Graft Copolymerization of Acrylamide onto Tamarind Kernel Powder in the Presence of Ceric ion

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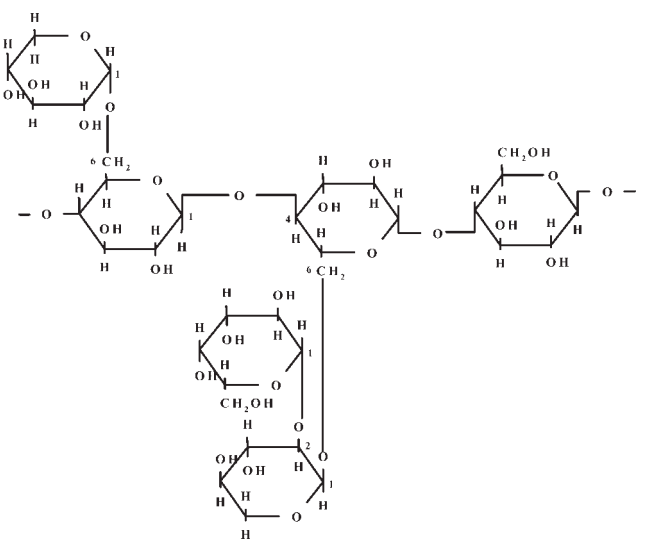
ABSTRACT: Tamarind kernel powder (TKP), a natural xyloglucan polysaccharide is derived from the seeds of *Tamarindus indica* Linn., a common and most important tree of India and South East Asia. TKP is used in cotton sizing, as a wet-end additive in the paper industry, as a thickening, stabilizing, and gelling agent in the food industry. Chemical modification of TKP through grafting has received considerable attention to impart new functional groups for different applications. Keeping this in view, graft copolymerization of acrylamide (AA) onto TKP was carried out in an aqueous medium using a ceric ammonium nitrate (CAN)-nitric acid initiation system. The reaction conditions were optimized for grafting with respect to the effect of the concentrations of CAN, nitric acid, TKP, AA, time, and reaction temperature. The maximum percentage grafting (%G) and percentage grafting efficiency (%GE) were found to be 231.45 and 93.66%, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3696–3701, 2008

Key words: tamarind kernel powder; graft copolymerization; acrylamide; ceric ammonium nitrate; free radical initiator

INTRODUCTION

Tamarind kernel powder (TKP) is derived from the seeds of *Tamarindus indica* Linn., a common and an economically most important tree of India and South East Asia. The seed is exalbuminous, consists of an outer hard and brown testa. The kernel constitutes about 70% of the weight of the seed. TKP is prepared by decorticating the seeds and pulverizing the creamy white kernels.[1] TKP, a crude extract of tamarind seeds, has been used as a replacement for starch in cotton sizing, and as a wet-end additive in the paper industry, where it replaces starches and galactomannans.[2] Refined tamarind seed polysaccharide is used as a thickening, stabilizing, and gelling agent in the food industry, particularly in Japan where it is a permitted food additive.[2,3] The polysaccharide is composed of a (1→4)-β-D-glucan backbone substituted with side chains of α-D-xylopyranose and β-D-galactopyranosyl (1→2)-α-D-xylopyranose linked (1→6) to glucose residues. Exact composition of polysaccharide is not fully known till date. The ratio of glucose : xylose : galactose in the polysaccharide has been reported by number of workers as ~ 3 : 2 : 1, 3 : 2.25 : 1, 2.25 : 1.25 : 1, 4 : 2 : 1, and 2.8 : 2.25 : 1.0.[2,3] Arabinose residues are frequently reported for tamarind seed polysaccharide but these probably arise from contaminating arabinans.[3] In India, TKP is one of the cheapest gums available. However, because of several drawbacks, such as unpleasant odor, dull color, presence of water insolubles, low solubility in cold water, and fast biodegradability, it is wanting in several specialty end-use properties.



Graft copolymerization of vinyl monomers onto naturally occurring polymers has gained importance in modifying the physical and chemical properties of polymers. Among chemical methods, redox-initiated grafting is advantageous because in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions.

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Grafting of acrylamide (AA) onto natural polymers such as starch,[4–7] sodium alginate,[8] dextran,[9,10] xanthan,[11] guar gum,[12] and *Cassia tora* gum[13] has been studied using different redox systems.

In our laboratory, seed gums (*Cassia tora*/*Cyamopsis tetragonoloba*/TKP) were modified via carboxymethylation,[14,15] carbamoylethylation,[16,17] cyanoethylation,[18] and grafting.[13,19,20] Interestingly, there is no work reported on the graft copolymerization of AA onto TKP in the presence of CAN as redox initiator. Therefore, reaction conditions for graft copolymerization of AA onto TKP were optimized with a view that grafted TKP may find better applications in comparison with native TKP.

EXPERIMENTAL

Materials and methods

TKP was obtained from M/S Sooraj Trading, KGF, Karnataka, India. AA (for synthesis, Loba Chemie, India), CAN, dimethylformamide, acetic acid, and methanol were of laboratory grade (S. D. Fine-Chem, Mumbai, India), and nitric acid (AR grade, Ranbaxy Laboratories, India) were used in this study. The infrared spectrum (IR) of grafted sample was measured in KBr pellets using a JASCO FT/IR-5300 spectrophotometer in the range 650–4000 cm^{-1}.

Graft copolymerization

The grafting reaction was carried out under nitrogen atmosphere in a 500-mL four-necked flask equipped with a reflux condenser, a stirrer, dropping funnel, and a gas inlet system immersed in a constant temperature water bath. In a typical reaction, TKP (0.012–0.031 mol) was dissolved in a definite volume of water with constant stirring and bubbling of a slow stream of nitrogen for 30 min at the desired temperature (20–40°C). After 30 min, a freshly prepared 10 mL solution of CAN (0.015–0.04 mol) in nitric acid (0.1–0.3*N*) was added and stirred for 10 min. Nitrogen gas was continuously passed through the reaction mass and AA (0.070–0.113 mol) was added. In all the reactions, total volume of the reaction was kept constant. The grafting reaction was carried out for varying time intervals (1–3 h). The zero time of the reaction was at the time of monomer addition. After completion of the reaction, the mixture was immediately poured into methanol for precipitation. The precipitated product was recovered by centrifugation and washed with pure methanol (2 × 50 mL). The crude copolymer thus obtained was dried till constant weight under vacuum at 40°C. The dried product was extracted with dimethylformamide/acetic acid mixture (1 : 1 by vol) for 48 h and washed with methanol to remove the homopolymer (polyacrylamide). The grafted TKP was dried to a constant weight under vacuum at 40°C. The percent grafting (%G) and percent grafting efficiency (%GE) were determined from the increase in the weight of TKP after grafting in the following manner:

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

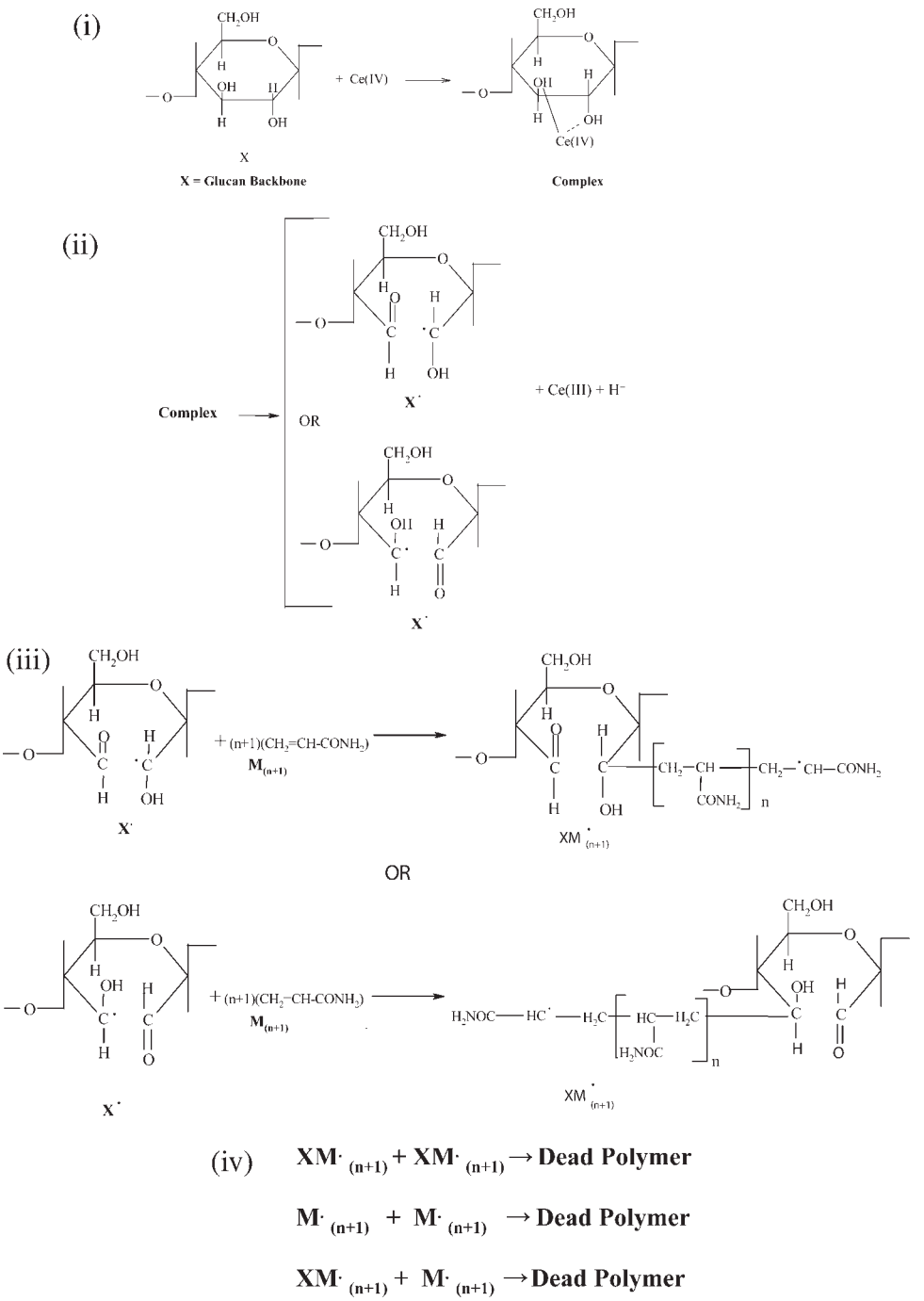
$$\%GE = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

RESULTS AND DISCUSSION

Ceric ammonium nitrate has been used extensively as the redox initiator for effective grafting of a variety of vinyl monomers onto biopolymers viz. guar gum,[12,20] cellulose,[21] and chitin.[22] Ceric ion enters into complex formation with biopolymers, and on disproportionation the complex generates free radicals on the backbone polymer where grafting of the appropriate vinyl monomer can occur. The formation of free radicals in ceric-treated biopolymers has been confirmed by electron spin resonance.[23] The mechanism by which cerium (IV) interacts with biopolymer to form free radical involves the formation of a coordination complex between the cerium (IV) and the hydroxyl group of biopolymer. The ceric (IV)-biopolymer complex then disproportionate forming a free radical on the biopolymer chain and cerium (III).[10,23] Evidence for complex formation has been obtained by kinetic and spectrophotometric methods for the oxidation of various alcohols and substrates containing alcohol groups by ceric ions in perchloric and nitric acids.[24–26] The postulated mechanism has been supported by the model compound studies of cerium (IV) oxidation of monohydric alcohols and 1,2-glycols, and suggest that the C_2–C_3 glycol and the C_6 hydroxyl of an anhydro-D-glucose unit may be preferred sites for free-radical generation.[24,27,28]

The relative rates of oxidation of the C_6 hydroxyl and the C_2–C_3 glycol were examined. Model compounds such as cyclohexanemethanol and tetrahydropyran-2-methanol were used for the C_6 hydroxyl, and *trans*-1,2-cyclohexanediol for C_2–C_3 glycol. The result indicates that diol group oxidized about six times faster than the C_6 hydroxyl. Thus cerium (IV) oxidation will occur mainly at the C_2–C_3 glycol unit and to some extent at the C_6 primary hydroxyl.[24]

The equilibrium constants for complex formation show that the presence of adjacent hydroxyl groups in the organic substrate causes a substantial increase in the stability of the complex compared to compounds with only one hydroxyl. Thus, the



Scheme 1 Mechanism of grafting of acrylamide onto TKP. (i) Complex formation. (ii) Chain initiation. (iii) Chain propagation. (iv) Chain termination.

equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols are considerably larger than for the monohydric alcohols. The greater stability of the complexes with the 1,2-glycols indicates that these compounds form a chelate complex with cerium (IV).[24]

Furthermore, the equilibrium constants for the *cis*- and *trans*-1,2-cyclohexanediols are consistent with chelate complex formation. In the stable conformations of these compounds, the separation of the hydroxyl groups is about the same, and a relatively large cerium (IV) ion can easily bridge this distance. The formation of a five-membered chelate ring fused to the cyclohexane ring resulting in a relatively rigid system with the *trans* isomer, whereas the complex with the *cis* isomer is relatively flexible because conformation interconversion can occur as readily in the complex as in the uncomplexed diol. This greater flexibility of the complex with the

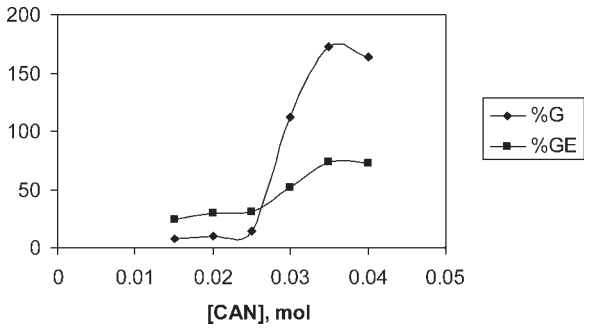


Figure 1 Effect of CAN concentration on %G and %GE. Reaction conditions: [TKP] 0.012 mol; [AA] 0.085 mol; [HNO_3] 0.3*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

cis isomer thus contributes to its somewhat greater stability.[24]

In view of the above, it is proposed that in the cerium (IV)-initiated graft copolymerization onto TKP, the oxidation reaction of cerium (IV) with TKP will occur preferably at the C_2–C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl as a result of one electron transfer process. The ceric ion (IV) initially forms a Ce (IV)-xyloglucan complex. This complex is then reduced to cerous ion (III) with a formation of free radical at either C_2 or C_3 on the backbone as shown in Scheme 1.[23] The free radical then react with the vinyl monomer, which is present in the reaction mixture to initiate graft copolymerization. The grafting occurs mainly at C_2–C_3 as discussed earlier. The grafting was also confirmed by the IR spectrum of the grafted sample which showed additional peaks at 3200 and 1665 cm^{-1} due to N—H stretching and C=O stretching and N—H bending, respectively. This testifies the existence of grafting.

Determination of the optimum reaction conditions

To optimize the conditions for grafting of AA onto TKP, the concentration of nitric acid, free radical initiator, monomer, TKP, time, and temperature were varied.

Effect of CAN concentration

The effect of variation in CAN concentration on %G and %GE is shown in Figure 1. CAN concentration was varied from 0.015 to 0.04 mol. It is evident from the data that the %G increases with an increase in the initiator concentration, and reaches a maximum value of 172.44% at 0.035 mol of CAN. Further increase in CAN concentration (0.04 mol) is accompanied by a decrease in the %G (163.96%). The observed increase in %G, with the CAN concentration ranging from 0.015 to 0.035 mol, may be due to the fact that in this concentration range, the increase in concentration of ceric ion results in an increase in the total number of Ce (IV)-xyloglucan complex which decompose to give more active sites. Thus, this activation along the backbone is immediately followed by graft copolymerization of monomer onto the backbone. At relatively higher concentration of the initiator, the number of backbone radicals increases. This will enhance the possibility of termination of the backbone radicals before grafting takes place. Furthermore, homopolymer formation at higher initiator concentration competes with the grafting reaction for available monomer, thereby leading to a decrease in %G.

Figure 1 also shows a decrease in %GE with 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. The higher the concentration of Ce (IV), the greater will be the termination of growing grafted chains resulting in reduction of %G as well as %GE.[13,19,20,29–31]

Effect of nitric acid concentration

The concentration of nitric acid was varied from 0.1 to 0.3*N*, keeping fixed the concentrations of all other reagents as well as time and temperature. The effect of acid concentration on %G and %GE is shown in Figure 2. It is observed that there exists an optimum concentration of nitric acid, which affords maximum percent grafting (187.28%). This corresponds to 0.2*N* in present case.

The role of nitric acid in grafting of AA onto TKP is explained by the fact that ceric ion in water is believed to react in the following manner:

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

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

Thus ceric ion exists as $[Ce]^{4+}$, $[Ce(OH)_3]^{3+}$, and $[Ce—O—Ce]^{6+}$ in aqueous solution. The concentration of these species is found to vary with the concentration of nitric acid. The %G and %GE increases with increase in acid concentration upto 0.2*N*. This is attributed to the increase in the concentrations of

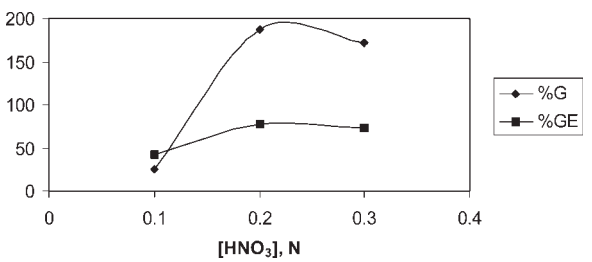


Figure 2 Effect of HNO_3 concentration on %G and %GE. Reaction conditions: [TKP] 0.012 mol; [CAN] 0.035 mol; [AA] 0.085 mol; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

$[Ce(OH)_3]^{3+}$and $[Ce]^{4+}$ at the expense of [Ce—O—Ce]$^{6+}$. Ceric ion $[Ce]^{4+}$ and $[Ce(OH)_3]^{3+}$, being smaller in size, are more effective in their ability to form complexes with TKP than [Ce—O—Ce]$^{6+}$. With further increase in acid concentration beyond 0.2*N*, it was observed that %G and %GE decreases. This is explained by the fact that as $[H^+]$ increases, the equilibria, eqs. (1) and (2) shift toward the formation of more and more $[Ce]^{4+}$ and $[Ce(OH)_3]^{3+}$. These species, at higher concentration of acid, affect the grafting adversely. Instead of propagating the polymeric chain, these species at higher concentration affect the termination steps, thus lowering the %G and %GE. Moreover, ceric ion has been reported to be involved in oxidative termination of growing monomeric chain as shown in eq. (3).[13,19,20,32,33]

$$Ce^{4+} + M_n \rightarrow Ce^{3+} + M_n + H^+ \quad (3)$$

Thus, nitric acid plays a definite role in promoting grafting of poly(acrylamide) onto TKP.

Effect of concentration of TKP

The effect of concentration of TKP on %G and on %GE was studied by varying the amount of TKP (0.012–0.031 mol) keeping other variables fixed. It can be seen from Figure 3 that %G and %GE increased initially with an increase in TKP concentration and reached a maximum value (195.05 and 80.60%, respectively) at 0.019 mol. With further increase in TKP concentration, both %G and %GE were found to be decreased. The initial rise may be due to an increase in the reactive sites with increasing concentration of the TKP. The decrease is due to the destruction of radical activity on the backbone soon after it is formed due to the termination between backbone–backbone and backbone-primary radicals. Similar results have also been reported in the literature.[13,19,20,34]

Effect of monomer concentration

The effect of monomer concentration on the grafting yields is represented in Figure 4. It is observed from the results that with increase in monomer concentration, %G increases and reaches the maximum value 229.68% at 0.099 mol. The enhancement of grafting by increasing the monomer concentration could be ascribed to the greater availability of grafting sites on TKP macroradicals to monomer molecules. However at higher monomer concentration, i.e., beyond 0.099 mol, there is a decrease in %G and %GE. This decrease can be attributed to the higher affinity of AA monomer for its homopolymer (polyacrylamide) over the TKP macroradicals. Thus, most of the monomer is preferentially used up in the formation of homopolymer on increasing the AA concentration, which is evident from the rise in viscosity of the reaction medium at higher concentration.[7,13,29,35]

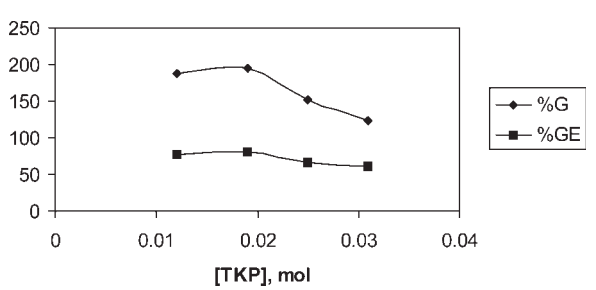


Figure 3 Effect of TKP concentration on %G and %GE. Reaction conditions: [CAN] 0.035 mol; [AA] 0.085 mol; $[HNO_3]$ 0.2*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

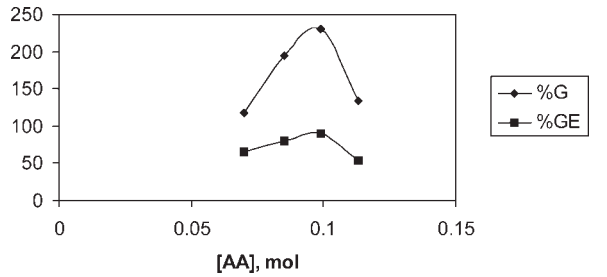


Figure 4 Effect of AA concentration on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [CAN] 0.035 mol; $[HNO_3]$ 0.2*N*; reaction time 3 h; reaction temperature 30°C; total reaction volume 100 mL.

Effect of reaction time

The effect of polymerization time on %G and %GE is shown in Figure 5. The percent grafting exhibits progressive improvement with the increase in reaction time and showed maximum %G (231.45%) at 2 h. This effect of time on grafting can be explained by the fact that more the contact time of monomer molecules with the TKP macroradicals sites, the higher will be the grafting, but the decrement in %G and %GE occurs beyond 2 h which can be rationalized

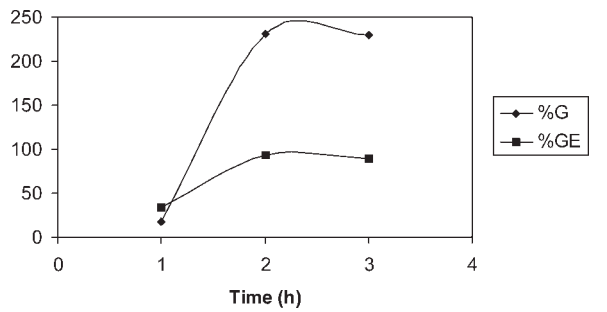


Figure 5 Effect of reaction time on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [CAN] 0.035 mol; [AA] 0.099 mol; $[HNO_3]$ 0.2*N*; reaction temperature 30°C; total reaction volume 100 mL.

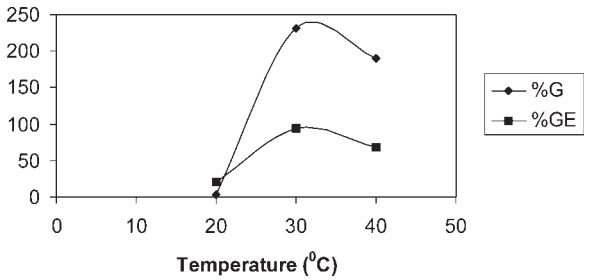


Figure 6 Effect of temperature on %G and %GE. Reaction conditions: [TKP] 0.019 mol; [CAN] 0.035 mol; [AA] 0.099 mol; [HNO_3] 0.2*N*; reaction time 2 h; total reaction volume 100 mL.

on account of depletion of monomer and initiator concentration with the progress of the reaction. Further with an increase in the reaction time, mutual annihilation of growing grafted chains also occurs leading to a decrease in %G and %GE.[13,19,20,36]

Effect of temperature

The grafting reactions were carried out at different temperatures (20–40°C), keeping other variables constant. The effect of temperature on %G and %GE is shown in Figure 6. The %G as well as %GE, increases with the rise of temperature from 20 to 30°C, but decreases with further increase in temperature. The maximum %G (231.45) was obtained at 30°C. The dependence of %G on temperature can be ascribed to the enhancement of the rate of diffusion of monomer. Increase in temperature beyond the optimum temperature (30°C in this case) leads to the graft copolymerization with poor selectivity, and various hydrogen abstraction and chain transfer reactions might be accelerated, leading to the decrease of %G and %GE.

Further at higher temperature, there may also be the acceleration of the termination process, which leads to the formation of more homopolymer. Similar results have been reported in the literature.[13,19,20,29,37]

CONCLUSION

Graft copolymerization of AA onto TKP in aqueous medium can be initiated effectively with CAN. The optimum reaction conditions obtained for grafting of AA onto TKP by using: [TKP] 0.019 mol; [CAN] 0.035 mol; [AA] 0.099 mol; [HNO_3] 0.2*N*; reaction time 2 h; reaction temperature 30°C, and total reaction volume 100 mL.

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