

# Graft Copolymerization of Starch–AN Initiated by Potassium Permanganate

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**ABSTRACT:** The initiating ability of the potassium permanganate in the graft copolymerization of acrylonitrile onto starch was studied. The results indicate that the grafting parameters, such as concentrations of potassium permanganate, acrylonitrile, starch, and catalyst acids, all have significant effects on the graft copolymerization and the components of the graft copolymers, and this offers methods to adjust the properties of the graft copolymers. The sources of starch and corn starch derivatives both affected the components of the graft copolymers, which showed the influence of functional group on the grafting ability of starch. The preheat treatment and preoxidation of starch, as well as the adding sequence of the reactants all influenced the graft copolymerization, from which some suggestions about the grafting procession could be obtained. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1965–1972, 1998

**Key words:** starch; potassium permanganate; acrylonitrile; graft copolymerization

## INTRODUCTION

Graft copolymerization is one of the effective methods to improve the properties of organic or inorganic materials,<sup>1,2</sup> especially for natural polymers, such as fiber,<sup>3,4</sup> cellulose,<sup>5,6</sup> gelatin,<sup>7,8</sup> chitosan,<sup>9</sup> and starch.<sup>10,11</sup> Transition metal is one of the popular initiators used in the graft copolymerization of natural polymers, of which ceric ammonium nitrate is the most used one because of its high initiating ability and wider applicability.<sup>12–14</sup>

Starch is a partial crystalline polymer. The outstanding characteristic of starch is its biodegradability in the environment. It can also be metabolized by human beings because of enzyme amylase thrived in the body. Amylase can break down starch into glucose and provide fuel for the need of body. As far as biodegradability is concerned, starch is a ideal polymer to be used as biodegrad-

able materials to reduce plastics pollution. But starch has some defects, such as low mechanical properties, that need to be modified through graft copolymerization. Ranby has reported the graft copolymerization of acrylonitrile or methyl methacrylate onto native starch under the initiating of manganic ions.<sup>15,16</sup> William has reviewed the research on this aspect in the US Department of Agriculture (USDA).<sup>17</sup> Foamed polystyrene is the main source of plastics pollution, together with packaging bags. Since styrene does not graft copolymerize with starch in the presence of ceric ion, two alternative methods were taken to prepare starch-*g*-PS.<sup>17</sup> In the first one, water–cornstarch–styrene was mixed to form a paste, and then the paste is irradiated with cobalt-60 or treated with potassium persulfate to initiator polymerization. The another method was to graft copolymerize starch–styrene by extrusion.

In our early articles, we reported the graft copolymerization of starch and gelatin.<sup>18,19</sup> The present article will systematically study the graft copolymerization of starch using potassium permanganate as an initiator.

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## EXPERIMENTAL

### Preparation of Starch Derivatives

The preparation of starch derivatives including carboxymethyl starch, hypochlorous acid starch, aldehyde starch, and crosslinking starch is described in Whistler et al.<sup>20</sup>

### Manufacture of Starch-AN Graft Copolymer

First, a weighed amount of starch and distilled water were poured into a three-neck flask under slow stirring and an N<sub>2</sub> atmosphere to form a paste, which was then preheated at a temperature of 75°C for 30 min before it was cooled to desired reaction temperature. Next, potassium permanganate solution was added into to allow starch to be preoxidized for a short time, and then monomer acrylonitrile and catalyst acid were added. The mixture reacted about 3 h before it was terminated. The rough products were precipitated, filtered, and dried to a constant at 60°C in a vacuum. The dried products were extracted with dimethylformamide in a Soxhlet apparatus for 72 h to remove homopolymer polyacrylonitrile (PAN), and then the extracted products were dried and weighed.

### Determination of Percentage of Grafting and Grafting Efficiency

The percentage of grafting (PG) and grafting efficiency (GE) were calculated as follows:

$$\text{PG}(\%) = \frac{\text{weight of grafted PAN}}{\text{weight of starch}} \times 100$$

$$\text{GE}(\%) = \frac{\text{weight of grafted PAN}}{\text{weight of reacted AN}} \times 100$$

### Calculation of Molecular Weight of Grafted PAN

The purified starch-*g*-PAN copolymer was hydrolyzed in 1 mol/L HCL solution at 105–110°C for 24 h to get the grafted side chains.

The solution viscosity of the grafted chains was determined with a Ubbelohde viscometer at 50°C with dimethyl sulfoxide as solvent, and the molec-

ular weight was consequently calculated according to the Mark-Houwink equation, below:

$$[\eta] = KM_v^\alpha$$

where  $K = 2.83 \times 10^{-4}$ , and  $\alpha = 0.758$ .

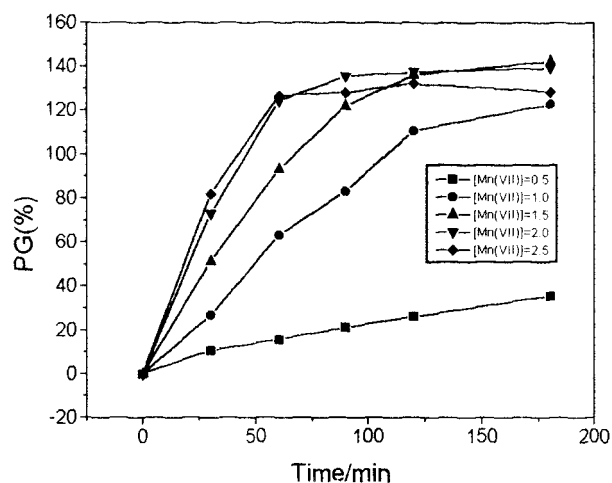
### Infrared Spectra

The infrared (IR) spectra of starch and graft copolymer St-*g*-PAN were tested with an Fourier transform IR spectrometer.

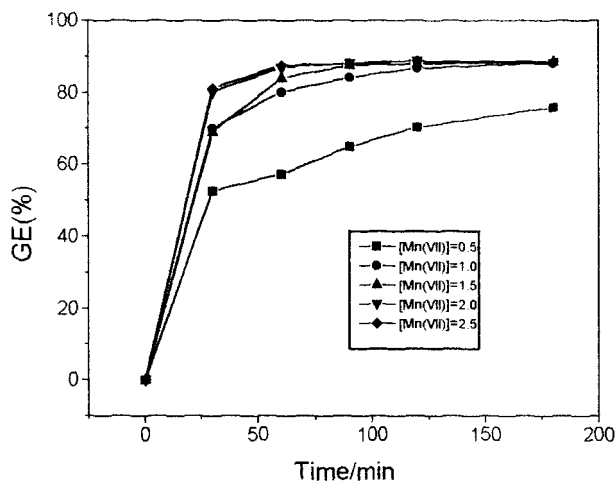
## RESULTS AND DISCUSSION

### Initiator Concentration

The concentration of initiator has great effect on the graft copolymerization. Figures 1 and 2 illustrate the changes in PG and GE when initiator concentration varied in the range of 0.5–2.5 × 10<sup>-3</sup> mol/L. PG and GE both increased first and then leveled off as the reaction went for each of initiator concentrations [Mn(VII)], but the absolute values of PG and GE were different as [Mn(VII)] changed. The final PG arrived at a maximum value at [Mn(VII)] of 1.5 × 10<sup>-3</sup> mol/L, while the final GE turned to be a constant value. When [Mn(VII)] was comparatively low, the reaction between initiator and starch to form radicals on the starch backbone was dominant, so more chance was offered to the monomers to graft if



**Figure 1** PG versus [Mn(VII)]: [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; [H<sup>+</sup>] = 0.1 mol/L; preheat temperature = 75°C; reaction temperature = 40°C.

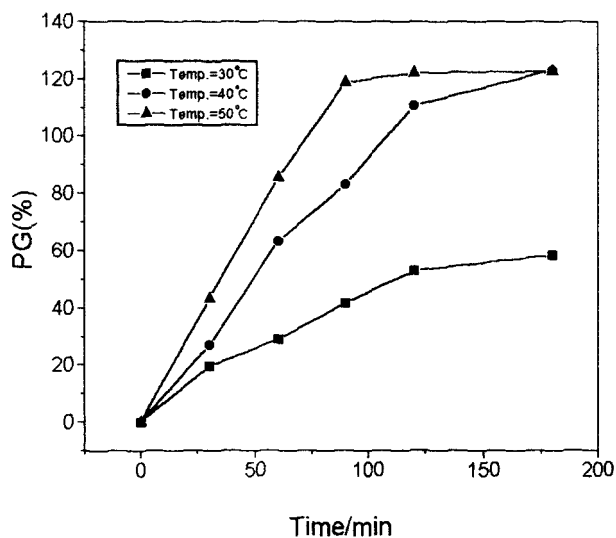


**Figure 2** GE versus  $[Mn(VII)]$ :  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature =  $75^\circ C$ ; reaction temperature =  $40^\circ C$ .

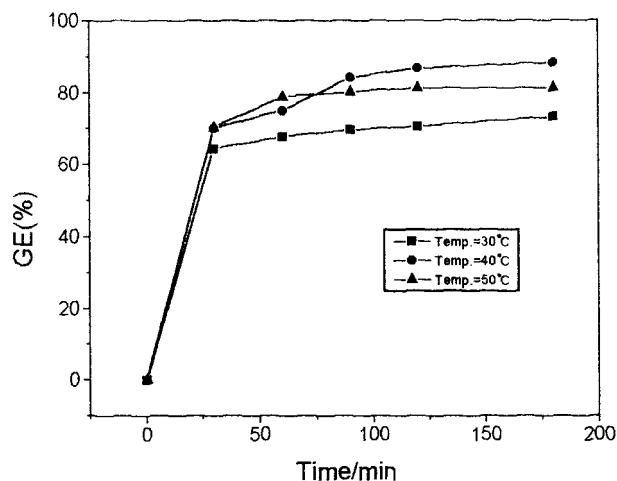
the concentration of initiator increased. But as  $[Mn(VII)]$  further rose, the inducing decomposition of the initiator became prominent, which caused the decrease of radicals on the backbone, so PG fell following the peak. Obviously, the rate of grafting at the beginning reaction period rose as initiator concentration increased.

#### Determination of Reaction Temperature

Figures 3 and 4 show the influence of reaction temperature on the grafting. GE showed a maxi-



**Figure 3** Effect of reaction temperature on PG:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature =  $75^\circ C$ .



**Figure 4** Effect of reaction temperature on GE:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature =  $75^\circ C$ .

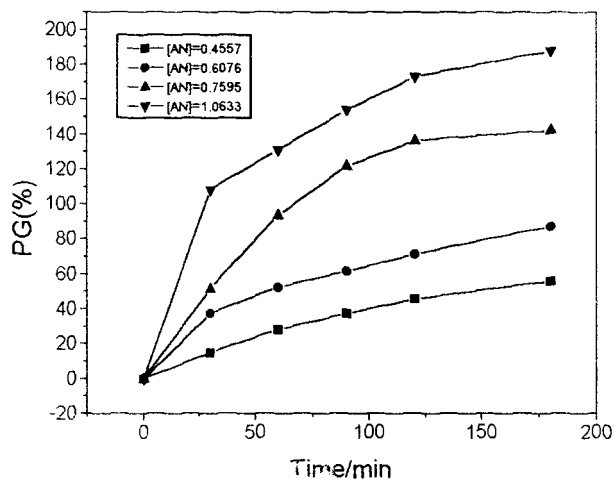
imum at temperature of  $40^\circ C$ , but PG values were almost the same at 40 and  $50^\circ C$ . This can be attributed to the following reasons.

1. When the temperature rises, the swelling level of starch becomes great, which is favorable to the diffusion of initiator and monomer to the backbone.<sup>3</sup>
2. The rising temperature leads to the increase of rates in initiation, propagation, and termination, and the grafting rate in early reaction stage grew evidently as reaction temperature rose.
3. The rising temperature is more favorable to the rate of homopolymerization than to that of graft copolymerization because the former has a higher activation energy.

#### The Relationship Between the Monomer Concentration and Components of Copolymers

Figures 5 and 6 show the PG and GE of the graft copolymerization when the monomer concentration changed in the range of 0.45–1.37 mol/L. PG and GE both increased as monomer concentration increased. This may be ascribed to the following facts.

1. Increasing  $[AN]$  can cause the increase of local  $[AN]$  in or around the swollen starch granules. This is favorable to the diffusion of monomer molecules onto radical site on the

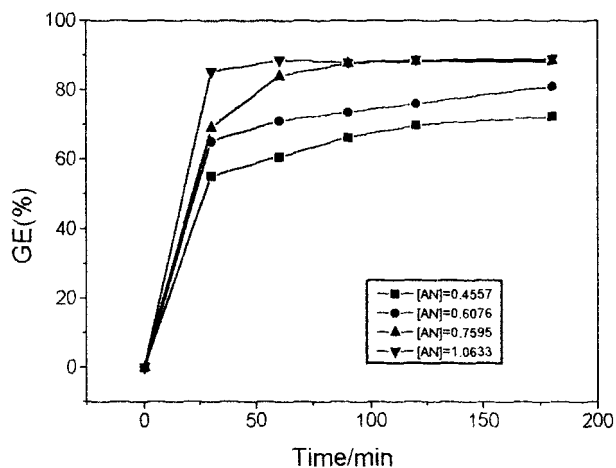


**Figure 5** Effect of [AN] on PG:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; [AGU] = 0.1086 mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature = 75°C; reaction temperature = 40°C.

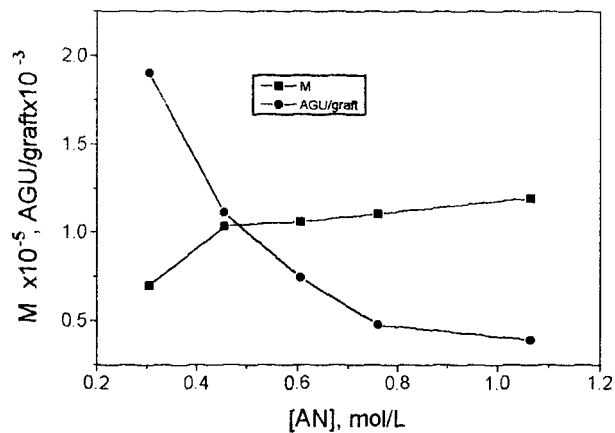
backbone, leading to the growth of PG and GE.

- Increasing [AN] contributes to the formation of accept-donor complex between starch and monomer,<sup>21,22</sup> which is beneficial to the orientation delivering of monomer.

Besides, the molecular weights of the grafted chains were measured, shown in Figure 7. The molecular weight of the grafted chain went up as the monomer concentration increased, but the



**Figure 6** Effect of [AN] on GE:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; [AGU] = 0.1086 mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature = 75°C; reaction temperature = 40°C.

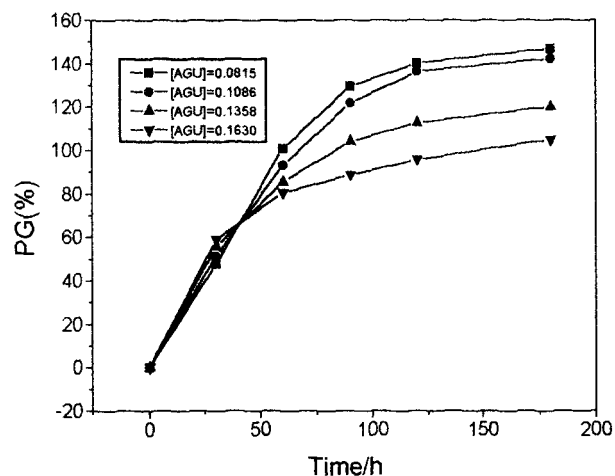


**Figure 7** Relationship between molecular weight and [AN]. Conditions are as in Figure 6.

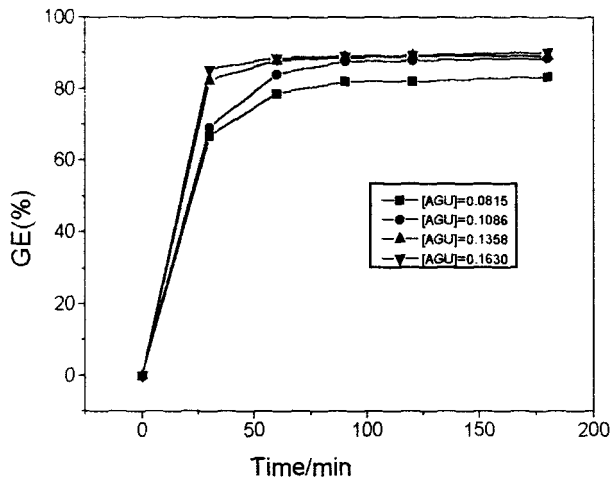
average glucose unit number between two grafting sites (AGU/graft) decreased. This means that both the grafting site number and the molecular weight grafted on these sites rose.

#### Effect of Starch Concentration on the Grafting

The effect of starch concentration on the graft copolymerization is illustrated in Figures 8 and 9. PG decreased steadily as [AGU] rose, while GE rose first constantly. When [AGU] rose, the reaction probability between the starch backbone and initiator, starch radicals, and monomer molecules increased, so GE grew. Since the concentration of the monomer [AN] did not change, the local [AN]



**Figure 8** PG versus [AGU]:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; [AN] = 0.7595 mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature = 75°C; reaction temperature = 40°C.

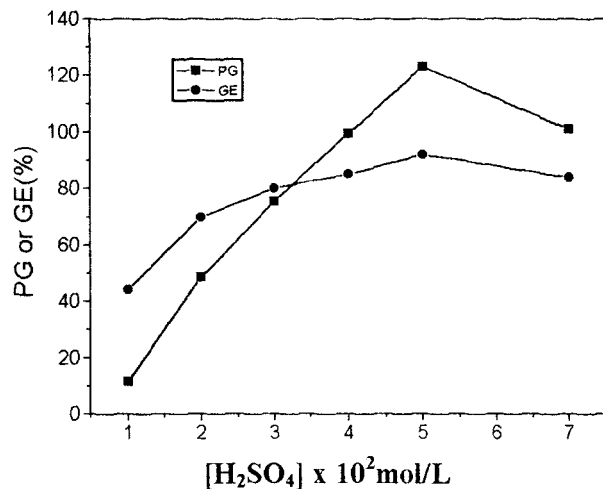


**Figure 9** GE versus [AGU]:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; [AN] = 0.7595 mol/L;  $[H^+] = 0.1$  mol/L; pre-heat temperature = 75°C; reaction temperature = 40°C.

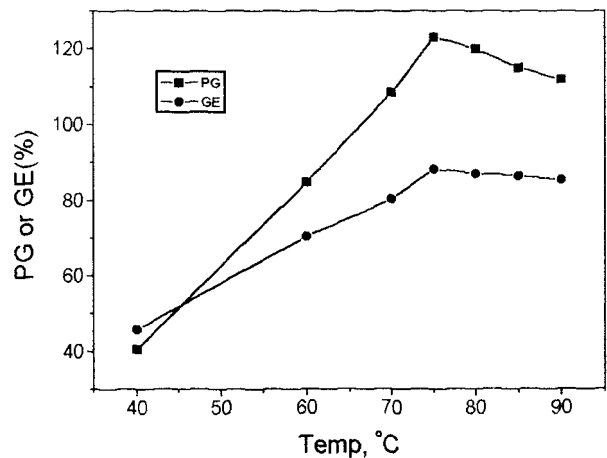
around each starch granule became lower as [AGU] increased, so PG lowered gradually.

#### Catalyst Acid

Sulfuric acid acts as catalyst in the graft copolymerization of starch with AN. As shown in Figure 10, PG and GE came to a maximum at the acid concentration of  $5.0 \times 10^{-2}$  mol/L. Acid can catalyze the graft copolymerization; but, at the same time, excessive hydrogen ion can react with produced  $MnO_2$  to form oxygen atom [O] that can



**Figure 10** Effect of acid concentration:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; pre-heat temperature = 75°C; reaction temperature = 40°C.



**Figure 11** Effect of preheat-treatment of starch:  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[H^+] = 0.1$  mol/L; [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; reaction temperature = 40°C.

terminate polymerization, besides the consumption of  $MnO_2$ , an effective initiator to react with starch and form radicals on the backbones.

#### Preheat Treatment of Starch

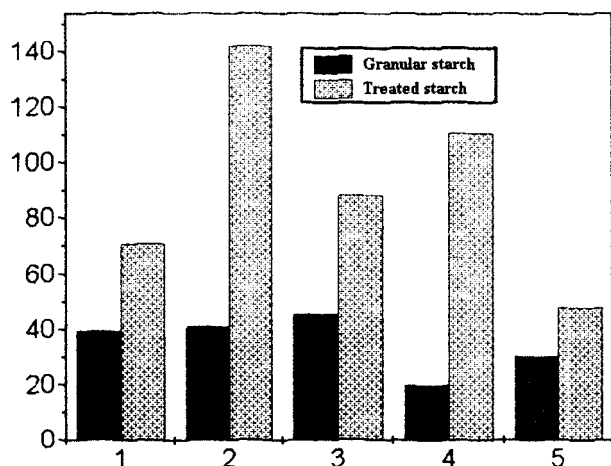
Starch was heat-treated at a desired temperature over 60°C before graft copolymerization. Figure 11 shows the effect of temperature of preheat treatment on the grafting. Starch is a partial crystal polymer and has a limited swelling ability at the low temperature. A rising temperature could increase both the swelling ability and solubility of starch in water, which was favorable to the graft copolymerization, so PG and GE grew.

#### Comparison of the Grafting Ability Between Granular Starch and Gelatinized Starch

Figure 12 is the grafting results of granular starch and gelatinized starch. Obviously, the gelatinized starch had a higher PG, GE, and PC (percentage conversion of monomer). Molecular weight ( $M$ ) of the branch chain grafted onto gelatinized starch and the average glucose unit number between two grafting sites (AGU/graft) were also higher comparing with granular starch. This relationship between molecular weight and AGU/graft was different from that in Figure 7.

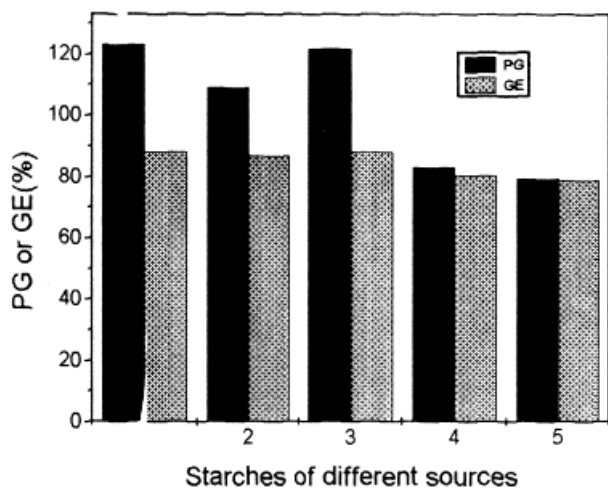
#### Grafting Abilities of Different Sources of Starches and Starch Derivatives

Different sources of starches have different grafting abilities as shown in Figure 13. Corn starch

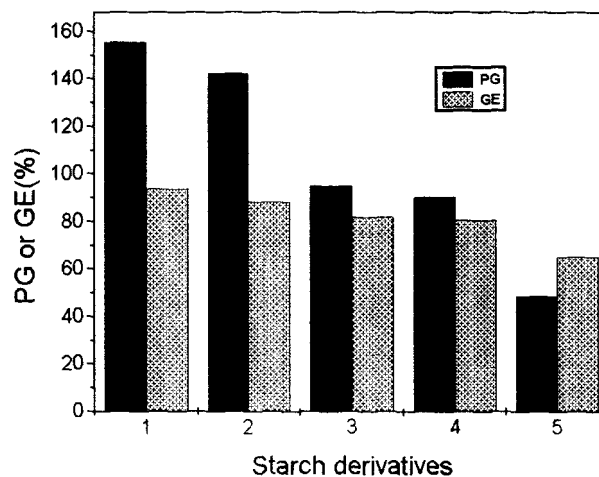


**Figure 12** Grafting ability of granular starch and preheat treatment starch:  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[H^+] = 0.1$  mol/L; reaction temperature =  $40^\circ C$ .

and cassava starch showed the highest grafting efficiency, while canna starch showed the lowest. This is related to the granular structure, crystallinity, and gelatinization properties of starch. Meanwhile, the grafting abilities of corn starch derivatives were also investigated and illustrated in Figure 14. When starches were introduced with different groups, they showed different grafting



**Figure 13** Grafting abilities of different sources of starches:  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[H^+] = 0.1$  mol/L; preheat temperature =  $75^\circ C$ ; reaction temperature =  $40^\circ C$ . Starch derivatives are as follows: (1) corn starch, (2) potato starch, (3) cassava starch, (4) wheat starch, and (5) canna starch.



**Figure 14** Grafting abilities of corn starch derivatives:  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[H^+] = 0.1$  mol/L; reaction temperature =  $40^\circ C$ . Starch derivatives are as follows: (1) aldehyde starch, (2) native starch, (3) hypochlorous starch, (4) carboxymethyl starch, and (5) crosslinking starch.

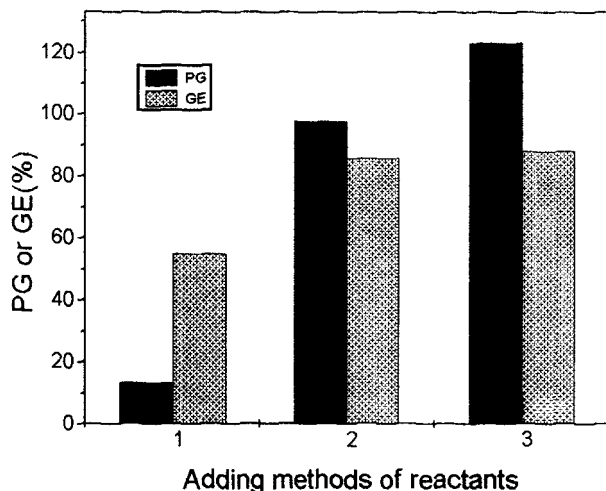
abilities. All the starch derivatives had lower grafting efficiency compared with native starch except aldehyde starch. In fact, the formed aldehyde group could easily transform to enol, which could further react with manganic ion to form radicals on the backbone.

#### Adding Sequence of Reactants

Three different adding sequences of reactants were taken in the graft copolymerization, and the results are shown in Figure 15. In method 1, potassium permanganate showed a high oxidation potential and caused the destruction of part of the double bond in monomers. If method 2 was taken, potassium permanganate could make the formed aldehyde group further oxidized to carboxy  $-COOH$ . But method 3 overcame the above shortcomings, so PG and GE were the highest among the 3 methods.

#### Effect of Preoxidation Time on the Grafting

The oxidation extent of starch depended both on the adding sequence of reactants and preoxidation time, as shown in Figure 16. It indicated that when starch was preoxidized for about 10 min, it had the highest grafting ability, which suggested

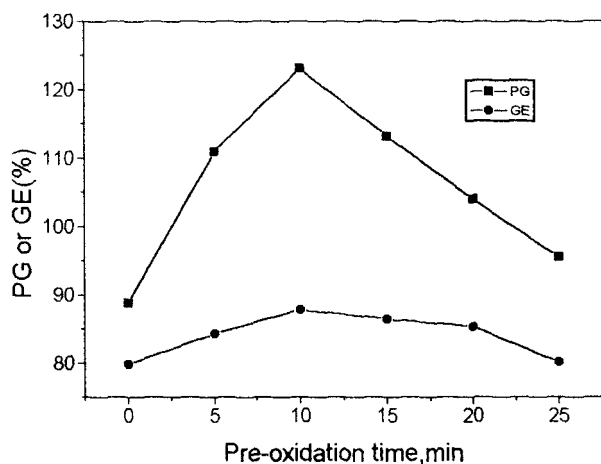


**Figure 15** Effect of adding sequence of reactants:  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L;  $[H^+] = 0.1$  mol/L; reaction temperature =  $40^\circ C$ . Sequences are as follows: (1) AN(1)  $\rightarrow$  acid (2)  $\rightarrow$  Mn(VII), (2) Mn(VII)  $\rightarrow$  acid (2)  $\rightarrow$  AN, and (3) Mn(VII) (1)  $\rightarrow$  AN (2)  $\rightarrow$  acid.

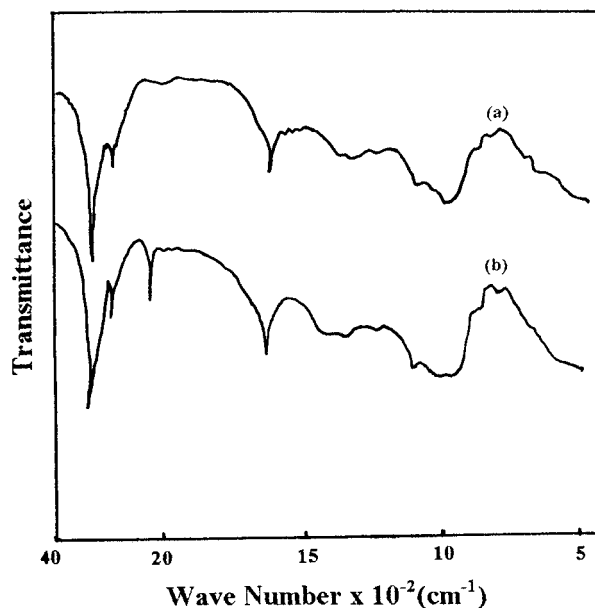
that the starch had a suitable oxidation degree or had the most aldehyde groups on its backbone.

#### Proof of Grafting

Figure 17 is the IR spectra of native starch [Fig. 17(a)] and purified starch-*g*-PAN [Fig. 17(b)]. The spectrum of the graft copolymer shows both the characteristic absorption of starch at  $3000-$



**Figure 16** Effect of preoxidation time:  $[AN] = 0.7595$  mol/L;  $[AGU] = 0.1086$  mol/L;  $[H^+] = 0.1$  mol/L;  $Mn(VII) = 1.0 \times 10^{-3}$  mol/L; reaction temperature =  $40^\circ C$ .



**Figure 17** IR spectra of (a) native starch and (b) St-*g*-AN.

$3800$   $cm^{-1}$  and characteristic absorption of PAN at  $2245$   $cm^{-1}$ , this confirms the existence of the graft copolymer starch-*g*-PAN.

#### CONCLUSION

1. Reaction conditions, such as concentration of reactants, reaction temperature, and preheat treatment, all affect the grafting ability, which offers the methods to adjust the component of the graft copolymers.
2. Different sources and derivatives of starch have different grafting abilities. The grafting ability increases when the aldehyde group is introduced to the starch.
3. The adding sequence of the reactants affects the grafting ability of the starch. This explains that the oxidation degree of starch is the key point that decides the grafting ability, and it also proves that the initiating action of potassium permanganate comes from the oxidation of starch and the formation of aldehyde group.
4. Potassium permanganate can be used as a cheap initiator to replace  $Ce^{4+}$  salt in manufacturing the starch-*g*-PAN copolymer, a raw material for water-absorbing materials.

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