Graft Copolymerization of Acrylonitrile onto *Cassia tora* Gum with Ceric Ammonium Nitrate–Nitric Acid as a Redox Initiator

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ABSTRACT: The graft copolymerization of acrylonitrile (AN) onto *Cassia tora* gum (CTG) was carried out in an aqueous medium with a ceric ammonium nitrate (CAN)–nitric acid initiation system. The percentage grafting and percentage grafting efficiency were determined as functions of the concentrations of CAN, nitric acid, AN, and CTG and the polymerization temperature and time. The results are discussed, and a reaction mechanism is proposed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 129–136, 2003

Key words: graft copolymers; initiator; modification; *Cassia fora* gum

INTRODUCTION

The chemical modification of natural macromolecules is an important area in polymer chemistry, and it has been used to impart more desirable properties to these substances. In recent years, the chemical modification of natural polymers through grafting has received considerable attention. The goal of these modifications is to impart or improve the properties of macromolecular substances for different end uses and to increase their consumption. The availability of a spectrum of polysaccharides thus provides an excellent opportunity for the development of fine-tuned products by chemical modification for broader applications.

Among chemical methods, redox-initiated grafting offers advantages, as grafting can be carried out under milder conditions with a minimum of side reactions. The grafting of acrylonitrile (AN) onto natural polymers such as guar gum,[1–3] *Leucaena glauca* gum,[4] starch,[5–8] and cellulose[9] through different redox initiators has been reported.

Cassia tora gum (CTG) is derived from the seeds of *Cassia tora Linn.,* a common herbaceous annual weed occurring throughout India. The pods are 15–22.5 cm long and up to 0.625 cm in diameter and contain flattened dark seeds. The *Cassia tora* seed is composed of hull (27%), endosperm (32%) and germ (41%). Methylation studies showed that the backbone of the polysaccharide has a fundamental structure consisting of a linear chain of β-D-(1→4)-linked mannopyranosyl residues substituted by α-D-galactopyranosyl groups mainly at O-6.[10] There have been very few reports on the chemical modification of CTG and its uses.[11–14] With the view that grafted CTG may find better applications in comparison to native CTG, we carried out the grafting of AN onto CTG in the presence of ceric ammonium nitrate (CAN) as a redox initiator; the reaction conditions for graft copolymerization were optimized and are reported in this article.

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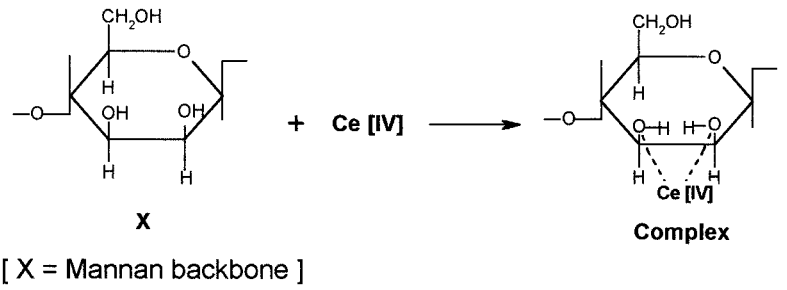
EXPERIMENTAL

Materials and methods

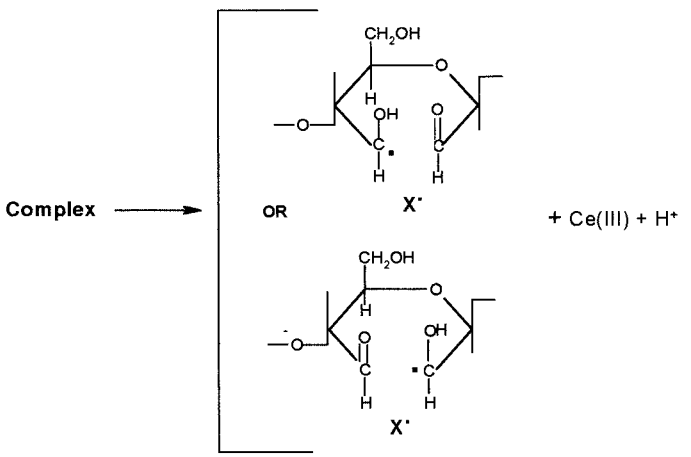
Gum from the *Cassia tora* seed was isolated as per a method described by Soni.[15] AN (for synthesis, Merck, Darmstadt, Germany), CAN (Aldrich Chemical Co., Milwaukee, WI), and nitric acid (analytical reagent (AR) grade, Ranbaxy Laboratories, Ltd., S.A.S. Nagar, India) were used in this study.

Graft copolymerization

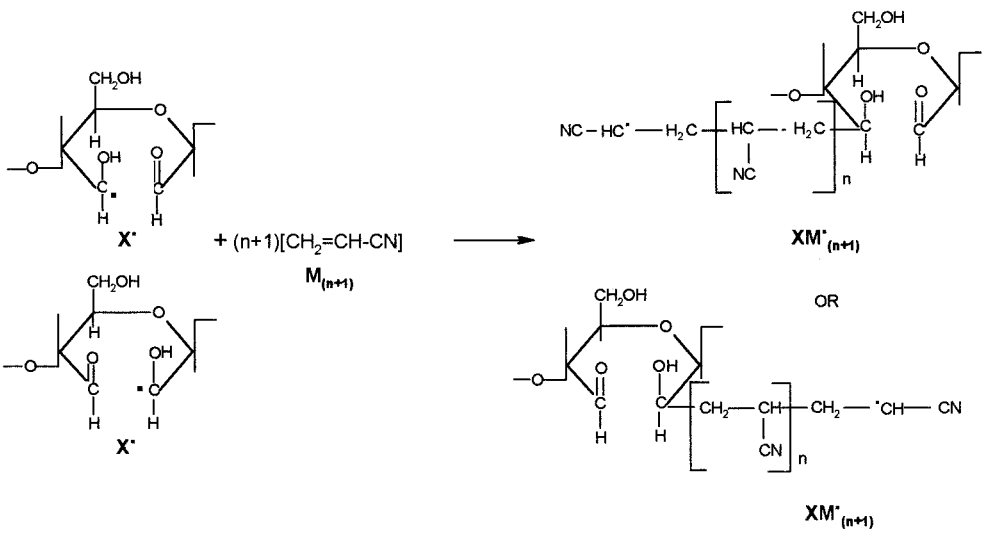
The grafting reaction was carried out under a nitrogen atmosphere in a 500-mL three-necked flask equipped with a stirrer, a gas inlet system, and a reflux condenser immersed in a constant-temperature water bath. In a typical reaction, CTG (2–5 g) was dissolved in water (200 mL) with constant stirring and the bubbling of a slow stream of nitrogen at the desired temperature. The freshly prepared 10-mL solution of CAN (0.01–0.04 mol) in nitric acid (0.1–0.4*M*) followed by AN (0.21–0.56 mol) was added, and a continuous supply of nitrogen was maintained throughout the reaction period. The grafting reaction was carried out



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

for varying periods of time (1–5 h). After the reaction was over, the reaction mixture was poured into methanol for precipitation. Centrifugation, washing with methanol, and filtration were carried out, and the product was dried in a vacuum dessicator. The dried product was extracted with a dimethylformamide/

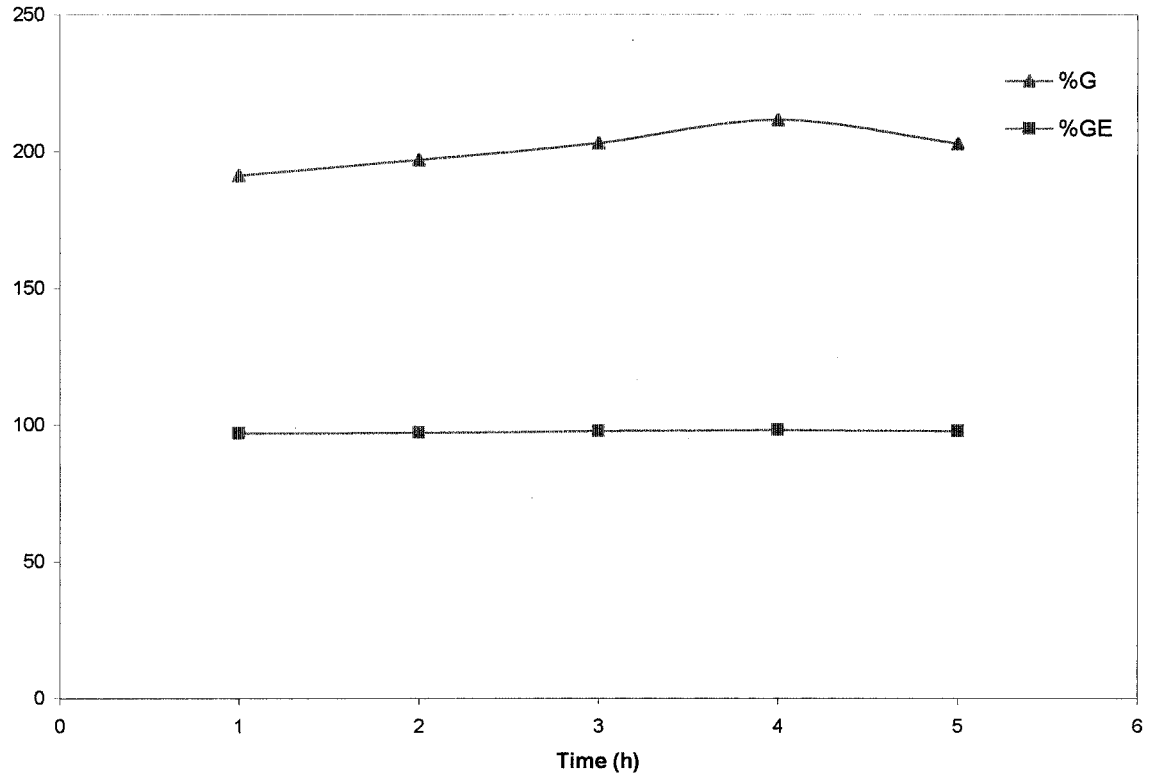


Figure 1 Effect of reaction time on %*G* and %*GE*.

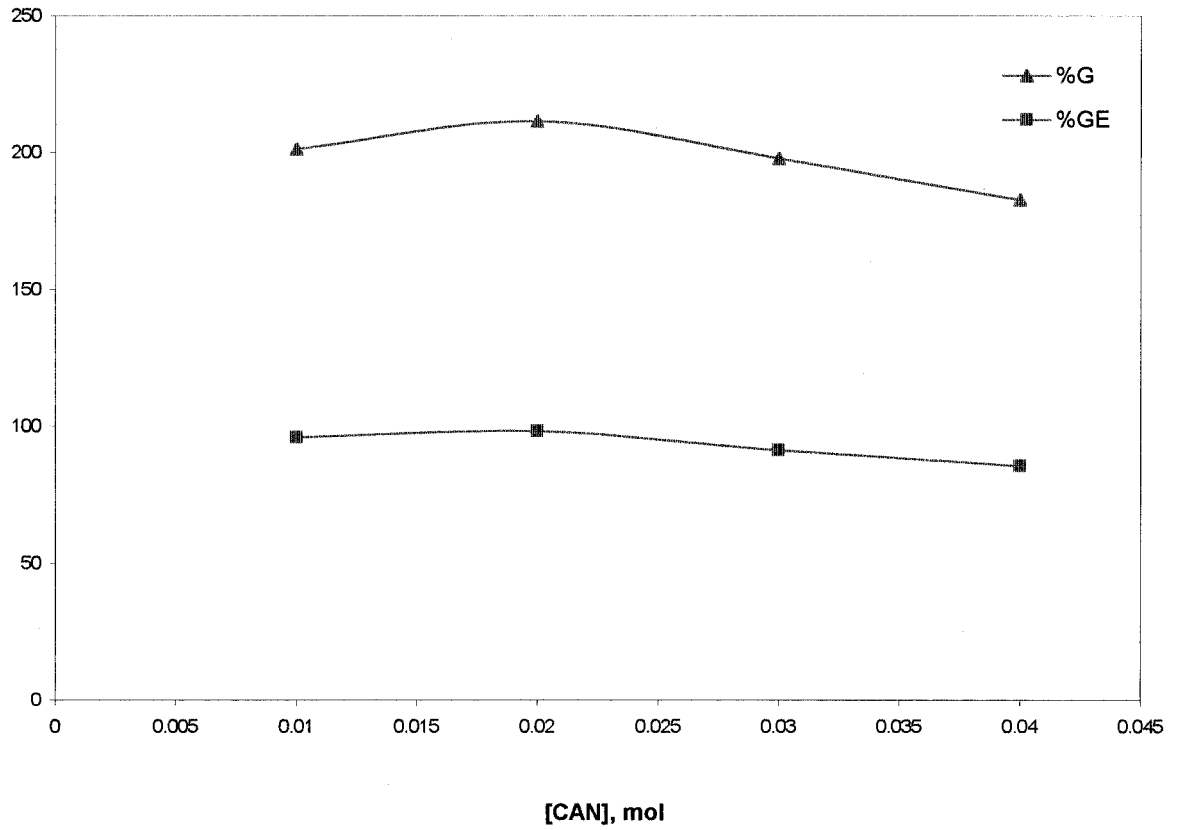


Figure 2 Effect of CAN concentration on %*G* and %*GE*.

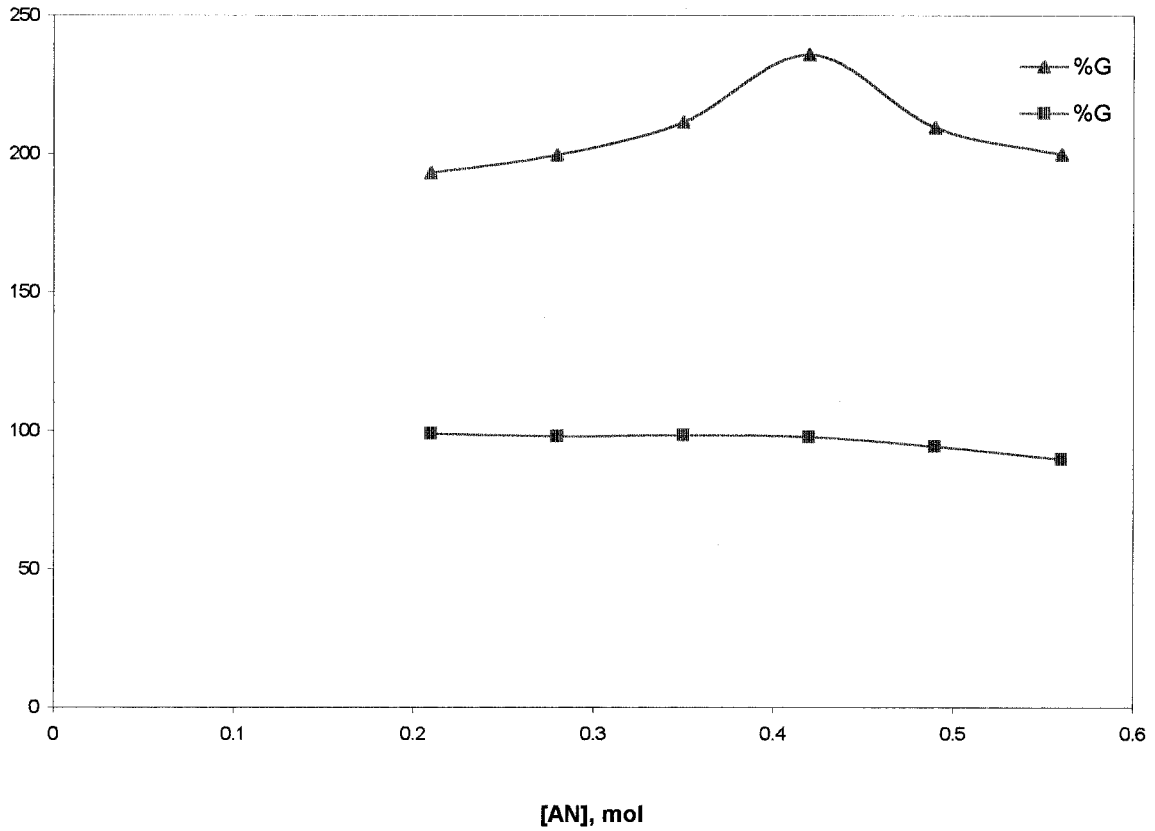


Figure 3 Effect of AN concentration on %*G* and %*GE*.

acetic acid mixture (1:1) for 48 h to remove the homopolymer (polyacrylonitrile). The grafted CTG was dried to a constant weight. The percentage grafting (%*G*) and percentage grafting efficiency (%*GE*) were calculated from the increase in weight of CTG after grafting in the following manner:

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

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

RESULTS AND DISCUSSION

The use of CAN for the chemical initiation of vinyl polymerization has been reported as part of the possible modification of biopolymers, namely, chitin,[16] starch,[17–19] cellulose,[20] and guar gum.[21] The formation of free radicals on these biopolymers by cerium(IV) has been demonstrated by electron spin resonance.[22] The mechanism by which cerium(IV) generates free radicals is believed to involve the formation of a coordination complex between the oxidant, that is, CAN, and the hydroxyl group of the biopolymer. The ceric(IV)–biopolymer complex then disproportionates, forming a free radical on the biopolymer chain and cerium (III).[22,23] Model compound studies of the cerium(IV) oxidation of monohydric alcohol and 1,2-glycols have supported the postulated mechanism and suggested that the C_2—C_3 glycol and the C_6 hydroxyl of the anhydro-D-glucose unit may be the preferred site for free-radical generation.[24–26] Evidence for the formation of a stable coordination complex has been obtained by kinetic and spectroscopic methods for the cerium(IV) oxidation of many compounds in perchloric and nitric acids.[25,27,28]

The relative reactivities of the C_6 hydroxyl and C_2—C_3 glycol were estimated by comparison of tetrahydropyran-2-methanol and cyclohexane methanol as models for the C_6 hydroxyl and with *trans*-1,2-cyclohexanediol for C_2—C_3 glycol units. The results showed that the relative rate of the ceric ion oxidation of *trans*-1,2-cyclohexanediol was six times higher than that of the primary hydroxyl.[25]

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 a relatively large Ce(IV) can easily bridge this distance. The formation of a five-member chelate ring fused to the cyclohexane ring results in a relatively rigid system with the trans isomer, whereas the complex with cis

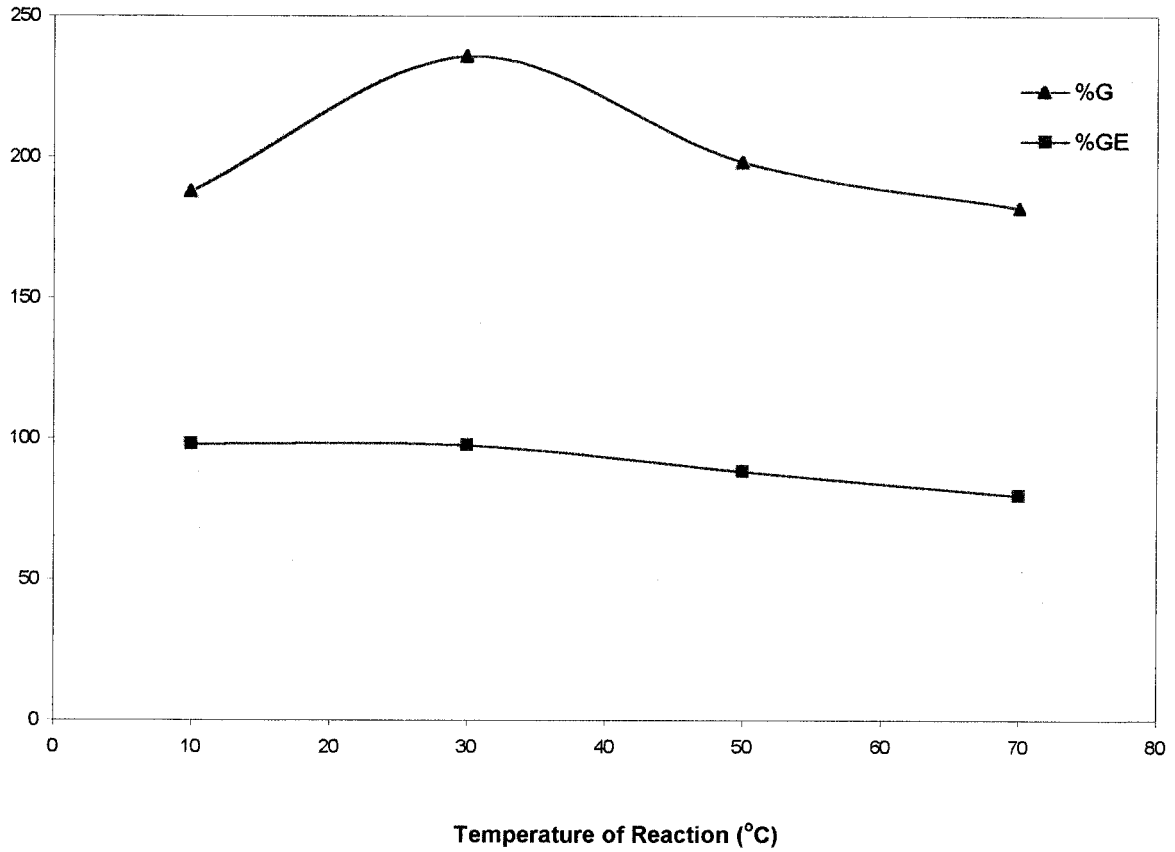


Figure 4 Effect of temperature on %*G* and %*GE*.

isomer is relatively flexible because 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).[25]

In view of this, we propose that the oxidation reaction of CTG occurs preferably at the C_2—C_3 glycol unit and to a very lesser extent at the C_6 hydroxyl because the mannan backbone of CTG contains a cis —OH group at C_2—C_3.

In the presence of ceric salts, namely, CAN $[Ce(NH_4)_2(NO_3)_6]$, as an initiator for graft copolymerization onto CTG, we propose that a ceric ion–CTG 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 Scheme 1.[20] The radical site on the galactomannan chain then initiates the graft copolymerization of the polar vinyl monomer, which is present in the reaction mixture. The grafting occurs mainly at C_2—C_3, as discussed previously.

Determination of the optimum reaction conditions

To optimize the grafting conditions of AN onto CTG, we varied the concentrations of nitric acid, the free-radical initiator, the monomer, and also the time and temperature.

Effect of reaction time

The effect of polymerization time on %*G* and %*GE* is shown in Figure 1. As shown in this figure, the %*G* increased rapidly with increasing time up to 4 h, after which it leveled off. The increase in %*G* was accounted for by the increase in the number of grafting sites in the initial stages of reaction.[29,30] The leveling off of grafting after 4 h could be attributed to a decrease in concentration of both the initiator and monomer and to a reduction in the number of sites on the backbone accessible for grafting as the reaction proceeded.

Also, %*GE* did not change appreciably during the course of reaction, as shown in Figure 1. The %*GE* pattern of AN onto CTG showed a similarity to the %*GE* pattern of vinyl monomers onto sodium alginate[31] and jute fiber[32] with ceric ion as the redox initiator. Thus, to obtain the maximum %*G*, the optimum reaction time was 4 h.

Effect of CAN concentration

The effect of variation in CAN concentration on %*G* and %*GE* is shown in Figure 2. CAN concentration

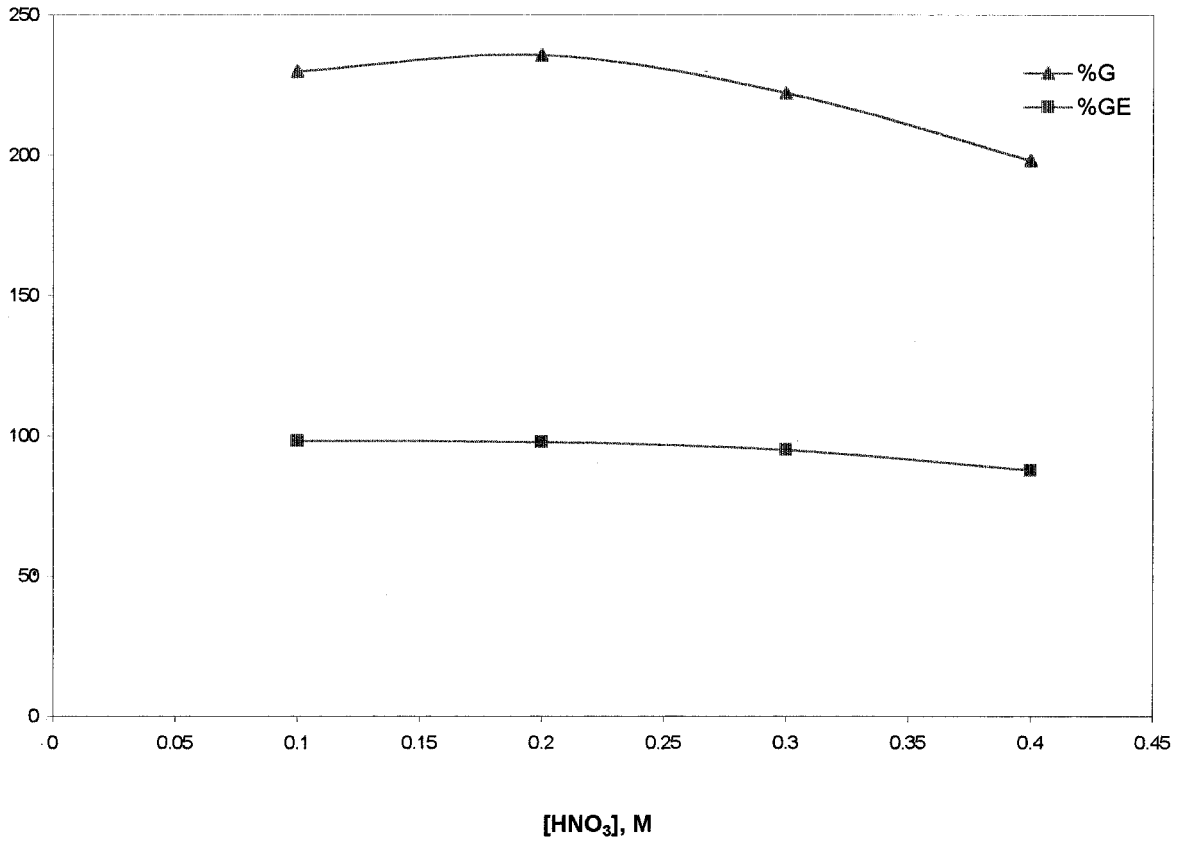


Figure 5 Effect of HNO_3 concentration on %*G* and %*GE*.

was increased from 0.01–0.04 mol. As is evident from Figure 2, the %*G* increased with increasing initiator concentration but reached a maximum value (211.57%) at 0.02 mol of CAN. A further increase in CAN concentration was accompanied by a decrease in the %*G*. The observed increase in %*G*, with the CAN concentration ranging from 0.01 to 0.02 mol, may have been due to the fact that in this concentration range, the activation along the backbone took place immediately, followed by the graft copolymerization of the monomer onto the backbone. A relatively high concentration of the initiator may have caused a reduction in grafting, due to an increase in the number of backbone radicals terminated before AN addition. Further, homopolymer formation at higher concentrations, which competed with the grafting reaction for available monomer, could have led to a decrease in %*G*. Similar observations have also been reported in the literature.[33–36]

Figure 2 also shows a decrease in %*GE* with increasing CAN concentration. The fast dissociation of CAN may have accounted for higher %*GE* in the initial stages because less Ce(IV) would have been available for initiation.[37] We propose that for ceric-ion-initiated graft copolymerization, the higher the concentration of Ce(IV) is, the greater will be the termination of growing grafted chains, which result in a reduction of %*G* and %*GE*.[38]

Effect of monomer concentration

The results reported in Figure 3 show that as the monomer concentration increased from 0.21 to 0.56 mol, there was an increase in %*G*, which reached a maximum at 0.42 mol and showed decreasing trend with any further increase in monomer concentration. The enhancement of %*G* by increasing monomer concentration to an optimum value could be ascribed to the greater availability of grafting sites to the monomer. However, the decreasing trend of %*G* beyond optimum monomer concentration may have been due to the competition between homopolymerization and graft copolymerization, where the former prevailed over the latter at higher AN concentrations.[39]

Figure 3 also shows that there was a decrease in %*GE* with increasing AN concentration. This decrease in %*GE* could be attributed to the higher affinity of the AN monomer for its homopolymer (polyacrylonitrile) over the CTG macroradicals. Thus, most of the monomer was preferentially used up in the formation of homopolymer when the AN concentration was increased.[40–42]

Effect of temperature

The grafting reactions were carried out at different temperatures (10–70°C) with the other variables kept constant. The effect of temperature on %*G* and %*GE* is

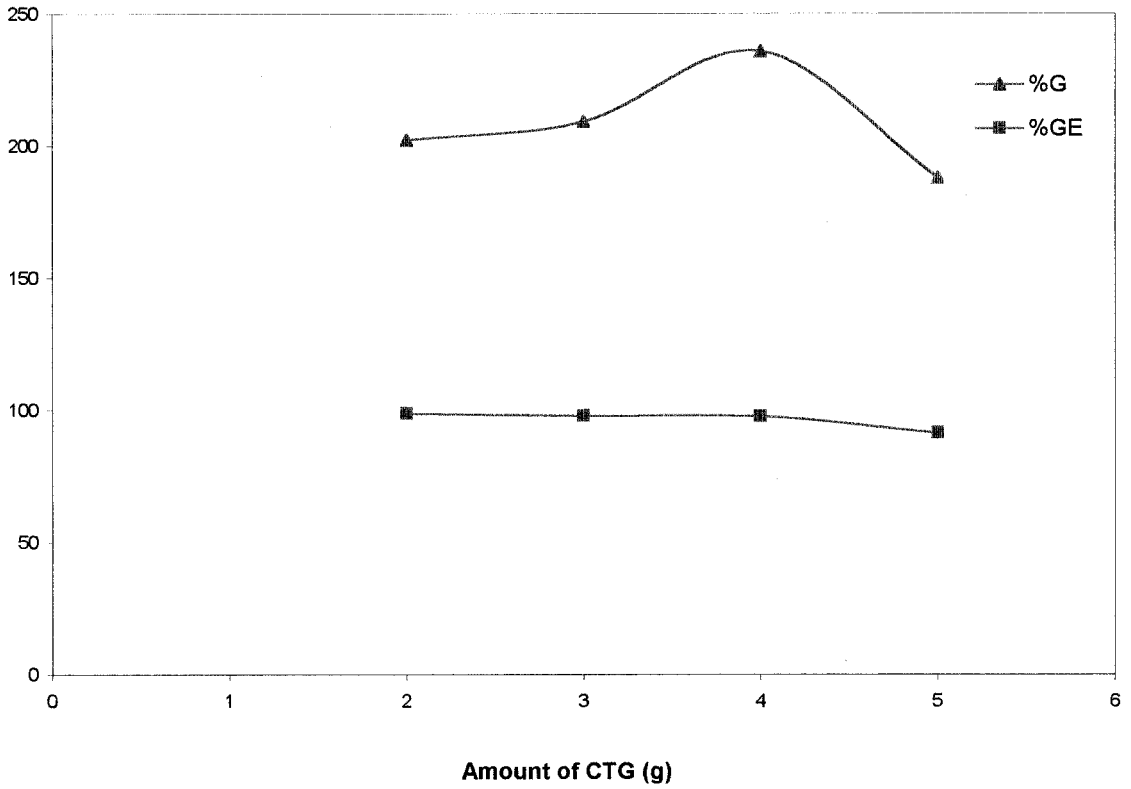


Figure 6 Effect of CTG concentration on %*G* and %*GE*.

shown in Figure 4. The results show that a maximum %*G* was obtained at 30°C, and %*G* decreased with any further increase in temperature. The dependence of %*G* on temperature could be ascribed to the enhancement of the rate of diffusion of the monomer. Any increase in temperature beyond the optimum temperature (30°C in this case) led to graft copolymerization with poor selectivity, as various hydrogen abstraction and chain-transfer reactions may have been accelerated, leading to a decrease in %*G*.

Figure 4 also shows the effect of temperature on %*GE*. It is clear from Figure 4 that as the temperature increased, %*GE* decreased. The decrease in %*GE* with increasing temperature could 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 led to the formation of more homopolymer. Similar results have been reported in literature.[33,34,43]

Effect of nitric acid concentration

The concentration of nitric acid was varied from 0.1 to 0.4*M*, with the concentrations of all other reagents, time, and temperature fixed. The effect of acid concentration on %*G* and %*GE* is shown in Figure 5. The %*G* increased with increasing acid concentration up to 0.2*M*, beyond which it decreased. This was due to the fact that there existed an optimum concentration of nitric acid that afforded maximum grafting. This corresponded to 0.2*M* in this case. Beyond the optimum concentration of nitric acid, the %*G* decreased in each case. The role of nitric acid in the grafting of vinyl monomers onto CTG is explained by the fact that ceric ion in water is believed to react in the following manner:

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

$$2[Ce(OH)_3]^{+3} \leftrightharpoons [Ce—O—Ce]^{+6} + H_2O \quad (2)$$

Thus, ceric ion exists as Ce^{+4}, $(Ce[OH]_3)^{+3}$ and $[Ce—O—Ce]^{+6}$ in aqueous solution. The concentration of these species was found to vary with the concentration of nitric acid.[44] In the beginning of the reaction, the %*G* increased with increasing $[H^+]$. This was attributed to the increase in the 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, were more effective in their ability to form complexes with CTG than $(Ce—O—Ce)^{+6}$. Further increases in nitric acid concentration beyond 0.2*M* decreased %*G*. This could be explained by the fact that as $[H^+]$ increased, the equilibria (Eq.1 and 2) shifted toward the formation of more $(Ce—O—Ce)^{+6}$.

Effect of CTG concentration

We studied the effect of CTG concentration on %*G* and on %*GE* by varying the amount of CTG (2–5 g) and

keeping other variables fixed. Figure 6 shows that %*G* and %*GE* increased with increasing amounts of CTG up to 4 g and further decreased with increasing amounts of CTG. The initial increase may have been to the fact that the reactive sites increased with increasing concentration of CTG. The decrease beyond the amount of 4 g could be attributed to the destruction of radical activity on the backbone soon after it was formed due to the termination between backbone–backbone and backbone–primary radicals. Similar results have also been reported in the literature.[3,45,46]

CONCLUSIONS

The graft copolymerization of AN onto CTG in aqueous medium was initiated effectively with CAN. The optimum reaction conditions obtained for the grafting of AN onto CTG were CTG amount = 4 g, [CAN] = 0.02 mol, [AN] = 0.42 mol, $[HNO_3]$ = 0.2*M*, reaction time = 4 h, and reaction temperature = 30°C.

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