

# Chlorohydrin Water Swellable Rubber Compatibilized by an Amphiphilic Graft Copolymer. I. Synthesis and Characterization of Compatibilizer PVA-*g*-PBA

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**ABSTRACT:** The graft copolymerization of butyl acrylate onto poly(vinyl alcohol) with ceric ammonium nitrate as redox initiator in a aqueous medium has been investigated. The formation of graft copolymer was confirmed by means of IR, scanning electron microscopy (SEM), and wide-angle X-ray diffraction (WAXD). The percentage of monomer conversion and percentage of grafting varied with concentrations of initiator, nitric acid, monomer, macromolecular backbone ( $X_n = 1750$ ,  $M = 80\,000$ ), reaction temperature and reaction time. Some inorganic salts and organic solvents have a great influence upon grafting. The reaction mechanism has been explored, and rate equations for the reaction are established. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 977–986, 2000

**Key words:** poly(vinyl alcohol); butyl acrylate; graft copolymerization; ceric ammonium nitrate; inorganic salt; organic solvent

## INTRODUCTION

Poly(vinyl alcohol) (PVA) has plenty of hydroxyl groups, which form strong intramolecular and intermolecular hydrogen bonds, and therefore crystallizes very easily; this also leads to weakened hydrophilicity. Grafting vinyl monomer onto PVA backbone can improve backbone hydrophilicity through destroying crystallizability of PVA.

Although grafting vinyl monomers onto PVA can be traced back to 1950s,<sup>1</sup> a lot of work has been done in this field.<sup>2–13</sup> Most of the grafting reactions were carried out in aqueous medium and initiated by ammonium persulfate,<sup>8</sup> potas-

sium persulfate,<sup>5</sup> ferric ion-hydrogen peroxide,<sup>9</sup> and ceric ammonium nitrate.<sup>1</sup> The grafted monomers involved hydrophilic species, such as acrylic acid<sup>7</sup> and acrylamide,<sup>1</sup> and hydrophobic species, such as acrylonitrile,<sup>10</sup> acrylates,<sup>11</sup> methyl acrylates,<sup>12</sup> styrene<sup>13</sup>, and so on. Grafting butyl acrylate onto PVA initiated by ceric ammonium nitrate in an aqueous medium has not been studied systematically and reported.

Poly (butyl acrylate) (PBA) has longer soft-side chains and a low glass-transition temperature and quite good elasticity. Grafting it onto PVA can greatly improve the properties of PVA. At the same time, the branched chains are hydrophobic. The amphiphilic graft copolymer, which is prepared using PVA as hydrophilic backbone and PBA as hydrophobic branched chains, has served as compatibilizer between hydrophobic rubber

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and hydrophilic water absorbent resin and has improved the water swelling abilities of chlorohydrin rubber/cross-linked polyacrylate blend in our next work.<sup>14</sup>

In this paper, we are going to discuss the effects of various reaction parameters, and the effects of some inorganic salts and organic solvents on percentage of monomer conversion and percentage of grafting. The effects of them on molecular weights of grafted PBA chains and grafting frequency will be investigated in the later work.

## EXPERIMENTAL

### Materials

PVA, analytical reagent (Qidong 2nd chemical factory, Jiangsu, China), with average degree of polymerization  $1750 \pm 50$  and molecular weight  $8 \times 10^4$  was used. Butyl acrylate (BA), analytical reagent (Yili Fine Chemicals Co. Ltd, Beijing, China), was distilled at reduced pressure under  $N_2$  to remove the inhibitor before use.

Ceric ammonium nitrate (CAN), analytical reagent, was used as received. All other reagents were of analytical reagent and were used without further purification.

### Graft Copolymerization

The graft reactions were carried out in a four-necked, round-bottom flask of 250-ml capacity, fitted with mechanical stirrer, a  $N_2$  gas inlet, a dropping funnel, and a reflux condenser. The reaction temperature was controlled by a super constant-temperature water bath.

In a typical experiment, a known amount of PVA was dissolved in 90 ml distilled water in the flask. After BA was added, the solution was stirred, flushed slowly with  $N_2$  for 30 min and adjusted to reaction temperature under  $N_2$ . Then a required amount of CAN solution in 10 ml  $HNO_3$  was added to initiate the copolymerization. The reaction was allowed to proceed for a desired period of time at reaction temperature under  $N_2$ . Acetone was added in excess to precipitate the polymer. The crude products were filtered and dried under vacuum. The dried products were extracted with acetone by means of Soxhlet extractor for 48 h to remove homo-PBA and then the left products, pure graft copolymers, were dried under vacuum and weighted.

### Determination of the Percentage of Monomer Conversion and the Percentage of Grafting

The percentage of monomer conversion ( $C_M\%$ ) and the percentage of grafting ( $G\%$ ) can be calculated by the dry weights of PVA, used monomer, crude products and grafted product:<sup>15,16</sup>

$$C_M\% = \frac{\text{wt of BA polymer}}{\text{wt of used BA}} \times 100$$

$$= \frac{\text{dry wt of crude product} - \text{dry wt of PVA}}{\text{dry wt of used BA}} \times 100$$

$$G\% = \frac{\text{wt of grafted BA polymer}}{\text{wt of PVA}} \times 100$$

$$= \frac{\text{dry wt of grafted product} - \text{dry wt of PVA}}{\text{dry wt of PVA}} \times 100$$

### IR Spectra

IR spectra of the pure PVA film, the pure PBA coated on KBr pellet, and the graft copolymer in KBr pellet specimen were recorded on a Nicolet FTIR-5PC spectrometer.

### Scanning Electron Microscopy

The surface morphology of the graft and pure PVA were observed from X-650 scanning electron microscope. The sample was sputter-coated with gold to improve electric conductivity.

### Wide-Angle X-ray Diffraction

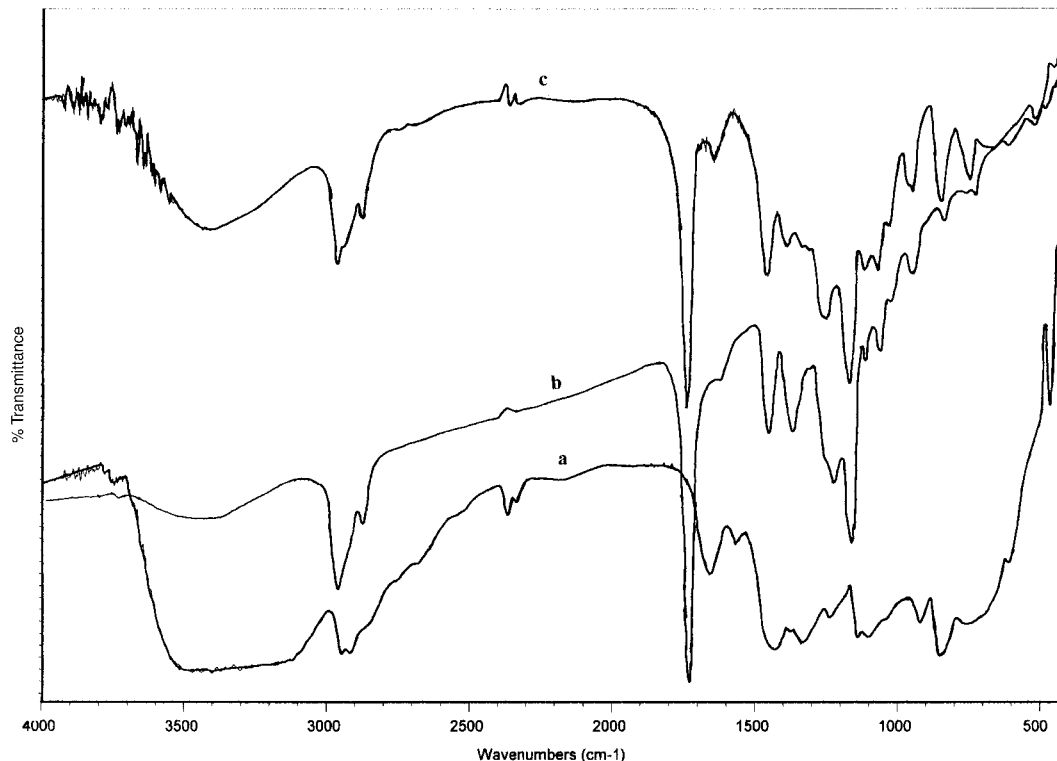
WAXD patterns were collected on a Rigaku D/Max- $\gamma$ A diffractometer, using Nickel-filtered  $CuK\alpha$  (radiation generated at 50 KV and 150 mA in the  $2\theta$  range of  $5 \sim 60^\circ$ ).

## RESULTS AND DISCUSSION

### Evidence of Grafting

#### Weight Gain

PVA is soluble in hot water, and homo-PBA is soluble in acetone. When a crude product was extracted by means of Soxhlet extractor with dis-



**Figure 1** IR spectra of (a) pure PVA, (b) pure PBA, and (c) PVA-g-PBA.

tilled water and acetone, alternatively, to remove the unreacted PVA and the homo-PBA, the insoluble solid, PVA-g-PBA, still remained and was heavier than the original PVA. The PBA grafted onto the PVA backbone leads to increased weight.

### IR Spectra

Figure 1 shows the IR spectrum of (a) pure PVA, the IR spectrum of (b) pure PBA, and the IR spectrum of (c) PVA-g-PBA purified by thorough extraction with acetone and distilled water. The IR spectrum of PVA reveals absorption bands at 3100–3600  $\text{cm}^{-1}$  (strong, very broad, —OH stretching), caused by intermolecular hydrogen bonds among the hydroxyl groups.<sup>17</sup> The IR spectrum of PBA indicates absorption band at 1734  $\text{cm}^{-1}$  (strong, C=O stretching). The IR spectrum of PVA-g-PBA shows a weakened and narrowed absorption band at 3410  $\text{cm}^{-1}$  (—OH stretching), which is characteristic of PVA, and a weakened band at 1736  $\text{cm}^{-1}$  (C=O stretching), which is the characteristic of PBA. These confirmed the formation of graft copolymer.

### Scanning Electron Microscopy

It is clear from SEM pictures (Figure 2) that the surface of ungrafted PVA is very rough and not

smooth (a), whereas the surface of BA-grafted PVA seems to be covered with a smooth layer of continuous paste. The base of PVA can still be seen through the layer of paste (b).

### Wide-Angle X-ray Diffraction

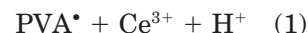
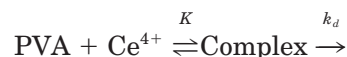
Figure 3 shows the WAXD patterns of (a) pure PVA and (b) PVA-g-PBA. It is evident that the WAXD pattern of pure PVA exhibits a sharp peak at 19.899, and two other peaks at 11.703 and 10.105, indicating high crystallinity. The PVA-g-PBA has a widened peak at 19.697 and the peaks at 13.964 and 8.837 become strong. These suggest that the grafting copolymerization affects the crystal structure of PVA.

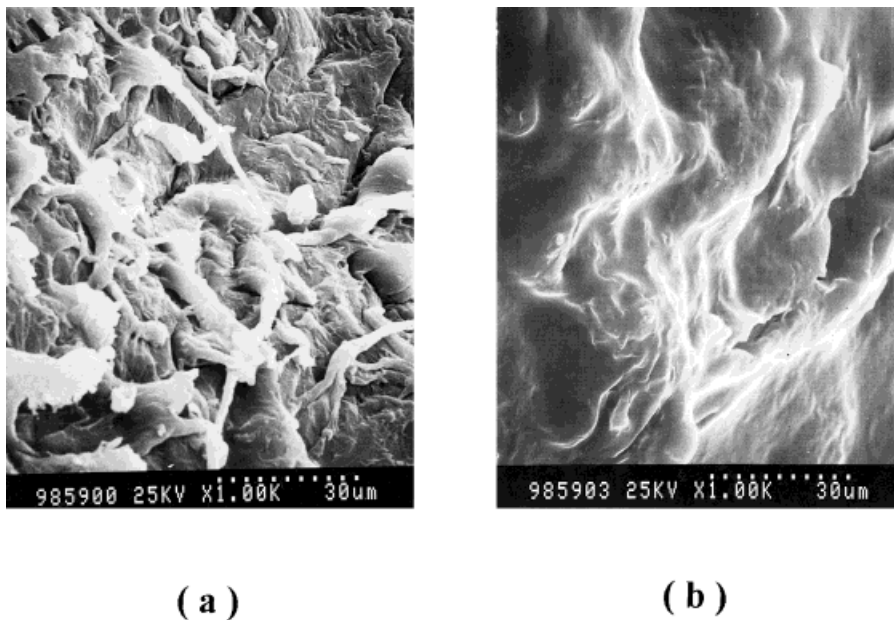
### Reaction Mechanism and Rate Equation

#### Reaction Mechanism

The graft copolymerization of BA onto PVA with ceric ammonium nitrate as a initiator is proposed to occur according to following mechanism:

#### 1. Initiation

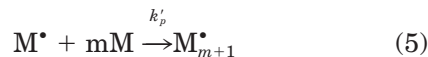
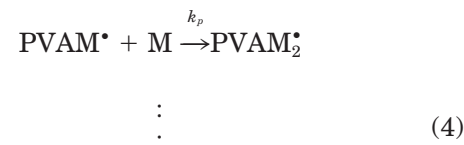




**Figure 2** Scanning electron micrographs of (a) pure PVA and (b) PVA-g-PBA.

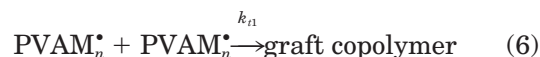


2. Propagation

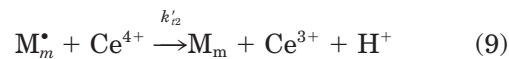


3. Termination

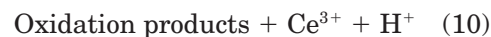
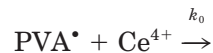
At lower  $[Ce^{4+}]$ , the termination of growing chain is mainly determined by coupling of two radicals:



At higher  $[Ce^{4+}]$ , the termination of growing chain is mainly determined by a single radical:



4. Oxidation



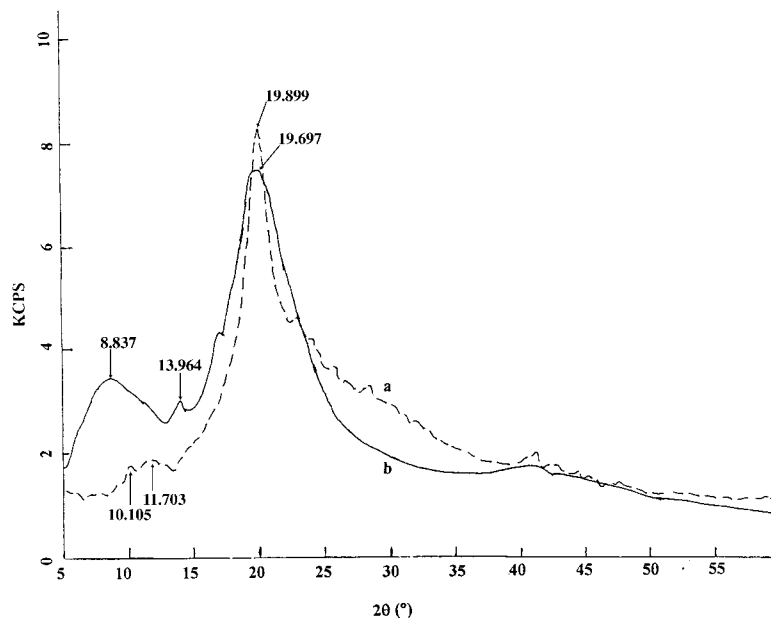


Figure 3 WAXD patterns of (a) pure PVA and (b) PVA-g-PBA.

Here PVA is the poly(vinyl alcohol) substrate, M is the monomer butyl acrylate.

### Rate Equation

It is generally presumed that radical reactivity is independent of chain length,  $k_p = k_p'$ ,  $k_{t1} = k_{t1}'$ ,  $k_{t2} = k_{t2}'$ ,

$$K = [\text{Complex}]/[\text{PVA}][\text{Ce}^{4+}]$$

$$\begin{aligned} -d[\text{PVA}^{\bullet}]/dt &= k_d[\text{Complex}] - k_i[\text{PVA}^{\bullet}][\text{M}] \\ &\quad - k_0[\text{PVA}^{\bullet}][\text{Ce}^{4+}] \\ &= k_dK[\text{PVA}][\text{Ce}^{4+}] - k_i[\text{PVA}^{\bullet}][\text{M}] \\ &\quad - k_0[\text{PVA}^{\bullet}][\text{Ce}^{4+}] \quad (11) \end{aligned}$$

$$\begin{aligned} -d[\text{PVAMn}^{\bullet}]/dt &= k_i[\text{PVA}^{\bullet}][\text{M}] \\ &\quad - k_{t1}[\text{PVAMn}^{\bullet}]^2 - k_{t2}[\text{PVAMn}^{\bullet}][\text{Ce}^{4+}] \quad (12) \end{aligned}$$

According to the basic hypothesis that the concentration of free radical becomes essentially constant in the polymerization, the disappearance rates of  $\text{PVA}^{\bullet}$  and  $\text{PVAMn}^{\bullet}$  are

$$-d[\text{PVA}^{\bullet}]/dt = 0 \quad -d[\text{PVAMn}^{\bullet}]/dt = 0 \quad (13)$$

At lower  $[\text{Ce}^{4+}]$ , the termination proceed in accordance with eq. (6). The  $[\text{PVA}^{\bullet}]$  oxidized by  $\text{Ce}^{4+}$  in

eq. (10) is negligible, so the  $k_0[\text{PVA}^{\bullet}][\text{Ce}^{4+}]$  in eq. (11) and the  $k_{t2}[\text{PVAMn}^{\bullet}][\text{Ce}^{4+}]$  in eq. (12) were so small that they can be neglected:

$$[\text{PVA}^{\bullet}] = k_d K[\text{PVA}][\text{Ce}^{4+}]/k_i[\text{M}]$$

$$[\text{PVAMn}^{\bullet}] = (k_dK/k_{t1})^{1/2}[\text{PVA}]^{1/2}[\text{Ce}^{4+}]^{1/2} \quad (14)$$

The total rate of graft reaction:

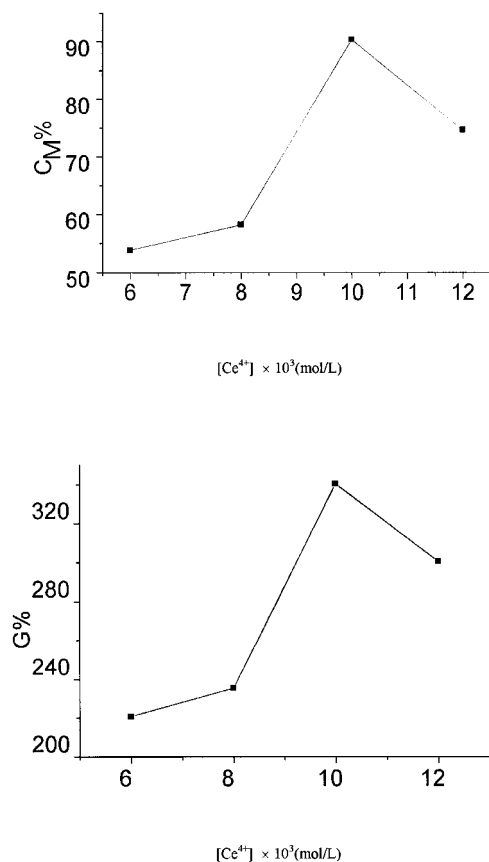
$$R_p = -d[\text{M}]/dt = k_i[\text{PVA}^{\bullet}][\text{M}] + k_p[\text{PVAMn}^{\bullet}][\text{M}] \quad (15)$$

The number of monomers used in initiation must be very small compared with that used in propagation, because macromolecular chains need to be obtained. So  $k_i[\text{PVA}^{\bullet}][\text{M}]$  is of negligible importance. Then

$$\begin{aligned} R_p &= k_p[\text{PVAMn}^{\bullet}][\text{M}] \\ &= k_p(k_dK/k_{t1})^{1/2}[\text{PVA}]^{1/2}[\text{Ce}^{4+}]^{1/2}[\text{M}] \quad (16) \end{aligned}$$

At higher  $[\text{Ce}^{4+}]$ , the termination proceed in accordance with eq. (8). The  $k_{t1}[\text{PVAMn}^{\bullet}]^2$  in eq.(12) is of negligible importance but  $[\text{PVA}^{\bullet}]$  oxidized by  $\text{Ce}^{4+}$  in eq. (10) is not negligible, hence from eqs. (11) and (12):

$$[\text{PVA}^{\bullet}] = k_dK[\text{PVA}][\text{Ce}^{4+}]/(k_i[\text{M}] + k_0[\text{Ce}^{4+}])$$



**Figure 4** Effect of  $[\text{Ce}^{4+}]$  on  $C_M\%$  and  $G\%$ .  $[\text{PVA}] = 2.5 \times 10^{-4}$  mol/L,  $[\text{BA}] = 0.702$  mol/L,  $[\text{HNO}_3] = 0.05$  mol/L,  $45^\circ\text{C}$ , 3.5 h.

$$[\text{PVAMn}^*] = \frac{k_d k / k_{t2} [\text{PVA}] [\text{M}]}{([\text{M}] + (k_o/k_i) [\text{Ce}^{4+}])} \quad (17)$$

The total rate of graft reaction would be:

$$R_p = k_p [\text{PVAMn}^*] [\text{M}]$$

$$= \frac{k_p k_d k / k_{t2} [\text{PVA}] [\text{M}]^2}{([\text{M}] + (k_o/k_i) [\text{Ce}^{4+}])} \quad (18)$$

### Effects of Reaction Parameters on Graft Copolymerization

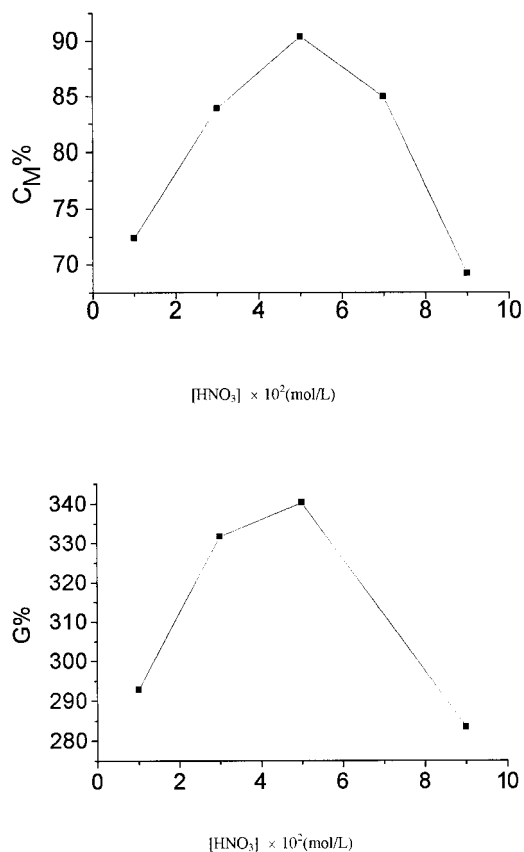
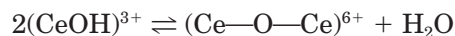
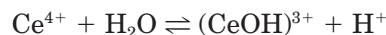
#### Initiator Concentration

Figure 4 exhibits that there existed a maximum (0.01 mol/L) for  $[\text{Ce}^{4+}]$  up to which  $C_M\%$  and  $G\%$  increased, and beyond this concentration both decreased. With the increase in  $[\text{Ce}^{4+}]$ , the complex of  $\text{Ce}^{4+}$ -PVA molecules also increased and produced more radical sites to initiate the copolymerization of the BA. Besides, termination reaction is

mostly determined by the recombination of double radicals (eq. 6) and the total rate of graft reaction is directly proportional to  $[\text{Ce}^{4+}]^{1/2}$  (eq. 16). Thereafter, the decrease in  $C_M\%$  and  $G\%$  may be attributed to the termination reaction mostly determined by a single radical (eq. 8). The total rate of graft reaction is inversely proportional to  $([\text{M}] + (k_o/k_i) [\text{Ce}^{4+}])$  (eq. 18). In the meantime, the termination of  $\text{PVA}^*$  by oxidation became important<sup>18</sup> (eq. 10)

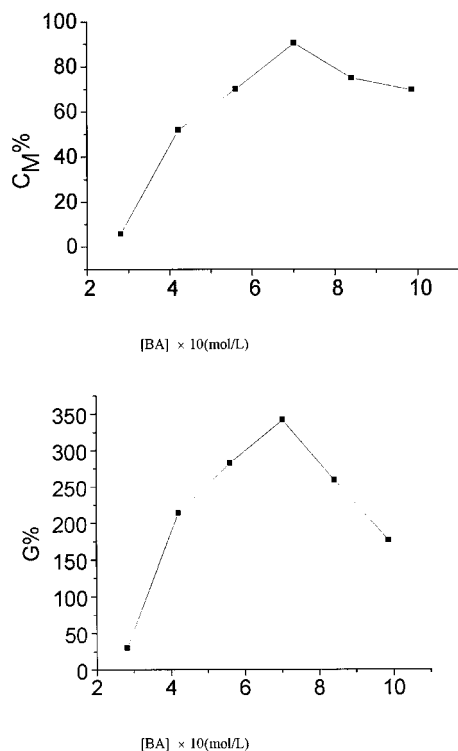
#### Nitric Acid Concentration

The effect of nitric acid concentration on  $C_M\%$  and  $G\%$  is shown in Figure 5,  $C_M\%$  and  $G\%$  initially increased on increasing  $[\text{HNO}_3]$  up to 0.05 mol/L, and decreased with further increase of  $[\text{HNO}_3]$ . According to the equilibria:<sup>19-21</sup>



**Figure 5** Effect of  $[\text{HNO}_3]$  on  $C_M\%$  and  $G\%$ .  $[\text{PVA}] = 2.5 \times 10^{-4}$  mol/L,  $[\text{BA}] = 0.702$  mol/L,  $[\text{Ce}^{4+}] = 1.0 \times 10^{-2}$  mol/L,  $45^\circ\text{C}$ , 3.5 h.





**Figure 6** Effect of [BA] on  $C_M\%$  and  $G\%$ . [PVA] =  $2.5 \times 10^{-4}$  mol/L,  $[Ce^{4+}] = 1.0 \times 10^{-2}$  mol/L,  $[HNO_3] = 0.05$  mol/L, 45°C, 3.5 h.

In acid solution, there exist three species of ceric ion,  $Ce^{4+}$ ,  $(CeOH)^{3+}$ , and  $(Ce-O-Ce)^{6+}$ . Owing to steric hindrance,  $(CeOH)^{3+}$  and  $(Ce-O-Ce)^{6+}$  cannot initiate graft copolymerization, only  $Ce^{4+}$  can initiate grafting. On adding nitric acid to the solution, both the equilibria above will shift to the left and the  $[Ce^{4+}]$  will increase. As a result, the  $C_M\%$  and  $G\%$  will become larger. The decrease in  $C_M\%$  and  $G\%$  at  $[HNO_3]$  beyond 0.05 mol/L may be explained as (1) the ionic strength of the medium increased as  $[HNO_3]$  increased, which led to the coagulation of the colloidal polymer particles.<sup>19, 21</sup> The coagulation causes the bimolecular termination rate to increase, or (2) when  $[Ce^{4+}]$  was too high, the oxidation (see eq. 10) occurred easily.

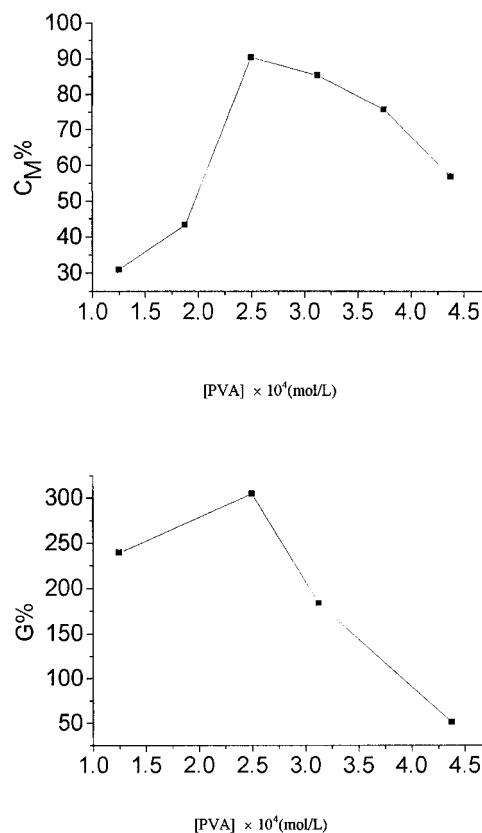
#### Monomer Concentration

As shown in Figure 6,  $C_M\%$  and  $G\%$  increased with an increase in [BA] (up to 0.702 mol/L) and after that  $C_M\%$  and  $G\%$  decreased. This is perhaps because the number of radical sites produced by decomposition of the complex between  $Ce^{4+}$  and PVA kept constant, therefore each site

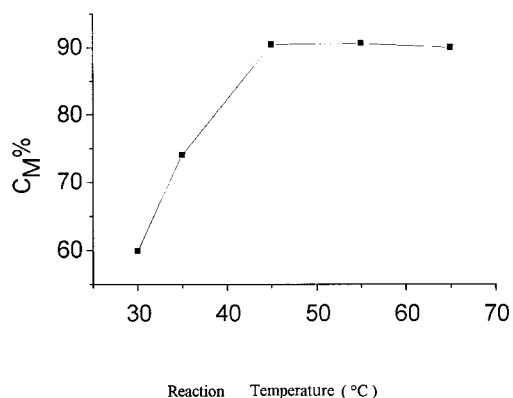
averaged higher availability of monomer molecules in the proximity of immobile PVA macroradicals with the increase of [BA].<sup>22</sup> With further increasing [BA], the monomers that reacted on PVA macroradicals tended to saturate and the conversion rate of monomers was slower than the increase of monomer concentration and  $C_M\%$  decreased; heterogeneous polymerization was unfavorable to dissolution and diffusion of monomer and  $G\%$  decreased.

#### Backbone Concentration

Figure 7 indicates that an increase in backbone concentration made more monomers and initiators easily accessible to the PVA surface and produced more number of grafting sites<sup>22</sup> resulting in an increase in  $C_M\%$  and  $G\%$ , which conformed with eq. (16). With a further increase in backbone concentration, the higher viscosity of the reaction solution made the diffusion of monomer more difficult, and more PVA macroradicals interacted with each other to terminate the reaction, conse-



**Figure 7** Effect of [PVA] on  $C_M\%$  and  $G\%$ . [BA] = 0.702 mol/L,  $[Ce^{4+}] = 1.0 \times 10^{-2}$  mol/L,  $[HNO_3] = 0.05$  mol/L, 45°C, 3.5 h.



**Figure 8** Effect of reaction temperature on  $C_M\%$  and  $G\%$ . [PVA] =  $2.5 \times 10^{-4}$  mol/L, [BA] = 0.702 mol/L, [Ce<sup>4+</sup>] =  $1.0 \times 10^{-2}$  mol/L, [HNO<sub>3</sub>] = 0.05 mol/L, 3.5 h.

quently, giving rise to an decrease in  $C_M\%$  and  $G\%$ .

### Temperature

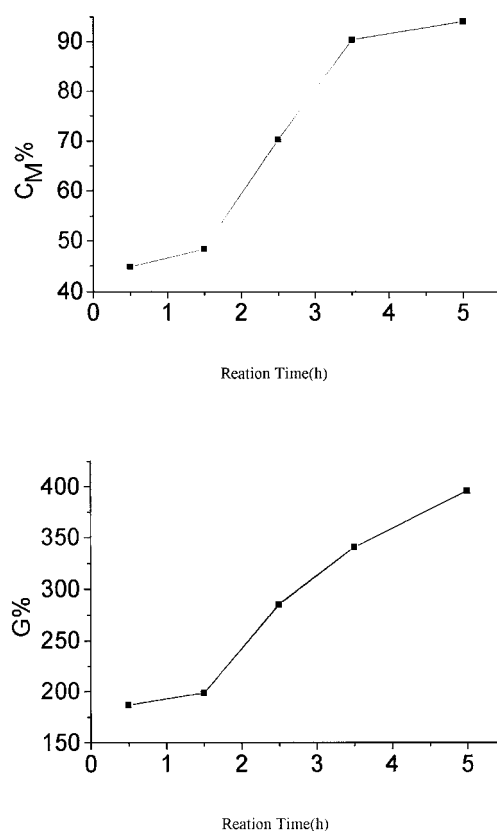
Raising temperature increased  $C_M\%$  and  $G\%$  up to 55°C and then leveled off (Figure 8). This was because raising temperature: (1) enhanced diffusion of BA into the PVA, (2) increased in the mobility of monomer molecules and their collision with PVA macroradicals,<sup>18</sup> and (3) increased initiation<sup>23</sup> and propagation of the graft reaction.

### Time

$C_M\%$  and  $G\%$  increased with reaction time (Figure 9). As reaction time was prolonged, more grafting sites along the backbone were produced and more monomers were grafted.

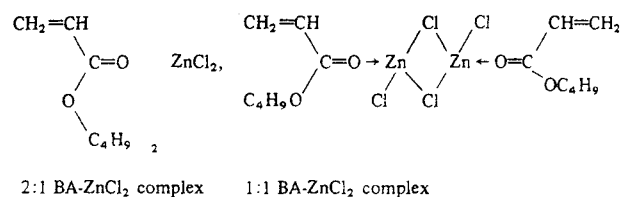
### Inorganic Salts

Table I shows that addition of K<sub>2</sub>SO<sub>4</sub> caused both  $C_M\%$  and  $G\%$  to decrease, and that addition of



**Figure 9** Effect of reaction time on  $C_M\%$  and  $G\%$ . [PVA] =  $2.5 \times 10^{-4}$  mol/L, [BA] = 0.702 mol/L, [Ce<sup>4+</sup>] =  $1.0 \times 10^{-2}$  mol/L, [HNO<sub>3</sub>] = 0.05 mol/L, 45°C.

ZnCl<sub>2</sub> to the reaction mixture made both  $C_M\%$  and  $G\%$  increase. It may be thought that a complex formed between the polar group of butyl acrylate and ZnCl<sub>2</sub>, giving rise to an increase in reactivity of the complexed monomer.



**Table I** Effect of Inorganic Salts on  $C_M\%$  and  $G\%$

| Inorganic Salts                | Concentration (mol/L) | $C_M\%$ | $G\%$  |
|--------------------------------|-----------------------|---------|--------|
| K <sub>2</sub> SO <sub>4</sub> | 0.02                  | 61.1    | 253.88 |
| ZnCl <sub>2</sub>              | 0.02                  | 87.6    | 370.69 |
| Blank                          | 0                     | 63.1    | 264.16 |

Condition: [PVA],  $2.5 \times 10^{-4}$  mol/L; [BA], 0.702 mol/L; [Ce<sup>4+</sup>],  $1.0 \times 10^{-2}$  mol/L; [HNO<sub>3</sub>], 0.05 mol/L; 35°C, 90 min.



**Table II** Effect of Organic Solvents on  $C_M\%$  and  $G\%$ 

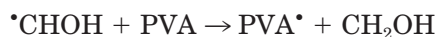
| Organic Additives | Concentration (mol/L) | $C_M\%$ | $G\%$  |
|-------------------|-----------------------|---------|--------|
| Methanol          | 0.2                   | 78.76   | 320.62 |
| Ethylene glycol   | 0.2                   | 78.90   | 336.10 |
| Blank             | 0                     | 63.09   | 264.16 |

Condition: [PVA],  $2.5 \times 10^{-4}$  mol/L; [BA], 0.702 mol/L;  $[Ce^{4+}]$ ,  $1.0 \times 10^{-2}$  mol/L;  $[HNO_3]$ , 0.05 mol/L; 35°C, 90 min.

When [BA] was high enough, the complexed monomer will accelerate the graft copolymerization. This is similar to the grafting of butyl acrylate onto gelatin by Zhichong Li et al.<sup>20</sup>

### Organic Solvents

From Table II, it is evident that  $C_M\%$  and  $G\%$  increased when water-miscible organic solvents such as methanol and ethylene glycol were added to the reaction solution. It was probable that  $Ce^{4+}$  reacted with the organic solvents to produce organic solvent radicals and then they were transferred to PVA backbone to form PVA macroradicals, which initiated graft copolymerization, and organic solvent radicals were reduced. The organic solvents transferred radicals, but less initiated homopolymerization. We propose that there existed reactions as follows:



### CONCLUSIONS

1. Butyl acrylate can be easily graft polymerized onto PVA using ceric ammonium nitrate as redox initiator in an aqueous medium. Weight gain, IR, SEM, and WAXD confirmed the formation of graft copolymer.
2. From reaction mechanism, it is inferred that at lower  $[Ce^{4+}]$ , the total rate of graft reaction is proportional to  $[PVA]^{1/2}$ ,  $[Ce^{4+}]^{1/2}$ , and  $[M]$ , and that at higher  $[Ce^{4+}]$ , the total rate

of graft reaction is proportional to  $[PVA]$  and  $[M]^2$ , but is inversely proportional to  $([M] + (k_0/k_i)[Ce^{4+}])$ . They accord with the experimental results at earlier period of polymerization.

3. The percentage of monomer conversion and percentage of grafting varied with  $[Ce^{4+}]$ ,  $[HNO_3]$ , [BA], [PVA], reaction temperature, and reaction time. The optimums within range of the experiment have been obtained. They are:  $[Ce^{4+}]$ , 0.01 mol/L;  $[HNO_3]$ , 0.05 mol/L; [PVA],  $2.5 \times 10^{-4}$  mol/L; [BA], 0.702 mol/L; temperature, 45°C; reaction time, 3.5 h.
4. The addition of  $ZnCl_2$ , methanol, and ethylene glycol to the reaction solution can increase  $C_M\%$  and  $G\%$ , whereas the addition of  $K_2SO_4$  retarded the graft copolymerization.

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