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COMPARISON OF TRANSITION METALS IN THE GRAFT COPOLYMERIZATION OF VINYL MONOMERS ONTO STARCH

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Key Words: Transition-metal, Starch Graft-copolymerization

ABSTRACT

The ability to graft acrylonitrile (AN) onto starch initiated by various transition metals such as Mn(VII), Cr(VI), V(V) and Fe(III) were compared in the existence of sulfuric acid in different concentrations. The results showed that the grafting potential of Fe(III) is the lowest, while Mn(VII) is the highest of these transition metals discussed. The catalyzing ability of varieties of acids, including perchloric acid, sulfuric acid, nitric acid and hydrochloric acid, in the graft copolymerization of acrylonitrile onto starch was studied; and the graft ability of monomers such as acrylaniide (AM), acrylic acid (AA) and methyl methacrylate (MMA), was compared. The experimental data indicates that the catalytic abilities of acids are related to their capability of providing protons. The granuluar structure of starch and it's graft copolymer were investigated with scanning electron microscopy, infrared spectroscopy, and thermogravietry.

INTRODUCTION

Graft copolymerization is one of the most efficient methods to modify, natural polymers, especially polysaccharides such as cellulose [1], starch [2] and fiber [3]. Initiator is the key factor that decides the graft efficiency of graft copolymerization of starch, so researchers have been making efforts to discover even more effective ones.

Transition metals and their chelates have attracted considerable attention because they can initiate and produce free radicals directly at the backbone through reactions with active groups of matrix [4-10]. Misra [11] has reported the use of transition metal acetyl acetonate chelates in the graft copolymerization of cellulose with various monomers. In our previous papers we have studied the graft copolymerization of N-vinylpyrrolinone onto gelatin [12], the graft modification of canna starch with methyl methacrylate and pullulan with butyl acrylate using manganic pyrophosphate as an initiator [13,14], the graft capacities of transition metal/thiourea redox systems in the graft copolymerization of starch [15]. As an extension, the present paper will compare the grafting ability of different metal ions in the graft copolymerization of starch with vinyl monomers.

EXPERIMENTAL

Materials

Starch containing 12% water, was provided by Tianjin Red-Flag Starch Plant. Monomers acrylamide (Linhai Chemical Plant), acrylic acid (Beijing Chemical Plant), methyl methacrylate and acrylanitrile (Tianjin Second Chemical Plant) were purified according to standard procedures before use. Other chemicals such as ferric chloride, chromic oxide, potassium permanganate, ammonium metavanadate were all tested and provided by Tianjin Chemical Co.

Manufacture of Starch Graft Copolymer

The slurry dissolved with a weighed amount of starch was poured into a three-neck flask and heated to 70°C. The system was maintained at temperature for half an hour under slow stirring and a N_2 atmosphere, and cooled to 40 °C. Then, the initiators (transifion metal ions), catalyst (acids), and vinyl monomers were added. The reaction mixture was permitted to react under slow stirring for 3 hours during which the flask was filled with N_2 gas. The products were precipitated out with alcohol, filtered, dried, and weighed.

TABLE 1. Extractants for Homopolymers

Homopolymers	PAN[9]	PAA[10]	PMMA[11]	PAM[12]
Extrantants	DMF	Methanol	Acetone	Glucol/glacial acetic acid

The raw graft products contained homopolymers formed during the graft copolymerization, and they were extracted from graft copolymers with extractants for several hours. The extractants pertinent to the different homopolymers and extracting conditions are listed in Table 1.

Calculation of Parameters

The percentage of grafting (PG) of graft copolymers, grafting efficiency (GE) of graft copolymerization and percent conversion of monomer (PC) were calculated by weighing the original starch and grafting products

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

$$GE(\%) = \frac{\text{weight of grafted polymer branch}}{\text{weight of monomer reacted}} \times 100$$

$$PC(\%) = \frac{\text{weight of monomer reacted}}{\text{weight of monomer added}} \times 100$$

Analysis of Graft Copolymer

The thermogravimetry of starch and starch graft copolymers were tested with a RigakuTG-TDA thermogravimeter. Infrared spectrum (IR) analysis is one of the effective methods to detect the reaction and formation of functional groups, and the IR spectra of starch and purified graft copolymers were determined with a 170 SXFT-IR spectrometer, and the photographs of scanning electron microscope of the starch samples were tested with a Hitachi X-650 scanning electron microscope after spraying with gold.

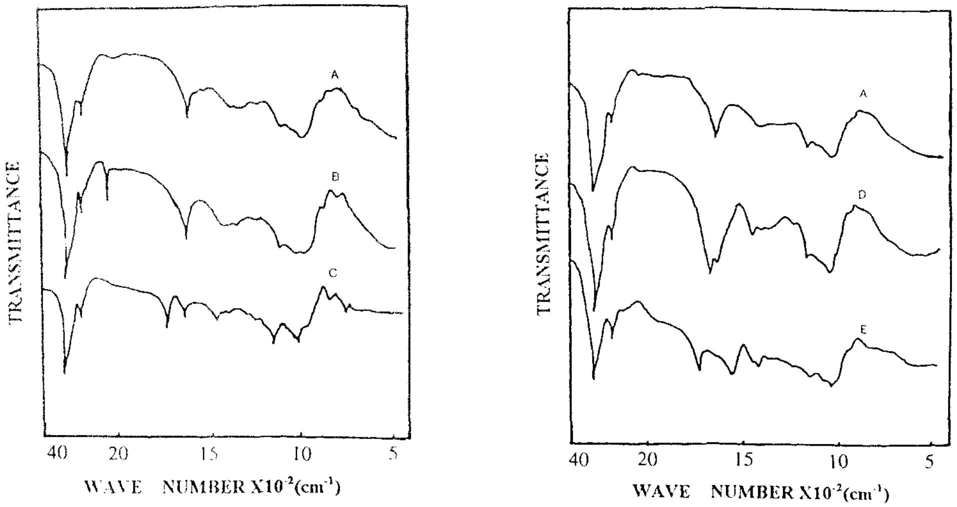


Figure 1. IR spectra of native corn starch (a), starch-g-PAA (b), starch-g-AM (c), starch-g-PMMA (d), starch-g-PAN(e).

RESULTS AND DISCUSSION

Proof of Graft Copolymerization

The IR spectra of starch (A) and starch graft copolymers starch-g-PAN (B). starch-g-PNMA (C), starch-g-PAM (D), starch-g-PAA (E) are shown in Figure 1. By observation, we found that the purified graft copolymers have both the characteristic absorption bands of starch and the characteristic bands of the corresponding branch polymers. This proves the existence of graft coplymerization.

Comparison of Transition Metal Ions in Grafting Acrylonitrile onto Starch

The capacities of transition metal ions, Mn(VII),Cr(VI), V(V) and Fe(IR), in initiating graft copolymerization of starch with acrylonitrile at two different sulfuric acid concentrations were studied. The experimental results are illustrated in Figure 2 with a sulfuric acid conentration of $5x10^{-2}$ mol/L, and Figure 3 with the concentration of $2x10^{-2}$ mol/L. By comparing data in the figures, we found that with the grafting percentage and efficiency there existed a maximum value with increasing the initiator concentration at two different acid concentrations for each of the four transition metal ions. The maximum values of PG and GE occurred at the same initiator concentration for each of the ions though the metal ions have different valences and properties. But the initiator concentration that corresponded to the

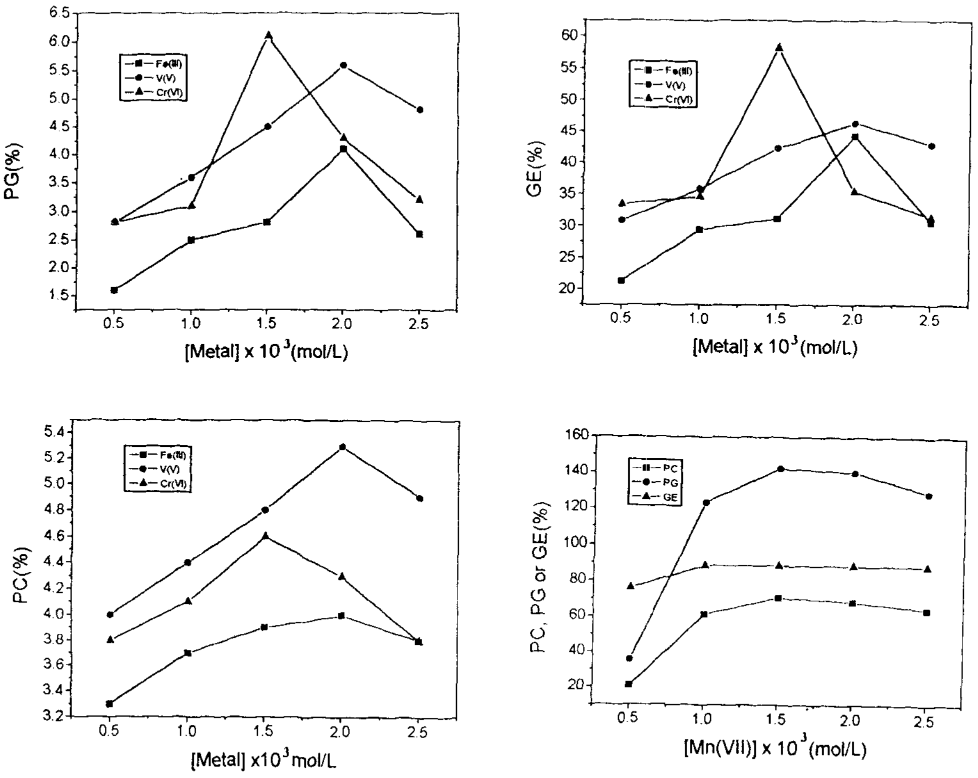


Figure 2. Effect of initiators on grafting. [AGU] = 0.1086 mol/L, [AN] = 0.7595 mol/L, [H$^+$] = 4x10^{-2}, Temp. = 40°C, time = 3 hours.

maximum value depended on the initiators. Evidently, V(V) was at a concentration of 1.5x10^{-2} mol/L, but the other three ions, Mn(VII), Cr(VI) and FE(III), were at the same concentration of 2x10^{-2} mol/L, which did not vary when sulfuric acid concentration changes from 5x10^{-2} mol/L to 2x10^{-2} mol/L. For each metal ion, the grafting percentage and efficiency trends were similar, and the PG and GE of the ions Fe(III), V(V), Cr(VI) were hardly affected by the decreasing of the sulfuric acid concentration with the exception of Mn(VU). Its maximum value of PG decreased over 20% as the sulfuric acid concentration decreased from 5x10^{-2} mol/L to 2x10^{-2} mol/L. Generally, the grafting abilities of Cr(VI), V(V), Fe(III) were similar and much lower than that of Mn(VII).

The above results indicate that the initiating abilities of the transition metal ions were different, and could be attributed to the redox potential of the transition

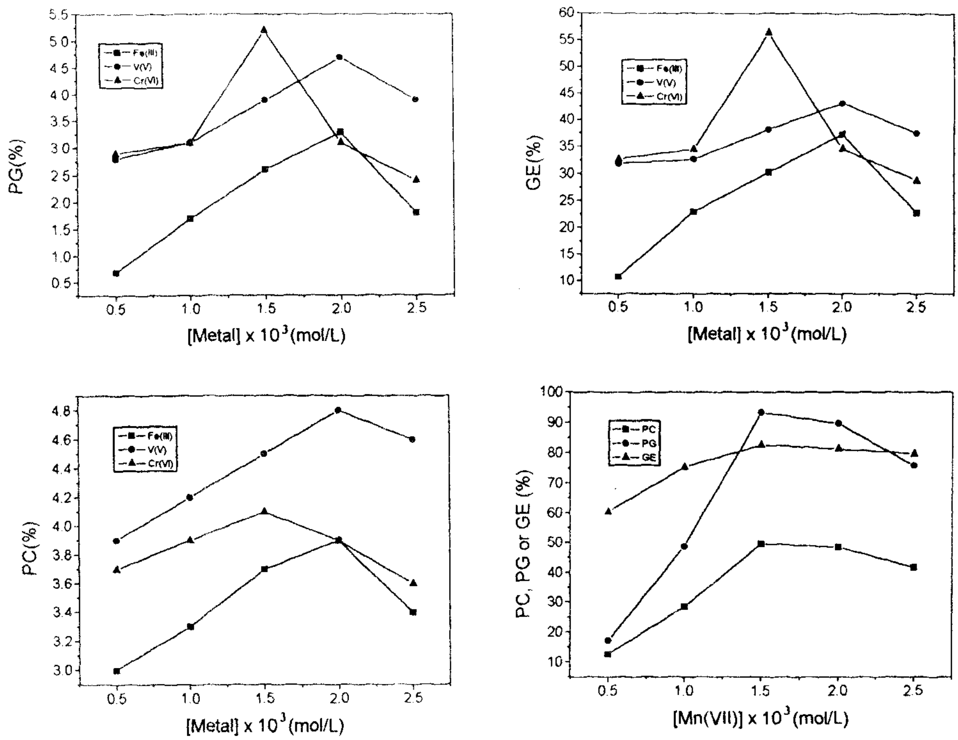


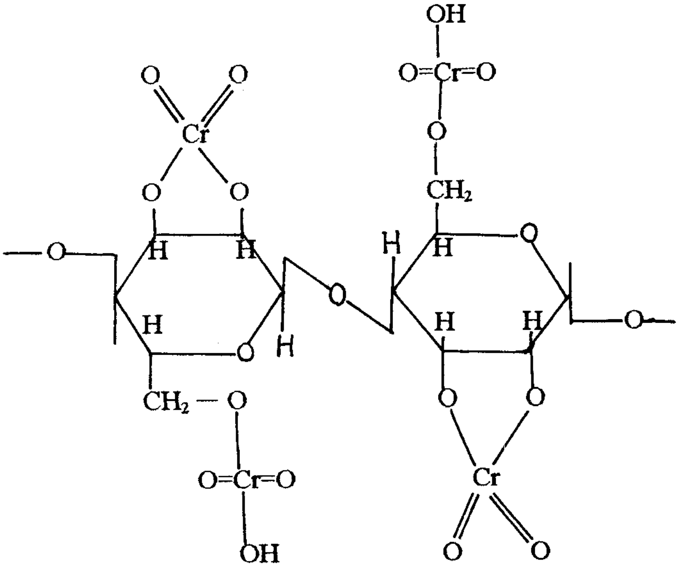
Figure 3. Effect of initiators on grafting. [AGU] = 0.1086 mol/L, [AN] = 0.7595 mol/L, $[H^+] = 10x10^{-2}$, Temp.= 40°C, time = 3 hours.

TABLE 2. Normal Redox Potential (NRP) of the Metal Ions

Redox	Mn^{7+}/Mn^{2+}	$Cr_2O_7^{2-}/Cr^{3+}$	VO_2^{+}/VO^{2+}	Fe^{3+}/Fe^{2+}
NRP	1.51	1.33	1.00	0.77

metals. Metal ions reacted with hydroxide groups and form free radicals directly on the starch backbone.

Evidently, the higher the redox potential of the metal ion, the greater the quantity the free radicals yielded by the above reaction. The numerous free radicals led to a chance of colliding monomers with the reaction site and a higher rate of graft copolymerization. The normal redox potential of the four metal ions are listed in Table 2. The redox potential of Mn(VII)/Mn(II) is the highest of the four metals, and this might provide an explanation as to why the initiating ability of Mn(VII) is higher than the other three metal ions. The ion Cr(VI) did not show a higher grafting ability than that of Fe(III), even though the redox potential of the former is much higher than that of the latter. This fact proved that the ion Cr(VI) could react, in acid medium, with starch and form a complex described below [8].



It is difficult for the complex to decompose in lower temperature. This also explains why the MnO_4^-/Mn^{2+} and CrO_7^{2-}/Cr^{3+} are so great, even though the between their redox potential is not significant.

The Catalytic Ability of Acids in the Graft Copolymerization of Acrylonitrile with Starch

Acids are effective catalysts that increase the initiating ability of transition metal ions in the graft copolymerization of vinyl monomers onto natural polymers such as starch, cellulose and gelatin. The effect of acids, including HCl, HNO_3, H_2SO_4 and $HClO_4$, on the reaction are different and the results at two acid concentrations are shown in Figure 4(a) with $[H^+]=4x10^{-2}$ and Figure 4(b) with $[H+=10X10^{-2}$. The data implies that the catalytic ability of the four acids is:

$$HCl < HNO_3 < H_2SO_4 < HClO_4$$

The catalytiic ability rose when the concentrations of the acids were increased, which is related to the potential to provide protons of the acids.

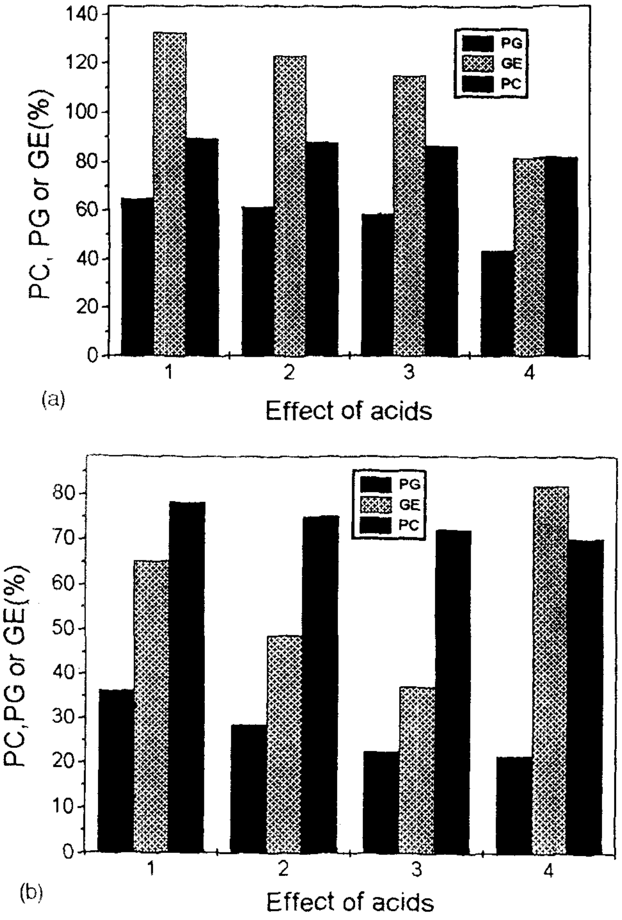


Figure 4. Catalytic ability of acids. (a) $[H^+] = 4 \times 10^{-2}$, (b) $[H^+] = 10 \times 10^{-2}$ Temp. = 40°C $[Mn(VII)] = 2 \times 10^{-3}$ mol/L, [AGU] = 0.1086 mol/L, [AN] = 0.7595 mol/L, time = 3 hours.

1. $HClO_4$, 2. H_2SO_4, 3. HNO_3, 4. HCl

Comparison of Monomers in the Graft Copolymerization with Mn(VII) as an Initiator

The graft of acrylonitrile, methyl methacrylate, acrylic acid and acrylamide onto starch, at two acid concentrations, under the same reaction conditions using Mn(VII) as an initiator, was studied, and the results are illustrated in Figure 5. The results indicate that different monomers did not show the same grafting ability, and the ability of the four monomers is:

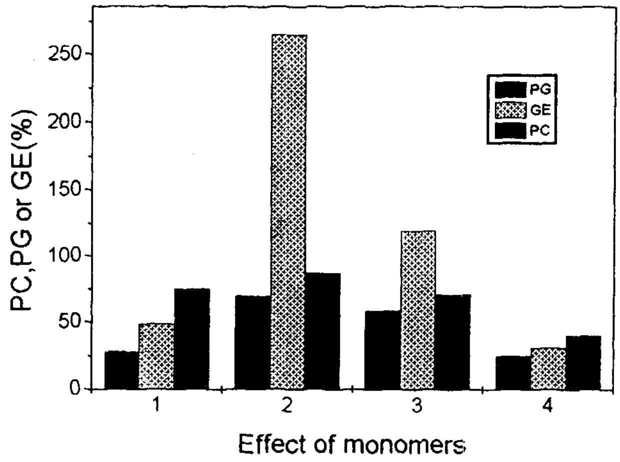


Figure 5. Initiating ability of monomers. [Mn(VII)] = 2 x 10^{-3} mol/L, [AN] = 0.7S9Smol/L,
Temp. = 40°C, time = 3hours.
1. AN, 2. MMA, 3. AM, 4. AA.

AA < AM < AN < MMA

The reason is not clear, it might be due to the formation of the complex between monomer and starch, which became convenient for the monomers to diffuse to the matrix of starch molecules, and consequently, help the monomers locate the reaction sites. The four monomers can form complexes with starch according to References 5 and 6 (Figure 6). But the capability of supplying an electron as a donator of the four monomers is in the following order:

MMA > AN > AM > AA

Evidently, the stability of complexes is in the same order, which makes the monomers exhibit a different grafting ability.

I > II > III > IV

Analysis of Scanning Electron Microscope (SEM) and Thermogravity (TG)

The SEM photos of native starch and its graft copolymers starch-g-PMMA, starch-gPAA, starch-g-PAN, starch-g-PAM are shown in Figure 7. The

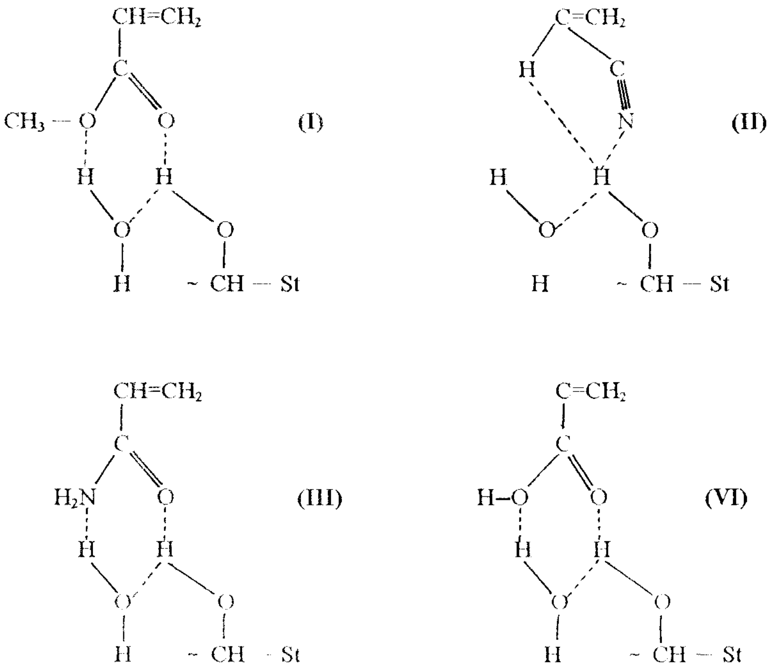


Figure 6. Complexes of starch with monomers.

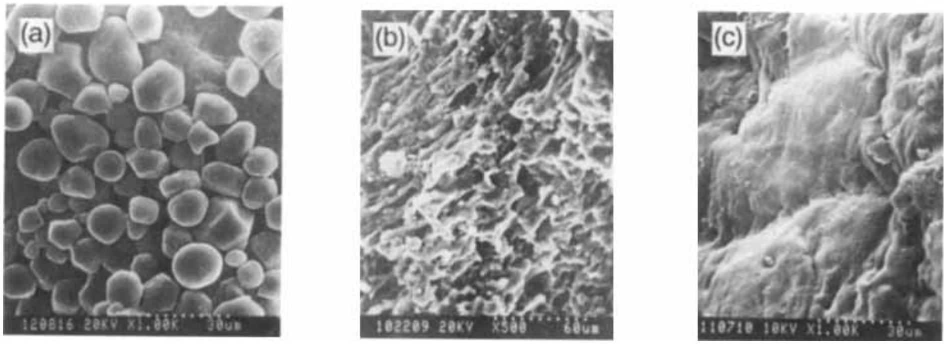


Figure 7. SEM of starch (a), starch-g-PAA b), starch-g-AM (c), starch-g-PMMA (d), starch-g-PAN (e).

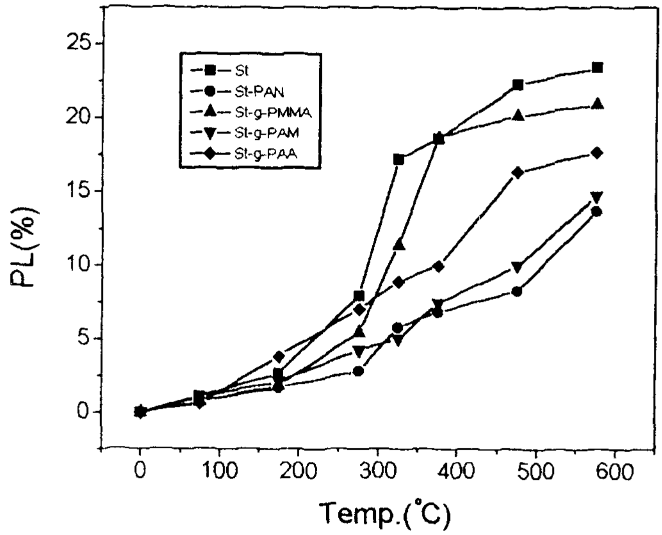


Figure 8. Thermogravities of samples.

starch granules were partly destroyed during the graft copolymerization and the grafted branch chains attached to the starch surface. The thermogravity diagrams of the native starch and four graft copolymers with different kinds of branch chains are illustrated in Figure 8. The curves tell us that the anti-thermal properties of the starch are improved after it grafted with monomers, and the thermal stability was arranged in the following order. This improvement is favorable for the graft copolymers to be used as biodegradable materials.

St-g-PAN > St-g-PAM > St-g-PAA > St-g-PMMA > St

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