

Ceric Ion-Induced Graft Copolymerization of Acrylamide on Cationic Guar Gum at Low Temperature

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ABSTRACT: The solution polymerization of acrylamide (AM) on cationic guar gum (CGG) under nitrogen atmosphere using ceric ammonium sulfate (CAS) as the initiator has been realized. The effects of monomer concentration and reaction temperature on grafting conversion, grafting ratio, and grafting efficiency (GE) have been studied. The optimal conditions such as 1.3 mol of AM monomer and 2.2×10^{-4} mol of CAS have been adopted to produce grafted copolymer (CGG1-g-PAM) of high GE of more than 95% at 10°C. The rates of polymerization (R_p) and rates of graft copolymerization (R_g) are enhanced with increase in temperature (<35°C). The R_p is enhanced from 0.43×10^{-4} mol L⁻¹ s⁻¹ for GG-g-PAM to 2.53×10^{-4} mol L⁻¹ s⁻¹ for CGG1-g-PAM (CGG1, degree of substitute

(DS) = 0.007), and R_g from 0.42×10^{-4} to 2.00×10^{-4} mol L⁻¹ s⁻¹ at 10°C. The apparent activation energy is decreased from 32.27 kJ mol⁻¹ for GG-g-PAM to 8.09 kJ mol⁻¹ for CGG1-g-PAM, which indicates CGG has higher reactivity than unmodified GG ranging from 10 to 50°C. Increase of DS of CGG will lead to slow improvement of the polymerization rates and a hypothetical mechanism is put forward. The grafted copolymer has been characterized by infrared spectroscopy, thermal analysis, and scanning electron microscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3715–3722, 2007

Key words: polysaccharides; modification; synthesis; copolymerization; activation energy

INTRODUCTION

Various vinyl monomers such as acrylamide (AM),¹ methacrylamide,² acrylonitrile,³ methacrylate,⁴ 4-vinylpyridine,⁵ and acrylic acid⁶ grafting onto guar gums were reported to incorporate favorable properties while retaining their desirable properties such as thickening, water/saline retention, and biodegradability. Grafted guar gum derivative is used as flocculant, heavy metal absorbent, and biodegradable drag reducing agent in industrial wastewater treatment, mining industry and oil field chemical treatment respectively. In particular, more reports have focused on guar gum, hydroxypropyl guar gum (HPG),⁷ and carboxymethyl guar gum (CMGG)-AM grafted copolymer. Ceric ion,⁸ peroxydiphosphate/metabisulphite,⁹ vanadium(v)/mandelic,¹⁰ Cu²⁺/mandelic acid¹¹ and Fe²⁺/BrO₃¹⁻,¹² potassium persulfate/ascorbic acid¹³ are used as initiators of polymerization. Ce(IV), being the highest active initiator with less homopolyacrylamide, is considered to combine with glycol linkages of polygalactomanna and lead to C—C bond cleavage (between C2 and C3) by electron donor-acceptor transferring reaction, and

macroradical groups are generated on the backbone. All the researches have paid more attention to the enhancement of grafting level than to molecular weight of grafted AM copolymer. Especially the copolymer of cationic guar gum (CGG) grafted AM has seldom been studied. Nayak and Singh,^{14,15} have reported the synthesis of HPG-g-PAM using ceric ammonium nitrate (CAN). The product had a molecular weight of 3,490,000 and good flocculation property. Huang and Liu¹⁶ discussed about the copolymer of CGG grafted AM in the presence of high concentration of CAN at 50°C with low grafting efficiency (GE), and this copolymer also had low molecular weight. CGG has been known as an excellent retention and drainability agent for papermaking industry because of its substantivity with cellulose and fines. However in our previous work, CGG could not improve handsheets' physical property. Thus this article discusses the aqueous graft copolymerization of AM onto CGG at 10°C using low concentration of ceric ammonium sulfate (CAS) to obtain the copolymer of high molecule weight which has not been reported before. Moreover it has been found that CGG shows better polymerization activity than unmodified guar gum. The rates of polymerization and grafting for CGG-g-PAM and GG-g-PAM have been evaluated under same conditions, and apparent activity energy has been calculated and compared.

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EXPERIMENTAL

Materials

CGG of various degree of substitute (DS) was made in our laboratory based on the methods described by Chowdhary¹⁷ and Yeh.¹⁸ The details were as follows: 50 g guar gum and quantitative ethanol were placed into a beaker with stirring. The required sodium hydroxide solution was added as the catalyst and alkalization lasted for 45 min, and then the 70% (w/v) solution of cationic 3-chloride-2-hydroxypropyl trimethyl ammonium chloride was added slowly for 30 min at room temperature. And then the mixture was heated and reacted for 2–5 h at 50–60°C. The products' characters were listed in Table I. AM, CAS, sodium hydroxyl, and 95% (v/v) ethanol used were of analytic agent grade.

Graft copolymerization

CGG-g-PAM was synthesized by grafting AM onto CGG through radical polymerization method in an aqueous system using Ce(IV)/nitric acid redox initiator. The procedure was as follows.

One gram of CGG was dissolved in distilled water (125 mL) in a three-neck flask under constant stirring. The flask was then flushed with nitrogen for 30 min. The required amount of AM and 10 mL distilled water was added. The solution was stirred for 15 min while being bubbled with nitrogen. The required amount of Ce(IV) solution (in 0.5 mol HNO₃) was added. The nitrogen was continued flowing for another 10 min, and the flask was sealed with tape. The reaction temperature was maintained at 10°C by immersing the flask in a constant temperature bath pan by adding ice-water continuously. And then the mixture was neutralized to pH 6.5–7 by addition of concentrated NaOH-ethanol solution (*c* (NaOH) = 0.05 mol). The white precipitate was filtered on a sintered glass filter with suction. The solid was thoroughly washed with 80% (v/v) ethanol solution, then 90% (v/v), and finally pure ethanol. The product was dried in vacuum to a constant weight at 65°C and –0.1 MPa.

TABLE I
Characteristics of CGG

–	W(N) (%) ^a	DS	η (dL/g)	Content of water (%)
GG	0	0	11.73	10.0
CGG1	0.06	0.007	10.02	9.45
CGG2	0.85	0.108	9.32	9.56
CGG3	1.11	0.146	8.95	9.41

^a The content of nitrogen of GG is 0.65%, the content of nitrogen of CGG1, CGG2, and CGG3 have subtracted the initial value of GG, and then the values have been listed.

Purification of the grafted copolymer

There were CGG-g-PAM, PAM, unreacted monomer, and residual initiator in the mixture. Therefore it was necessary to separate the grafted copolymer from the crude product. The extraction of occluded PAM was carried out by solvent extraction using a mixture of glycol and ice acetic acid (6 : 4 by volume). The detailed procedure was as follows: 2 g of crude graft copolymer was taken in a 250 mL beaker. Then 100 mL of the solvent was added and kept at 30°C for 24 h. Before the mixture was filtered by using Buchner funnel the residue was washed with same solvent mixture for 2–3 times to remove the PAM thoroughly. The product was washed with ethanol again and kept for 12 h. Finally it was dried at 65°C in a vacuum oven.

Grafting parameters and rate equations

The compositional parameters, including monomer conversion (%C_t), grafting ratio (G), and %GE are calculated by the following formula:

$$C_t = \frac{TP - IG}{M} \times 100$$

$$G = \frac{GS - IG}{IG}$$

$$GE = \frac{GS - IG}{TP - IG} \times 100$$

where *M*, TP, GS, IG denotes mass (g) of monomer charged, total product, grafted copolymer and CGG, respectively.

Rates of polymerization (*R_p*) and rates of graft copolymerization (*R_g*) could be evaluated by measurements of the monomer disappearance rate using the following equations:

$$R_p = \frac{TP}{M \times T \times V} \times 1000$$

$$R_g = \frac{GS}{M \times T \times V} \times 1000$$

where *M* is the molar mass of the monomer used. *T* and *V* denote total reaction time (s) and total volume (mL) of the reaction mixture.

Intrinsic viscosity and molecular weight measurements

The molecular weight (MW) of the pure grafted copolymer was determined from the intrinsic viscosity [η] measurements. Ubbelohde viscometer was used

to measure viscosity at 25°C in 1 mol NaNO₃ solution. The weight-average MW was then calculated from $[\eta]$, dL/g values using the following Mark-Houwink equation.

$$[\eta] = 6.31 \times 10^{-5} \times [\text{Mw}]^{0.08}$$

Due to the high mass ratio of AM/CGG (>9) during the polymerization of CGG-g-PAM, the percentage of CGG was very small. So the contribution of CGG was neglected when measuring the Mw of grafted product.

Study of Fourier transform infrared, differential thermal gravimetric, and scanning electron microscopy

The structure of CGG-g-PAM, GG, CGG, and PAM were determined by FTIR spectra. The thermal analysis of GG, CGG, and CGG1-g-PAM were carried out by NETZSCH TG209 F1 (DTG, Germany). The heating rate was uniform in all cases at 10°C/min in an atmosphere of nitrogen, starting from room temperature up to 600°C. SEM pictures were obtained

by XL-30 ESEM (Philip Company, Holland). The samples, in the powered form, were mounted on the specimen stubs and coated with gold ion using IB.5 Ion Sputtering Apparatus. The voltage was 10 kV and the micrographs were taken at a magnification of 800.

RESULTS AND DISCUSSION

Characterization of graft copolymers

IR spectra

The IR spectra of GG, CGG, PAM, and CGG1-g-PAM are shown in Figure 1. In the case of CGG, absorption band at 1480 cm⁻¹ is for the CH₃ bending vibration of quaternary ammonium. The IR spectra of CGG1-g-PAM shows that two bands around 1668 and 1413 cm⁻¹ are related to C=O and N-H stretching vibration bands of the amide group which is correlated with 1670 and 1400 cm⁻¹ band of PAM, respectively. As PAM copolymer has been removed from grafted products, the presence of above bands in the graft copolymer is a strong evidence of grafting.

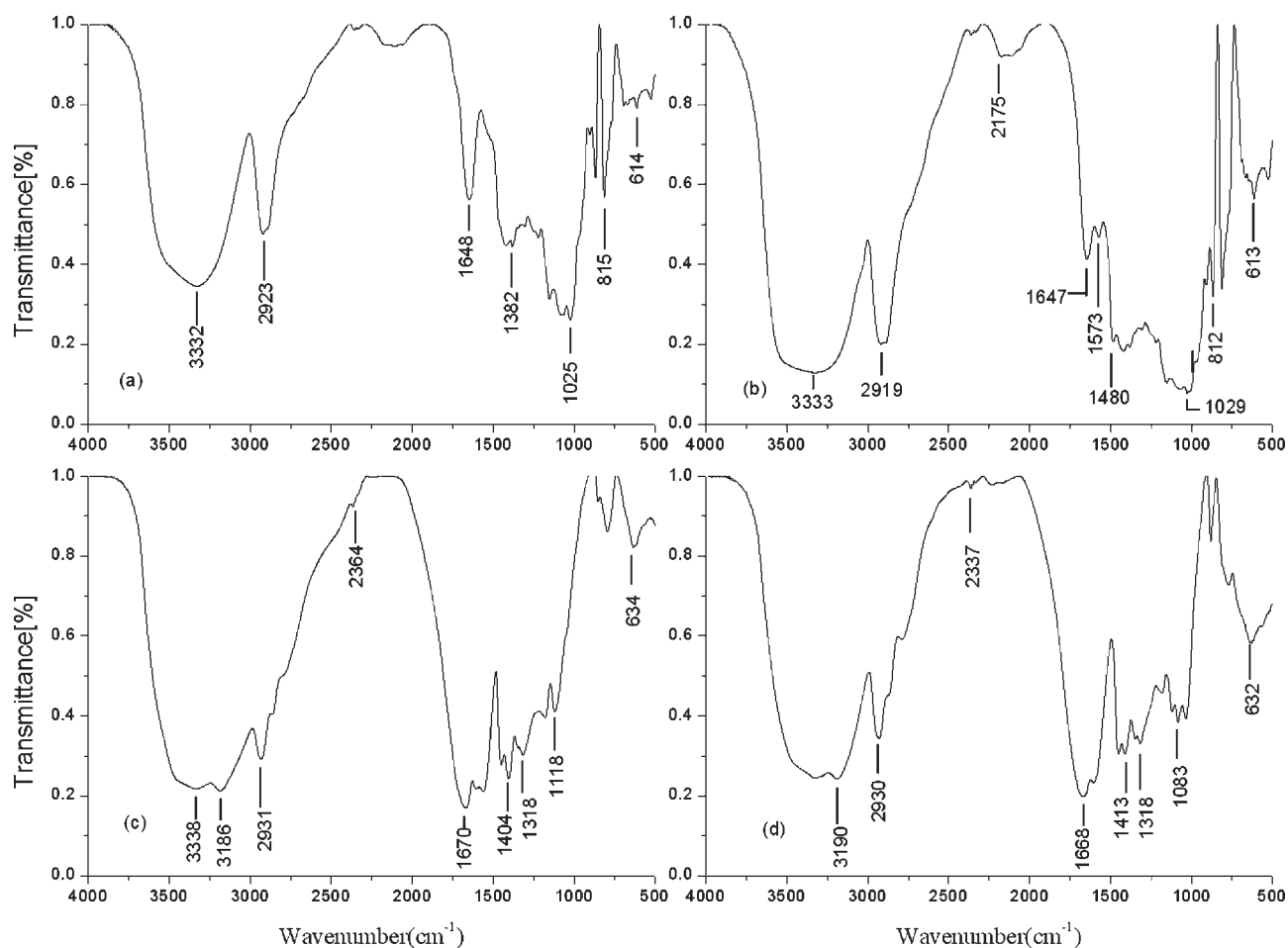


Figure 1 IR Spectra for (a) guar gum, (b) cationic guar gum, (c) PAM, and (d) CGG1-g-PAM.

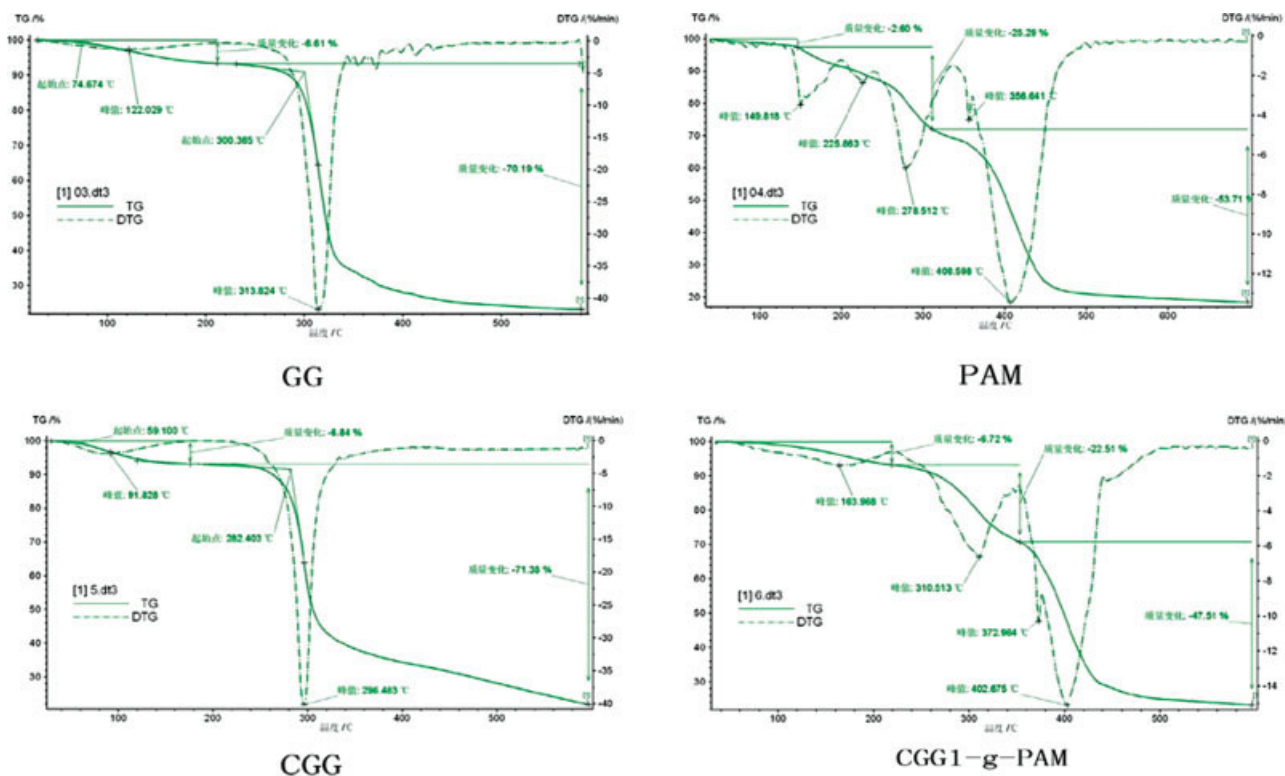


Figure 2 DTG of grafted copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

DTG analysis

Figure 2 shows that two distinct zones are observed where the weight to be lost in case of GG and CGG1. The initial weight loss of 6.61% begins at 74.67 and 59°C, which is due to evaporation of solvent such as ethanol and water in these two samples. The second degradation zone is at 333.37 and 282.40°C respectively, where the polymer decomposition takes place. These data show that CGG has the worse heat-resistance property because the quarter ammonium is easy to break up. However, the DTG curve for PAM indicates a characteristic pattern distinctly different from the base polysaccharide, e.g., GG and CGG. After the initial loss of weight because of solvent, there is a continuous loss of weight with an increase in temperature up to 140°C. Later the maximum weight loss of 53.71% happens at 300.15°C due to the loss of NH_2 group in the form of ammonium. When

AM has been grafted onto the backbone of CGG, the degradation of the copolymer takes place in three stages. The first stage is as the same as GG, CGG, and PAM below 100°C. The second stage of decomposition (starting from 201.5°C) is for the degradation of both PAM and CGG chains. The loss of weight is increased with further increasing of temperature. At the third stage, the copolymer degrades at the starting temperature of 362.18°C which is higher than PAM, meanwhile the weight loss of 47.51% of the CGG1-g-PAM is lower than that of 53.71% of PAM. From the DTG curves it can be concluded that the grafting of PAM chains onto the polysaccharide backbone enhances the thermal stability of the polysaccharide, which can indicate that the grafted copolymer was synthesized successfully. All details of weight loss and corresponding temperatures are summarized in Table II.

TABLE II
DTG Analysis of Samples

Sample	Stage 1		Stage 2		Stage 3		Temperature (°C) of the biggest weight loss
	Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)	
GG	74.67	6.61	333.37	70.19			313.82
CGG1	59.1	6.84	282.40	71.38			296.48
PAM	80.24	2.6	140.8	25.29	300.15	53.71	406.60
CGG1-g-PAM	81.25	6.72	201.5	22.51	362.18	47.51	402.67

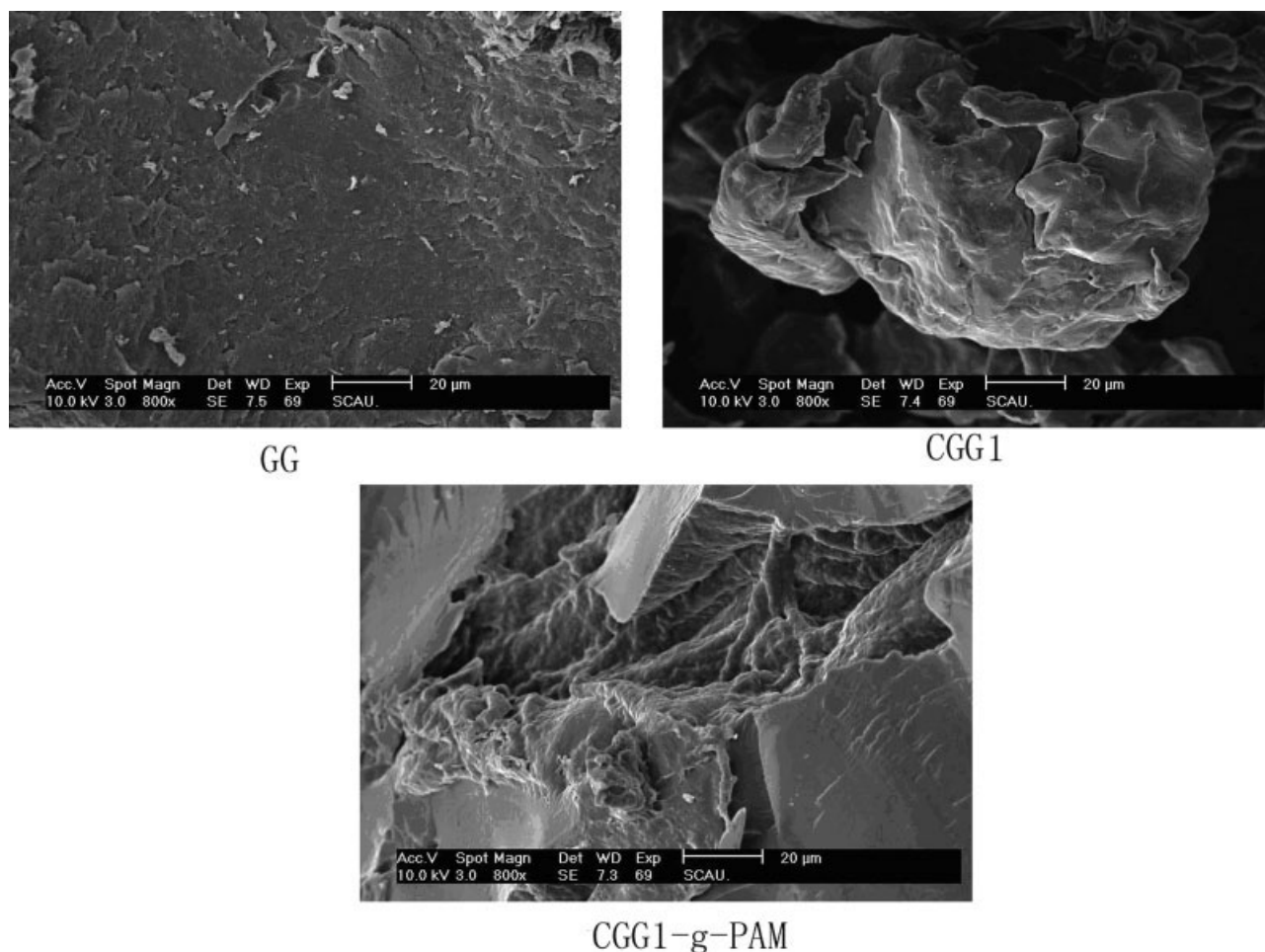


Figure 3 SEM of GG, CGG1, and CGG1-g-PAM.

Scanning electron micrographs

Figure 3 shows the SEM pictures of GG, CGG and, CGG1-g-PAM. Surface morphology of GG is smooth and tight. However, CGG shows different microcosmic structure which is coarse, loose, and wrinkled. The surface of CGG1-g-PAM displays piece, more coarse and clustered tuber existing on the surface. The distinct difference in the micrographs of these products indicates that grafting has taken place.

Effect of monomer concentration on grafting parameters and molecular weight

According to radical polymerization theory, the process is influenced by concentration of initiator and monomer, reaction temperature, and reaction time. To synthesize product of high MW and GE the effects of monomer concentration on grafting parameters and MW were studied. The experimental results are plotted on Figures 4 and 5 under the same conditions.

Figure 4 shows that conversion percentages ($\%C_t$) increases up to 100% with increases in monomer

concentration from 0.37 to 0.55 mol, after which it keeps 100% with further increase in AM concentration (<1.3 mol). This could be because of the enhanced contact opportunity of monomer and macroradical at higher monomer concentration. However $\% C_t$ decreases beyond 1.3 mol because the macromolecule makes the solution sticky and limits the movement of monomer molecule. The other reason is that combination and disproportion of macroradicals occur more frequently. The grafting ratio shows the same trend as conversion percentage. GE keeps about 95% at all various concentrations which is attributed to the decrease of AM homopolymerization at 10°C .

Figure 5 indicates that the MW of grafted copolymer initially increases, but thereafter decreases by altering the AM concentration from 0.37 to 1.99 mol. This is because propagation rate and initiation rate are higher and reaction solution becomes stickier rapidly when comparing with lower AM concentration. Thus the higher MW of copolymer is obtained. The decrease is attributed to a faster rate of termination and transferring. Thus, there are more unreacted

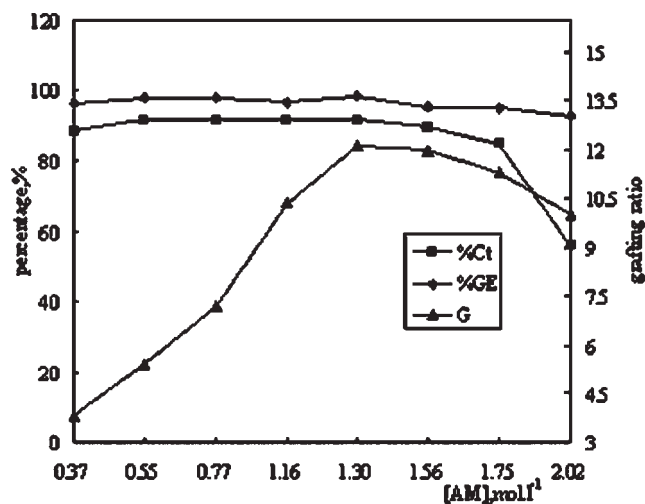


Figure 4 Effect of monomer concentration on grafting parameters $T = 10^{\circ}\text{C}$, $[\text{CGG}] = 8 \text{ g L}^{-1}$, $t = 12 \text{ h}$, $[\text{CAS}] = 2.1 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}^{+}] = 0.01 \text{ mol L}^{-1}$.

monomers at higher AM concentration in the mixture leading to the reduction of MW.

Effect of reaction temperature on grafting parameters, molecular weight, and polymerization rate

The graft copolymerization of AM onto CGG was investigated at 10, 20, 30, 40, and 50°C when concentration of all reagents was kept constant. It is observed that in Figures 6 and 7, all the grafting parameters and MW, except %GE, increase with increasing of temperature from 10 to 35°C and then decrease from 35 to 50°C . The increase is because of higher mobility of monomer molecules, resulting in

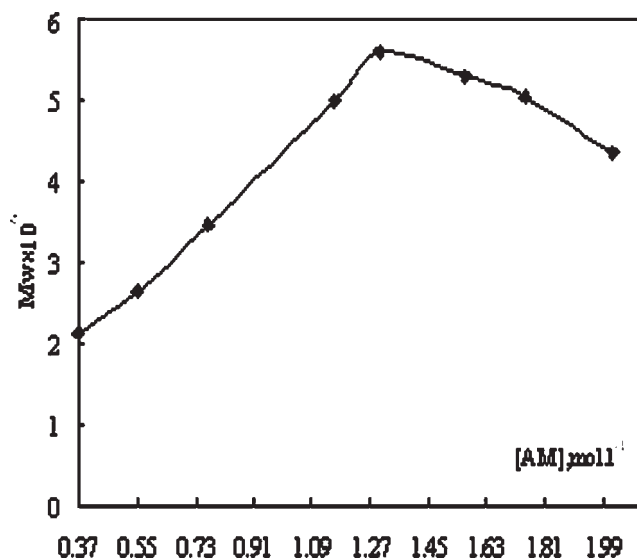


Figure 5 Effect of monomer concentration on MW of copolymer $T = 10^{\circ}\text{C}$, $[\text{CGG}] = 8 \text{ g L}^{-1}$, $t = 12 \text{ h}$, $[\text{CAS}] = 2.1 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}^{+}] = 0.01 \text{ mol L}^{-1}$.

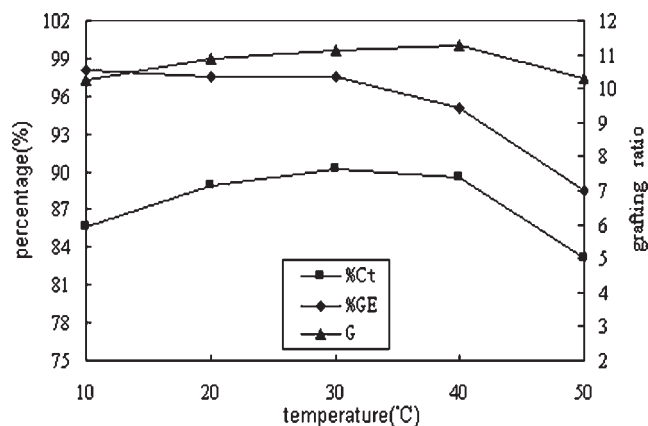


Figure 6 Effect of temperature on grafting parameters $[\text{CGG}] = 8 \text{ g L}^{-1}$, $[\text{AM}] = 1.3 \text{ mol L}^{-1}$, $t = 4 \text{ h}$, $[\text{CAS}] = 2.1 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}^{+}] = 0.01 \text{ mol L}^{-1}$.

enhanced diffusion rate in the vicinity of guar gum macroradical at higher temperature. The decrease in MW is ascribed to improvement of propagation rate and termination rate of macroradical group with solvent. The MW of graft copolymer is 4,350,000 at 50°C . %GE decreases slowly due to the enhancement of homopolymer at high temperature. Thus it could be concluded that temperature has a significant effect on the graft copolymerization reaction. Considering products of high MW and %GE with low energy consumption, the optimum temperature of 10°C is chosen.

Experiments show that rates of polymerization (R_p) and rates of graft copolymerization (R_g) go up quickly during 30 min from the addition of initiator. Weight method is adopted to calculate the average polymerization rate at various temperature. The Arrhenius plot (Fig. 8) of R_p versus $1/T$ is a straight line (the curve is experimental data. The line is treated by computer). The activation energy of

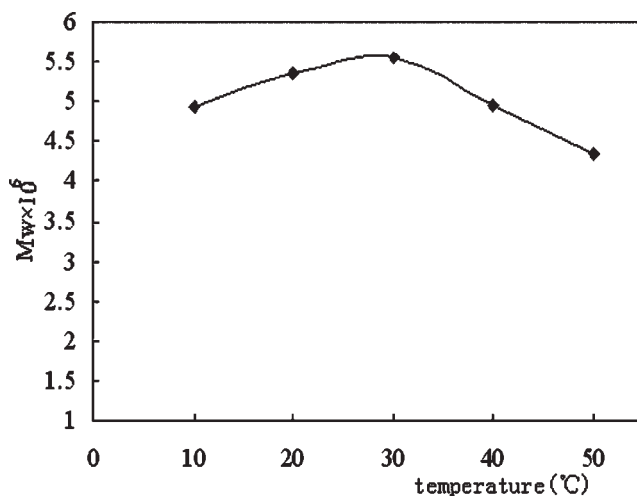


Figure 7 Effect of temperature on MW of copolymer. The experimental conditions are the same as Figure 6.

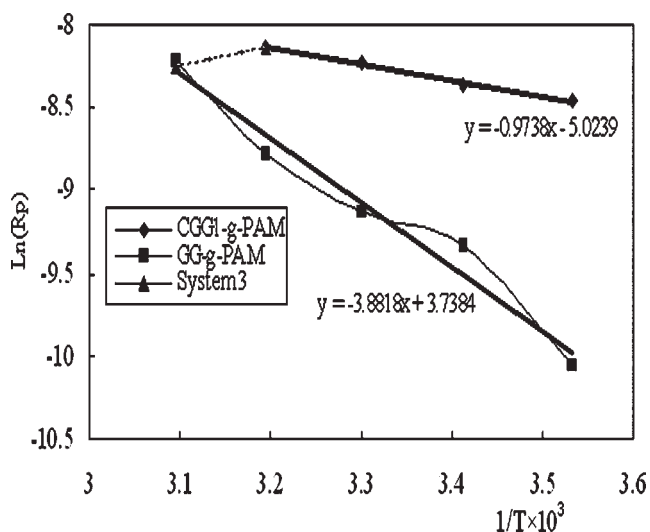


Figure 8 Effect of temperature on R_p [CGG1] = 8 g L⁻¹, [AM] = 0.77 mol L⁻¹, [CAS] = 2. × 10⁻⁴ mol L⁻¹, [H⁺] = 0.01 mol L⁻¹, t = 0.5 h.

CGG1-g-PAM and GG-g-PAM is calculated to be 8.07 and 32.2 kJ mol⁻¹, respectively.

Thus ΔE_a for CGG1-g-PAM (CGG, DS = 0.007) is much lower than that for GG-g-PAM. So R_p for CGG-g-PAM is quicker than that for GG-g-PAM. The hypothetical mechanism will be put forward later.

Comparative study of R_p and R_g of GG and CGG of various DS grafted by AM

Figures 9 and 10 show the reaction rates of GG-g-PAM and CGG-g-PAM polymerization under the same conditions. Unmodified guar gum has worse polymerization performance than CGG at 10°C. For CGG1-g-PAM R_p increases from 0.43 × 10⁻⁴ mol L⁻¹ s⁻¹ for GG-g-PAM to 2.53 × 10⁻⁴ mol L⁻¹ s⁻¹ and

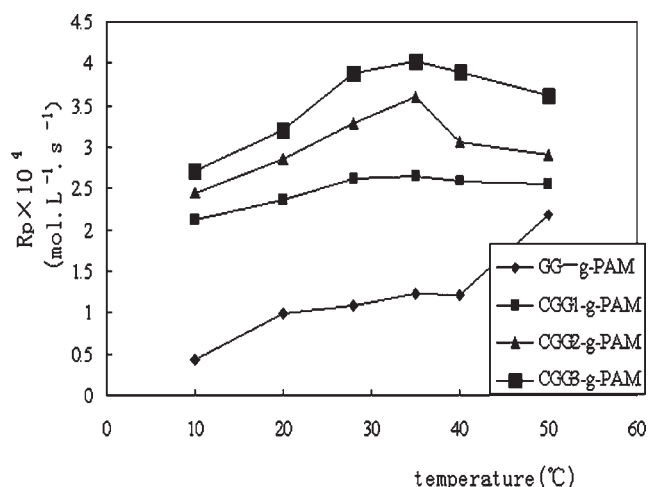


Figure 9 Effect of substrates on R_p [CGG1] = 8 g L⁻¹, [AM] = 0.77 mol L⁻¹, [CAS] = 2.1 × 10⁻⁴ mol L⁻¹, [H⁺] = 0.01 mol L⁻¹, t = 0.5 h.

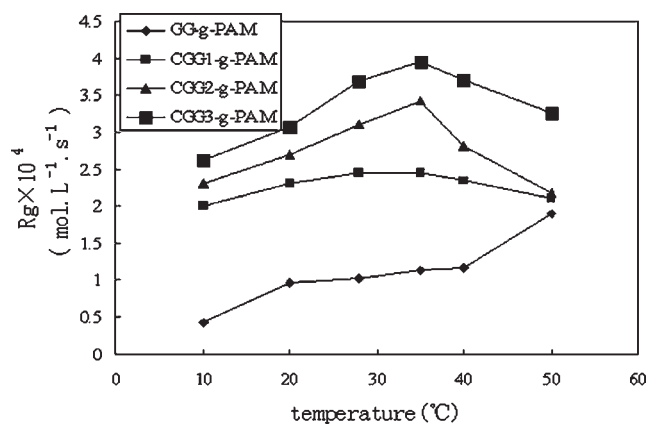


Figure 10 Effect of substrates on R_g [substrate] = 8 g L⁻¹, [AM] = 0.77 mol L⁻¹, [CAS] = 2.1 × 10⁻⁴ mol L⁻¹, [H⁺] = 0.01 mol L⁻¹.

R_g from 0.42 × 10⁻⁴ to 2.00 × 10⁻⁴ mol L⁻¹ s⁻¹. Moreover R_p and R_g can enhance further with weak trend when the DS of CGG ranges between 0.007 and 0.146.

With increasing of reaction temperature, R_p and R_g for both GG and CGG can go up from 10 to 35°C, which is consistent with radical polymerization theory, i.e., enhancement of reaction temperature accelerates the initiation of ceric ion and propagation polymerization. However the difference between GG-g-PAM and CGG-g-PAM decreases at higher temperature because R_p for GG-g-PAM increases more quickly than that for CGG-g-PAM.

Figures 9 and 10 also show that R_p and R_g are observed to decrease at higher temperature from 35 to 50°C for CGG of various DS. Especially R_g drops more rapidly than R_p which is ascribed to more homopolymerization. The degradation of CGG at higher temperature will shorten the length of mannose backbone. Therefore the amounts of macroradical induced by electron transfer reaction of ceric ion go down and lead to low initiation and propagation rate. However as for GG-g-PAM R_p and R_g keep going up due to the better heat-resistance of GG. This can be confirmed by DTG curve (Fig. 2).

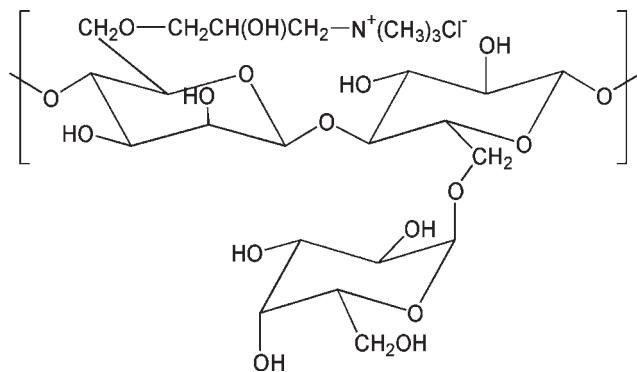


Figure 11 Structure of CGG.

Thus, the following reaction mechanism was proposed for the graft copolymerization of AM onto CGG basing on these experimental phenomena. First, CGG molecule (Fig. 11) has positive charge after the —OH in the C6 position is etherized by cationic monomer. Thus CGG is easier to dissolve in water at room temperature and its aqueous solution is clearer than unmodified GG. Therefore its molecule is easy to spread and apt to complex with Ce(IV). Second, ammonium compound may independently act as a reductive agent to lower the initiation active energy of Ce(IV). Therefore CGG can generate more free groups than GG under the same conditions. It is also found that R_p fall off with further increase of DS. This is attributed to steric hinderance of cationic monomer.

CONCLUSIONS

Graft copolymerization of AM onto CGG at 10°C has been synthesized using CAS as initiator under nitrogen atmosphere. It shows that high concentration of AM and lower temperature can benefit copolymer of high molecular weight and GE. The optimal conditions such as 1.3 mol of AM and 2.2×10^{-4} mol of CAS has been adopted to produce grafted copolymer (CGG-g-PAM) of high GE (>95%) at 10°C. Compared with unmodified guar gum, CGG of various DS have the superior polymerization performance. In case of CGG1 of low DS (DS = 0.007), the polymerization rate of CGG1-g-PAM increases from 0.43×10^{-4} mol L⁻¹ s⁻¹ for GG-g-PAM to 2.53×10^{-4} mol L⁻¹ s⁻¹ at 10°C for 0.5 h reaction time, as well as R_g for CGG1-g-PAM

increases from 0.42×10^{-4} mol L⁻¹ s⁻¹ for GG-g-PAM to 2.00×10^{-4} mol L⁻¹ s⁻¹. The apparent activation energy for CGG1-g-PAM decreases from 32.27 kJ mol⁻¹ for GG-g-PAM to 8.09 kJ mol⁻¹. The R_p and R_g can enhance further with weak trend for CGG of DS ranging from 0.007 to 0.146.

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