Graft Copolymers of Methy Methacrylate onto Canna Starch Using Manganic Pyrophosphate as an Initiator

JIAN-PING GAO,* RU-CHUAN TIAN, JIU-GAO YU, and MENG-LIN DUAN

Department of Chemistry, Tianjin University, Tianjin 300072, Republic of China

SYNOPSIS

In this article, the graft copolymerization of methy methacrylate with canna-starch under the initiating of manganic pyrophosphate was investigated systemly. It was found that the percentage of grafting, grafting efficiency, and rate of grafting were all dependent, to some extent, on the concentration of the initiator, monomer and starch, as well as reaction time and temperature. The rate equation of graft copolymerization established from the experimental results was similar to the equation derived from the reaction mechanism. The graft copolymer was investigated with an infered spectroscope, scanning electron microscope, and x-diffraction methods. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization of starch and other natural macromolecular can be initiated by transition metal ions,[1,2] of which Fe^{3+}, Cu^{2+}, Co^{3+}, Ce^{4+}, V^{3+}, Cr^{6+} as well as their complexies are the most commonly used initiator. Especially, Ce^{4+} was widely used in the graft modification of cellulose,[3] fiber,[4] gelatin,[5] and starch.[6] Misra[7,8] has reported the usage of transition metal acetyl acetonate chelates such as $Zn(acac)_2$, $Mn(acac)_3$, $Fe(acac)_3$, and $Al(acac)_3$ in the graft copolymerization of cellulose with various monomers, and found that the initiating capability of initiators was related to the monomers used.

Meanwhile, Ranby and his co-workers[9-11] studied the graft copolymerization of acrylonitrile or methy methacrylate onto granular native potato starch using manganic pyrophosphate as an initiator, and indicated that this initiator was efficient in this specific system. In our early work, we studied the graft copolymerization of pullulan with butyl acrylate,[12] corn starch with acrylonitrile initiated by manganic pyrophosphate,[13] and the results achieved were satisfied.

As an extension, this article will present the study on the graft copolymerization of methy methacrylate (MMA) onto canna starch with manganic pyrophosphate as an initiator.

EXPERIMENT

Material

Canna-starch was supplied by Zizong Starch Plant of Sichuang, China. Methy methacrylate, T. C. Co., China, was purified before usage.[10] All other chemicals were analytical grade reagents from T. C. Co., China.

Preparation of Initiator

The preparation of manganic pyrophosphate refers to the literature.[9]

Preparation of Graft Copolymer

A known weight of canna starch was slurried in 150 mL distilled water in a three-neck flask, which was equipped with a stirer and a thermometer. The starch slurry was preheated at 80°C for about half an hour under the atmosphere of N_2 gas, and then was cooled to the reaction temperature desired. After that, initiator was added first, followed by monomer after 10 min. The above reaction mixture was stirred and reacted for some hours, and then was terminated

by adding hydrochinone. The products were poured into alcohol to precipitate it, washed thoroughly with alcohol, dried, and weighed.

The above crude products were extracted with acetone in a Soxhlet apparatus for 72 h to remove homopolymer (PMMA), and the residue was dried and weighed.

Determination of Molecular Weight of PMMA Grafted

The purified graft copolymer was hydrolyzed in 1 mol/L HCl solution at 105–110°C for 24 h to obtain the grafted side chains.

The viscosity of the grafted chains solution was determined with an Ubbelohde viscometer at 25°C using acetone as solvent. The molecular weight was calculated according to the equation below:

$$[\eta] = KM^{\alpha}$$

where $K = 9.6 \times 10^{-3}$ $\alpha = 0.69$.

Definition of some Parameters

Percentage of grafting (PG), grafting efficiency (GE), and rate of grafting (Rg) were used to evaluate the graft copolymerization

$$PG(\%) = \frac{\text{Weight of PMMA grafted}}{\text{Weight of starch}} \times 100.$$

$$GE(\%) = \frac{\text{Weight of PMMA grafted}}{\text{Weight of monomer reacted}} \times 100.$$

$$R_g = \frac{\text{Weight of PMMA grafted}}{\text{MW of MMA} \times \text{reaction time (s)} \times \text{reaction volume (m}^3\text{)}}$$

RESULTS AND DISCUSSION

Identification of Grafting

Figure 1 is the IR spectra of canna-starch and grafting sample (starch-g-PMMA). The spectrum of the
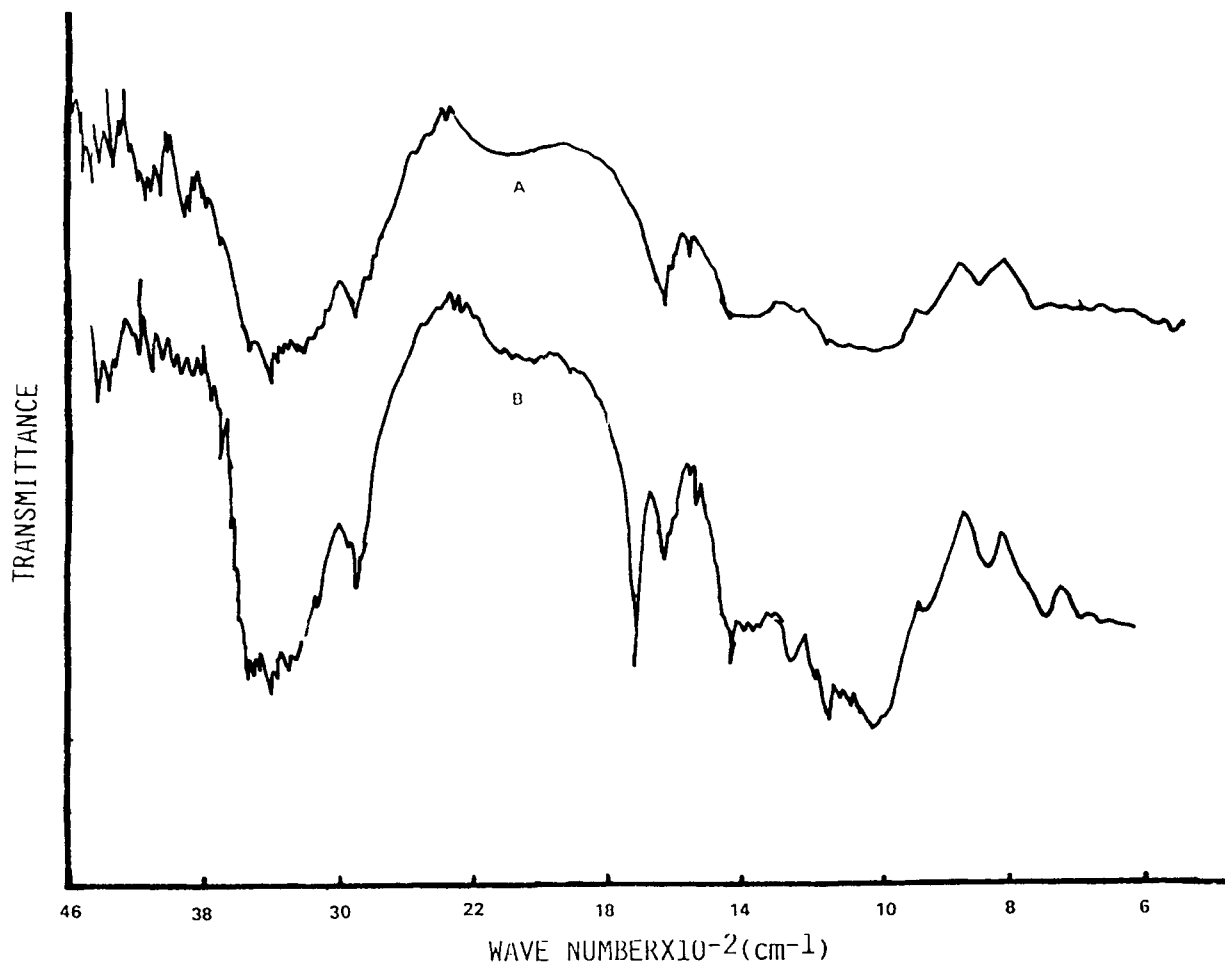

Figure 1 IR spectra of (A) root-starch, (B) graft sample (Starch-g-PMMA).
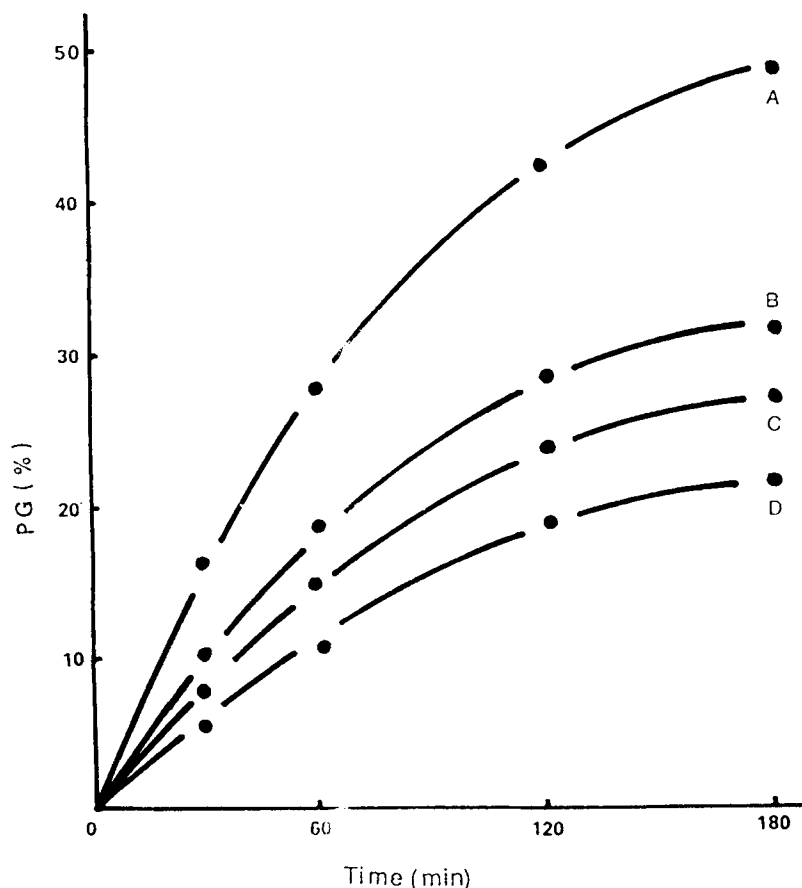
Figure 2   Effect of initiator concentration on grafting. [AGU] = 0.123 mol/L, [MMA] = 0.189 ml/L, [H_2SO_4] = 0.05 mol/L Temp. = 30°C. (A) [Mn(III)] = 3 × 10^{-3} mol/L; (B) [Mn(III)] = 4 × 10^{-3} mol/L; (C) [Mn(III)] = 2 × 10^{-3} mol/L; (D) [Mn(III)] = 1 × 10^{-3} mol/L.

grafting sample (curve B) showed both the characteristic absorption of starch at 3000–3800 cm^{-1} and the characteristic absorption of methy methacrylate homopolymer at 1737 cm^{-1}. This testified the existence of grafting.

Effect of Initiator Concentration

The effects of initiator concentration on the percentage of grafting are shown in Figure 2. It indicated that the PG increased with the increasing of [Mn(III)] at the beginning, and then decreased with further increasing of [Mn(III)] over 3.0 × 10^{-3} mol/L.

Meanwhile, the molecular weight of the grafted side chains was also determined, and the results were listed in Table I. It showed that the molecular weight of the grafted side chains decreased with the increase of an initiator concentration.

Effect of Monomer Concentration

The effects of monomer concentration on PG were illustrated in Figure 3. With the increase of [MMA] from 0.1 mol/L to 0.3 mol/L, the PG increased because of the rising of grafting rate, and a maximum PG was achieved at [MMA] = 0.3 mol/L. With the further increase of [MMA], the chain transfer from starch macroradical onto monomer increased, leading to the lowering of PG. Besides, the PG increased rapidly with the increase of reaction time, and became almost a constant value after reacting 3 h.

Table I   Molecular Weight of PMMA Grafted

[Mn(III)] × 10^3 mol/L	1	2	3	4
M × 10^5	33.4	17.2	7.5	5.2

50

40

PG (%)

30

20

10

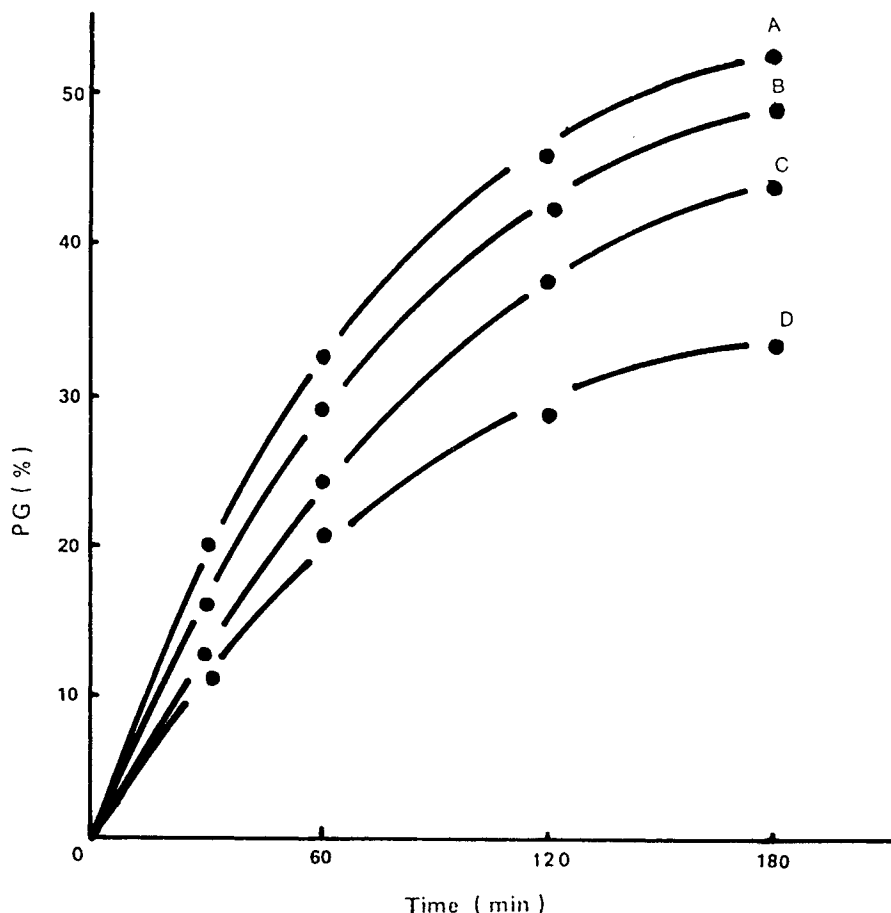0   60   120   180

Time (min)

A
B
C
D

Figure 3 Effect of monomer concentration on grafting [AGU] = 0.123 mol/L, [Mn(III)] = 3 × 10⁻³ mol/L, [H₂SO₄] = 0.05 mol/L, Temp. = 30°C. (A) [MMA] = 0.314 mol/L; (B) [MMA] = 0.189 mol/L; (C) [MMA] = 0.441 mol/L; (D) [MMA] = 0.126 mol/L.

Effect of Canna Starch Concentration

The changes of percentage of grafting and grafting efficiency, with variance of canna starch concentration [AGU] from 0.1 to 0.4 mol/L, were shown in Figures 4 and 5. The PG decreased steadily with [AGU] increasing, owning to the lowering ratio of monomer to canna starch, but the graft efficiency increased with the increase of [AGU] and achieved a maximum value at [AGU] = 0.3 mol/L.

Effect of Reaction Temperature

Reaction temperature is another important reaction condition in the graft copolymerization. The effects of temperature on PG and GE were shown in Figure 6. PG and GE both increased when the reaction temperature changed from 20 to 50°C. Considering our early works,[13] we think it quite possible that the following changes may be occurred with the rise in temperature: (1) improving the swelling capability of canna starch, (2) increasing the diffusion rate of the monomer and initiator onto and into starch granular, (3) raising the rate of grafting.

Kinetics and Mechanism

The rate of graft copolymerization is largely dependent on the concentration of the initiator, monomer, and starch.

Figure 7 showed the effects of the initiator [Mn(III)] on the grafting rate (Rg). The plot of Rg vs. $[Mn(III)]^{1/2}$ is linear.

Similarly shown in Figures 8 and 9, the relationships between Rg and [MMA] and Rg and $[AGU]^{1/2}$ were also linear. Therefore, the following reaction rate equation was established:

$$Rg = K[MMA][Mn(III)]^{1/2}[AGU]^{1/2} \quad \text{(a)}$$

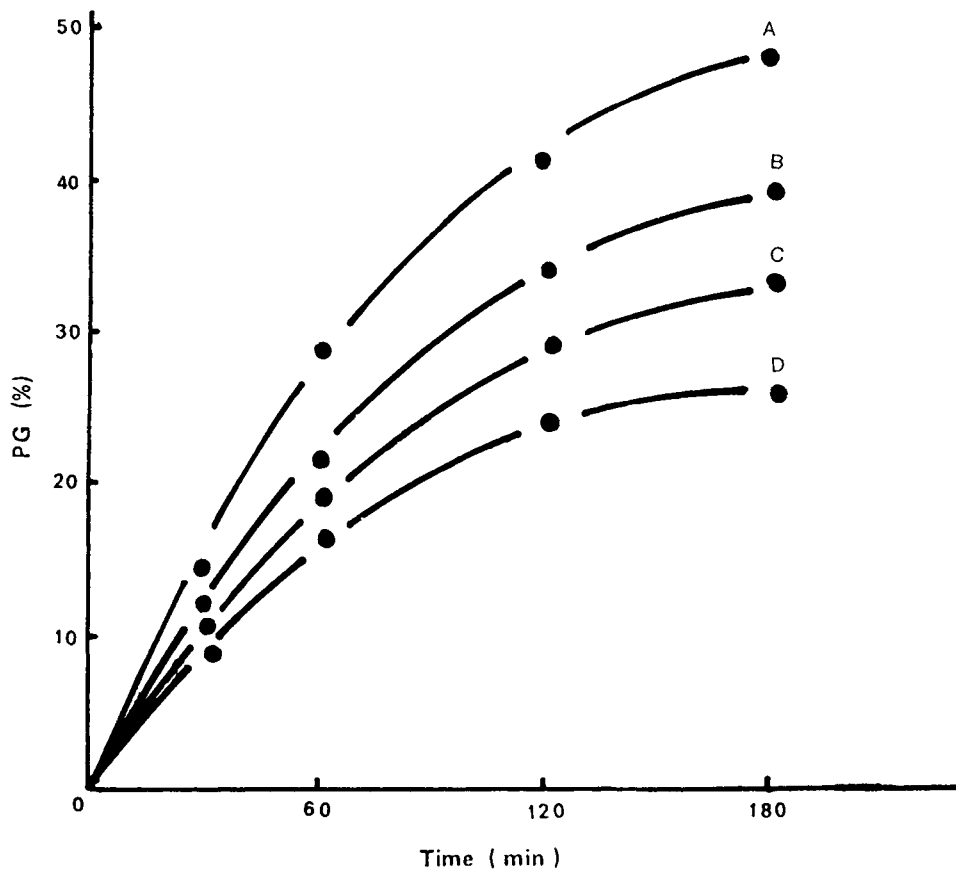**Figure 4** Effect of starch concentration on grafting [MMA] = 0.189 mol/L, [Mn]$^{3+}$ = 3 × 10^{-3} mol/L, [H$_2$SO$_4$] = 0.05 mol/L, Temp. = 30°C. (A) [AGU] = 0.123 mol/L; (B) [AGU] = 0.208 mol/L; (C) [AGU] = 0.288 mol/L; (D) [AGU] = 0.370 mol/L.
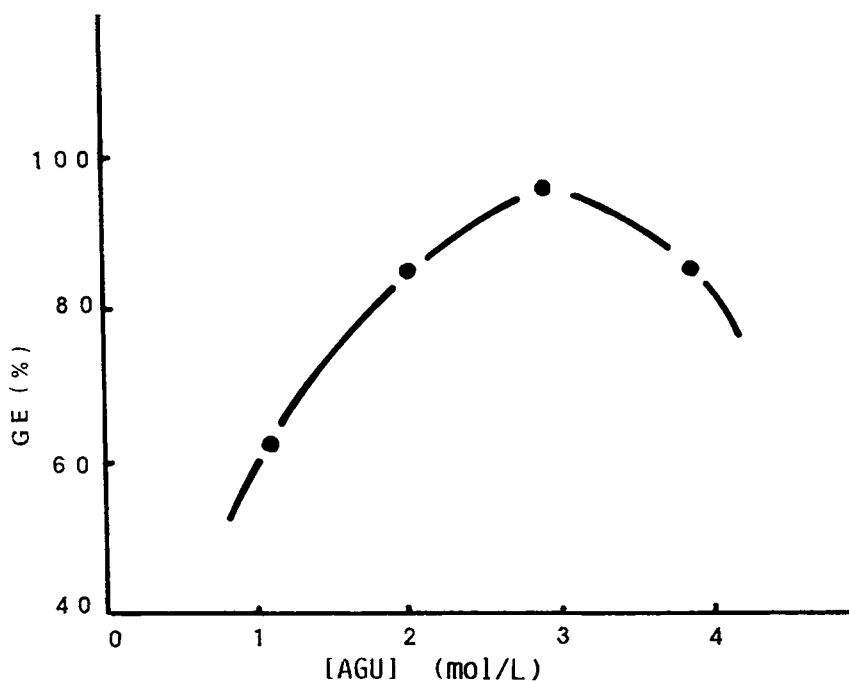

Figure 5 Effect of starch concentration on grafting efficiency; other conditions as in Figure 4.

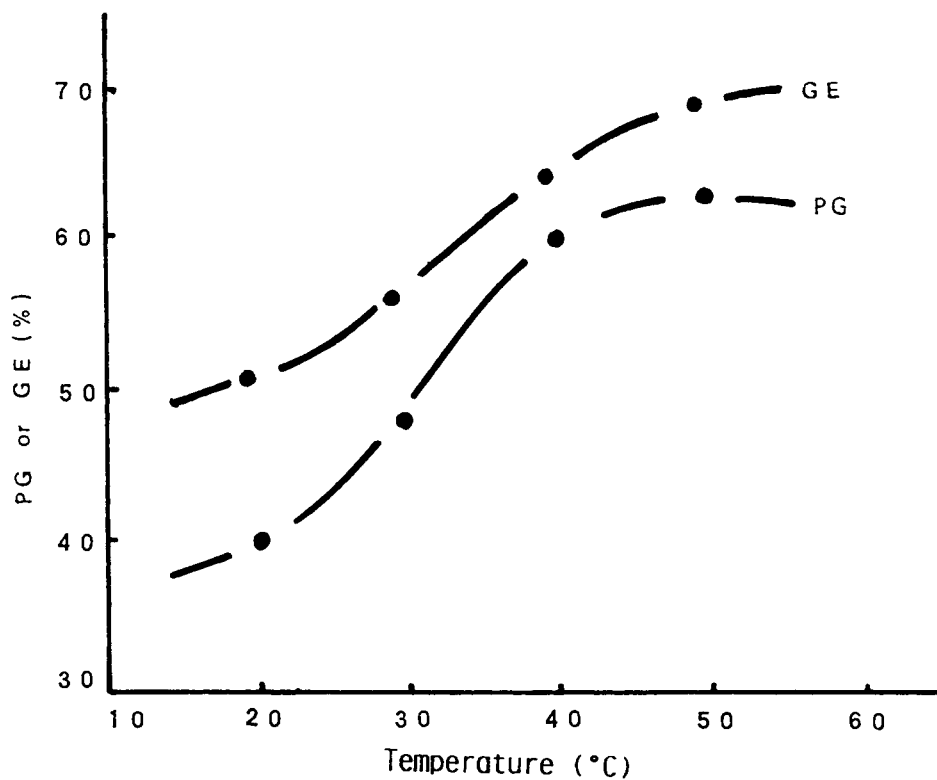**Figure 6**   Effect of reaction temperature [AGU] = 0.123 mol/L, [MMA] = 0.189 mol/
L, [Mn]$^{3+}$ = 3 × 10^{-3} mol/L.
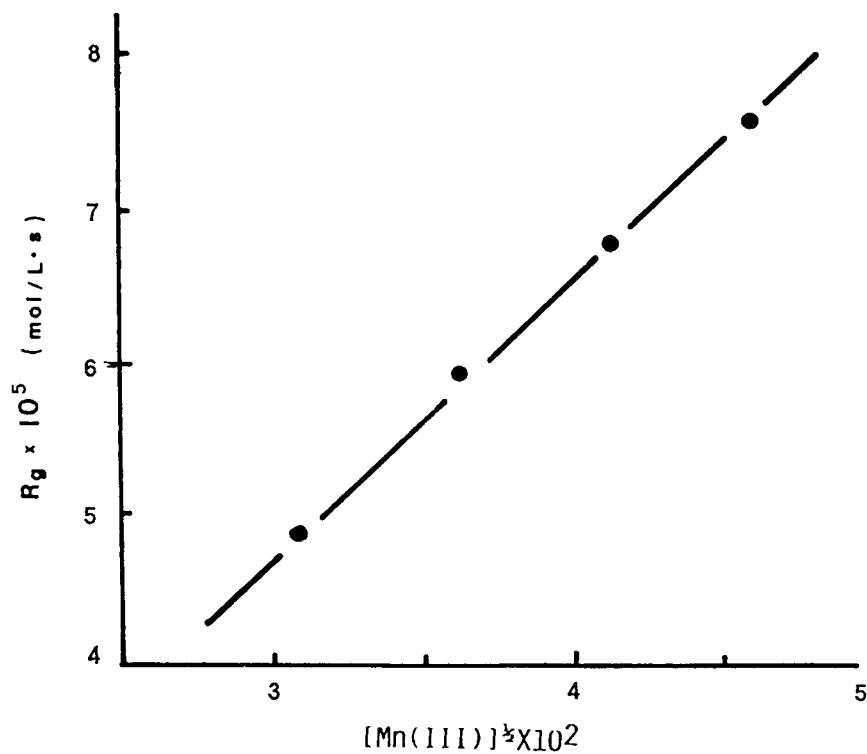
Figure 7   Plot of Rg vs. [Mn(III)]$^{1/2}$. Other conditions as in Figure 2.
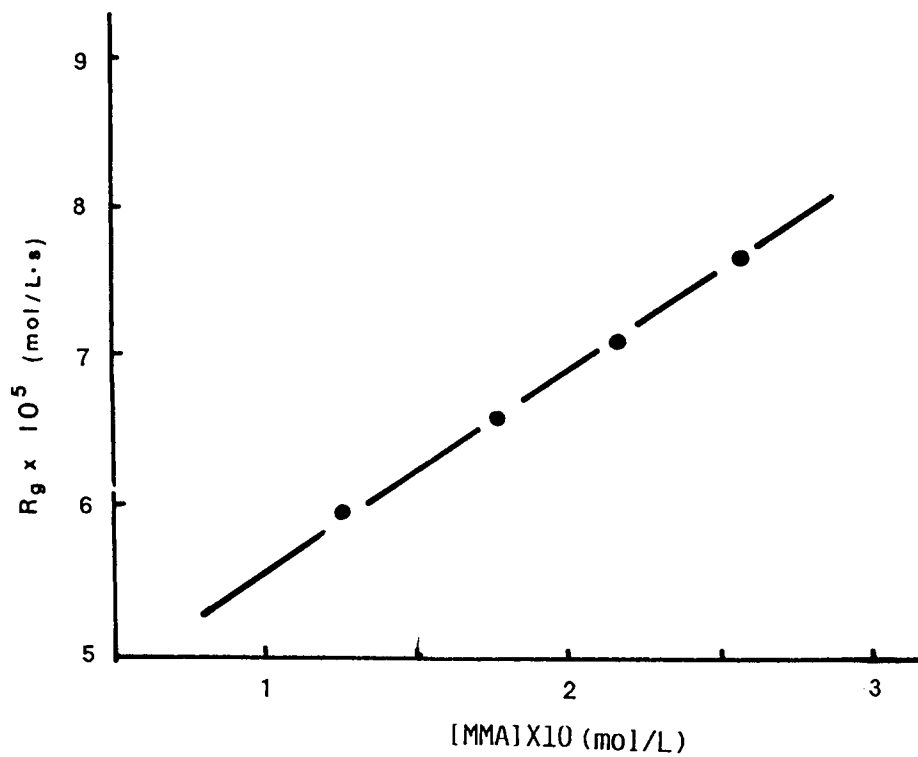
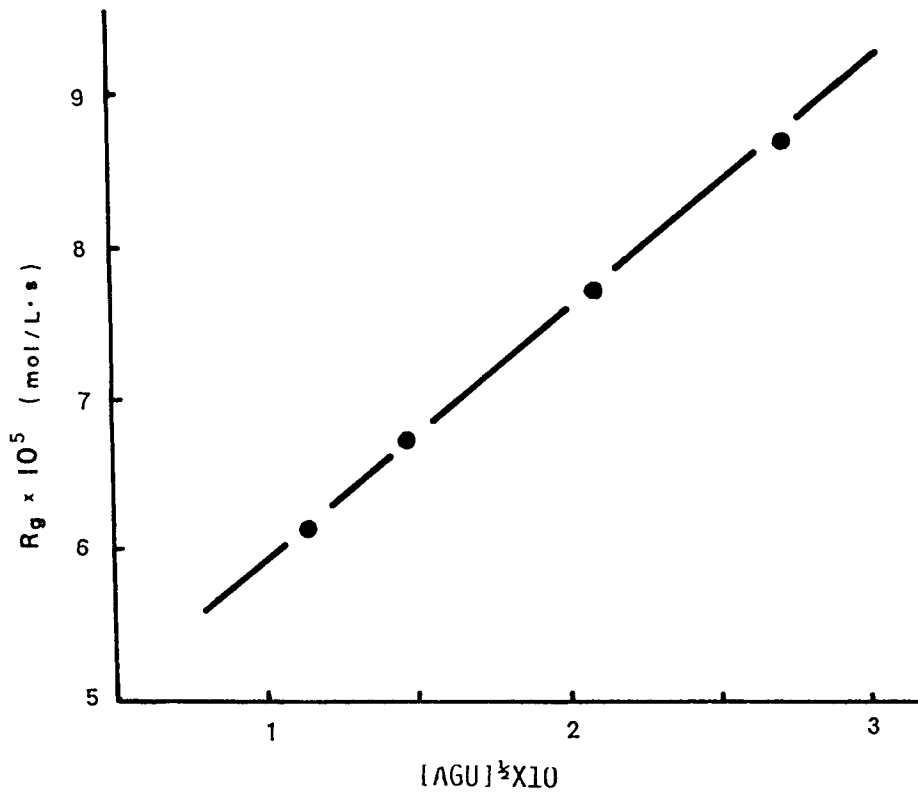**Figure 8**   Plot of Rg vs. [MMA]. Other conditions as in Figure 3.

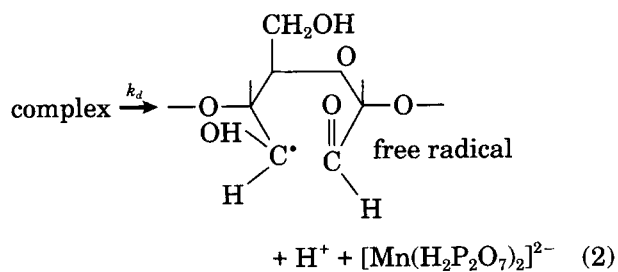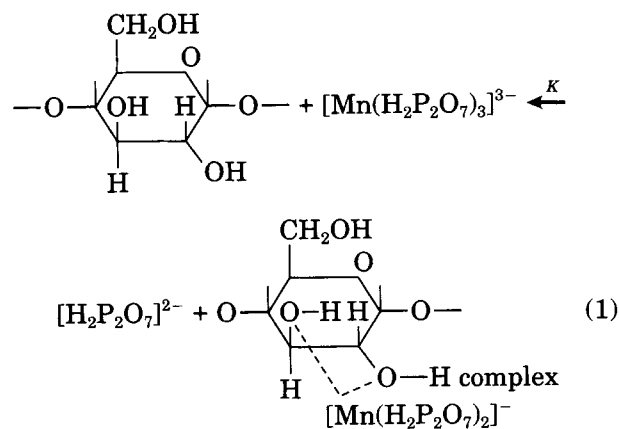**Figure 9**   Plot of Rg vs. $[AGU]^{1/2}$. Other conditions as in Figure 4.

Table II Effect of Temperature on Rg

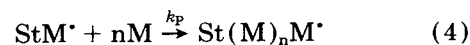| Temperature °C	20	30	40	50
Rg × 10⁵		5.51	7.51	10.5	14.2

For other reaction condtions, see Figure 6.

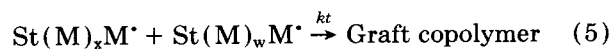The mechanism of grafting reaction was suggested as follows[9]:

Initiation:

$$-O-\overset{CH_2OH}{\underset{H}{\bigcirc}}-O- + [Mn(H_2P_2O_7)_3]^{3-} \overset{K}{\longleftarrow}$$

$$[H_2P_2O_7]^{2-} + O-\overset{CH_2OH}{\bigcirc}-O- \quad (1)$$

complex
$[Mn(H_2P_2O_7)_2]^-$

$$\text{complex} \overset{k_d}{\longrightarrow} -O-\overset{CH_2OH}{\bigcirc}-O- \quad \text{free radical}$$

$$+ H^+ + [Mn(H_2P_2O_7)_2]^{2-} \quad (2)$$

$$St^\cdot + M \overset{k_1}{\rightarrow} StM^\cdot \quad (3)$$

Propagation:

$$StM^\cdot + nM \overset{k_p}{\rightarrow} St(M)_nM^\cdot \quad (4)$$

Termination:

$$St(M)_xM^\cdot + St(M)_wM^\cdot \overset{k_t}{\rightarrow} \text{Graft copolymer} \quad (5)$$

On the basis of the above reaction scheme and three basic hypotheses in free-radical polymerization, the following expressions were derived

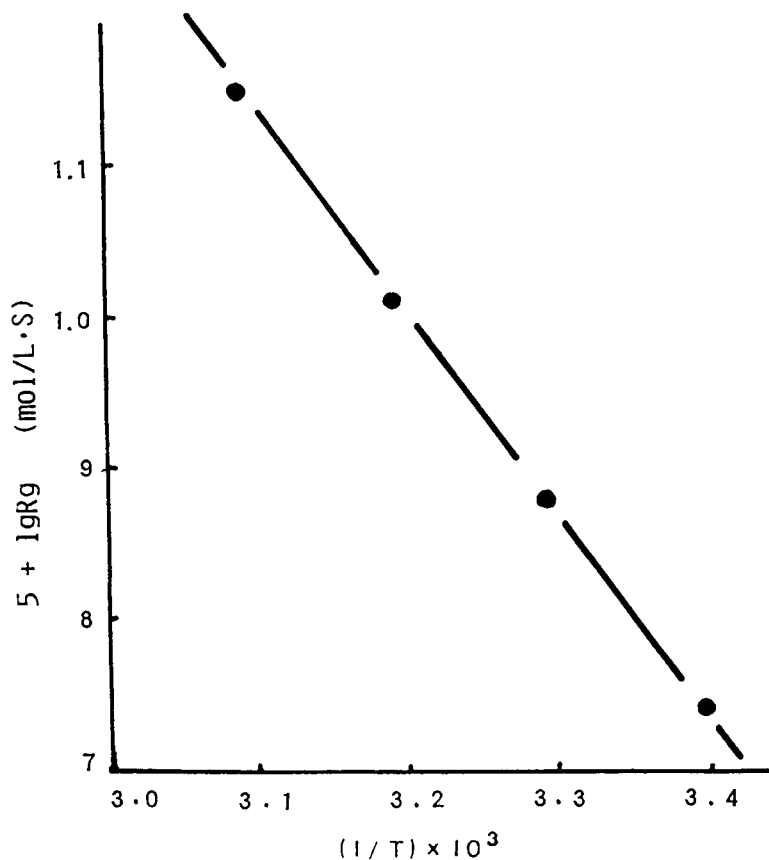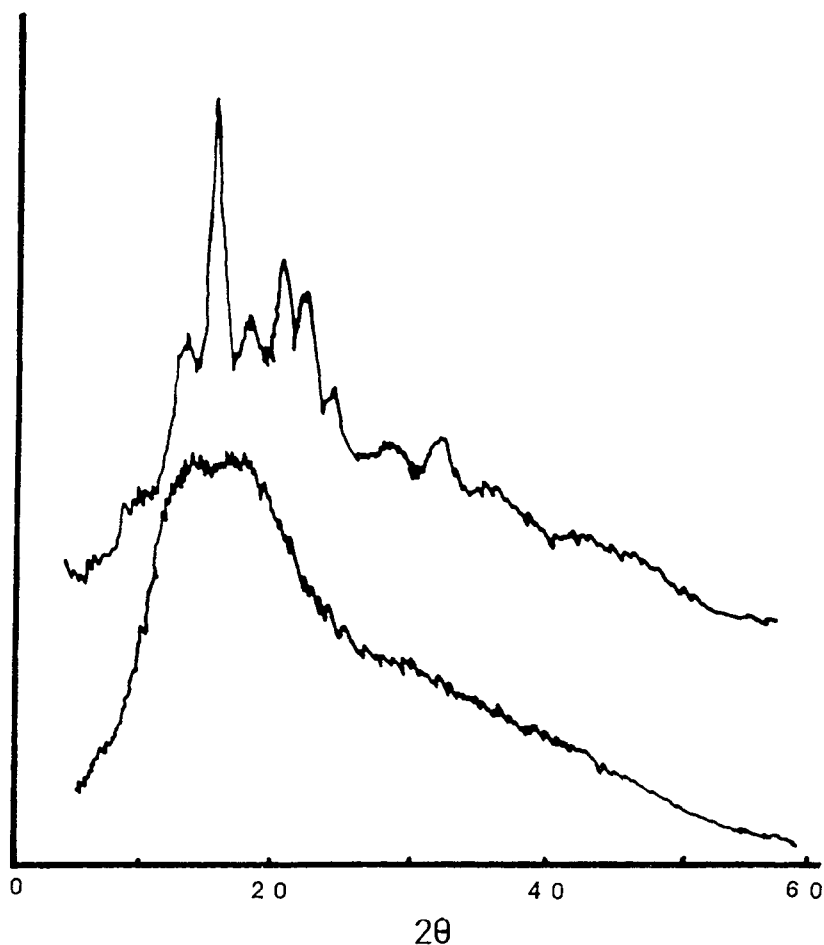**Figure 10** Plot of lgRg vs. 1/T. Other conditions as in Figure 6.

Figure 11   X-Ray analysis. (A) canna starch; (B) starch-g-PMMA.

$$\frac{d[\text{St}^\bullet]}{dt} = Kk_d[\text{St}][\text{Mn(III)}] - k_i[\text{St}^\bullet][\text{M}]$$

$$[\text{St}^\bullet] = \frac{Kk_d[\text{St}][\text{Mn(III)}]}{k_i[\text{M}]} \qquad (6)$$

$$\frac{d[\text{StM}^\bullet]}{dt} = k_i[\text{St}^\bullet][\text{M(III)}] - k_t[\text{StM}^\bullet]^2$$

$$[\text{StM}^\bullet] = \left(\frac{Kk_d[\text{St}][\text{Mn(III)}]}{k_t}\right)^{1/2} \qquad (7)$$

$$Rg = k_P[\text{StM}^\bullet][\text{M}]$$

$$= k_P\left(\frac{Kk_d}{kt}\right)^{1/2}[\text{St}]^{1/2}[\text{M}][\text{Mn(III)}]^{1/2} \qquad (8)$$

Where M, [St], and Mn(III) represent monomer MMA, starch and initiator $[\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3]^3$, respectively, but the [St] was often replaced by [AGU].

Equation (8) is identical with Eq. (a), established from the experiment. This indicated that the reaction mechanism suggested above was acceptable.

Besides, the effect of the reaction temperature on the grafting rate within the range of 20 to 50°C was shown in Table II and Figure 10. According to the Arrhennius equation, the apparent activation energy for graft copolymer (Eg) was obtained:

$$Eg = 27.1 \text{ kJ/mol}$$

Analysis of X-Ray Diffraction and Micropolariscope

Figure 11 is the results of x-ray diffraction analysis of native starch and graft copolymer St-g-PMMA. It can be seen that the x-ray graph of the native starch shows four sharp crystal peaks, but after the starch was grafted with MMA, the four crystal peaks were merged into a smooth peak. This result suggested that the crystal phase was also involved in the grafting reaction except for the amorphous
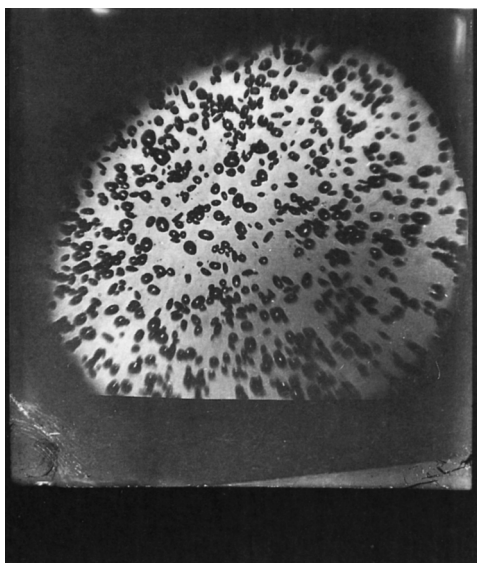
(a)
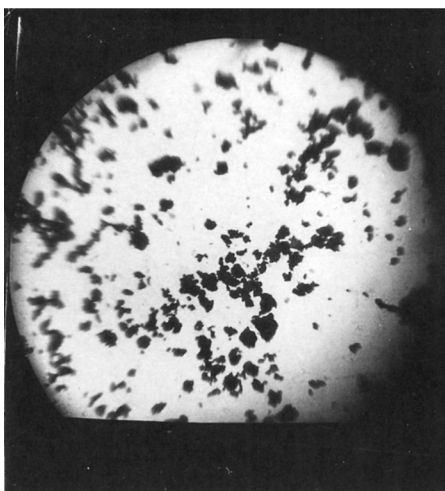
(b)

Figure 12 Analysis of micropolariscope. (A) canna starch; (B) starch-g-PMMA.

phase. This suggestion was also demonstrated by the micropolariscope photos of the native starch and st-g-PMMA, as shown in Figure 12. The photo of the native canna starch showed a deformed polarized crossline, but this crossline disappeared in the photo of St-g-PMMA. This further indicated that the graft reaction was connected with the crystal phase of starch.

**Study of Scanning Electron Microscope**

The SEM photos of canna starch and graft copolymer St-g-PMMA were shown in Figure 13. The photos explained that the granular structure of native canna starch was not maintained after graft copolymerization.

## Determination of the TG Diagram

The thermogravimetric diagrams of starch and St-g-PMMA were measured by a Rigaku-TG-TDA analyzer with the rising rate of 6°C/min. The curves in Figures 14 and 15 showed that the thermostability of St-g-PMMA was similar to that of native canna starch.

CONCLUSION

Manganic pyrophosphate can initiate the graft copolymerization of canna starch with methy methacrylate efficiently, and the PG and Rg can be ad-

051503 10KV X300 100um

(a)

051512 10KV X500 60um
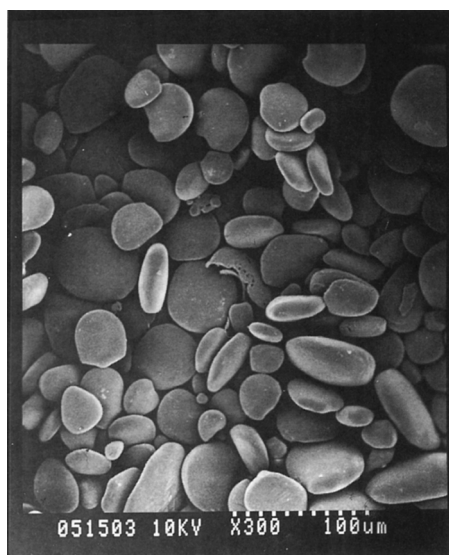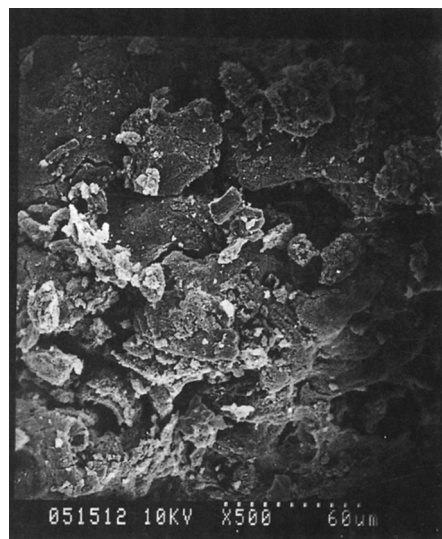
(b)

Figure 13 SEM photos of canna starch and graft sample. (A) canna starch; (B) starch-g-PMMA.
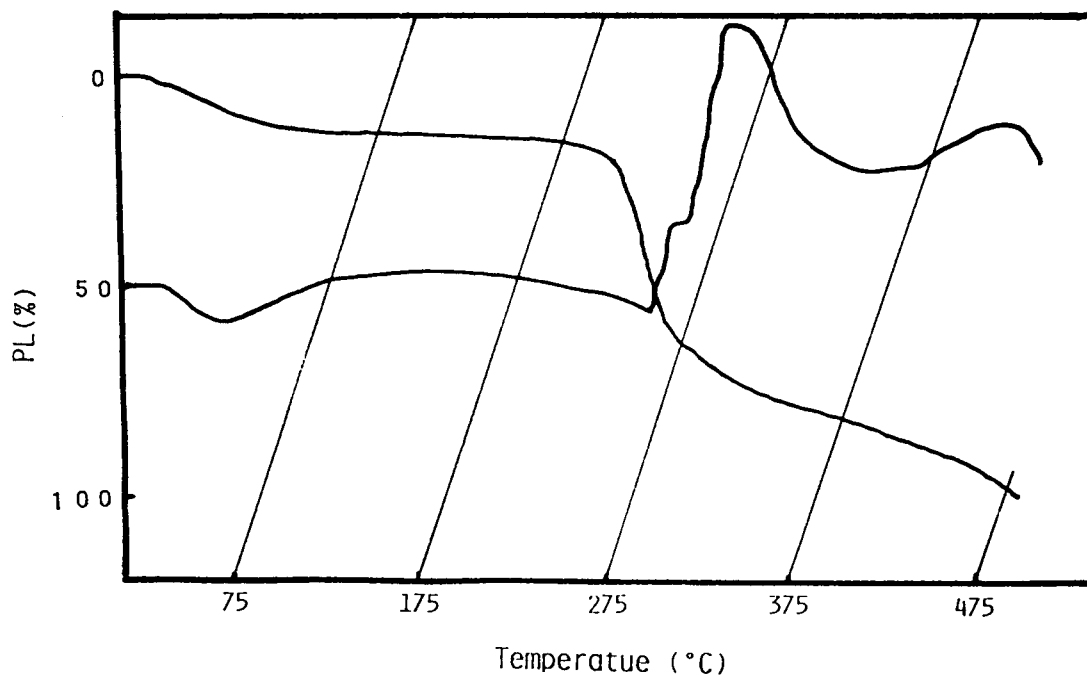
Figure 14   TG analyses of canna starch.

justed by changing the reaction conditions such as reaction temperature, concentration of monomer initiator, and starch.

Under the experiment condition, a suitable rate equation was proposed

$$Rg = K[MMA][Mn(III)]^{1/2}[AGU]^{1/2}$$

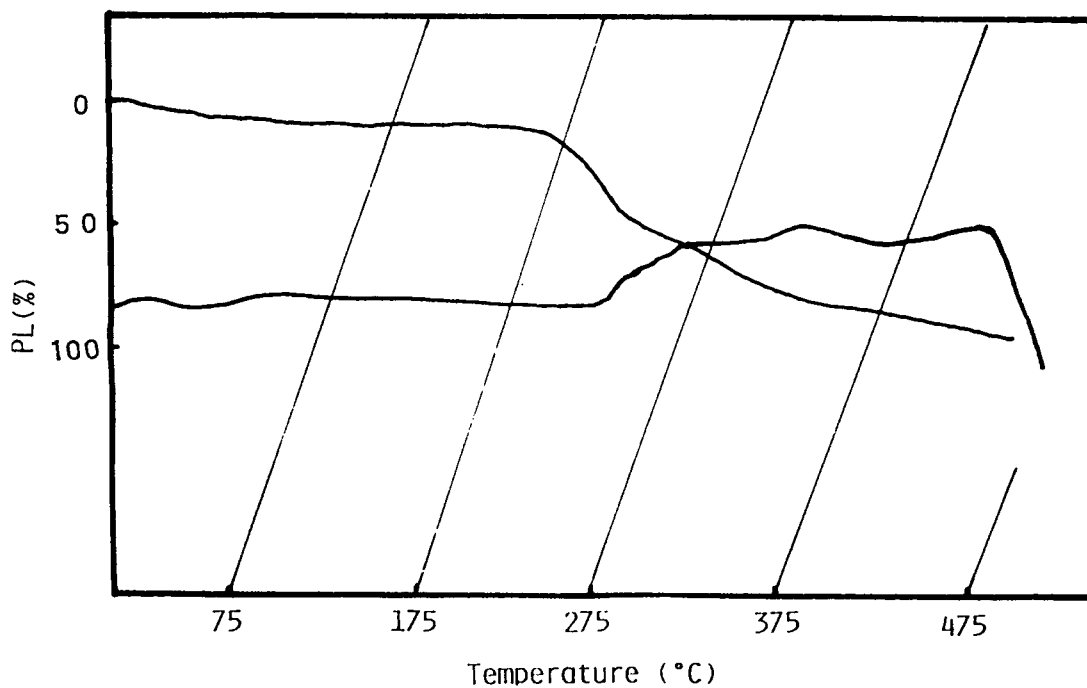and the apparent activation energy was

$$Eg = 27.1 \text{ kJ/mol}$$

Figure 15   TG analyses of starch-g-PMMA.

Not only the amorphous, but also crystal phase of starch was involved in the graft copolymerization.

REFERENCES

1. S. N. Bhattacharyya and Maldas, *Prog. Polym. Sci.,* **10,** 171–270 (1984).
2. O. B. Wurzburg, *Modified Starches,* CRC Press, Inc., Boca Raton, FL, 1980.
3. O. Y. Mansour and A. Nagaty, *J. Polym. Sci., Polym. Chem. Edn.,* **13,** 2785 (1975).
4. M. M. Huge, M. D. Habibuddowla, A. J. Mahmood, and A. J. Mian, *J. Polym. Sci., Polym. Chem. Edn.,* **18,** 1447 (1988).
5. R. C. Khetarpal and K. D. Gill, *J. Macromol. Sci. Chem.,* **A18**(3), 445 (1982).
6. L. A. Gugliemelli, W. M. Doane, C. R. Russell, and C. L. Swanson, *J. Polym. Sci., Polym. Lett. Ed.,* **10,** 415 (1972).
7. B. N. Misra and C. S. Pande, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 2369 (1973).
8. B. N. Misra and L. K. Jassal, *J. Macromol. Sci. Chem.,* **A16,** 1093 (1981).
9. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **21,** 1647 (1977).
10. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **21,** 3407 (1977).
11. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **22,** 2991 (1978).
12. R. C. Tian, J. P. Gao, J. G. Ru, and M. L. Duan, *J. Appl. Polym. Sci.,* **45,** 591 (1992).
13. R. C. Tian and Y. C. Wei, *Acta Polym. Sinica,* **2,** 1 (1990).