Graft Mechanism of Acrylonitrile onto Starch by Potassium Permanganate

Liming Zhang,[1]* Jianping Gao,[1] Ruchuan Tian,[1] Jiugao Yu,[1] Wei Wang[2]

[1] School of Science, Tianjin University, Tianjin 300072, People's Republic of China
[2] School of Chemical Engineering, Tianjin University, Tianjin 300072, People's Republic of China

ABSTRACT: The graft mechanism of acrylonitrile (AN) onto starch under the initiation of potassium permanganate was investigated. The relationships of the grafting rate and the concentrations of potassium permanganate, AN, and backbone starch, as well as the reaction temperature, were established. On this basis, the equation for the rate of the graft copolymerization was derived, and the apparent activation energy for the graft copolymerization was obtained. Through the study of the oxidation reaction of starch with manganic ions, the valence changes of manganic ions during the graft copolymerization, and the grafting ability of different starch derivatives, together with electron spin resonance analysis, the grafting mechanism for the graft copolymerization of AN onto starch under the initiation of potassium permanganate was determined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 146–152, 2003

Key words: starch; acrylonitrile; graft polymerization

INTRODUCTION

Starch is one of the most plentiful renewable natural resources. It has been widely applied in the paper, textile, and food industries.[1] Because it is biodegradable in the environment, starch can be added to synthetic plastics to reduce white pollution[2,3] or can be used as a polyamide in the oil industyr.[4,5] Because the compatibility of starch with synthetic plastics, along with its processing and mechanical properties, is not good enough, chemical or physical modification is necessary.

Graft copolymerization is one of the most effective ways to improve the comprehensive properties of polymer materials, and it is especially suitable for natural macromolecules such as cellulose,[6] gelatin,[7,8] starch,[9,10] pullulan,[11] and chitosan.[12,13] Generally, free-radical initiators used for synthetic polymerization can be applied to the graft modification of starch;[14] common initiators such as peroxide and redox systems are often used in the graft copolymerization of natural macromolecules.[15,16] Some transition-metal ions with high valence can also be used to initiate the graft copolymerization of starch.[17–20] Ghosh and Paul[21,22] applied potassium pervanadate or potassium trioxalatomanganate as an initiator to graft poly(methyl methacrylate) (PMMA) onto starch. Manganic ions, like Ce^{4+}, can initiate the graft copolymerization of starch.[23,24] Mehrotra and Ranby[25] reported the graft copolymerization of acrylonitrile (AN) onto starch with Mn^{3+}, and they found that the pretreatment temperature had no effect on the monomer conversion and addition. The average molecular weights of the grafts showed, however, an increase by a factor of nearly 10. Hebeish et al.[26] reported the graft copolymerization of AN onto starch with potassium permanganate as the initiator, and they briefly discussed the formation of free radicals on the backbone and the effect of various conditions on the graft copolymerization. In our early articles, we reported the graft copolymerization of PMMA onto canna starch with manganic pyrophosphate as an initiator,[27] and we found that it was an effective initiator for the graft copolymerization of starch with methyl methacrylate. We compared the initiating abilities of different transition ions in the graft copolymerization of starch,[28] and we also studied the grafting efficiency (GE) of polyacrylonitrile (PAN) onto starch with different transition-metal-ion/thiourea systems.[29] We also investigated using potassium permanganate to initiate the graft copolymerization of starch with AN, and we discussed the effects of various reaction conditions on graft copolymerization.[30] As an extension of our previous studies, this article focuses on the reaction rate and reaction mechanism of the graft copolymerization of PAN onto starch initiated by potassium permanganate.

EXPERIMENTAL

Materials

Maize starch was acquired from the Redflag Starch Plant (Tianjin, China), and aldehyde starch and hypo-

chlorous acid-oxidized starch were prepared in our laboratory according to a literature procedure.[1] AN and potassium permanganate were obtained from the Tianjin Second Reagent Plant (Tianjin, China), and MnO_2 was prepared in our laboratory as described in the literature.[31]

Graft copolymerization and makeup of starch-*graft*-polyacrylonitrile (St-*g*-PAN)

Weighed amounts of starch and distilled water were put into a three-necked flask under slow stirring and an atmosphere of N_2 to form a paste, which was then preheated at 75°C for about 30 min before it was cooled to the desired reaction temperature. A certain volume of a potassium permanganate solution was added into the vessel to allow the starch to be preoxidized for a short time, and then the monomer AN and the catalyst sulfuric acid were added. The reactants were allowed to react about 3 h before the reaction was terminated. The rough products were precipitated with ethanol, filtered, and dried to a constant weight at 60°C in a vacuum. The dried products were extracted with dimethylformamide in a Soxhlet apparatus for 72 h for the removal of the homopolymer PAN, and the extracted products were finally dried and weighed.

Calculation of the percentage of grafting (PG) and GE

The PG and GE were calculated with the following equation after the St-*g*-PAN, PAN branches, and reacted starch were weighed:

$$PG\ (\%) = \frac{\text{Weight of grafted PAN}}{\text{Weight of St-}g\text{-PAN}} \times 100$$

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

Determination of the average reaction rate (R_g) of the graft copolymerization

The rate of the graft copolymerization of AN onto starch under the initiation of potassium permanganate was calculated with the following equation:

$$R_g\ (\text{mol/L min}) = \frac{\text{Amount of branch PAN grafted}}{M_{AN} \times \text{Reaction time} \times \text{Volume}}$$

where M_{AN} represents the molecular weight of AN.

Valence analysis of manganic ions during the graft copolymerization

Electron spin resonance (ESR) analysis was used to trace the valence changes of the manganic ions during
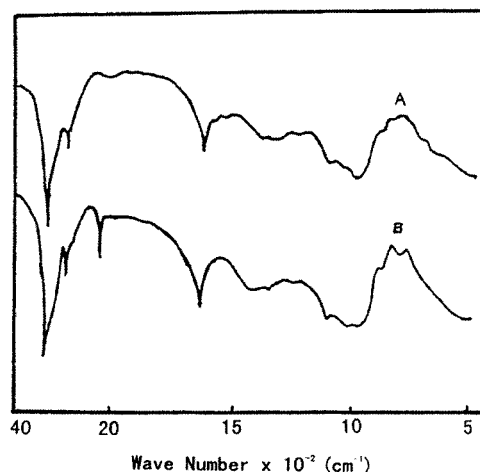

Figure 1 IR spectra of (A) native starch and (B) St-*g*-PAN.

the grafting reaction to explain the initiating mechanism of potassium permanganate for the graft copolymerization of AN onto starch. The graft copolymerization of starch was carried out as usual. An aqueous starch paste was first preheated at 75°C for about 30 min and then was cooled to the desired reaction temperature. After a $KMnO_4$ solution was added, a capillary about 1 mm in diameter was used to take samples from the vessel for *in situ* ESR analysis with a JES-3BX ESR instrument, with a glass capillary used as an interior control. After the catalyst sulfuric acid and the monomer AN were added, the capillary was used repeatedly to take samples from the vessel every 20 min up to 140 min.

Infrared (IR) spectra of the St-*g*-PAN copolymer

The IR spectra of the starch and graft copolymer St-*g*-PAN were obtained with a Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

Identification of St-*g*-PAN

IR is an effective way of identifying organic compounds or polymers, especially for chemical bonds newly formed during a reaction. Figure 1 shows the IR spectra of native starch and purified St-*g*-PAN. The spectrum of the graft copolymer shows the characteristic absorption of starch at 3000–3800 cm^{-1} and also the characteristic absorption of PAN at 2245 cm^{-1}. This proves the grafting reaction of AN onto starch by the initiation of potassium permanganate.

Relationship between R_g and the reaction parameters

Relationship between R_g and the initiator concentration

The initiating route for metal ions in graft copolymerizations is different from that of common free-radical
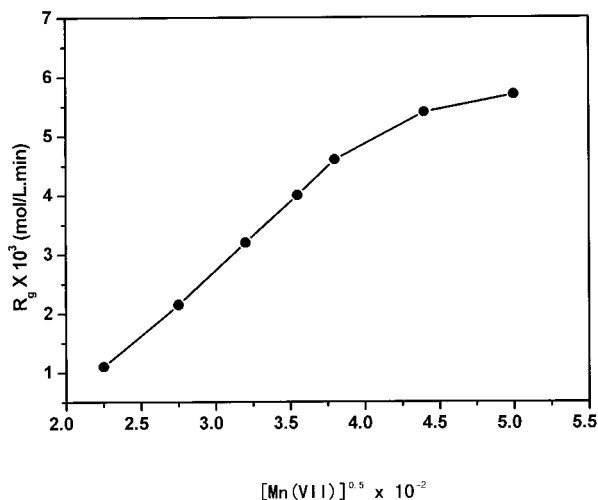
Figure 2 Relationship between R_g and the concentration of potassium permanganate ([AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; [H$^+$] = 0.1 mol/L; preheating temperature = 75°C; reaction temperature = 40°C).

initiators such as peroxides, which first decompose and form free radicals; these free radicals react with the monomer and start the propagation of the chain. Therefore, when peroxides are used in the graft copolymerization of starch, the produced free radicals can react with both the monomer and the backbone, and the former may lead to the formation of the homopolymer. In this way, graft copolymerization and homopolymerization become competitive reactions. When a metal ion with high valence, such as Mn^{7+}, is applied to the graft copolymerization, Mn^{7+} directly oxidizes the —OH groups on the starch backbone to form free radicals, and these free radicals initiate monomer molecules to graft onto the backbone and form reactive radical centers on the backbone. However, some of the free radicals on the backbone may have chain-transfer reactions onto the monomer or initiator, and this leads to the formation of the homopolymer. In this case, there is still a pair of competitive reactions, graft copolymerization and homopolymerization. As shown in Figure 2, as the initiator concentration changed from 0.5×10^{-3} to 2.5×10^{-3} mol/L, the graft rate continually increased. When the initiator concentration was less than 1.5×10^{-3} mol/L, the relationship between R_g and the KMnO$_4$ concentration was linear, but when the initiator concentration was greater than 1.5×10^{-3} mol/L, the R_g data deviated from the line and deflected to the x axis. This could be attributed to the fact that the termination reaction was mainly caused by double-end termination when the KMnO$_4$ concentration was lower, whereas when the KMnO$_4$ concentration was greater than 1.5×10^{-3} mol/L, single-end termination, caused by a chain-transfer reaction with the initiator, happened at the same time, and it became much

more dominant as the KMnO$_4$ concentration was further increased.

Relationship between R_g and the monomer concentration

In the monomer concentration range of 0.4–1.3 mol/L, R_g apparently increased as the AN concentration grew (see Fig. 3) because the local AN concentration in or around the swollen starch granules increased, and this helped the diffusion of the monomer molecules into the radical centers on the backbone.

Relationship between R_g and the concentration of the backbone

With the initiator and monomer concentrations specified, the relationship between R_g and the starch concentration ([AGU]) is illustrated in Figure 4. R_g had a linear relationship with [AGU]$^{0.5}$, increasing as the starch concentration grew. Our earlier article showed that PG was reduced if the amount of starch was increased because the ratio of the monomer to the starch was lowered. This led to a decrease in the AN concentration in every starch molecule, even though the graft rate became fast because of the greater number of radical centers being formed on the backbone as a whole.

In summary, the rate of the graft copolymerization of AN onto starch by potassium permanganate at a comparatively lower initiator concentration can be derived as follows:
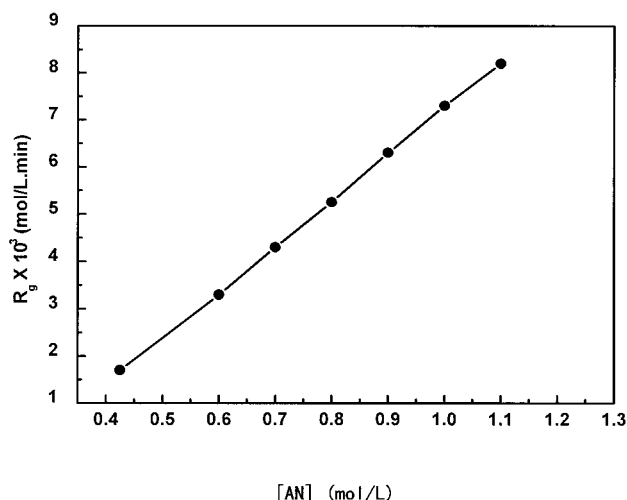
$$R_g = k[KMnO_4]^{1/2}[AN][AGU]^{1/2}$$

Figure 3 Relationship between R_g and the concentration of AN ([Mn(VII)] = 1.0×10^{-3} mol/L; [AGU] = 0.1086 mol/L; [H$^+$] = 0.1 mol/L; preheating temperature = 75°C; reaction temperature = 40°C).
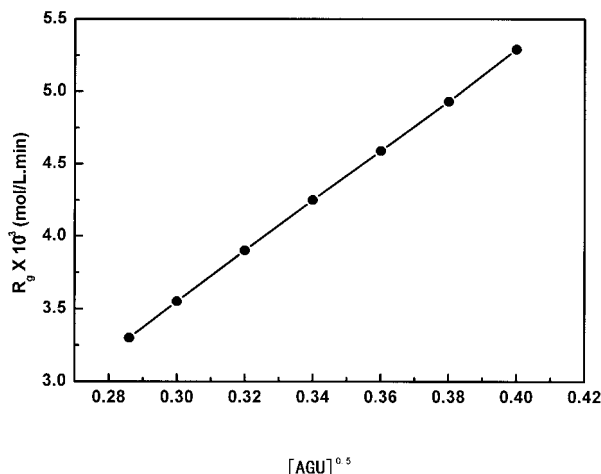
Figure 4 Relationship between R_g and the concentration of starch ([Mn(VII)] = 1.0×10^{-3} mol/L; [AN] = 0.7595 mol/L; [H$^+$] = 0.1 mol/L; preheating temperature = 75°C; reaction temperature = 40°C).

Effect of the reaction temperature on R_g

When the reaction temperature was changed in the range of 30–60°C, the grafting rate grew as the temperature was raised. The Arrhenius equation describes the relationship between the grafting rate and the reaction temperature (T):

$$\log R_g = \log k - (E/2.303R)(1/T)$$

Figure 5 gives the plot of $\log R_g \sim 1/T$, from which the apparent activation energy (E_{ag}) was roughly calculated with the slope of the line:
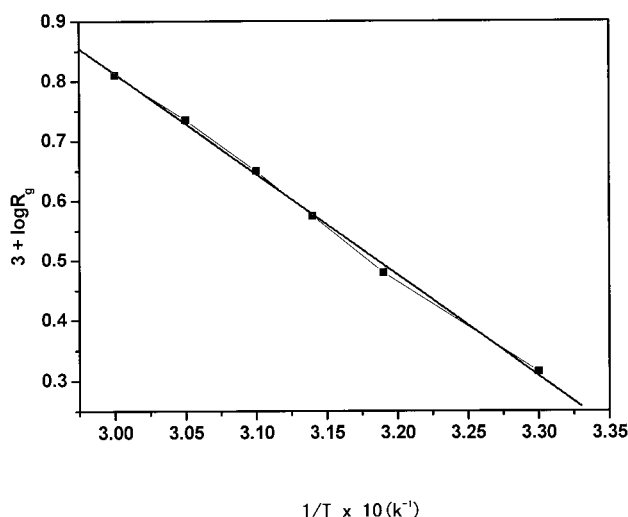
$$E_{ag} = 30.74 \text{KJ/mol}$$

Figure 5 Effect of the reaction temperature on R_g ([Mn-(VII)] = 1.0×10^{-3} mol/L; [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; [H$^+$] = 0.1 mol/L; preheating temperature = 75°C).
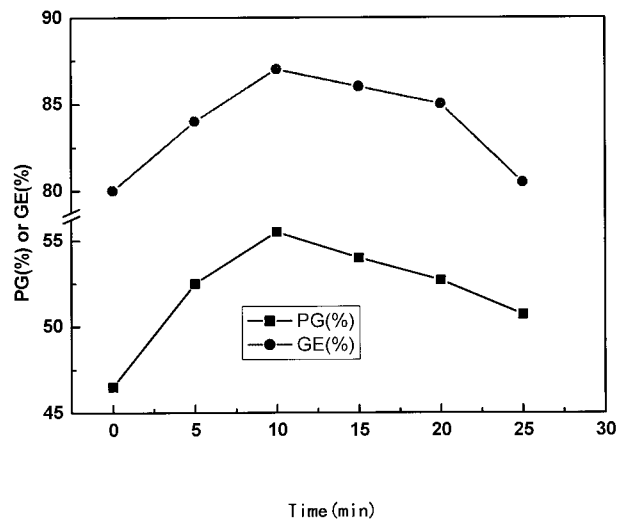

Figure 6 Preoxidation of starch and grafting ability ([Mn-(VII)] = 1.0×10^{-3} mol/L; [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; [H$^+$] = 0.1 mol/L; preheating temperature = 75°C; reaction temperature = 40°C).

Graft mechanism

Oxidation of starch by potassium permanganate

The oxidation reaction of starch by potassium permanganate was investigated under the same reaction conditions, except for the addition of the monomer. After a short time of mixing and reacting, the product was rinsed several times and filtered, and then the aldehyde groups formed during the oxidation reaction were tested. There were about 6.5 aldehyde groups per 100 glucose units. This indicated that the starch macromolecules reacted with potassium permanganate, and some of the —OH groups were transformed into aldehyde groups. These aldehyde groups were involved in the subsequent graft copolymerization of starch with monomer molecules.

Effect of the preoxidation time on the grafting ability of starch

Some starch was added to a four-necked flask, potassium permanganate was added, the oxidation reaction was allowed for a period of time, and then the monomer and acid were poured into the flask to start the graft copolymerization. Figure 6 shows the effect of the preoxidation time on the grafting ability of starch. Each datum in Figure 6 is the average value of five measurements, and the standard deviations are all less than 0.5. The data tell us that the preoxidation time obviously affected the grafting ability of starch, and about 10 min of oxidation before the graft copolymerization gave the highest grafting ability. When potassium permanganate was added to the starch slurry, some of the hydroxide groups (—OH) on the starch backbone were oxidized into aldehyde groups, just as
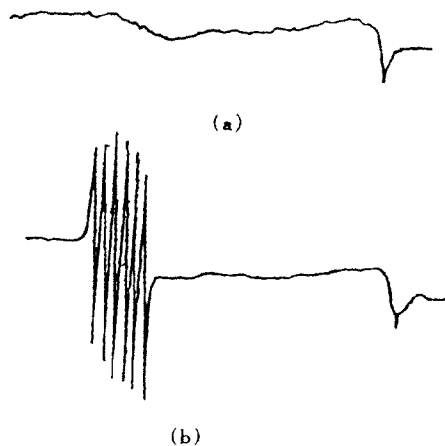
Figure 7 ESR spectra of manganic ions during graft copolymerization.

previously discussed. The produced aldehyde groups reacted with high-valence manganic ions to form free radicals on the starch backbone, so the graft copolymerization could be carried out. As the preoxidation time got longer, many more aldehyde groups on the backbone were produced, so the grafting ability of starch was higher. However, the aldehyde groups could be further oxidized into carboxyl groups, and this caused a decrease in the rate.[30]

Valence changes of manganic ions during the graft copolymerization

To trace the valence changes of manganic ions during the graft copolymerization, we used a certain addition sequence of the reactants. Potassium permanganate was first added to the starch slurry. After a period of time, the monomer AN and the catalyst acid were poured into the mixture separately. Just after $KMnO_4$ was added, the color of MnO_2 was observed, and it indicated that Mn^{7+} had reacted with starch and had been reduced from a valence of +7 to +4. However, after the addition of the monomer and catalyst and a further period of time of graft copolymerization, the purple-red color of the complex ion of $[Mn(H_2P_2O_7)_3]^{3-}$ could be observed if $Na_4P_2O_7$ was added to the vessel. This explains the existence of Mn^{3+}, which was formed by the reduction of Mn^{4+}. The purple-red color gradually became weaker and almost disappeared at the end of the graft copolymerization. This

tells us that Mn^{3+} was further reduced to Mn^{2+}. These phenomena indicate a series of valence changes in manganic ions during the graft copolymerization:

$$Mn(VIII) \rightarrow Mn(IV) \rightarrow Mn(III) \rightarrow Mn(II)$$
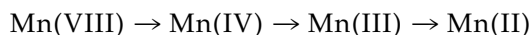
To further prove the aforementioned valence changes, we used ESR analysis to trace the graft copolymerization *in situ*. When potassium permanganate was just added to the flask containing starch, an ESR signal was obtained, as shown in Figure 7(a). It just gives a characteristic peak of the glass reference, indicating that the manganic ions did not have magnetism or that the *d*-orbital had no unpaired electron. After a period of time, the signal of the manganic ions appeared in the ESR spectrum, as shown Figure 7(b). The right part is still the signal of the glass reference (Gla), whereas the left part shows the characteristic peak of manganic ions (Mn). The signal strength of the manganic ions was evaluated by a comparison of the manganic ions and glass reference, or Mn/Gla, as shown in Table I and Figure 8. The data of Mn/Gla first increased and then declined as the graft copolymerization proceeded. After potassium permanganate was added to and reacted with starch, it was reduced to Mn^{4+} at a high self-rotation state, so the Mn/Gla value increased as formed Mn^{4+} grew. Meanwhile, Mn^{4+} was further reduced to Mn^{3+} or Mn^{2+}, which stayed at a low self-rotation state because of the existence of —CN groups in AN,[32] leading to the decrease in the Mn/Gla value. It was the opposite action of Mn^{4+}, Mn^{3+}, and Mn^{2+}, with the existence of —CN groups on the ESR signal deciding the trend of Mn/Gla during the graft copolymerization.

Grafting ability of the different starch derivatives under the initiation of MnO_2

The grafting ability of different maize starch derivatives was studied, and the results are listed in Table II. All the starch derivatives had a lower GE than native maize starch, except for aldehyde starch, and this indicated the important role of the aldehyde group in the graft copolymerization. Meanwhile, MnO_2, instead of $KMnO_4$, was used to initiate the graft copolymerization of AN onto various starch derivatives, including dialdehyde starch, hypochlorous acid-oxi-

TABLE I
Strength of the ESR Signal

	Time (min)								
	0	10	20	40	60	80	100	120	140
Gla	12.0	29.5	29.5	25	27.5	26.5	23.5	25.5	28.5
Mn	0	34.5	66.5	56.5	85.0	82.0	69.5	71.4	73.8
Mn/Gla	0	1.16	2.22	2.24	3.09	3.09	2.95	2.80	2.59
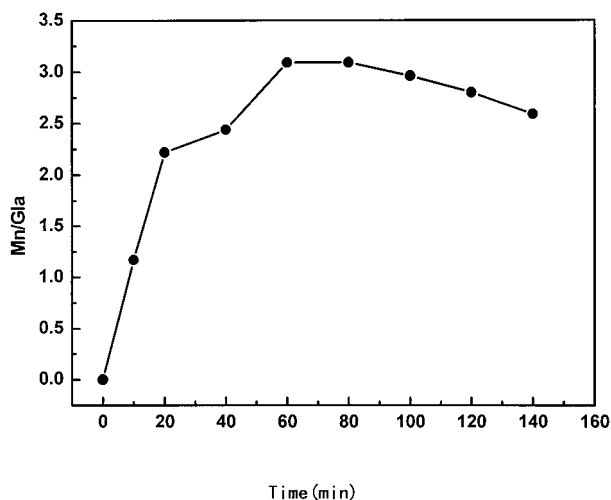
Figure 8 Signal strength of ESR of manganic ions during graft copolymerization.
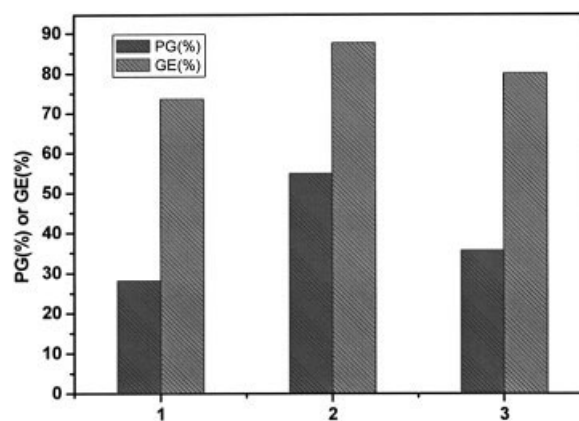

Figure 9 Graft copolymerization of starches initiated by MnO_2 ($[MnO_2] = 1.0 \times 10^{-3}$ mol/L; [AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; $[H^+]$ = 0.1 mol/L; preheating temperature = 75°C; reaction temperature = 40°C): (1) native starch, (2) aldehyde starch, and (3) hypochlorous acid-oxidized starch.

dized starch, and native maize starch as a control; the results are shown in Figure 9, in which each datum is the average value of five measurements, and the standard deviations are all less than 0.5. Obviously, the grafting ability of dealdehyde starch was much higher than that of hypochlorous acid-oxidized starch, but the grafting ability of hypochlorous acid was much higher than that of native maize starch. This shows that the aldehyde group on the starch and Mn^{4+} played important roles in the graft copolymerization.

Graft mechanism

Radical formation on starch macromolecules is a key issue in discussing the graft mechanism. Hebeish[26] studied the graft copolymerization of AN onto starch with potassium permanganate as an initiator and believed that radical formation in a polymerization system initiated by potassium permanganate in the presence of an acid seemed likely to occur through the reduction of Mn^{4+} to Mn^{3+}, Mn^{2+}, or both Therefore, the creation of free radicals during the graft copolymerization of AN onto starch was suggested as follows:

$$St{\rm —}OH + Mn^{4+} \rightarrow St{\rm —}O^{\bullet} + Mn^{3+} + H^+$$

$$St{\rm —}OH + Mn^{3+} \rightarrow St{\rm —}O{\cdot} + Mn^{2+} + H^+$$

From these experimental results, we roughly know the valence changes of the manganic ions and the redox reactions that occurred during the graft copolymerization, from which the grafting mechanism of AN onto starch backbones by $KMnO_4$ could be assumed. The graft copolymerization began with the oxidation of starch by $KMnO_4$, or the hydroxide groups —OH were oxidized into aldehyde groups; meanwhile, the manganic ion Mn^{7+} was reduced to Mn^{4+}:

$$St{\rm —}OH + KMnO_4 \longrightarrow St{\rm —}CH_2{\rm —}\overset{\overset{\textstyle H}{|}}{C}{=}O + Mn^{4+}$$
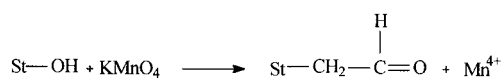
However, the aldehyde group was not stable, rearranging and transforming into an enol structure:

$$St{\rm —}CH_2{\rm —}\overset{\overset{\textstyle H}{|}}{C}{=}O \longrightarrow St{\rm —}CH{=}\overset{\overset{\textstyle H}{|}}{C}{\rm —}OH$$
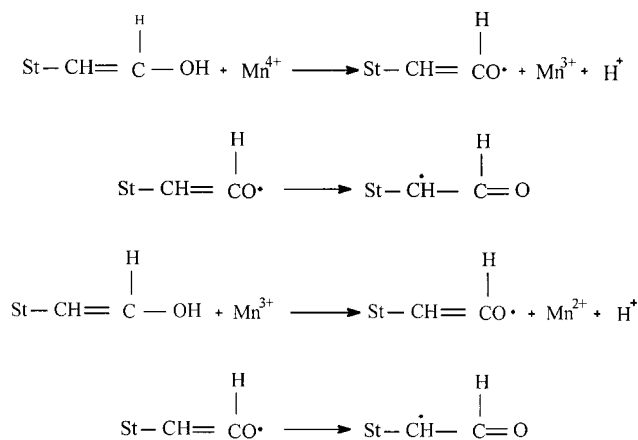
The enol structure reacted with Mn^{4+} to form free radicals on the starch backbone, and Mn^{4+} reduced to Mn^{3+}, which could accordingly react with the enol structure, like Mn^{4+}, to form free radicals on the starch chains:

TABLE II
**Grafting Abilities of Maize Starch Derivatives**

	Native starch	Aldehyde starch	Hypocholorous starch	Carboxymethy starch	Crosslinking starch
PE (%)	58.3	61.0	49.2	47.4	28.6
GE (%)	92.0	87.2	85.1	84.0	65.4

[AN] = 0.7595 mol/L; [AGU] = 0.1086 mol/L; [Mn(VII)] = 1.0×10^{-3} mol/L; $[H^+]$ = 0.1 mol/L; reaction temperature = 40°C.

$$\text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{C}}-\text{OH} + \text{Mn}^{4+} \longrightarrow \text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{CO}}\cdot + \text{Mn}^{3+} + \text{H}^{+}$$

$$\text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{CO}}\cdot \longrightarrow \text{St}-\overset{\cdot}{\text{CH}}-\underset{\underset{H}{|}}{\text{C}}=\text{O}$$

$$\text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{C}}-\text{OH} + \text{Mn}^{3+} \longrightarrow \text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{CO}}\cdot + \text{Mn}^{2+} + \text{H}^{+}$$

$$\text{St}-\text{CH}=\underset{\underset{H}{|}}{\text{CO}}\cdot \longrightarrow \text{St}-\overset{\cdot}{\text{CH}}-\underset{\underset{H}{|}}{\text{C}}=\text{O}$$

The free radicals consequently initiate the polymerization of the monomer AN and introduce AN branch chains onto the starch backbone:

$$\text{St}\cdot + \text{AN} \rightarrow \text{graft copolymer}$$
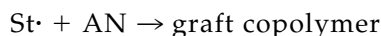
This is a speculated graft mechanism and need to be further supported by substantiating data.

CONCLUSIONS

1. The reaction rate for the graft copolymerization of AN onto starch under the initiation of potassium permanganate was as follows: $R_g = k[\text{KMnO}_4]^{1/2}[\text{AN}][\text{AGU}]^{1/2}$.
2. The manganic ion Mn^{7+} underwent a series of valence changes during the graft copolymerization: $\text{Mn(VII)} \rightarrow \text{Mn(IV)} \rightarrow \text{Mn(III)} \rightarrow \text{Mn(II)}$.
3. Aldehyde groups that formed on the starch macromolecules by the redox reaction with Mn^{7+} played an important role in the graft copolymerization of starch initiated by potassium permanganate.

References

1. Whistler, R. L.; Bemiller, J. N.; Paschall, E. F. Starch Chemistry and Technology, 2nd ed.; Academic: Orlando, FL, 1975.
2. Gao, J. P.; Wang, S. M.; Yu, J. G. Macromol Symp 1999, 144, 323.
3. William, M. Starch 1992, 44, 293.
4. Gao, J. P.; Lin, T.; Wang, W. Macromol Symp 1999, 144, 179.
5. Gao, J. P.; Yu, J. G.; Wang, W. J Appl Polym Sci 1998, 69, 791.
6. Aggour, Y. A.; Abdel-Razik, E. A. Eur Polym J 1999, 35, 2225.
7. Gao, J. P.; Li, Z. C. J Appl Polym Sci 1995, 55, 1291.
8. Gao, J. P.; Li, Z. C.; Wang, W.; Huang, M. G. J Appl Polym Sci 1998, 68, 1485.
9. Choi, W. M.; Jung, I. D.; Kwon, S. K.; Ha, C. S.; Cho, W. J. Polym Degrad Stab 1998, 61, 15.
10. Fanta, F.; Doane, W. M. Modified Starches: Properties and Uses; CRC: Boca Raton, FL, 1986.
11. Tian, R. C.; Gao, J. P.; Yu, J. G. J Appl Polym Sci 1992, 45, 591.
12. Kurita, K. Prog Polym Sci 2001, 26, 1921.
13. Singh, D. K.; Ray, A. R. J Membr Sci 1999, 155, 107.
14. Fanta, F. Polymeric Materials Encyclopedia; CRC: Boca Raton, FL, 1996; Vol. 10.
15. Fakhru, I. R. Z.; Qudsieh, I. Y. M.; Yunus, W. M. Z. W. J Appl Polym Sci 2001, 82, 1375.
16. Vazquez, B.; Goni, I.; Gurruchage, M. J Polym Sci Part A: Polym Chem 1989, 27, 595.
17. Rahman, L.; Silong, S.; Zin, W. M. J Appl Polym Sci 2000, 76, 516.
18. Lenka, S.; Mishra, M. K. J Appl Polym Sci 1980, 25, 1323.
19. Samal, R. K.; Sahoo, P. K. J Appl Polym Sci 1984, 29, 309.
20. Fanta, F.; Burr, R. C.; Doane, W. M. J Polym Sci Polym Chem Ed 1983, 21, 2095.
21. Ghosh, P. J.; Paul, S. K. J Macromol Sci Chem 1983, 20, 261.
22. Ghosh, P. J.; Paul, S. K. J Macromol Sci Chem 1983, 20, 179.
23. Singh, H.; Thampy, R. T.; Chipalkatti, V. B. J Polym Sci Part A: Gen Pap 1965, 3, 4289.
24. Palit, S. R.; Kornar, R. S. J Polym Sci 1962, 57, 609; 1962, 58, 85.
25. Mehrotra, R.; Ranby, B. J Appl Polym Sci 1978, 22, 2991.
26. Hebeish, A.; Ei-Thalouth, I. A.; Ei-Kashouti, M. A.; Fattah, S. H. A. Angew Makromol Chem 1979, 78, 101.
27. Gao, J. P.; Tian, R. C. J Appl Polym Sci 1994, 53, 1091.
28. Gao, J. P.; Yu, J. G.; Wang, W. J Macromol Sci Pure Appl Chem 1998, 35, 483.
29. Gao, J. P.; Tain, R. C.; Chang, L. M. Chin J Polym Sci 1996, 14, 163.
30. Gao, J. P.; Yu, J. G.; Wang, W. J Appl Polym Sci 1998, 68, 1965.
31. Zhao, H. M. Handbook for Synthetic Inorganic Compounds; Chemical Industry: Beijing, 1983; Vol. 1.
32. Zhao, C. D. Mass Structure; High Education Press: Beijing, 1985.