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Ceric-induced grafting of acrylate monomers onto sodium alginate

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The graft copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) onto sodium alginate (SA) with ceric ammonium nitrate (CAN) as a redox initiator in an aqueous medium has been studied. The optimized reaction conditions affording the maximum percentage of grafting of MA and MMA onto SA are determined by varying the concentrations of nitric acid, ceric ammonium nitrate, SA, MA and MMA, and also temperature and time. A comparison of the reactivity of the acrylate monomers with that of acrylonitrile has been made.

INTRODUCTION

In recent years, grafting as a technique for modifying chemical and physical properties of natural polymers as well as its derivatives, has attracted much interest from a practical and fundamental point of view. In our laboratory we have successfully grafted different vinyl monomers onto the sodium salt of partially carboxymethylated amylose (Na-PCMA) (Patel *et al.*, 1991, 1992, 1993*a*,*b*) and sodium salt of partially carboxymethylated starch (Na-PCMS) (Sinha *et al.*, 1992, 1993; Patel *et al.*, 1993*c*) using chemical as well as radiation methods. The water absorbency of the different saponified grafted samples of Na-PCMA has also been determined (Shah *et al.*, 1992*a*).

In our previous papers, we reported ceric-induced (Shah *et al.*, 1992*b*) and Fenton's reagent initiated (Shah *et al.*, 1994*a*,*b*) grafting of acrylonitrile onto sodium alginate and investigated the biodegradable behaviour of sodium alginate graft acrylonitrile by studying its interactions with different microorganisms (Shah *et al.*, 1994*c*). In continuation of our earlier work on the grafting of ethyl acrylate onto sodium alginate (Shah *et al.*, 1994*d*,*e*), we report here the study on the grafting of different acrylate monomers onto sodium alginate in the presence of Ce^{+4}.

EXPERIMENTAL

Materials

Sodium alginate (SA) used in the present work was kindly supplied by Wilson and Co., Bombay. Methylacrylate (CDH) and methyl methacrylate (Samir Tech. Chem) were washed with 2% (w/v) NaOH aqueous solution, followed by washing with distilled water. These were then dried over anhydrous sodium sulphate and finally distilled under nitrogen at atmospheric pressure. Ceric ammonium nitrate (CAN), Analar grade, Glaxo was used. Fresh solutions of the initiator were used by dissolving the required amount of CAN in HNO_3. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passage through freshly prepared alkaline pyrogallol solution. Deionized water was used for the preparation of solutions and in polymerization reactions.

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Graft copolymerization

The grafting reactions were carried out under nitrogen atmosphere in a 250 ml three-necked flask equipped with a reflux condenser, a stirrer and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, different amounts ($0{\cdot}5 \times 10^{-3}$–$3{\cdot}0 \times 10^{-3}$ kg, dry basis) of sodium alginate (SA) were dispersed in deionized water (100 ml) with constant stirring and bubbling a slow stream of nitrogen for 30 min at the desired temperature (15–50°C). A freshly prepared 10 ml solution of CAN (0·05–0·35 M) in nitric acid (0·05–0·60 N) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction mass and freshly distilled methyl acrylate/methyl methacrylate (0·1–9·0 ml) was added. The grafting reactions were carried out for varying time intervals (0·5–24 h). After completion of the reaction, the mixture was immediately filtered and the crude copolymer product was washed with nitric acid solution and deionized water. The crude

copolymer samples, namely SA-g-PMA and SA-g-PMMA were dried at 40°C under vacuum.

PMA-containing and PMMA-containing crude graft copolymers were freed from grafted PMA and PMMA by extraction with acetone and toluene, respectively, for 48 h. After complete removal of the homopolymers the residues were dried at 40°C under vacuum until constant weight was obtained.

The percentage grafting (% G), percentage grafting efficiency (% GE) and the rates of polymerization (R_p), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated with the help of the following expressions as reported earlier (Patel *et al.*, 1991).

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

$$\text{Percentage grafting efficiency (\% GE)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

$$\text{Rate of polymerization } (R_p) \text{ (mol } l^{-1}s^{-1}) = \frac{\text{Weight of polymer grafted} + \text{Weight of homopolymer}}{\text{Mol. wt of monomer} \times \text{Reaction time (s)} \times \text{Volume of the reaction mixture (ml)}} \times 1000$$

$$\text{Rate of graft copolymerization } (R_g) \text{ (mol } l^{-1}s^{-1}) = \frac{\text{Weight of polymer grafted}}{\text{Mol. wt of monomer} \times \text{Reaction time (s)} \times \text{Volume of the reaction mixture (ml)}} \times 1000$$

$$\text{Rate of homo polymerization } (R_h) \text{ (mol } l^{-1}s^{-1}) = \frac{\text{Weight of homopolymer}}{\text{Mol. wt of monomer} \times \text{Reaction time (s)} \times \text{Volume of the reaction mixture (ml)}} \times 1000$$

IR Spectra

IR spectra of SA, PMA, PMMA, SA-g-PMA and SA-g-PMMA were taken in KBr pellet form using a Perkin-Elmer model 983 spectrophotometer.

RESULTS AND DISCUSSION

Evidence of grafting

(a) Infrared spectral data of sodium alginate (SA), SA-g-PMA, SA-g-PMMA, PMA and PMMA have been utilized to prove grafting. The presence of a peak around 1740 cm^{-1} in each of SA-g-PMA and SA-g-PMMA samples indicates that grafting has taken place.

(b) The simplest method to prove the formation of the graft copolymer is based on the differences in solubility between the graft copolymer and the ungrafted homopolymer. SA is soluble in water while PMA and PMMA are soluble in acetone and toluene, respectively. When SA-g-PMA and SA-g-PMMA were soxhlet extracted with acetone and water as well as toluene and water alternatively for 48 h, insoluble solid still remained. A physical mixture of SA and PMA as well as SA and PMMA were treated in the same way and were found to dissolve completely. It is, therefore, apparent that SA-g-PMA and SA-g-PMMA samples obtained were not a simple physical mixture, some chemical bonds must exist between SA and PMA as well as SA and PMMA macromolecules.

(c) The physical mixtures of sodium alginate and benzene solutions of PMA and PMMA were prepared by stirring 1.0×10^{-3} kg of sodium alginate sample in 100 ml of benzene solution of PMA and PMMA for 24 h at room temperature. The sodium alginate was separated by filtration and the residue was subjected to extraction by benzene for 48 h and dried to a constant weight and 0.992×10^{-3} and 0.993×10^{-3} kg of sodium alginate sample was recovered from the respective physical mixtures. This indicated that the homopolymer, namely PMA as well as PMMA is completely removed from the respective physical mixture by benzene extraction.

Optimum reaction conditions

In the present investigation, various conditions were used to discover those optimum for grafting. Variables studied were concentrations of nitric acid and ceric ammonium nitrate (CAN), backbone concentration, monomer concentration, reaction time and temperature.

(a) Effect of acid concentration

Figure 1 shows the effect of nitric acid concentration on % grafting (% G) and % grafting efficiency (% GE) in

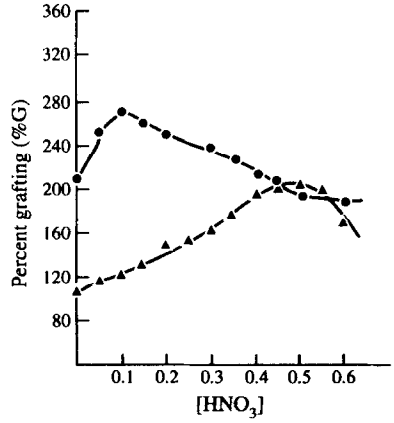

Fig. 1. Effect of nitric acid concentration on % grafting (% G) (●) MA; (▲) MMA.

the case of grafting of MA as well as MMA onto SA. It can be seen from Fig. 1 that there exists an optimum concentration of nitric acid which affords maximum percent grafting. This corresponds to 0·1 N with MA and 0·45 N with MMA. Beyond the optimum concentration of nitric acid, the percent grafting decreases. Interestingly (Fig. 1) even at zero concentration of nitric acid the value of percent grafting is found to be 207·04 and 106·46 with MA and MMA, respectively. This may be due to the possibility that, even in the absence of acid, sodium alginate in aqueous medium ionizes fully to a greater extent which facilitates the diffusion of monomer as well as initiator leading to a higher value of grafting.

In the beginning the percentage of grafting (% G) increases with increase in $[H^+]$ for MA and MMA (Fig. 1). This is attributed to the increase in the concentrations of $[Ce(OH)_3]^{+3}$ and Ce^{+4} at the expense of $(Ce\text{-}O\text{-}Ce)^{+6}$. Ceric ($Ce^{+4}$) and $[Ce(OH)_3]^{+3}$, being smaller in size, are more effective in their ability to form complexes with sodium alginate than $(Ce\text{-}O\text{-}Ce)^{+6}$. With further increase in nitric acid concentration beyond 0·1 N with MA and 0·45 N with MMA, it was observed that % G (Fig. 1) decreases. This could be attributed to the corresponding reduction in the ceric–sodium alginate complex formation as well as an increase in polymer termination rates. Nitric acid, thus, plays a definite role in promoting grafting of poly (methacrylate) and poly (methyl methacrylate) onto sodium alginate.

(b) Effect of initiator concentration

From Fig. 2 it can be seen that MA and MMA give rise to 292·36 and 237·12% grafting, respectively. It is further observed from this figure that with an increase in ceric ion concentration the percent grafting increases and reaches a maximum value at $[Ce^{+4}] = 0{\cdot}1$ mol/l for both MA and MMA. However, with further increases in the $[Ce^{+4}]$, the percent grafting decreases.

The observed increase in percent grafting within the CAN concentration range of 0·05–0·1 mol/l may be due to the fact that in this concentration range, activation along the backbone takes place immediately, followed by graft copolymerization of monomer onto the backbone. At relatively higher concentrations 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 a higher initiator concentration competes with the grafting reaction for available monomer and could also lead to a decrease in percent grafting. Similar observations have been reported (Pati *et al.*, 1979; Misra *et al.*, 1980; Egboh *et al.*, 1988).

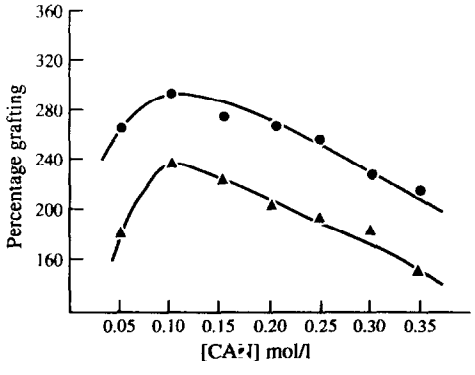

Fig. 2. Effect of ceric ammonium nitrate (CAN) concentration on % grafting (% G): (●) MA; (▲) MMA.

(c) Effect of sodium alginate concentration

The variation of sodium alginate concentration has a profound effect on percent grafting, grafting efficiency as well as on the rates of polymerization, grafting and homopolymerization as represented in Figs 3–6.

The percent grafting and percent grafting efficiency

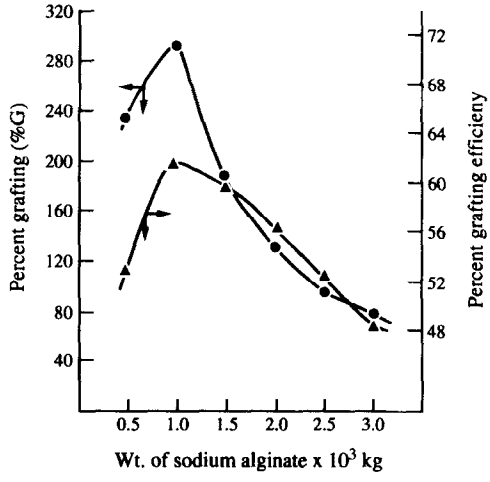

Fig. 3. Influence of amount of sodium alginate (SA) on: (●) % G; or (▲) % GE in the case of MA.

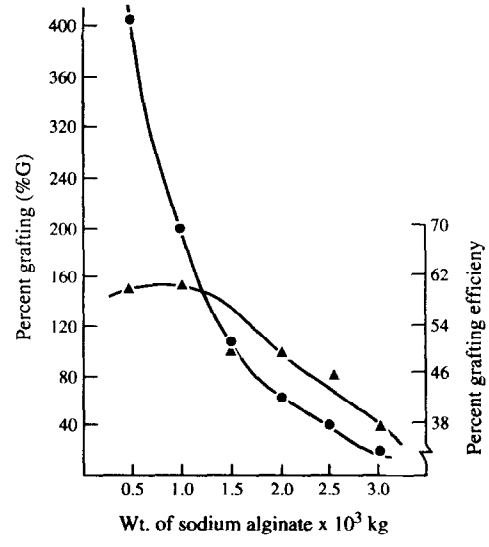

Fig. 4. Influence of amount of sodium alginate (SA) on: (●) % G; or (▲) % GE in the case of MMA.

have been plotted as a function of sodium alginate concentration for MA and MMA in Figs 3 and 4, respectively. It can be seen from Fig. 3 that % G and % GE increased initially with an increase in sodium alginate concentration, and reached a maximum value at [SA] = $1{\cdot}0 \times 10^{-3}$ kg for MA. With a further increase in sodium alginate concentration, both % G and % GE are found to be decreased. The initial rise may be due to an increase in the reactive sites with increasing concentration of the sodium alginate. The decrease is due to the destruction of radical activity on the backbone soon after it is formed due to termination between backbone–backbone and backbone–primary radicals. This is in agreement with the results obtained in the grafting of acrylonitrile onto starch (Mehrotra *et al.*, 1977), carboxymethyl amylose (Patel *et al.*, 1992), carboxymethyl starch (Sinha, 1990) and grafting of methylacrylate (Nagabhushanan *et al.*, 1978) and ethylacrylate (George *et al.*, 1989) onto gelatin.

In the case of grafting of MMA onto sodium alginate (Fig. 4), it has been observed that with increasing sodium alginate concentration, % G decreases steadily and % GE has a maximum. It may be explained because although the weight of the grafted side chains may increase with the increase in sodium alginate concentration and cause % GE to increase, the decrease in monomer-to-backbone ratio lowers % G. When the concentration of sodium alginate is increased further, the rate of graft copolymerization will be hindered by the high viscosity of the reaction system. Besides, high sodium alginate concentrations can produce more sodium alginate macroradicals which can interact with each other to terminate the reaction, thus lowering both % G and % GE. Similar results have been obtained in the case of graft copolymerization of butyl acrylate onto gelatin (Li Zhi-Chong *et al.*, 1988).

The effects of sodium alginate concentration on R_p, R_g and R_h for the grafting of MA and MMA onto sodium alginate are shown in Figs 5 and 6, respectively.

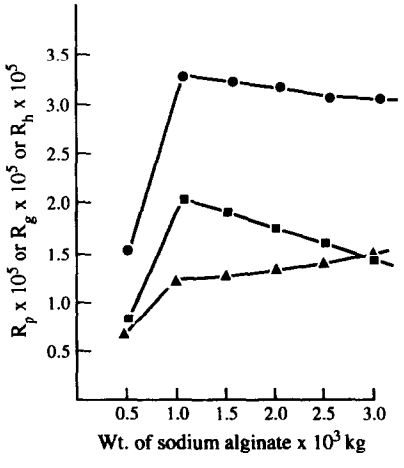

Fig. 5. Effect of amount of sodium alginate (SA) on: (●) $R_p \times 10^5$; (■) $R_g \times 10^5$; or (▲) $R_h \times 10^5$ in the case of MA.

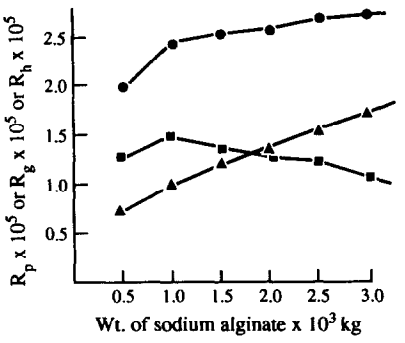

Fig. 6. Effect of amount of sodium alginate (SA) on: (●) $R_p \times 10^5$; (■) $R_g \times 10^5$; or (▲) $R_h \times 10^5$ in the case of MMA.

As shown in these figures the rate of polymerization (R_p) increases initially. This may be due to an increase either in the rate of graft copolymerization (R_g) or the rate of homopolymerization (R_h) or both. This is evidenced by the increase in both R_g and R_h (Figs 5 and 6) initially. This can be explained by the fact that an increase in sodium alginate concentration leads to a higher number of grafting sites, thereby increasing the rate of polymerization. The decrease in R_g might be due to the destruction of radical activity on the backbone soon after it is formed due to its higher concentration. Deactivation of backbone radicals may also occur through combination and/or interaction with the primary radicals. Similar observations have also been reported by other investigators (Patel, 1990).

(d) Effect of monomer concentration

Figures 7 and 8 show the effect of monomer concentration on grafting of MA and MMA, respectively. From these figures it can be seen that an increase in concentration of MA and MMA results in an increase in percent grafting to maximum values of 292·36 and 237·12% for MA and MMA at monomer concentrations of 0·483 and 0·407 mol/l, respectively. A further increase in monomer concentration leads to a decrease

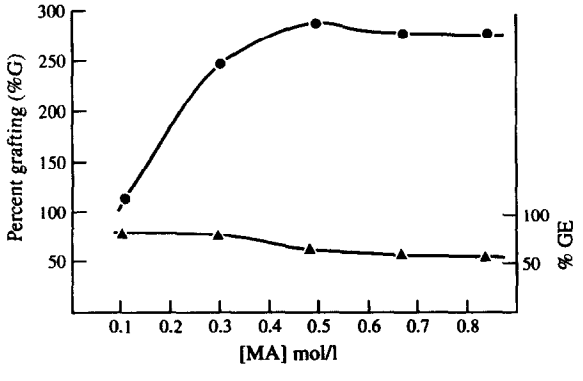

Fig. 7. Effect of methylacrylate (MA) concentration on: (●) % G; or (▲) % GE.

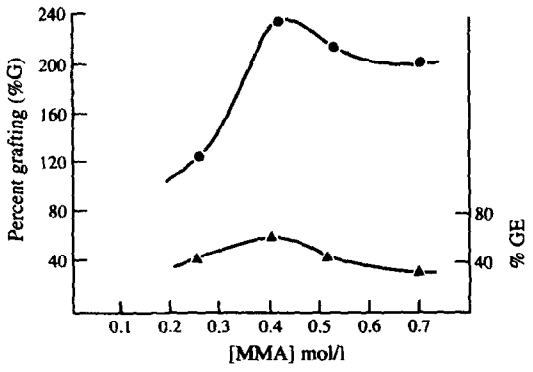

Fig. 8. Effect of methyl methacrylate (MMA) concentration on: (●) % G; or (▲) % GE.

in percent grafting for both the monomers. The enhancement of grafting by increasing the monomer concentration could be ascribed to the greater availability of grafting sites to monomer. However, at higher monomer concentrations, the concentration of monomer macroradicals increases and the rate of their combination and disproportionation is faster than the rate of their combination with sodium alginate molecules; percent grafting is decreased. Similar types of observations have also been reported previously (Lenka *et al.*, 1982).

(e) Effect of reaction time

Figures 9 and 10 represent the influence of reaction time on the percentage of grafting of MA and MMA, respectively. The percentage of grafting increases rapidly in the beginning up to 4 h and thereafter it decreases. This may indicate that with an increase in reaction time, mutual annihilation of growing grafted chains occurs and leads to a decrease in the percent grafting. A similar behaviour has been reported by Misra *et al.* (1981) as well as Nagabhushanan *et al.* (1978) during grafting of MA, EA and MA onto gelatin using CAN as an initiator as well as during grafting of EA onto gelatin in the presence of persulphate initiator. It can be seen from Figs 9 and 10 that % GE does not change appreciably during the course of the reaction.

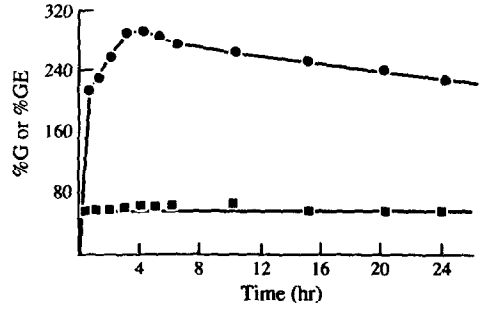

Fig. 9. Influence of reaction time on: (●) % G; or (■) % GE in the case of MA.

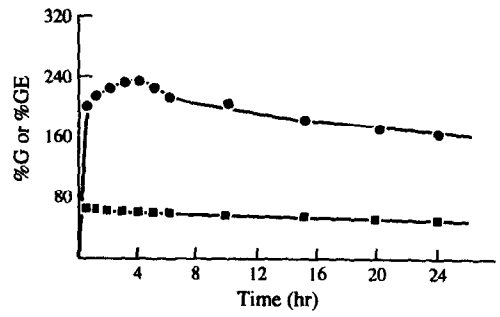

Fig. 10. Influence of reaction time on: (●) % G; or (■) % GE in the case of MMA.

The optimized reaction time is 4 h for both MA and MMA (Figs 9 and 10) and the maximum percentages of grafting reached within 4 h are 292·36% and 237·12% with MA and MMA, respectively.

(f) Effect of reaction temperature

The grafting reactions were carried out at different temperatures between 15 and 50°C, keeping the other variables constant. It can be seen from Fig. 11 that the percentage grafting increases with a temperature rise from 15 to 30°C for MMA and from 15 to 25°C for MA, but decreases to some extent with further increases of temperature to 50°C. Thus, an increase in temperature seems to cause a higher rate of dissociation of initiator, enhanced ionization of sodium alginate (which attracts more ceric ions) as well as the diffusion and mobility of the monomer from the aqueous phase to the backbone, resulting in considerable improvement in the grafting yield. With a further increase of temperature graft copolymerization occurs with poor selectivity, and various hydrogen abstraction and chain transfer reactions might be accelerated leading to the decrease of percent grafting. Patel *et al.* (1991) have also observed

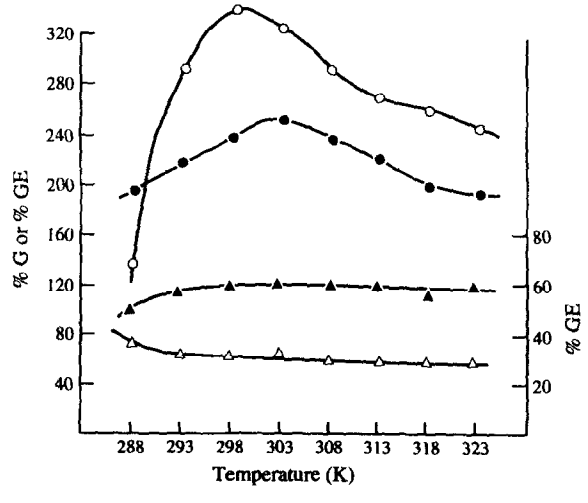

Fig. 11. The plots of % G or % GE vs temperature. For: (○) % G; (△) % GE. For MMA: (●) % G; (▲) % GE.

similar behaviour regarding the effect of temperature on percent grafting in the case of grafting of AN onto Na-PCMA using CAN as the initiator.

Figures 12 and 13 show the effect of temperature on the rates of polymerization, graft copolymerization and homopolymerization for grafting of MA and MMA onto SA, respectively. An increase in the reaction temperature is found to increase R_p initially and then to decrease it. A rise in temperature increases both the ionization of sodium alginate and the mobility of monomer leading to the substantial formation of graft and increasing R_g. The decrease in R_p and R_g after optimum temperature may be due to the fast rate of termination.

Increasing temperature causes a significant decrease in grafting efficiency in the case of MA (Fig. 11). This may be attributed to the solubility of monomer in the aqueous phase at higher temperature and also to the acceleration of the termination process which leads to the formation of more homopolymer and this is indicated by a steady increase in the rate of homopolymerization (Fig. 12). However, for MMA the grafting efficiency increases in the beginning and remains almost constant (Fig. 11). The initial increase

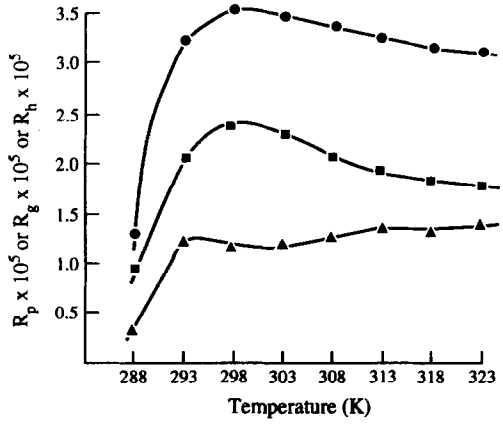

Fig. 12. Plot of (●) $R_p \times 10^5$; or (■) $R_g \times 10^5$; or (▲) $R_h \times 10^5$ vs temperature in the case of MA.

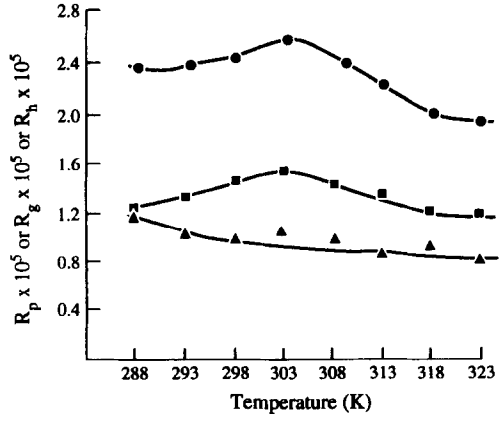

Fig. 13. Plot of (●) $R_p \times 10^5$; or (■) $R_g \times 10^5$; or (▲) $R_h \times 10^5$ vs temperature in the case of MMA.

Table 1. Maximum percent grafting of different vinyl monomers onto sodium alginate under optimum conditions[a]

Monomer	% Grafting (% G)	% Grafting efficiency (% GE)	% Homopolymer	Reference
AN	563·31	87·44	15·06	Shah *et al.*, 1992*b*
MA	341·05	67·33	34·63	Present work
MMA	254·93	59·72	36·73	Present work

[a]Optimum conditions for AN: HNO_3, 0·4 mol/l; CAN, 0·25 mol/l; time, 4 h; H_2O, 200 ml; SA, $1·5 \times 10^{-3}$ kg (dry basis); temp, 30°C; AN, 0·679 mol/l; total volume, 230 ml. MA: HNO_3, 0·1 mol/l; CAN, 0·10 mol/l; time, 4 h; H_2O, 100 ml; SA, $1·0 \times 10^{-3}$ kg (dry basis); temp, 25°C; AN, 0·483 mol/l; total volume, 115 ml. MMA: HNO_3, 0·45 mol/l; CAN, 0·10 mol/l; time, 4 h; H_2O, 100 ml; SA, $1·0 \times 10^{-3}$ kg (dry basis); temp, 30°C; AN, 0·407 mol/l; total volume, 115 ml.

may be due to the fact that the reactive sites increase with increasing temperature.

Comparison of the reactivity of monomers

The values of the maximum percentage grafting of AN (Shah *et al.*, 1992*b*), MA and MMA onto sodium alginate obtained under optimum conditions are shown in Table 1. A comparison of the results of Table 1 clearly shows the following reactivity order of monomers:

AN > MA > MMA.

This difference in monomer reactivities might depend on solubility, polarity molecular size, chemical nature etc.

The reduced reactivity of MA compared with AN is explained by the fact that $-COOCH_3$ having greater steric requirement makes this monomer less reactive than AN. In the case of MMA, the additional, $-CH_3$ group at the vinylic position probably offers more steric hindrance than MA and explains why it is less reactive than MA. The lowest reactivity of MMA, could be attributed to its lower solubility in the reaction medium and also the effect of the two methyl groups in MA making growth of the polymer chain sterically more difficult. Similar results have also been reported in the literature (Patel, 1990; Varma & Sarkar, 1974).

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