Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Ce(IV)-Ion Initiated Graft Copolymerization of Methyl Methacrylate onto Guar Gum

Brij Raj Sharma[a]; Vineet Kumar[a]; P. L. Soni[a]
[a] Center of Advance Studies in Chemistry of Forest Products, Forest Research Institute, Dehra Dun, India

To cite this Article Sharma, Brij Raj , Kumar, Vineet and Soni, P. L.(2003) 'Ce(IV)-Ion Initiated Graft Copolymerization of Methyl Methacrylate onto Guar Gum', Journal of Macromolecular Science, Part A, 40: 1, 49 — 60

To link to this Article: DOI: 10.1081/MA-120016673

URL: http://dx.doi.org/10.1081/MA-120016673

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 1, pp. 49–60, 2003

Ce(IV)-Ion Initiated Graft Copolymerization of Methyl Methacrylate onto Guar Gum

Brij Raj Sharma, Vineet Kumar,* and P. L. Soni*

Center of Advance Studies in Chemistry of Forest Products,
Forest Research Institute, Dehra Dun, India

ABSTRACT

Graft copolymerization of methyl methacrylate onto guar gum was carried out in an aqueous medium using a ceric ammonium nitrate–nitric acid initiation system. The percent grafting (%G) and percent grafting efficiency (%GE) were determined as functions of the concentrations of ceric ammonium nitrate, nitric acid, methyl methacrylate, guar gum, polymerization temperature and time. Results are discussed and a reaction mechanism is proposed.

Key Words: Guar gum; Graft copolymerization; Methyl methacrylate; Ceric ammonium nitrate.

INTRODUCTION

Natural polysaccharides, also known as *Cinderella of biopolymers*, undoubtedly provide a rich and renewable reservoir of structurally and functionally different biopolymers. However, the possibility of functional groups in polysaccharides to undergo a wide range of chemical reactions is an additional advantage for the extension of their applications. The availability of a spectrum of polysaccharides thus provides an excellent

---

*Correspondence: Vineet Kumar and P. L. Soni, Center of Advance Studies in Chemistry of Forest Products, Forest Research Institute, Dehra Dun—248006, India; E-mail: vineetkmadan@yahoo.co.in; sonil@icfre.org.

DOI: 10.1081/MA-120016673
1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

opportunity for the development of fine tuned products by chemical modification for broader applications. In recent years, chemical modification of natural polysaccharides through grafting has received considerable attention.

Guar gum (GG) is derived from the seeds of guar plant *Cyamopsis tetragonolobus*, a pod bearing legume grown commercially in India, Pakistan and the southwestern United States. Seed is composed of hull (15%), germ (45%), and endosperm (40%). The endosperm contains 75–85% guaran, the functional polysaccharide in guar gum, has a chain of $(1 \rightarrow 4)$-linked-β-D-mannopyranosyl units with single α-D-galactopyranosyl units connected by $(1 \rightarrow 6)$ linkages to, on the average, every second main chain unit. The ratio of D-mannopyranosyl to D-galactopyranosyl units is about 1.8:1. The average molecular weight of guaran is in the range of $1-2 \times 10^6$ dalton. GG forms viscous, colloidal dispersion when hydrated in water. It is being used as a viscosity builder and water binder in many industries such as textile, food, paper, petroleum, mining, explosives, pharmaceuticals etc.[1,2]

Grafting of methyl methacrylate onto natural polymers such as starch,[3–5] cellulose,[6–8] *Leucaena glauca* seed gum,[9] sodium alginate,[10,11] jute fiber,[12] chitin,[13] wool and silk[14] has been studied using different redox systems, but there is no report on the graft copolymerization of methyl methacrylate (MMA) onto GG in the presence of ceric ammonium nitrate (CAN) as redox initiator. Reaction conditions for graft copolymerization of MMA onto GG were optimized in our laboratory with a view that grafted GG may find better applications in comparison to native GG.

EXPERIMENTAL

Materials and Methods

Guar gum was supplied by Hindustan Gum and Chemicals Ltd., Bhiwani, Rajasthan, India. Methyl methacrylate, ceric ammonium nitrate (for synthesis, Aldrich Chemical Co.) and nitric acid (AR grade, Ranbaxy Laboratories Ltd., India) were used in this study. Methyl methacrylate was distilled before use.

Graft Copolymerization

The grafting reaction was carried out in inert atmosphere in a 500 mL, three-necked round bottom flask equipped with a stirrer, a gas inlet system and a reflux condenser immersed in a constant temperature water bath. In a typical reaction, GG (0.5–2.0 g) was dissolved in water (90 mL) with continuous stirring and bubbling of a slow stream of nitrogen at the desired temperature. The freshly prepared 10 mL solution of CAN (0.005–0.04 mol/L) in nitric acid (0.1–0.4 M) followed by MMA (0.14–0.49 mol/L) was added and a continuous supply of nitrogen gas was maintained throughout the reaction period. The grafting reaction was carried out for a varying period of time intervals (1–5 h). After the reaction was over, the reaction mixture was poured in methanol. Centrifugation, washing with methanol and filtration processes were carried out, and the product was dried in a vacuum desiccator. The dried product was extracted with benzene for 24 h. After

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

complete removal of homopolymer (polymethyl methacrylate), the grafted product was dried to a constant weight. The %G and %GE were calculated from the increase in weight of GG after grafting in the following manner:

$$\%\mathrm{G} = \frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100$$

$$\%\mathrm{GE} = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

RESULTS AND DISCUSSION

The use of CAN for chemical initiation of vinyl polymerization has been shown in the possible modification of biopolymers viz. Chitin,[13] starch,[15–17] cellulose,[18] guar gum,[19] etc. The formation of free-radicals on these biopolymers by cerium(IV) has been demonstrated by electron spin resonance.[20] The mechanism by which cerium(IV) generates free-radicals is believed to involve the formation of coordination complex between the oxidant i.e., CAN and the hydroxyl group of biopolymer. The ceric(IV)–biopolymer complex then disproportionates forming a free-radical on the biopolymer chain and cerium(III).[20,21] Model compound studies of cerium(IV) oxidation of monohydric alcohol and 1,2-glycols support the postulated mechanism and suggest that the C_2–C_3 glycol and the C_6 hydroxyl of anhydro-D-glucose unit may be preferred site for free-radical generation.[22–24] Evidence for the formation of stable coordination complex has been obtained by kinetic and spectroscopic methods for cerium(IV) oxidation of many compounds in perchloric and nitric acids.[23,25,26]

Relative reactivity of the C_6 hydroxyl and C_2–C_3 glycol was estimated by comparing the tetrahydropyran-2-methanol and cyclohexanemethanol as models for the C_6 hydroxyl and with *trans*-1,2-cyclohexanediol for C_2–C_3 glycol units. The results show that the relative rate of the ceric ion oxidation of *trans*-1,2-cyclohexanediol was six times higher than the primary hydroxyl.[23]

Furthermore, equilibrium constants for *trans*-1,2-cyclohexanediol and *cis*-1,2-cyclohexanediol are consistent with chelate complex formation. In the stable conformations of these compounds the separation of the hydroxyl groups is almost the same and the relatively large Ce(IV) can easily bridge this distance. The formation of a five-membered chelate ring fused to the cyclohexane ring results in a relatively rigid system with the *trans* isomer, whereas the complex with *cis* isomer is relatively flexible since conformation interconversion can occur as readily in the complex as in the uncomplexed diol. The greater flexibility of the complex with the *cis*-isomer thus contributes to its somewhat greater stability (more positive entropy of formation).[23]

In view of the above, it is proposed that the oxidation reaction of GG will occur preferably at the C_2–C_3 glycol unit and to a much less extent at the C_6 hydroxyl since mannan backbone of GG contains *cis*-OH group at C_2–C_3.

In the presence of ceric salts viz. CAN $[Ce(NH_4)_2(NO_3)_6]$, as initiator on graft copolymerization onto GG, it is proposed that a ceric ion–GG complex is initially formed as a result of electron transfer. Then the ceric ion(IV) is reduced to cerous ion(III), and a free-radical is created on the galactomannan backbone as shown in Sch. 1.[18] The radical site on the galactomannan chain then initiates graft copolymerization of a polar vinyl monomer, which is present in the reaction mixture. The grafting occurs mainly at C_2-C_3 as discussed above.

Determination of Optimum Reaction Conditions

To optimize the conditions for grafting of MMA onto GG, the concentration of CAN, nitric acid, monomer, time and temperature were varied.

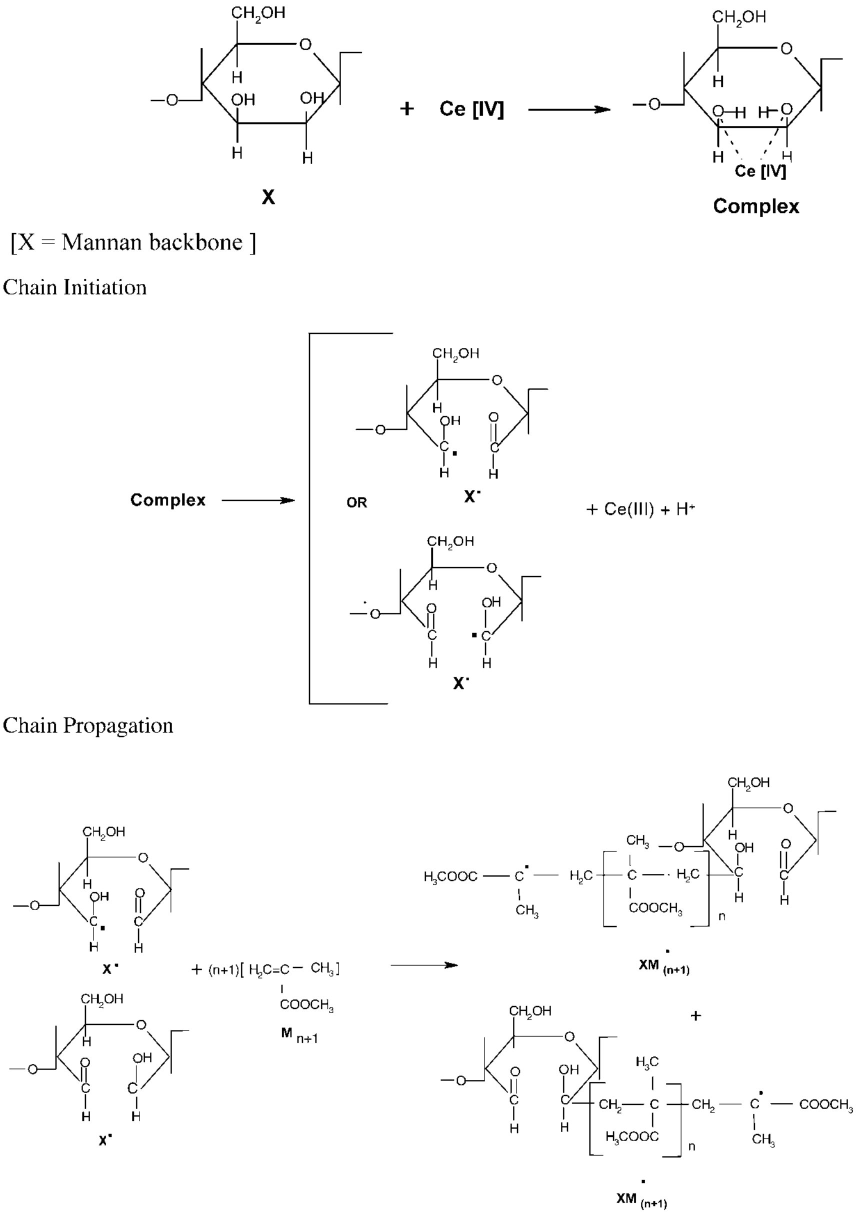
Effect of Reaction Time

The effect of polymerization time on %G and %GE is shown in Fig. 1. It can be seen from Fig. 1 that the %G increases rapidly with an increase in time up to 3 h, after which it levels off. The increase in %G is accounted for by the increase in number of grafting sites in the initial stages of reaction.[10,27] The leveling off of grafting after 3 h could be attributed to a decrease in concentration for both initiator and monomer, thereby a reduction in the number of sites on the backbone accessible for grafting as the reaction proceeds.

It has also been observed that %GE does not change appreciably during the course of reaction as shown in Fig. 1. The slight change in %GE with time occurs due to an increase in the homopolymer formation on account of lesser available sites on the backbone for grafting. The GE pattern of MMA onto GG shows the similarity to the GE pattern of vinyl monomers onto sodium alginate,[10] jute fiber[12] with ceric ion as redox initiator. Thus, to obtain the maximum %G, the optimum reaction time is 3 h.

Effect of CAN Concentration

The effect of variation in CAN concentration on %G and %GE is shown in Fig. 2. CAN concentration was increased from 0.005–0.04 mol/L. It is evident from the Fig. 2 that the %G increases with an increase in the initiator concentration and reaches maximum value 197.86% at 0.02 mol/L of CAN. A further increase in the CAN concentration is accompanied by a decrease in the %G. The observed increase in %G, within the CAN concentration ranging from 0.005 to 0.02 mol/L, may be due to the fact that in this concentration range the activation along the backbone takes place immediately, followed by graft copolymerization of monomer onto the backbone. A relatively high concentration of the initiator may cause a reduction of grafting, due to an increase in the number of backbone radicals terminated prior to MMA addition. Further, homopolymer formation at higher concentration which competes with the grafting reaction for available monomer could lead to a decrease in %G. Similar observations have also been reported in the literature.[4,15,28]



[X = Mannan backbone]

Chain Initiation

Chain Propagation

Chain Termination

$XM^{\bullet}_{(n+1)} + XM^{\bullet}_{(n+1)} \longrightarrow$ Dead Polymer

$M^{\bullet}_{(n+1)} + M^{\bullet}_{(n+1)} \longrightarrow$ Dead Polymer

$XM^{\bullet}_{(n+1)} + M^{\bullet}_{(n+1)} \longrightarrow$ Dead Polymer

Scheme 1.

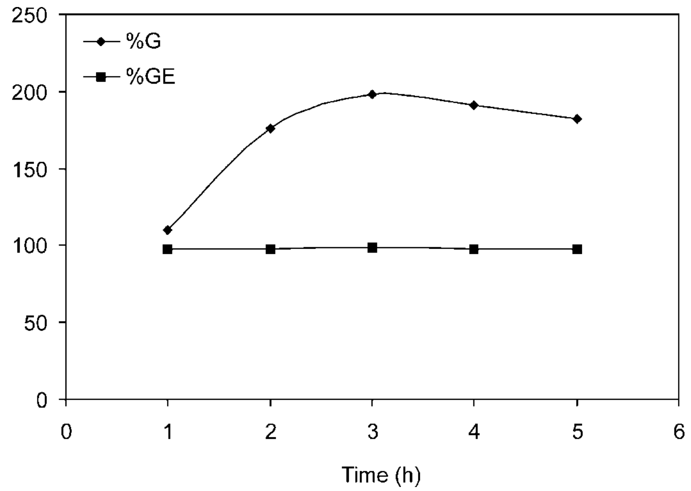


Figure 1. Effect of duration of reaction on %G and %GE. Reaction conditions: GG = 0.05 g/L, [CAN] = 0.02 mol/L, [MMA] = 0.21 mol/L, $[HNO_3]$ = 0.2 M, reaction temperature = 30°C, reaction volume = 100 mL.

Fig. 2 also shows that there is a decrease in %GE with an increase in the CAN concentration. The fast dissociation of CAN may account for higher %GE in the initial stages, since the total amount of Ce(IV) would be available for initiation. It is proposed that for ceric ion initiated graft copolymerization, the higher the concentration of Ce(IV),

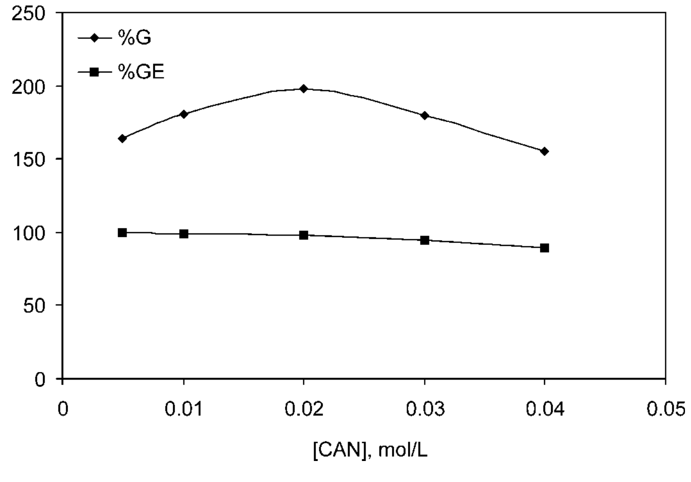


Figure 2. Effect of concentration of CAN on %G and %GE. Reaction conditions: GG = 0.05 g/L, [MMA] = 0.21 mol/L, $[HNO_3]$ = 0.2 M, reaction temperature = 30°C, reaction time = 3 h, reaction volume = 100 mL.

the greater will be the termination of growing grafted chains resulting in reduction of %G as well as %GE. It is reasonable to expect a similar termination with an increase in initiator concentration, the consequence of which leads to a steady decrease in %GE.[15,29] Furthermore, the decrease in %GE with an increase of CAN concentration could be due to the formation of more homopolymers at higher CAN concentration, which in turn leads to a decrease in %GE.[30,31]

Effect of Monomer Concentration

The results reported in Fig. 3 show that as the monomer concentration increases from 0.14 to 0.35 mol/L, there is an increase in %G, reaching a maximum and shows decreasing trend with further increase in monomer concentration beyond 0.35 mol/L. The enhancement of %G by increasing monomer concentration to a certain value could be ascribed to the greater availability of grafting sites to monomer. However, the decreasing trend of %G beyond certain monomer concentration may be due to the competition between homopolymerization and graft copolymerization, where the former prevails, the latter at a higher MMA concentration.[32]

Fig. 3 also shows that an increase in MMA concentration decreases the %GE. This decrease in %GE can be attributed to the higher affinity of MMA monomer for its homopolymer (polymethyl methacrylate) over the GG macro radicals. Thus, most of the monomer is preferentially used up in the formation of homopolymer on increasing the MMA concentration.[28,29,33]

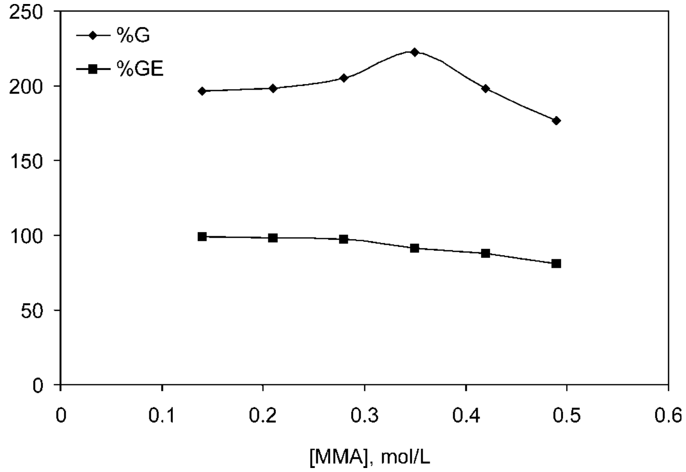


Figure 3. Effect of monomer concentration on %G and %GE. Reaction conditions: GG = 0.05 g/L, [CAN] = 0.02 mol/L, $[HNO_3] = 0.2$ M, reaction temperature = 30°C, reaction time = 3 h, reaction volume = 100 mL.

Effect of Temperature

The grafting reactions were carried out at different temperatures (10–70°C) keeping the other variables constant. The effect of temperature on %G and %GE is shown in Fig. 4. Results show that maximum %G obtained at 30°C and decreases with a further increase in temperature. The dependence of %G on temperature can be ascribed to the enhancement of the rate of diffusion of monomer. With an increase in temperature beyond 30°C, graft copolymerization occurs with poor selectivity and various hydrogen abstraction and chain transfer reactions may be accelerated, leading to the decrease of %G.

Fig. 4 also shows the effect of temperature on %GE. It is clear from the Fig. 4 that as the temperature increases, %GE decreases. The decrease in %GE with increasing temperature may be attributed to the increased solubility of monomer in the aqueous phase at higher temperatures, and also to the acceleration of the termination process which leads to the formation of more homopolymers. This is in agreement with the results reported in the literature.[4,33]

Effect of Nitric Acid Concentration

The concentration of nitric acid was varied from 0.1–0.4 M, keeping fixed the concentrations of all other reagents, time and temperature. The effect of acid concentration on %G and %GE is shown in Fig. 5. It is seen that the %G increases with an increase of acid concentration up to 0.2 M beyond which it decreases. This is due to the fact that there exists an optimum concentration of nitric acid, which affords maximum grafting. This corresponds to 0.2 M in the present case. Beyond the optimum concentration of nitric acid,

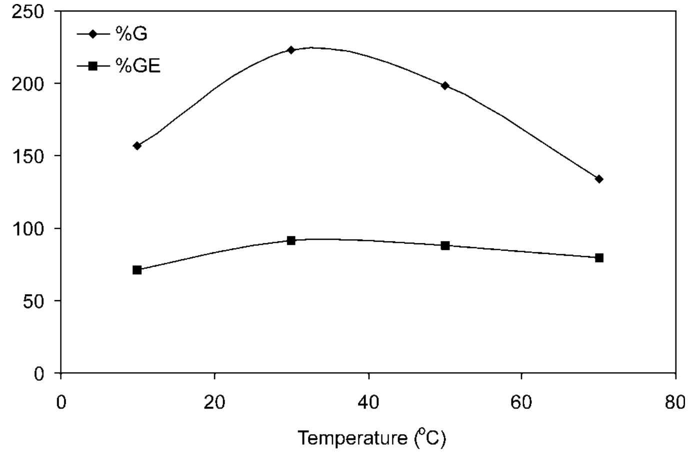


Figure 4. Effect of temperature on %G and %GE. Reaction conditions: GG = 0.05 g/L, [CAN] = 0.02 mol/L, [MMA] = 0.35 mol/L, [HNO_3] = 0.2 M, reaction time = 3 h, reaction volume = 100 mL.

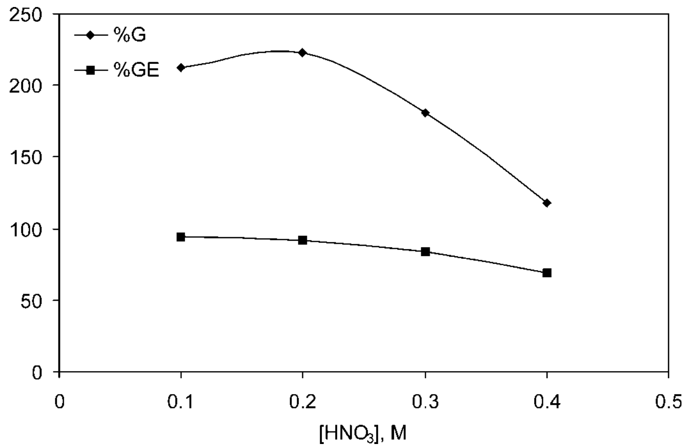


Figure 5. Effect of nitric acid concentration on %G and %GE. Reaction conditions: GG = 0.05 g/L, [CAN] = 0.02 mol/L, [MMA] = 0.35 mol/L, reaction time = 3 h, reaction temperature = 30°C, reaction volume = 100 mL.

the %G decreases in each case. The role of nitric acid in grafting of vinyl monomers onto GG is explained by the fact that ceric ion in water is believed to react in the following manner:

$$Ce^{+4} + H_2O \Leftrightarrow [Ce(OH)_3]^{+3} + H^+ \tag{1}$$

$$2[Ce(OH)_3]^{+3} \Leftrightarrow [Ce{-}O{-}Ce]^{+6} + H_2O \tag{2}$$

Thus, ceric ion exists as Ce^{+4}, $(Ce[OH]_3)^{+3}$ and $[Ce{-}O{-}Ce]^{+6}$ in aqueous solution. The concentration of these species is found to vary with the concentration of nitric acid.[34]

In the beginning, the %G increases with an increase in $[H^+]$. This is attributed to the increase in concentration of Ce^{+4} and $(Ce[OH]_3)^{+3}$ at the expense of $(Ce{-}O{-}Ce)^{+6}$. Ceric ions $(Ce)^{+4}$ being smaller in size are more effective in their ability to form complexes with GG than $(Ce{-}O{-}Ce)^{+6}$. A further increase in nitric acid concentration beyond 0.2 M decreases %G. This may be explained by the fact that as $[H^+]$ increases, the equilibria (Eqs. 1 and 2) shift towards formation of more $(Ce{-}O{-}Ce)^{+6}$.

Effect of Concentration of Guar Gum

The effect of concentration of GG on %G and on %GE was studied by varying the amount of GG (0.05–0.2 g/L) keeping other variables fixed. Fig. 6 shows that %G and %GE increases with increase in amount of GG up to 0.1 g/L and further decreases with increase in amount of GG. The initial increase may be due to the fact that the reactive sites increase with increase in the concentration of GG. The decrease beyond the amount of 0.1 g/L may be attributed to the destruction of radical activity on the backbone soon after it is formed due to the termination between backbone–backbone and backbone–primary

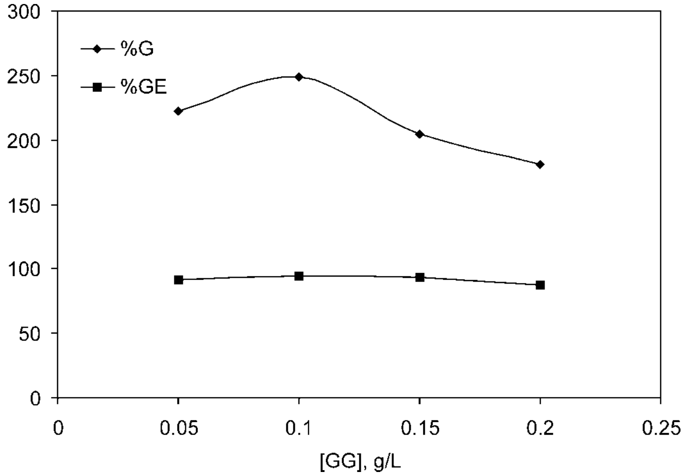


Figure 6. Effect of backbone concentration on %G and %GE. Reaction conditions: [CAN] = 0.02 mol/L, [MMA] = 0.35 mol/L, $[HNO_3] = 0.2$ M, reaction time = 3 h, reaction temperature = 30°C, reaction volume = 100 mL.

radicals. This is in agreement with the results obtained in grafting of methyl methacrylate onto sodium alginate[10] and grafting of acrylamide onto xanthan gum.[27]

CONCLUSION

Graft copolymerization of methyl methacrylate onto guar gum in aqueous medium can be initiated effectively with ceric ammonium nitrate. The optimum reaction conditions obtained for grafting of MMA onto GG were: amount of GG = 0.1 g/L, [CAN] = 0.02 mol/L, [MMA] = 0.35 mol/L, $[HNO_3] = 0.2$ M, reaction time = 3 h and temperature of reaction = 30°C.

REFERENCES

1. *The Wealth of India*; *First Supplement Series (Raw Materials)*; National Institute of Science Communication, CSIR: New Delhi, 2001; Vol. 2, 296–317.
2. Maier, H.; Anderson, M.; Karl, C.; Magnuson, K.; Whistler, R.L. Guar, locust bean, tara and fenugreek gum. In *Industrial Gums: Polysaccharides and Their Derivatives*, 3rd Ed.; Whistler, R.L., BeMiller, J.N., Eds.; Academic Press, Inc.: London, 1993; 181–221.
3. Fanta, G.F.; Burr, R.C.; Doane, W.M.; Russel, C.R. Influence of starch granule swelling on graft copolymer composition. A comparison of monomers. J. Appl. Polym. Sci. **1971**, *15*, 2651–2660.

4. Ghosh, P.; Paul, S.K. Graft copolymerization of methyl methacrylate onto potato starch using potassium trioxalatomanganate as initiator. J. Macromol. Sci.—Chem. **1983**, *A20* (2), 179–188.
5. Brockway, C.E.; Moser, K.B. Grafting of poly(methyl methacrylate) to granular corn starch. J. Polym. Sci., Part A **1963**, *1*, 1025–1039.
6. Ghosh, P.; Banerjee, M.; Ghosh, T.K. A simple method for the determination of the degree of true grafting in graft copolymerization of a vinyl monomer on cellulose or oxycellulose. J. Macromol. Sci.—Chem. **1982**, *A18* (4), 607–613.
7. Ogiwara, Y.; Igeta, K.; Kubota, H. Studies on the ability of cellulosic materials to initiate graft copolymerization. J. Appl. Polym. Sci. **1971**, *15*, 1119–1128.
8. Bianchi, E.; Bonazza, M.A.E.; Russo, S. Free radical grafting onto cellulose in homogeneous conditions. 2. Modified cellulose–methyl methacrylate system. Carbohydr. Polym. **2000**, *41*, 47–53.
9. Raval, D.K.; Patel, M.V.; Patel, R.G.; Patel, V.S. Perspective study of vinyl grafting onto *Leucaena glauca* seed gum and guar gum by hydrogen peroxide initiation. Starch/Stärke **1991**, *43* (12), 483–487.
10. Shah, S.B.; Patel, C.P.; Trivedi, H.C. Ceric-induced grafting of acrylate monomers onto sodium alginate. Carbohydr. Polym. **1995**, *26*, 61–67.
11. Trivedi, H.C.; Patel, C.P.; Shah, S.B. Grafting of vinyl monomers onto sodium alginate. Trends Carbohydr. Chem. **1996**, *2*, 1–22.
12. Huque, M.M.; Habibuddowla, Md.; Mahmood, A.J.; Mian, A.J. Graft copolymerization onto jute fiber: ceric ion-initiated graft copolymerization of methyl methacrylate. J. Polym. Sci., Polym. Chem. Ed. **1980**, *18*, 1447–1458.
13. Ren, L.; Tokura, S. Structural aspects of poly(methyl methacrylate)-grafted β-chitin copolymers initiated by ceric salts. Carbohydr. Polym. **1994**, *23*, 19–25.
14. Arai, K.; Negishi, M.; Okabe, T. Infrared spectroscopy of graft polymers separated from graft copolymers of wool and silk with methyl methacrylate. J. Appl. Polym. Sci. **1968**, *12*, 2585–2596.
15. Athawale, V.D.; Lele, V. Synthesis and characterization of graft copolymers of maize starch and methacrylonitrile. Carbohydr. Polym. **2000**, *41*, 407–416.
16. Carr, M.E. Preparation and application of starch graft poly (vinyl) copolymers as paper coating adhesives. Starch/Stärke **1992**, *44*, 219–223.
17. Chinnaswamy, R.; Hanna, M.A. Extrusion-grafting starch onto vinylic polymers. Starch/Stärke **1991**, *43* (10), 219–223.
18. Gurdag, G.; Yasar, M.; Gurkaynak, M.A. Graft copolymerization of acrylic acid on cellulose: reaction kinetics of copolymerization. J. Appl. Polym. Sci. **1997**, *66*, 929–934.
19. Deshmukh, S.R.; Singh, R.P. Drag reduction effectiveness, shear stability and biodegradation resistance of guar gum-based graft copolymers. J. Appl. Polym. Sci. **1987**, *33*, 1963–1975.
20. Reyes, Z.; Rist, C.E.; Russell, C.R. Grafting vinyl monomers to starch by ceric ion. I. Acrylonitrile and acrylamide. J. Polym. Sci., A1 **1966**, *4*, 1031.
21. McCormick, C.L.; Park, L.S. Water-soluble copolymers. III. Dextran-g-poly (acrylamides) control of grafting sites and molecular weight by Ce(IV)-induced initiation in homogeneous solutions. J. Polym. Sci., Polym. Chem. Ed. **1981**, *19* (9), 2229–2241.

22. Mino, G.; Kaizerman, S.; Rasmussen, E.J. The oxidation of pinacol by ceric sulfate. J. Am. Chem. Soc. **1959**, *81*, 1494–1496.
23. Hintz, H.L.; Johnson, D.C. The mechanism of oxidation of cyclic alcohols by cerium(IV). J. Org. Chem. **1967**, *32*, 556.
24. Pottenger, C.R.; Johnson, D.C. Mechanism of cerium(IV) oxidation of glucose and cellulose. J. Polym. Sci., Part A-1 **1970**, *8*, 301–318.
25. Duke, F.R.; Forist, A.A. The theory and kinetics of specific oxidation. III. The cerate-2,3-butanediol reaction in nitric acid solution. J. Am. Chem. Soc. **1949**, *71*, 2790–2792.
26. Duke, F.R.; Bremer, R.F. The theory and kinetics of specific oxidation. IV. The cerate-2,3-butanediol reactions in perchlorate solutions. J. Am. Chem. Soc. **1951**, *73*, 5179–5181.
27. Behari, K.; Pandey, P.K.; Kumar, R.; Taunk, K. Graft copolymerization of acrlamide onto xanthan gum. Carbohydr. Polym. **2001**, *46*, 185–189.
28. Zhang, L.-M.; Chen, D.-Q. Grafting of 2-(dimethylamino)ethyl methacrylate onto potato starch using potassium permagnate/sulfuric acid initiation system. Starch/Stärke **2001**, *53*, 311–316.
29. Athawale, V.D.; Vidyagauri. Graft copolymerization onto starch. 3: Grafting of acrylamide using ceric ion initiation and preparation of its hydrogels. Starch/Stärke **1998**, *50* (10), 426–431.
30. Hu, Z.-H.; Zhang, L.-M. Water soluble ampholytic grafted polysaccharides. II. Synthesis and characterization of graft terpolymers of starch with acrylamide and [2-(methacryloylox)] ethyl dimethyl (3-sulfopropyl) ammonium hydroxide. J. Macromol. Sci.—Pure Appl. Chem. **2002**, *A39* (5), 419–430.
31. Zhang, L.-M.; Tan, Y.-B.; Huang, S.-J.; Chen, D.-Q.; Li, Z.-M. Water soluble ampholytic grafted polsaccharides. 1. Grafting of the zwitterionic monomer 2-(2-methacrylo ethyl dimethyl ammonio) ethanoate onto hydroxyethyl cellulose. **2000**, *A37* (10), 1247–1260.
32. Hebeish, A.; Refie, M.H.; Higazy, A.; Ramadon, M. Synthesis, characterization and properties of polyacryamide–starch composites. Starch/Stärke **1996**, *48* (5), 175–179.
33. Patel, B.K.; Sinha, V.K.; Trivedi, H.C. Graft copolymerization of sodium salt of partially carboxymethylated amylose with acrylonitrile. J. Polym. Mater. **1991**, *8*, 321–328.
34. Sood, D.S.; Kishore, J.; Misra, B.N. Grafting onto wool. XXVII. Graft copolymerization of mixed vinyl minimers by use of ceric ammonium nitrate as redox initiator. J. Macromol. Sci.—Chem. **1985**, *A22* (3), 263–278.

Received March 29, 2002
Revised July 15, 2002