

Synthesis and Biodegradation of St-g-poly(MMA-co-VAc) Initiated by Manganic Pyrophosphate*

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Methyl methacrylate(MMA) and vinyl acetate(VAc) were grafted onto corn starch with manganic pyrophosphate{[Mn(H₂P₂O₇)₃]³⁻} as the initiator and water as the reaction medium. The influences of reaction conditions, including pH value, initiator concentration, monomer concentration and its composition, on percent grafting and grafting efficiency were investigated. The graft copolymer was characterized by means of IR spectroscopy, scanning electron micrograph(SEM) and ¹H NMR spectroscopy. The biodegradation experiment showed that the degradation of corn starch-g-poly(MMA-co-VAc) was mainly from starch. However, after poly VAc in the side chain was transformed into poly vinyl alcohol(PVA), both starch and the grafted side chain could be degraded completely.

Keywords Starch, Graft copolymerization, Manganic pyrophosphate, Biodegradation

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Introduction

Starch is an abundant natural resource which is renewable and biodegradable. The graft copolymerization of starch with some vinyl monomers presents a potential way for the production and application of biodegradable materials, thereby protecting the environment. Various initiators can be used to prepare starch graft copolymers. Ceric ions are efficient but costly^[1]; persulfates are nontoxic and low-cost but inefficient^[2]; in some redox systems it is difficult to determine the suitable proportion of oxidant to reductant^[3]. Comparatively, manganic pyrophosphate is an efficient initiator with good selectivity, low cost and few side reactions. Accordingly, it can be used instead of the expensive ceric ammonium nitrate(CAN) in mass production^[4].

In our study, MMA was grafted onto corn starch because of the transparency of poly(MMA)(PMMA). However, it was confirmed that only the starch portion of this copolymer could be biodegraded while PMMA portion could not. In order to make PMMA portion degraded, poly VAc(PVAc) segments were introduced into the side chain by copolymerizing VAc with MMA. PVAc could be

transformed to PVA under alcoholysis or fungal attack, and PVA could be easily biodegraded. Thus, the degradation of the grafted side chain could be improved greatly. This article presents the first successful attempt to graft the copolymer of MMA and VAc onto corn starch by [Mn(H₂P₂O₇)₃]³⁻ initiation and biodegradation of corn starch-g-P(MMA-co-VAc), the results are satisfying.

Experimental

1 Materials

Corn starch(Food grade) was dried at 80 to a constant weight. MMA, from Beijing Chemical Reagent Company, was washed with a 5% sodium hydroxide solution and distilled water before distillation at a reduced pressure in the atmosphere of nitrogen, to remove the inhibitor hydroquinone. VAc was distilled at atmospheric pressure through a 30 cm Vigreux column. Both the monomers were stored in a refrigerator for future use. The initiator was prepared according to literature[4]. Peptone was supplied by Shanghai Medical Factory, and bacillus subtilis from the Biology Department of Henan Normal University.

2 Grafting Procedure

Dried starch(2 g) was dispersed in 70 mL of

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acidified water in a four-necked flask, preheated at 80 °C under the atmosphere of N₂ for 30 min then cooled to the desired temperature. The initiator solution of 10 mL was added to the reaction vessel, followed by the addition of VAc. Five minutes later, MMA was dropped into the mixture within 30 min. The reaction was carried out under the atmosphere of nitrogen for 4 h. At the end of the reaction, the mixture was poured into ethanol, washed with ethanol and distilled water, filtered, dried and weighed. The crude product was extracted with acetone in a Soxhlet apparatus for 48 h to remove homopolymers PMMA, PVAc and copolymer P(MMA-co-VAc).

3 Acid Hydrolysis of Graft Copolymer

The starch grafted copolymer (approximately 1 g) was weighed accurately and hydrolyzed in 150 mL of 0.5 mol/L hydrochloric acid solution at 95–97 °C for 3 h, all the starch went into the solution, leaving behind the grafted side chain. The percentage of grafting and grafting efficiency were calculated by means of the following equations:

$$G(\%) = m [\text{P(MMA-co-VAc) grafted}] / m(\text{starch reacted}) \times 100$$

$$E_g(\%) = m [\text{P(MMA-co-VAc) grafted}] / m(\text{monomer reacted}) \times 100$$

4 Biodegradation

Corn starch-g-P(MMA-co-VAc) ($E_g = 60\%$) and the correspondent side chains were used as samples. The graft copolymer with 5% poly-chloroethylene was dissolved in dimethylsulfoxide then spread on the sheet of polytetrafluoroethylene to obtain a film. The grafted side chain was dis-

solved in acetone and made into a film in the same manner^[5].

4.1 The Degradation of Corn Starch-g-P(MMA-co-VAc) and the Side Chain

Peptone of 0.5 g, 0.25 g beef grease and 0.5 g sodium chloride were dissolved in 100 mL of distilled water. The pH value of the solution was adjusted to 7 with NaOH. *Bacillus subtilis* together with 0.5 g grafted copolymer or the side chain were added to the solution at room temperature.

4.2 Degradation of Corn Starch-g-poly(MMA-co-VAc) (VA Refers to Vinyl alcohol).

Corn starch-g-P(MMA-co-VAc) of 1 g was added to 20 mL of a 5% NaOH solution of methanol and stirred for 12 h at room temperature. PVAc in the side chain changed into PVA. The product was dispersed in 500 mL of natural water and put in a shady place.

Results and Discussion

1 Identification of Grafting

Table 1 shows the IR spectral data of corn starch, starch-g-P(MMA-co-VAc) and grafted side chain. It could be seen that the grafted starch shows both the characteristic absorption of starch at 3800–3000, 850, 750 cm⁻¹ and that of carbonyl at 1735 cm⁻¹; the grafted side chain shows both the characteristic absorption of PMMA at 1243, 1192, 1149 cm⁻¹ and that of PVAc at 1375, 1243, 1022 cm⁻¹[6,7]. It could also be seen from the SEM photos (Fig. 1) that the surface of starch was smooth and it is granular while the surface of St-g-P(MMA-co-VAc) was rough and irregular. Again the incidence of grafting was testified.

Table 1 IR spectra data

Sample	$\tilde{\nu}$ cm ⁻¹
Starch	3720–3040, 2930, 1630, 915, 850, 755, 560
St-g-P(MMA-co-VAc)	3720–3060, 2931, 1735, 1638, 1378, 1245, 1154, 1022, 932, 856, 762, 707
P(MMA-co-VAc)	3420, 2999, 2952, 2854, 1735, 1447, 1378, 1243, 1192, 1149, 1076, 1022,

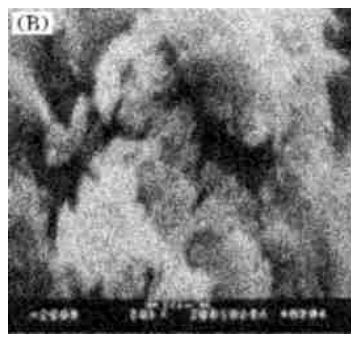
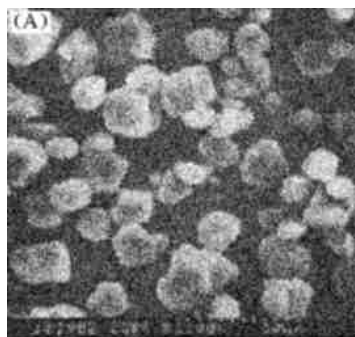
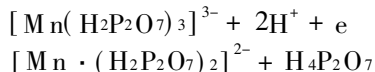


Fig. 1 SEM images of corn starch(A) and St-g-P(MMA-co-VAc)(B).

2 pH Values

Fig. 2 shows the effect of pH values on G and E_g . On the one hand, when pH is below 2.7, a poor grafting yield is obtained. This could be ascribed to the following reaction of initiator:



The newly produced $\text{Mn}(\)$ ions have no initiating ability. Besides, the excessive H^+ holds back the production of the starch free radicals, whereas the starch free radicals are the key to produce starch graft copolymers. High acid concentration also leads to partial hydrolysis of starch and the monomers. On the other hand, when pH is over 4.0, G and E_g are low because oxidation-reduction potential of Mn^{3+} is reduced, the initiating efficiency decreases accordingly. The proper range of pH values is between 2.7 and 4.0.

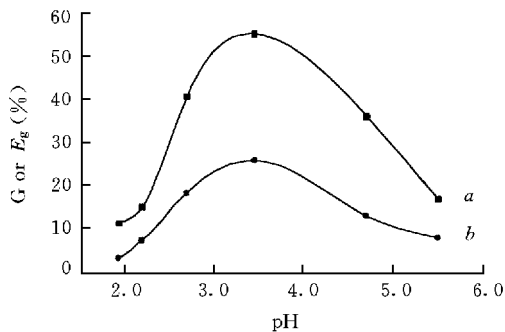


Fig. 2 Effect of pH values on $G(a)$ and $E_g(b)$.

3 Initiator Concentration

Fig. 3 shows the effect of initiator concentration on G and E_g . When $[\text{Mn}^{3+}]$ is below 0.2×10^{-3} mol/L, G and E_g are low because of the poor reacting rate. With the increase of $[\text{Mn}^{3+}]$ from 0.2×10^{-3} mol/L to 0.8×10^{-3} mol/L, G and E_g increase and reach the maximum. The decrease in the grafting yield, when $[\text{Mn}^{3+}]$ is over 0.8×10^{-3} mol/L, might be due to the acceleration of homopolymerization and terminal reactions.

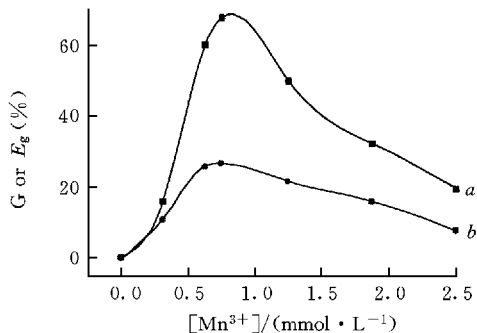


Fig. 3 Effect of $[\text{Mn}^{3+}]$ on $G(a)$ and $E_g(b)$.

4 Monomer Concentration and Its Composition

Fig. 4 shows the effect of the total monomer concentration on the grafting. G and E_g increase as the monomer concentration is increased, *i.e.*, the increase of local monomers in or around the swollen starch granules. With further increase of the monomer concentration, G and E_g decrease because of the enhanced rate of the homopolymerization. Further studies also disclosed that with increasing MMA content in the two monomers, G and E_g increase rapidly and reach almost a constant value when the molar ratio of MMA to VAc is over 60/40, as is shown in Fig. 5. This is due to the different competitive polymerization rate (r) between MMA and VAc. For example^[8], at 60, $r_{\text{MMA}} = 20$, $r_{\text{VAc}} = 0.015$, which shows that MMA is much more active than VAc.

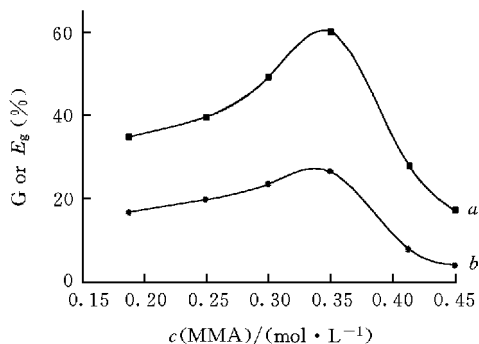


Fig. 4 Effect of monomer concentration on $G(a)$ and $E_g(b)$.

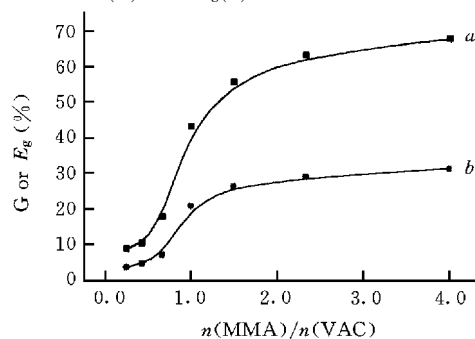


Fig. 5 Effect of molar ratios of MMA to VAc on $G(a)$ and $E_g(b)$.

5 Composition of Grafted Side Chains

As is shown in Fig. 6, the δ 3.6 peak of PMMA unit and the δ 1.8—2.1 multiplet of PVAc unit were integrated for determination according to the following equation: $n(\text{MMA})/n(\text{VAc}) = S_{3.6}/S_{1.8-2.1}$ (S refers to the proportion of the peaks). The results are given in Table 2. It could be seen that the molar ratio of MMA to VAc in the polymer varies slightly with the variation of the molar ratio of MMA to VAc in monomer, the value approximates to 2/1. However, the possible reason

is still under further study.

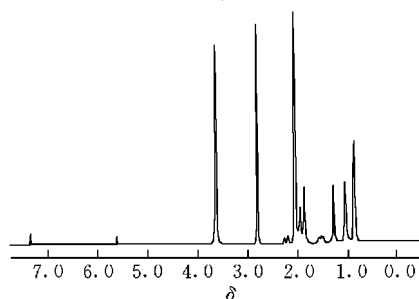


Fig. 6 ^1H NMR spectrum of grafted chain [P(MMA-co-VAc)].

Table 2 Composition of monomer and polymer

$n(\text{MMA})/n(\text{VAc})$ in monomer	20/80	40/60	50/50	60/40	80/20
$n(\text{MMA})/n(\text{VAc})$ in polymer	1.97/1	1.99/1	2.00/1	2.01/1	2.01/1

Biodegradation

1 Biodegradation of Starch-g-P(MMA-co-VAc) and Poly MMA-co-VAc through *Bacillus Subtilis* Attack

Fig. 7 illustrates the degradation behavior of starch-g-P(MMA-co-VAc) and P(MMA-co-VAc) in the presence of *bacillus subtilis*. It is obvious that the graft copolymer demonstrates a rapid degradation rate, the mass loss is 9% after one day and it reaches a maximum of 61% after 28 days. However, the mass loss of the side chain is less than 8% after 28 d. It is probable that *bacillus subtilis* could produce starch enzyme, so the starch portion of the grafted copolymer could be degraded

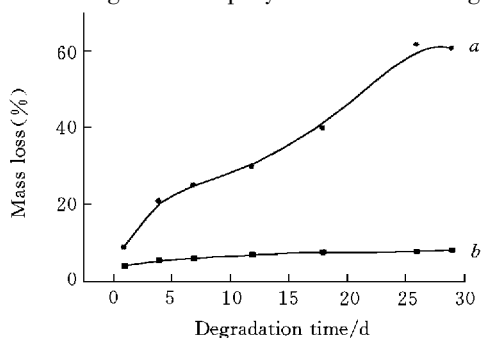


Fig. 7 Degradation of starch-g-P(MMA-co-VAc) (a) and P(MMA-co-VAc) (b).

easily, while the side chain could hardly be degraded.

2 Biodegradation of Starch-g-P(MMA-co-VAc) in Natural Water

Fig. 8 shows the degradation rate of starch-g-P(MMA-co-VAc) in natural water. It could be seen that the mass loss of the sample increases rapidly as degradation time increases. After 30 d the mass loss is over 80%. This indicates starch-g-P(MMA-co-VAc) could almost be degraded completely. Since PVAc could be also transformed into PVA via fungal attack, starch-g-P(MMA-co-VAc) could be degraded under certain conditions. Therefore, the materials made from it would demonstrate a good property of biodegradation.

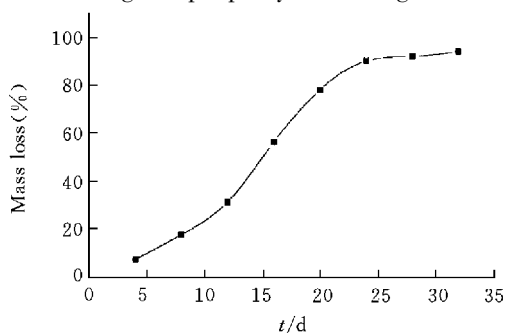


Fig. 8 Degradation in soil lixivium.

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