to the facile reaction path through the intermediacy of a new redox system formed by added Ag(I). Ag(I) is known to form colorless adducts with oxygen-containing compounds like alcohols, acids, and so forth. In the present case, Ag(I) may form an adduct with polymers like GA in the initial step followed by its oxidation with Ce(IV) to form an Ag(II) adduct which subsequently undergoes internal oxidation to provide grafting sites at a faster rate when compared to polymer alone. Thus, the increase in the rate of graft copolymerization with Ag(I) is due to the production of more numbers of initiating radicals. It is also possible that the Ag(II) intermediate can directly initiate the reaction, since it is known to be a more powerful oxidizing agent. Similar observations that were also made in Ce(IV)-isopropyl alcohol redox system initiated polymerization of acrylonitrile in the presence of Ag(I) [18].

3.3.2. Effect of $[Ce(IV)]$ on Grafting. In the presence of Ag(I), R_g and grafting efficiency were determined for the concentration range of 2.5×10^{-3} – $12.5 \times 10^{-3}\text{ M}$ (Table 2). An induction period was noticed and this period decreased with the increase in the concentration of Ce(IV). The grafting efficiency and rate of grafting were higher in the presence of catalyst. The decrease in R_g with the increase in $[Ce(IV)]$ was explained by assuming the participation of Ce(IV) in the termination step.

3.3.3. Effect of $[AN]$ on Grafting. The rate of graft copolymerization and grafting efficiency increased with the increase in [AN] in the presence of Ag(I) (Table 2) and the order in [AN] was 1.44. It is well known that order in [monomer] can be explained either by linear or mixed terminations of polymer-grafted chains.

3.3.4. Effect of $[GA]$ on Grafting. Increasing the percentage of polymer (w/v), the rate of grafting as well as grafting efficiency increased (Table 2). The order in [GA] in the presence of Ag(I) was found to be 0.70 as evident from the plot $5 + \log R_g$ versus $2 + \log [GA]$ (Figure 2). The deviation from unit order is due to the complexation of polymer with Ag(I). The order thus leads to linear termination of grafted polymer chains.

From the above results and discussion, it is concluded that the grafting is initiated by the primary radicals as well as the Ag(II) adduct and the termination by Ce(IV) is linear.

3.3.5. Mechanism of Graft Copolymerization in the Absence of Ag(I). Production of initiating species:



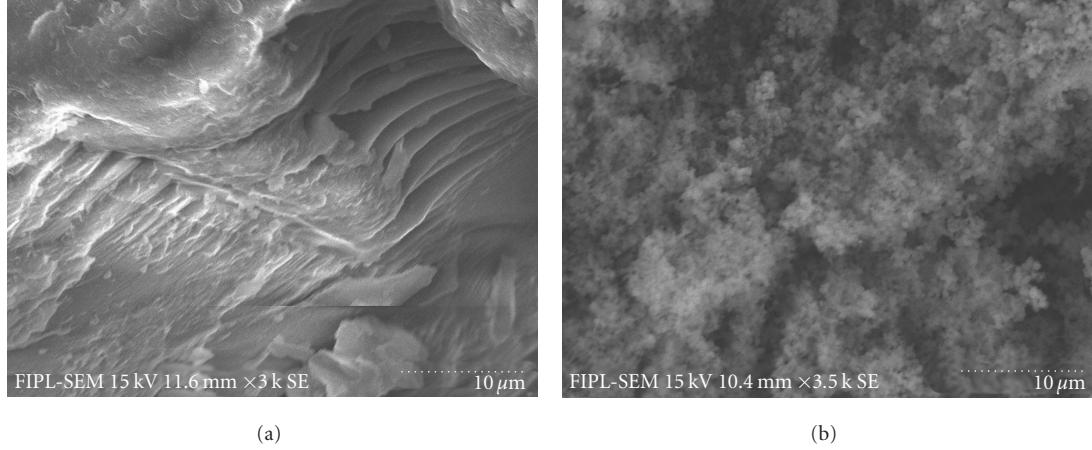


FIGURE 3: SEM images of (1) GA and (2) GA-g-acrylonitrile.

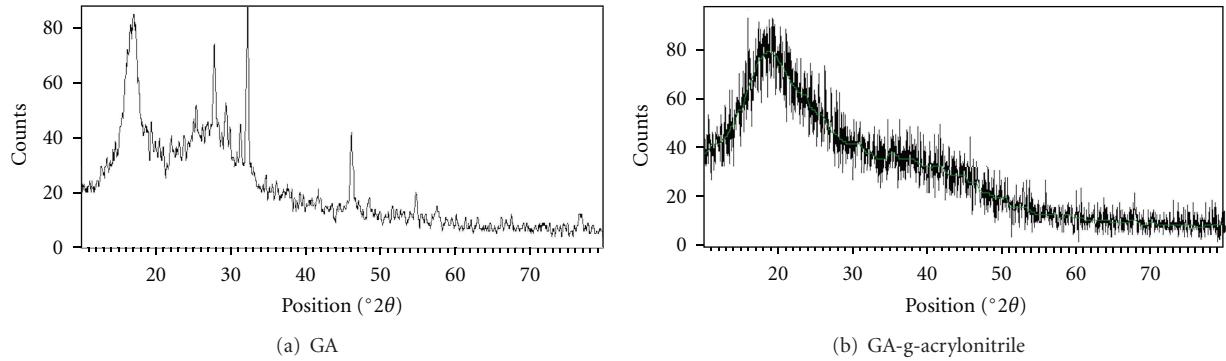
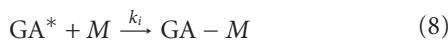


FIGURE 4: XRD.

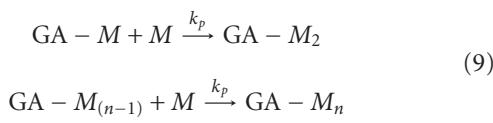
Reaction of primary radicals with Ce(IV) to give products:



Initiation of graft copolymerization by GA^* :



Propagation:



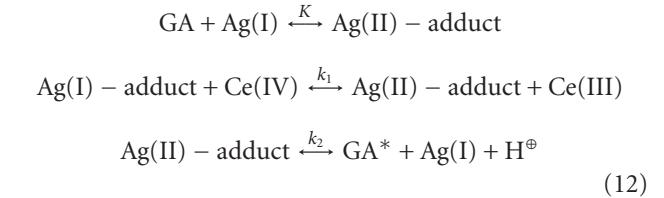
Termination by Ce(IV):



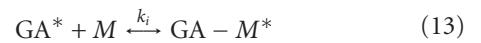
Applying steady-state principle, the rate law derived is:

$$R_g = -\frac{d[M]}{dt} = \frac{k_p k_i k_r [\text{GA}] [M]^2}{k_t \{k_0 [\text{Ce(IV)}] + k_i [M]\}}. \quad (11)$$

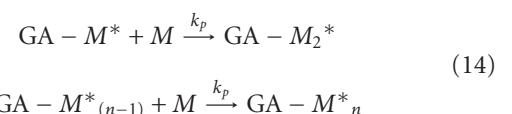
3.3.6. Mechanism of Graft Copolymerization in Presence of Ag(I). Production of initiating species:



Initiation of graft copolymerization by GA^* :



Propagation:



Termination by Ce(IV):



Consumption of GA^* by Ce(IV)



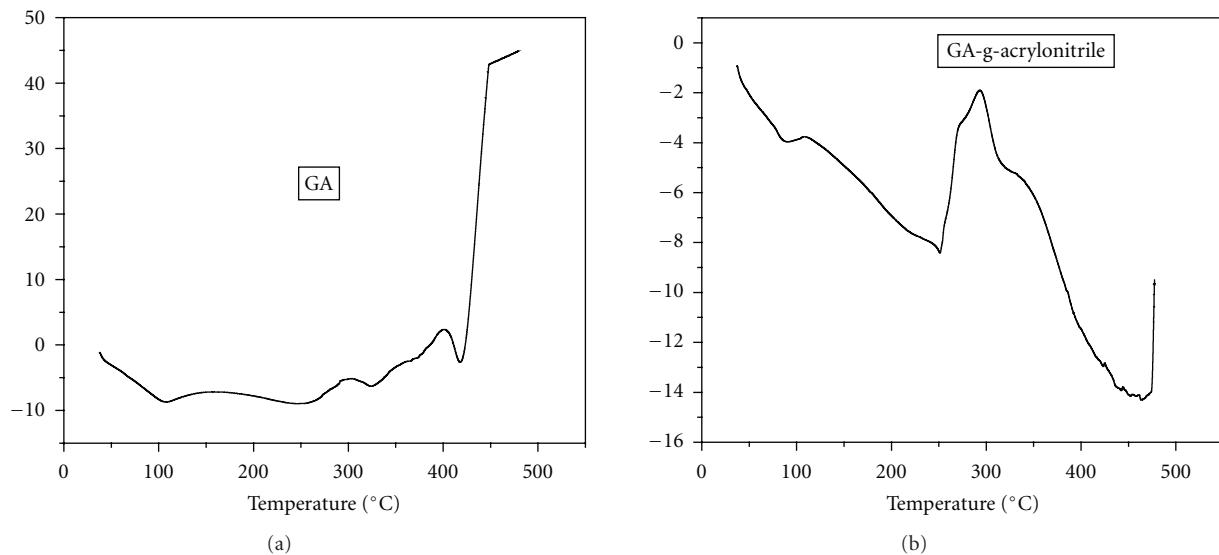


FIGURE 5: DSC.

Applying steady state principle, the rate law derived is

$$\begin{aligned} R_g &= -\frac{d[M]}{dt} \\ &= \frac{k_p k_i k_0 [GA][M]^2 [Ag(I)]}{k_i \{k_0 [Ce(IV)] + k_i [M]\} + \{K[Ag(I)] + K[GA]\}}. \end{aligned} \quad (17)$$

3.4. Characterization of Gum Arabic-g-Acrylonitrile

3.4.1. IR Spectra. IR spectra of GA show typical absorption of polysaccharide, ν_{max} 3419 cm⁻¹ (stretching of –OH group), and ν_{max} 2931 cm⁻¹ (C–H stretching), ν_{max} 1654 cm⁻¹, and the absorption at ν_{max} 2249 cm⁻¹ is –CN group of AN. Hence, the spectral data supports the grafting of AN onto GA.

3.4.2. SEM. The surface topography of the GA-g-acrylonitrile was studied by SEM and compared with the GA. The extreme surface of the graft polymer appears porous and different from that of the polymer GA. This evidence supports grafting of acrylonitrile onto GA (Figure 3).

3.4.3. XRD Spectra. XRD of GA (Figure 4) shows crystallinity in the region of 15–35°, while the graft polymer shows amorphous nature confirming the grafting of acrylonitrile onto backbone of GA.

3.4.4. DSC Spectra. DSC curve of GA (Figure 5) showed two endothermic transitions at about 322°C and 419°C. The thermogram of graft copolymer has new endothermic transitions at 252°C and 464°C and this may be due to the enhanced interaction between backbone polymer and the acrylonitrile. These results confirm the grafting of monomer onto polymer.

4. Conclusion

A novel approach of synthesis has been proposed with the aim of preparing graft copolymers without any homopolymer. The adopted methodology is to initiate polymerization by polymer radicals formed due to interaction of Ce(IV) with polymer. Ce(IV) participates in the initiation and termination steps of polymerization. The grafting was carried out in acidic medium by varying concentration of monomer, polymer, and Ag(I) and the grafting yields were found to be higher in the presence of Ag(I). The grafting mechanism has been explained satisfactorily by the linear termination of grafted polymers.

References

- [1] C. Radhakumary, P. D. Nair, S. Mathew, and C. P. Reghunadhan Nair, "Biopolymer composite of chitosan and methyl methacrylate for medical applications," *Trends in Biomaterials and Artificial Organs*, vol. 18, no. 2, pp. 117–124, 2005.
- [2] A. Bhattacharya and B. N. Misra, "Grafting: a versatile means to modify polymers: techniques, factors and applications," *Progress in Polymer Science*, vol. 29, no. 8, pp. 767–814, 2004.
- [3] A. Gopalan, T. Vasudevan, A. Ramasubramanian, and S. S. Hariharan, "Peroxosalts initiated graft copolymerization of aniline onto rayon," *Journal of Applied Polymer Science*, vol. 56, p. 1299, 1995.
- [4] G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, "Graft polymerization of vinyl acetate onto starch-g-poly(vinyl alcohol)," *Journal of Applied Polymer Science*, vol. 23, no. 1, pp. 229–240, 1979.
- [5] E. U. Ikuoria, A.S. Folayan, and F. E. Okieimen, "Studies in the graft copolymerization of acrylonitrile onto cassava starch by ceric ion induced initiation," *International Journal for Biotechnology and Molecular Biology Research*, vol. 1, no. 1, pp. 10–14, 2010.
- [6] V. Singh, A. Tiwari, S. Pandey, and S. K. Singh, "Peroxydisulphate initiated synthesis of potato starch-g-polyacrylonitrile

- under microwave irradiation," *Express Polymer Letters*, vol. 1, pp. 51–58, 2007.
- [7] R. Khullar, V. K. Varshney, S. Naithani, and P. L. Soni, "Grafting of acrylonitrile onto cellulosic material derived from bamboo (*Dendrocalamus strictus*)," *Express Polymer Letters*, vol. 2, no. 1, pp. 12–18, 2008.
 - [8] A. Jideonwo and H. A. Adimula, "Graft copolymerization of Acrylamide onto cellulose using enhanced Ferric/peroxide redox initiator system," *Journal of Applied Polymer Science*, vol. 10, no. 3, pp. 151–155, 2006.
 - [9] S. C. Jana, S. Maiti, and S. Biswas, "Graft copolymerization of acrylonitrile onto poly(vinyl alcohol) in presence of air using ceric ammonium nitrate-natural gums," *Journal of Applied Polymer Science*, vol. 78, no. 9, pp. 1586–1590, 2000.
 - [10] M. T. Taghizadeh and M. A. Darvishi, "Kinetics and mechanism of heterogeneous graft polymerization of acrylonitrile onto polyvinyl alcohol initiated with ceric ammonium nitrate," *Iranian Polymer Journal*, vol. 10, no. 5, pp. 283–292, 2001.
 - [11] J. Banerjee, A. Srivastava, A. Srivastava, and K. Behari, "Synthesis and characterization of xanthan gum-g-N-vinyl formamide with a potassium monopersulfate/Ag(I) system," *Journal of Applied Polymer Science*, vol. 101, no. 3, pp. 1637–1645, 2006.
 - [12] M. J. Zohuriaan-Mehr, A. Pourjavadi, and M. Sadeghi, "Modified CMC: part1-optimized synthesis of carboxymethyl cellulose-g-polyacrylonitrile," *Iranian Polymer Journal*, vol. 14, no. 2, pp. 131–138, 2005.
 - [13] M. Yiğitoğlu, N. Işıklan, and R. Özmen, "Graft copolymerization of N-vinyl-2-pyrrolidone onto sodium carboxymethylcellulose with azobisisobutyronitrile as the initiator," *Journal of Applied Polymer Science*, vol. 104, no. 2, pp. 936–943, 2007.
 - [14] B. A. El-Hady and M. M. Ibrahim, "Graft copolymerization of acrylamide onto carboxymethylcellulose with the xanthate method," *Journal of Applied Polymer Science*, vol. 93, no. 1, pp. 271–278, 2004.
 - [15] A. Sand, M. Yadav, and K. Behari, "Preparation and characterization of modified sodium carboxymethyl cellulose via free radical graft copolymerization of vinyl sulfonic acid in aqueous media," *Carbohydrate Polymers*, vol. 81, no. 1, pp. 97–103, 2010.
 - [16] S. B. Shah, C. P. Patel, and H. C. Trivedi, "Ceric-induced grafting of acrylonitrile onto sodium alginate," *High Performance Polymers*, vol. 4, no. 3, pp. 151–160, 1992.
 - [17] M. U. Chhatbar, R. Meena, K. Prasad, and A. K. Siddhanta, "Agar/sodium alginate-graft-polyacrylonitrile, a stable hydrogel system," *Indian Journal of Chemistry*, vol. 48, no. 8, pp. 1085–1090, 2009.
 - [18] P. Srinivas, K. Nageswar Rao, B. Sethuram, and T. Navneeth Rao, "Polymerisation of acrylonitrile initiated by cerium isopropyl alcohol redox system in presence and absence of Silver," *Journal of Macromolecular Science*, vol. 18, p. 261, 1982.

