# Graft Copolymerization of 4-Vinyl Pyridine onto Konjac Glucomannan Initiated by Ammonium Persulfate

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**ABSTRACT:** The grafting of 4-vinyl pyridine (4-VP) onto konjac glucomannan (KGM) by ammonium persulfate (APS) as the initiator was studied in an acid aqueous solution under an inert atmosphere. The grafting ratio ($G\%$) and grafting efficiency ($E\%$) were evaluated comparatively. The dependence of these parameters on the initiator concentration, sulfuric acid concentration, ratio of monomer to KGM, temperature, and reaction time was also investigated. Under conditions of $[KGM] = 1.00$ g/L, $[APS] = 1.00 \times 10^{-2}$ mol/L, $[4\text{-}VP] = 9.32 \times 10^{-2}$ mol/L, $[H^+] = 5.00 \times 10^{-2}$ mol/L, temperature $= 35°C$, and time $= 120$ min, the optimum $G\%$ and $E\%$ were 307.27 and 52.75%, respectively. The proof of grafting was obtained from thermogravimetric analysis and infrared spectra. Preliminary research of the graft's adsorption capacity for heavy-metal ions [Cr(VI), Cu(II), Pb(II), and Cd(II)] was done. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2339–2345, 2009

**Key words:** adsorption; blends; graft copolymers; polysaccharides; radical polymerization

## INTRODUCTION

The modification of natural polymers by graft copolymerization is an attractive and cost-effective technique for the preparation of new biomaterials. This is a quite promising method for improving the potential applications by introducing desired properties and thus enlarging the scope of abundantly available polysaccharides.[1]

Konjac glucomannan (KGM) is a high-molecular-weight, water-soluble nonionic polysaccharide, which can be extracted from tubers of the amorphophallus konjac plant in large quantities. It is a linear random copolymer of β-(1,4)-linked D-mannose and D-glucose, and the ratio of mannose to glucose is 1.6 : 1 (Fig. 1).[2] There are some branching points at the C-3 position of the mannoses, and an acetyl group is attached to 1 per 19 sugar residues.[3] Konjac is a kind of agricultural product with a high yield. It is widely planted in the mountainous areas in China at low cost and has long been used as a healthy food in China and Japan,[4] as it is abundant, inexpensive, and easily available. Recently, studies of KGM, with its applications in the food industry[5–7] and drug release,[8–10] have been extensive and have made much progress.

4-Vinyl pyridine (4-VP) is an important monomer, and its homopolymers are known catalysts. The presence of a reactive pyridine nitrogen on the repeating unit of poly(4-vinyl pyridine) [P(4-VP)] makes the polymer attractive as a reagent. The weakly basic nitrogen atom makes possible a variety of reactions on vinyl pyridine polymers, such as reaction with acids, quaternization, and complexation of metals. Therefore, P(4-VP) has extensive applications as a reducing agent, oxidizing agent, classified ion exchanger, heavy-metal-ion remover, and so forth.[11–18] Numerous studies on the grafting of 4-VP have been done, such as with guar gum,[19] chitosan,[20] polyamide,[21] and cellulose.[22] However, very few studies have been reported on the grafting of 4-VP onto KGM.

This polymer has been prepared because P(4-VP) has been found to have extensive applications.[11–18] Similarly, KGM also enjoys a wide range of use in industrial applications. Because of the poor hydrophilic properties and costly price of P(4-VP), KGM-*g*-(4-VP) (KGM–4-VP) would be more environmentally friendly and cost effective than P(4-VP) by grafting and would hold better properties of metal-ion uptake, a flocculent, and an antimicrobial resin than KGM.[19] As the graft copolymerization is a heterogeneous reaction, grafting may be accomplished with 4-VP onto some polymers, but the rate and extent of grafting are usually very low because of hindered diffusion of 4-VP at the surface of some polymers.[22] Hence, grafting onto KGM is accomplished by the addition of quantitative ethanol as a dispersant, 4-VP is dispersed effectively in deionized water, and phase
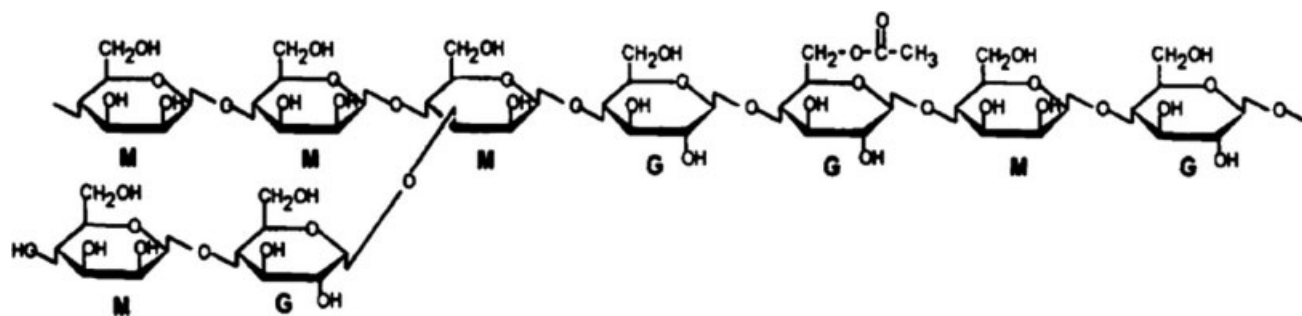
**Figure 1** Molecular structure of KGM (M = mannose; G = glucose).

conglomeration is hindered effectively, so that high grafting of 4-VP onto KGM is achieved. In this article, we report on the preparation and characterization of a novel polymer by the grafting of 4-VP onto KGM with ammonium persulfate (APS) as the only initiator. The dependence of the optimum grafting ratio ($G\%$) and grafting efficiency ($E\%$) on the initiator concentration, hydrogen ion concentration, ratio of monomer to KGM, temperature, and reaction time was investigated. Preliminary research on the graft's adsorption capacity for heavy-metal ions [Cr(VI), Cu(II), Pb(II), and Cd(II)] was done.

## EXPERIMENTAL

### Materials

KGM was purchased from the market (Zhongxin, Yunnan Zhongxin Co., Yunan, China). 4-VP, from ALFA Aesar (USA), was distilled under reduced pressure just before use (bp = 52°C). APS, which was an analytical-grade reagent, was recrystallized before use. Other substances, which were analytical-grade reagents, were used as received.

### Graft copolymerization

For each experiment, the weighed amount of KGM (0.10 g) was added to rapidly stirred deionized water in a three-necked flask. Throughout the course of the reaction, the reaction mixture was purged with purified nitrogen and was kept at a constant temperature. Defined amounts of APS solution and sulfuric acid were added to the reactor. 4-VP was dissolved by deionized water and 2.5 mL of ethanol as a dispersant, and then, the 4-VP solution was dropped into the reactor with an isobaric burette in at various times. The total liquid volume was kept at 100 mL each time. The reaction mixture was adjusted to pH 7.0 (to remove the $SO_4^{2-}$) and poured into 100 mL of ethanol, where the graft copolymer precipitated out and P(4-VP) remained in the solution.[23] The precipitate (KGM–4-VP) was separated, dried, and weighed. P(4-VP) was precipitated according to the method of Maria et al.[24]

The grafting parameters, $G\%$ and $E\%$, were defined and calculated as follows:

$$G\% = \frac{\text{Weight of polymer in the graft} - \text{Weight of the polymer backbone}}{\text{Weight of the polymer backbone}} \times 100$$

$$E\% = \frac{\text{Weight of polymer in the graft} - \text{Weight of the polymer backbone}}{\text{Weight of the polymer formed}} \times 100$$

### Thermal analysis

The stability of the pure KGM, homopolymer P (4-VP), and graft copolymers (KGM–4-VP) were determined by thermogravimetric analysis (TGA) behavior on a TA-SDTQ600 (Texas Instruments, Inc., New Castle, DE) at a heating rate of 10°C/min under a nitrogen atmosphere.

### IR spectra

The infrared spectra of the pure KGM, homopolymer P(4-VP), and graft copolymers (KGM–4-VP) were recorded on a Bruker TENSOR27 (Bruker Instruments, Inc., Ettlingen, Germany) spectrophotometer with the potassium bromide technique.

### Adsorption of heavy-metal ions

Static equilibrium adsorption experiments of four heavy-metal ions were done. These heavy-metal ions [Cr(VI), Cu(II), Pb(II), and Cd(II)] were the typical for metal contamination in water, so we chose them to test metal-ion sorption. Cr(VI), Cu(II), Pb(II), and Cd(II) stock solutions (1000 mg/L) were prepared with potassium dichromate ($K_2Cr_2O_7$), copper sulfate ($CuSO_4$), lead nitrate [$Pb(NO_3)_2$], and cadmium chloride ($CdCl_2$), respectively. All the working solutions were prepared by dilution of the standard stock solution with deionized water. The KGM–4-VP copolymer (10 mg) was placed in contact with 25-mL solutions of 20 mg/L concentrations of Cr(VI), Cu(II), Pb(II), and Cd(II) for the adsorption. The initial pH of the solution was adjusted with 0.01 mol/L HCl or NaOH. Because most of the metal ions are
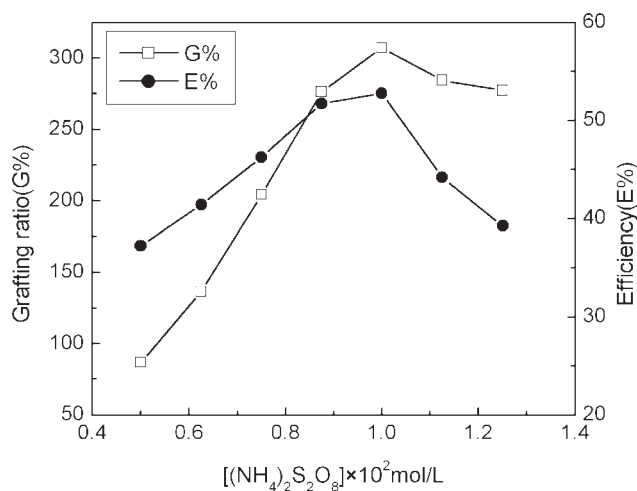
**Figure 2** Effect of the APS concentration: [KGM] = 1.00 g/L, [4-VP] = $9.32 \times 10^{-2}$ mol/L, [H$^+$] = $5.00 \times 10^{-2}$ mol/L, temperature = 35°C, and time = 120 min.

prone to precipitation at higher pH, investigations were limited to those pH values where precipitation was just prevented. The adsorbed amount of heavy-metal ion was measured with inductively coupled plasma-atomic emission spectometry (ICP-AES, TPS-7000, Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

## RESULTS AND DISCUSSION

### Effect of APS

The effect of APS on graft copolymerization was studied by the variation of its concentration from $0.50 \times 10^{-2}$ to $1.25 \times 10^{-2}$ mol/L, as shown in Figure 2. $G\%$ and $E\%$ increased significantly with increasing concentration of APS from $0.50 \times 10^{-2}$ to $1.00 \times 10^{-2}$ mol/L, but beyond the aforementioned concentration range, homopolymerization increased obviously, whereas $G\%$ and $E\%$ decreased slightly. The increase of $G\%$ and $E\%$ may have been due to the increase in macroradicals. With the increase in initiator concentration, more APS attacked the saccharide unit of KGM, more KGM macroradicals were generated, and thus, more active sites of KGM reacted with 4-VP and initiated the propagation reaction of 4-VP. However, an abundance of primary radicals may have accelerated the rate of both termination by coupling and chain transfer to 4-VP. At the same time, an excess of APS may have also increased the chance of encounters between 4-VP and 4-VP and initiated more 4-VP homopolymerization.[25] The slight decrease in $G\%$ and $E\%$ may have been caused by the increase in the concentration of APS up to $1.00 \times 10^{-2}$ mol/L.
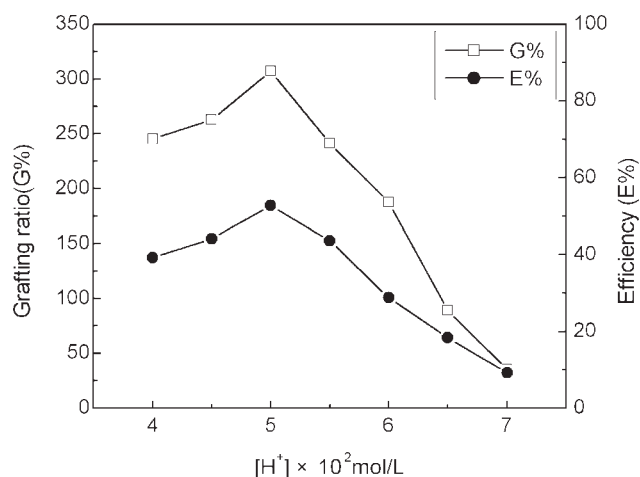
### Effect of hydrogen ions

Figure 3 shows the effect of the hydrogen ion concentration on $G\%$ and $E\%$. The variation of hydrogen ion concentration (total added H$^+$ amount) was affected by the addition of sulfuric acid to the reaction mixture. The variation of the hydrogen ion concentration from $4.00 \times 10^{-2}$ to $7.00 \times 10^{-2}$ mol/L indicated that $G\%$ and $E\%$ increased with increasing hydrogen ion concentration from $4.00 \times 10^{-2}$ up to $5.00 \times 10^{-2}$ mol/L. The formation of lots of grafting sites on the KGM backbone through oxidation by APS was beneficial. However, too many hydrogen ions may have induced the decomposition of APS and the degradation of KGM; thus, $G\%$ and $E\%$ decreased when the hydrogen ion concentration was above $5.00 \times 10^{-2}$ mol/L.

### Effect of the monomer-to-KGM ratio

We investigated the effect of 4-VP on the graft copolymerization by changing the concentration of 4-VP from $4.66 \times 10^{-2}$ to $11.65 \times 10^{-2}$ mol/L. Figure 4 suggests that the grafting parameters increased initially with the increase of 4-VP and declined thereafter. The initial increasing trend may have been due to the higher availability of monomer molecules in close proximity to the KGM macroradicals.[25] The decrease of $G\%$ and $E\%$ with the increase of 4-VP concentration after saturation may have been due to the decrease in the available 4-VP concentration and a reduction in the active sites on the KGM backbone as the graft copolymerization proceeded. Second, the decrease of $G\%$ and $E\%$ may have been due to the amount of 4-VP, which was more helpful to homopolymerization than grafting in the concentrations determined.[25] Third, the decline of the parameters at higher 4-VP/KGM ratios may have been due to the increase in the viscosity of the medium at high concentrations of the monomer and the homopolymer formed along with graft copolymers, which induced the decrease in the rate of diffusion of monomer



**Figure 3** Effect of the hydrogen ion concentration: [APS] = $1.00 \times 10^{-2}$ mol/L, [KGM] = 1.00 g/L, [4-VP] = $9.32 \times 10^{-2}$ mol/L, temperature = 35°C, and time = 120 min.
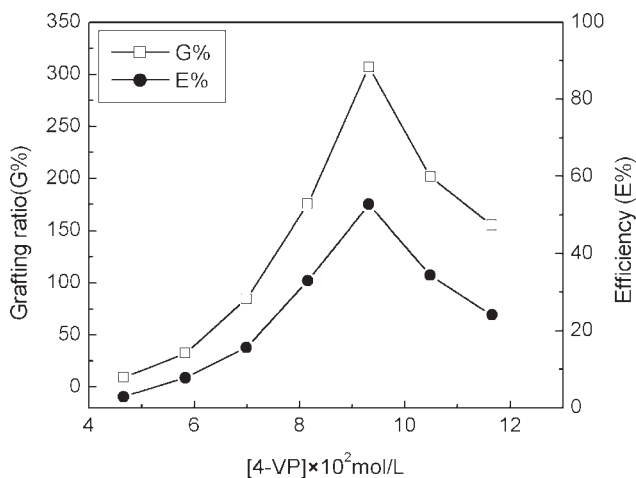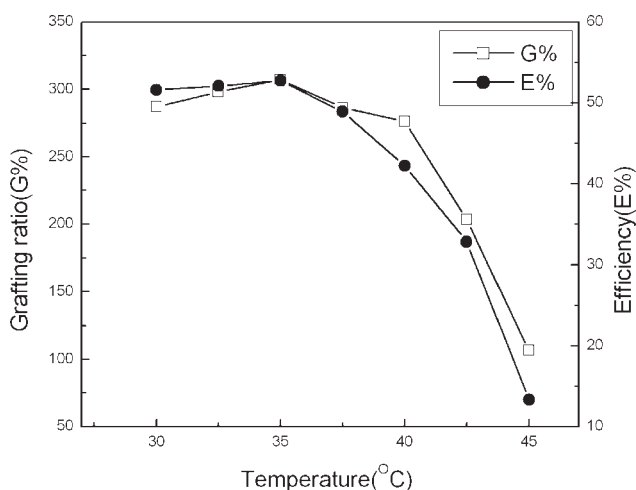
**Figure 4** Effect of the 4-VP concentration: [APS] $= 1.00 \times 10^{-2}$ mol/L, [KGM] $= 1.00$ g/L, [H$^+$] $= 5.00 \times 10^{-2}$ mol/L, temperature $= 35°$C, and time $= 120$ min.

molecules to the growing chains; hence, the graft ratio showed a decreasing trend.[1,19,26] On the other hand, 4-VP had a high affinity for its homopolymer substrate, which meant that the homopolymerization occurred in the polymer phase to a large extent. Thus, it is likely that homopolymerization had more chances to occur, and as a result, a decrease in G% and E% was observed.

## Effect of the temperature

The graft copolymerization was carried out at different temperatures ranging from 30 to 45°C. The relationship between the grafting parameters and temperature is shown in Figure 5. As the temperature increased from 30 to 45°C, G% and E% incipiently increased and then decreased. When the temperature
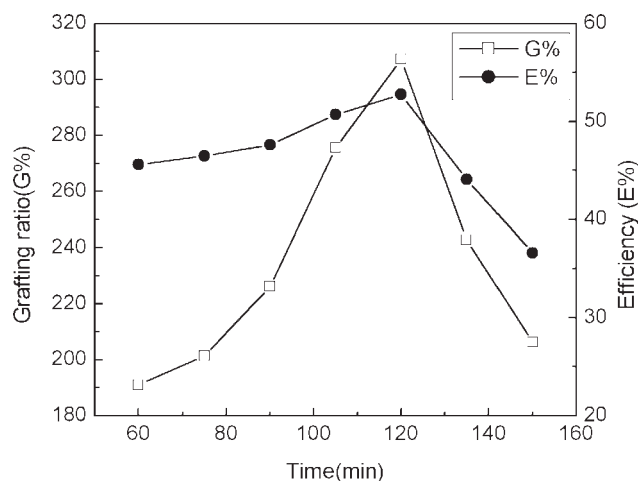
was low, APS could not provide enough free radicals, whereas with increasing temperature, the collision chances of KGM and APS increased and resulted in an increase in KGM macroradicals and enhanced the graft polymerization. G% and E% showed decreases above this optimum temperature, which was related to the following facts:

1. At a higher reaction temperature, the thermal decomposition rate of APS increased and gave out O$_2$; this acted as a scavenger for free radicals. The small radicals obtained were helpful to the homopolymerization of 4-VP.[25,26]
2. The mobility of macroradicals was enhanced and may have led to termination at a higher temperature.[25,26]

## Effect of the time

To analyze the effect of the reaction time on the grafting parameters, the graft copolymerization was conducted at different time intervals, with all other conditions kept constant. As shown in Figure 6, the grafting parameters increased with the reaction time up to 120 min, decreased thereafter, and then reached a saturation grafting value. The increasing trend clearly indicated that new graft sites were formed on the active sites of the KGM backbone along with the time. However, with increasing reaction time, the concentration of monomer and free radicals in the system decreased and resulted in decreases in G% and E%.[25] On the other hand, after 120 min, the APS was almost consumed, and oxidative degradation of the KGM backbone and that of the grafted chains occurred in the acid medium,[26] which resulted in the decreasing trend.



**Figure 5** Effect of the temperature: [APS] $= 1.00 \times 10^{-2}$ mol/L, [KGM] $= 1.00$ g/L, [4-VP] $= 9.32 \times 10^{-2}$ mol/L, [H$^+$] $= 5.00 \times 10^{-2}$ mol/L, and time $= 120$ min.



**Figure 6** Effect of the time: [APS] $= 1.00 \times 10^{-2}$ mol/L, [KGM] $= 1.00$ g/L, [4-VP] $= 9.32 \times 10^{-2}$ mol/L, [H$^+$] $= 5.00 \times 10^{-2}$ mol/L, and temperature $= 35°$C.
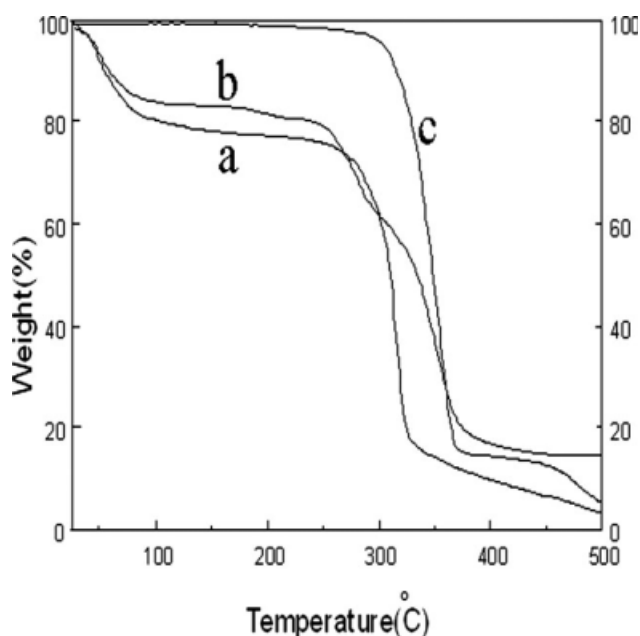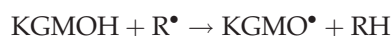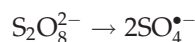
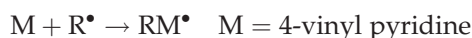**Figure 7** TGA curves of (a) KGM, (b) KGM-*g*-(4-VP) (*G*% = 206.30%), and (c) P(4-VP).

## Mechanism

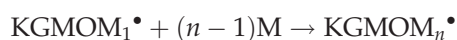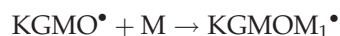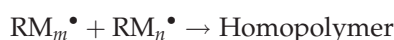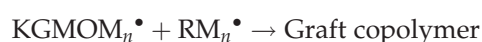The following mechanism is proposed for the graft copolymerization of 4-VP on to KGM.

Initiation

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$$

$$KGMOH + R^{\bullet} \rightarrow KGMO^{\bullet} + RH$$

where $R^{\bullet}$ is $SO_4^{\bullet-}$ and KGMOH is KGM.

$$M + R^{\bullet} \rightarrow RM^{\bullet} \quad M = \text{4-vinyl pyridine}$$

Propagation

$$KGMO^{\bullet} + M \rightarrow KGMOM_1^{\bullet}$$

$$KGMOM_1^{\bullet} + M \rightarrow KGMOM_2^{\bullet}$$

$$KGMOM_1^{\bullet} + (n-1)M \rightarrow KGMOM_n^{\bullet}$$

$$RM_{n-1}^{\bullet} + M \rightarrow RM_n^{\bullet}$$

Termination

$$KGMOM_n^{\bullet} + KGMOM_n^{\bullet} \rightarrow \text{Graft copolymer}$$

$$KGMOM_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{Graft copolymer}$$

$$RM_m^{\bullet} + RM_n^{\bullet} \rightarrow \text{Homopolymer}$$

## Proof of grafting

### TGA

As shown in Figure 7, KGM had an initial small mass loss step before actual pyrogenation occurred; this was due to the removal of adsorbed moisture. Decomposition of KGM started at 228°C; only 1.8% char yield was obtained at 500°C. The major thermal decomposition of KGM acted as one step, whereas that of the grafted copolymers (KGM–4-VP) took place in two degradation steps, referred to as *actual pyrolysis* (the second stage) and *carbonization* (the third stage). The final decomposition temperature (FDT), polymer decomposition temperature (PDT), the temperature at a maximum rate of mass loss ($T_{max}$), and integral procedural decomposition temperature (IPDT) of KGM, KGM-4-VP, and P(4-VP) were calculated from the TGA results and are shown in Table I. IPDT was calculated with the following equation:

$$IPDT(^{\circ}C) = A^* K^* (T_f - T_i) + T_i$$

where $A^*$ is the area ratio of the total experimental curve divided by the total TGA thermogram, $K^*$ is the coefficient of $A^*$, and $T_i$ and $T_f$ are the initial and final experimental temperatures, respectively. The thermogravimetric parameters of the grafting polymer were higher than that of KGM, which indicated that the grafting of 4-VP improved the thermal stability of the grafting polymer because the H bonding between the N of the pyridine ring and the O—H of KGM may have led to an enhancement of the thermal stability of the final material. The characterization of the graft copolymer provided evidence that poly(vinyl pyridine) was incorporated into the KGM backbone. We concluded that after the polymer was grafted with 4-VP, its thermal stability improved greatly. At 500°C, a 16% residual weight was obtained, which was more than that of KGM, which indicated that the prepared graft copolymer was thermally more stable than KGM.

### Fourier transform infrared spectra

The existence of grafting was evidenced by the weight increase and the difference in the IR spectra of the pure KGM and the graft copolymer. The Fourier transform infrared spectra of these polymers are shown in Figure 8. The spectrum of the graft
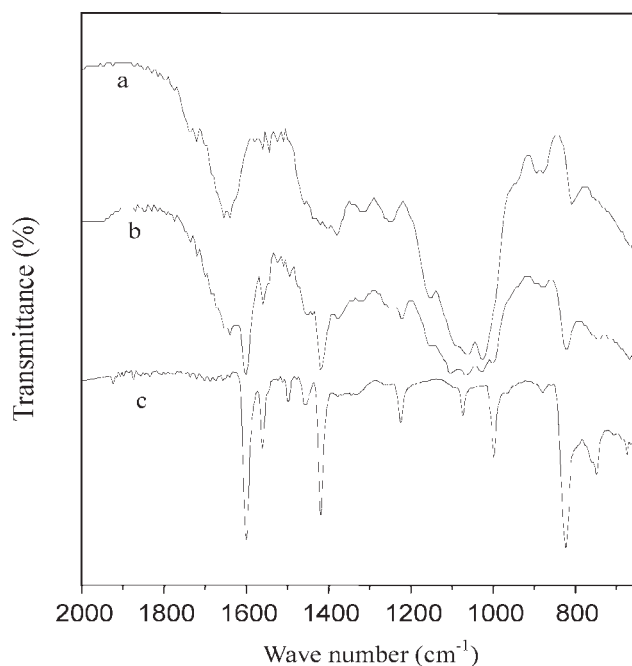
**TABLE I**
**TGA of the Polymers**

| Sample | PDT (°C) | FDT (°C) | $T_{max}$ (°C) | IPDT (°C) |
|---|---|---|---|---|
| KGM | 228 | 325.4 | 317.4 | 141 |
| KGM-4-VP | 167 | 420 | 352 | 262 |
| P(4-VP) | 292 | 374 | 354 | 266 |

copolymer showed a difference corresponding to the appearance of bands at 1601.55 and 1558.98 cm$^{-1}$ corresponding to the C=N asymmetrical stretching vibration of 4-VP.[27] Two characteristic bands for the C—H bending of the aromatic ring of the vinyl pyridine moiety that appeared around 750 and 823.47 cm$^{-1}$ were very indicative of the presence of the poly(vinyl pyridine) polymer in the graft.[16] The stretching vibration of C=C hypsochromic shifted from 1408 to 1418.04 cm$^{-1}$.[27] Consequently, we concluded that the grafting of 4-VP onto KGM took place at the site of the hydroxyl groups onto the KGM backbone.[19]

## Adsorption for heavy-metal ions

We obtained the amounts of adsorbed heavy metals by calculating the difference in the concentration of the heavy-metal ions before and after adsorptions. Via the preliminary research, the optimal results of adsorption for heavy-metal ions (based on these metal ions) are shown in Table II. As shown in Table II, the adsorption for anions ($Cr_2O_7^{2-}$) was at lower pH; it is possible that 4-VP was protonated at lower pH values and had more attractive electrostatic interactions for anions than amine–N. So the graft copolymer had good adsorption ability for Cr(VI) at lower pH.[28] The adsorption for metal positive ions was at higher pH. Because the heavy-metal ions we adsorbed by coordinate linkage, when the pH was higher, the electron pair on the N atom of the pyridine ring led to an enhanced coordinate linkage

**TABLE II**
**Adsorption of Heavy-Metal Ions on the Graft Copolymer**

| Heavy-metal ion | pH | Time (min) | Temperature (°C) | Removal (%) | Adsorption capacity (mg/g) |
|---|---|---|---|---|---|
| Cr(VI) | 3.03 | 30 | 25 | 93.06% | 37.23 |
| Cu(II) | 6.40 | 60 | 30 | 89.65% | 44.83 |
| Pb(II) | 7.52 | 60 | 25 | 84.90% | 42.45 |
| Cd(II) | 8.19 | 60 | 25 | 18.40% | 9.20 |

between the metal positive ions and corresponding interaction sites. However, the removal percentage of metal ions from $Cu^{2+}$ to $Cd^{2+}$ decreased. This may have been due to the decrease in the equilibrium constant for the formation of metal ions from $Cu^{2+}$ to $Cd^{2+}$. An in-depth study of adsorption for heavy-metal ions should be carried out.

## CONCLUSIONS

The graft copolymerization of 4-VP onto KGM in an aqueous medium initiated by APS was carried out with satisfactory results. It is generally believed that APS, which initiates the polymerization of vinyl monomers onto water-soluble polysaccharides, cannot reach a high graft ratio in aqueous media. However, when we used ethanol as a dispersant, 4-VP was dispersed effectively in deionized water and phase conglomeration was effectively hindered, graft copolymers with high $E\%$ and $G\%$ were obtained. The optimum $G\%$ and $E\%$ values were 307.27 and 52.75%, respectively, and the optimal parameters were found at [KGM] = 1.00 g/L, [APS] = 1.00 × $10^{-2}$ mol/L, [4-VP] = 9.32 × $10^{-2}$ mol/L, [H$^+$] = 5.00 × $10^{-2}$ mol/L, temperature = 35°C, and time = 120 min. Proof of grafting was obtained from gravimetric estimation and IR analysis. The grafted production was thermally more stable than pure KGM on the basis of the TGA results. The preliminary research of the adsorption capacity for heavy-metal ions suggested that the copolymer could be used as a sorbent commendably.



**Figure 8** IR spectra of (a) KGM, (b) KGM-*g*-(4-VP) ($G\%$ = 206.30%), and (c) P(4-VP).

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