

Graft Copolymerization of Butyl Acrylate onto Pullulan Using Manganic Pyrophosphate as Initiator

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SYNOPSIS

The graft copolymerization of butyl acrylate onto pullulan using manganic pyrophosphate as initiator in aqueous medium was studied. The effects of concentration of initiator, monomer, pullulan, and sulfuric acid on the percentage of grafting, the grafting efficiency, as well as the rate of graft copolymerization were investigated. The rate equation was derived and a suitable reaction mechanism was proposed. Finally, the grafted samples were characterized by IR spectral measurement.

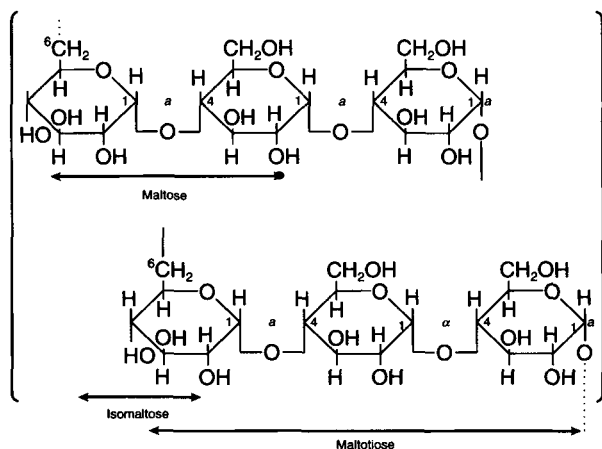
INTRODUCTION

Pullulan, a sort of amorphous polysaccharide, is produced out of the bacterial body by *Aureobaidium pullulans*. It was found by Wallenfels¹ in the seventies to be a linear micromolecule composed of α -1.6-linked maltotriose units.

Pullulan is a water-soluble powder with many advantageous properties.² Especially the properties of nontoxin, plasticity, lower permeability of oxygen gas, and so on make it widely used in food packaging, pharmacy, and other industries. Nevertheless, in some ways the usages of pullulan were limited by its solubility in water, and so it needs to be modified. This could be achieved by treating pullulan with a crosslinking agent, ester agent, and ether agent, blending pullulan with other polymers, or grafting various monomers onto pullulan.

Graft copolymerization of natural polymer is one of the valuable methods to improve the properties of the polymer, and has been extensively used in the graft modification of gelatin,³ cellulose,⁴ fiber,⁵ starch,⁶ and so on. By comparison, the graft copolymerization of pullulan was seldom reported. Domato⁷ has grafted the Et acrylate or styrene onto pullulan using $K_2S_2O_8$ as initiator and used the products as bonding of rayon-polyester nonwoven fabrics. Other monomers such as butyl-2-propenoate, ethenyl acetate, and methy-2-methyl-2-propenoate⁸ were also reported to be grafted onto pullulan. The utilization of these copolymers will

Formula:



become more profitable in wood, paper, and other products.

In this study the graft copolymerization of butyl acrylate onto pullulan was carried out in water medium with manganic pyrophosphate as initiator. The effects of various reaction parameters on the percentage of grafting P , grafting efficiency G , and grafting rate R_g are discussed; the grafted samples are characterized by IR spectral measurements.

EXPERIMENTAL

Materials

Pullulan is a product of the Institute of Microbe, China.

Butyl acrylate (BA), chemically pure, was first washed with 5% sodium hydroxide to remove the

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inhibitor, then washed with distilled water to remove alkali, and finally dried over anhydrous calcium chloride. Purification of this dried BA was carried out by distillation at vacuum, and the middle fraction of it was collected and used.

Initiator, manganic pyrophosphate $[\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3]^{3-}$, was prepared following the procedure of Rakesh.⁹

Preparation of Graft Copolymers

A weighted amount of pullulan was placed into a three-necked round-bottom flask of 250 mL, then dissolved with distilled water to obtain an aqueous solution of required concentration. The content in the flask was stirred and bubbled with nitrogen gas for 20 min before monomer and initiator were added in order. The reaction proceeded at a fixed temperature under N_2 gas. After the desired period of time, the reaction was ended. The content of flask was poured into alcohol and precipitated. These samples were filtered, dried at 60°C at vacuum and weighed.

The dried samples were extracted with acetone for 72 h to remove the homopolymers PBA. The purified graft copolymers were then dried at 60°C at vacuum and weighed.

Removal of Grafted Side Chain

An amount of graft copolymer was refluxed in 1 mol HCl aqueous at $105\text{--}108^\circ\text{C}$ for 12 h to remove the grafted side chain from the backbone. The precipitates were washed with distilled water, dried at 60°C at vacuum and weighed.

The percentage of grafting (P), grafting efficiency (G), and rate of graft copolymerization (R_g) would be calculated as follows:

$$P(\%) = \frac{\text{Weight of grafted PBA chain}}{\text{Weight of graft copolymer}}$$

$$G(\%) = \frac{\text{Weight of grafted PBA chain}}{\text{Weight of grafted PBA} + \text{weight of homo-PBA}}$$

$$R_g = \frac{\text{Weight of grafted PBA}}{M_w \text{ of BA} \times \text{reaction time (s)} \times \text{reaction volume (L)}} \times 1000$$

IR Spectra

The infrared spectra of pullulan, homo-PBA, and graft copolymer were determined with a FT-IR spectrometer.

RESULT AND DISCUSSION

Effect of Initiator Concentration

The effects of initiator concentration on percentage of grafting P and grafting efficiency G are illustrated in Figure 1. It indicated that with increasing the concentration of initiator $[\text{Mn}(\text{III})]$, the P increased and G decreased. That may be due to the fact that with the addition of $[\text{Mn}(\text{III})]$ the rates of graft copolymerization and homopolymerization both increased, and the latter increased even faster, leading to these results.

Effect of Monomer Concentration

The results in Figure 2 show that with increasing monomer concentration (BA) P and G both increased initially. The rapid increase in P at lower (BA) can be attributed to the increasing rate of graft copolymerization (R_g) with (BA) increasing [see Eq. (7) and Fig. 8]. But at higher monomer concentrations beyond 0.23 mol/L , the chain transfer to the monomer increased, resulting in more homopolymer formation, therefore, decreased G .

Effect of Pullulan Concentration

The results are shown in Figure 3, in agreement with the grafting of butyl acrylate onto gelatin.³ With an increase in pullulan concentration $[\text{AGU}]$, P decreased steadily, while G had a maximum at $[\text{AGU}] = 0.1 \text{ mol/L}$. This may be explained that with $[\text{AGU}]$ increasing the ratios of monomer to backbone (pullulan) were lower, causing P to decrease, though the weight of grafted side chain may be increased, which causes G to increase at the beginning.

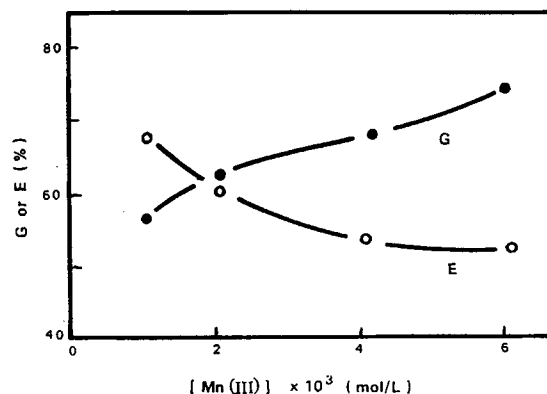


Figure 1 Effect of $[\text{Mn}(\text{III})]$ on grafting. $[\text{BA}] = 0.23 \text{ mol/L}$; $[\text{AGU}] = 0.12 \text{ mol/L}$; $[\text{H}_2\text{SO}_4] = 0.05 \text{ mol/L}$; 30°C , time = 3 h.

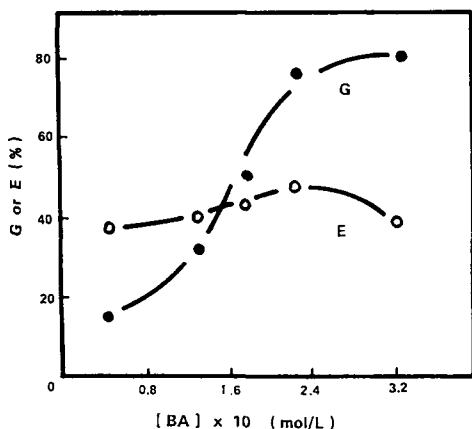


Figure 2 Effect of [BA] on grafting. $[\text{Mn(III)}] = 2 \times 10^{-3}$ mol/L; $[\text{AGU}] = 0.12$ mol/L; $[\text{H}_2\text{SO}_4] = 0.05$ mol/L; 30°C , time = 3 h.

With a further increase, the rate of graft copolymerization may have been hindered by the high viscosity of the system. In addition, high pullulan concentration may produce more pullulan macroradicals, which can interact with each other to terminate the reaction, or transfer to the monomer, thus lowering both P and G .

Effect of Sulfuric Acid

It is indicated (Table I) that the effect of $[\text{H}^+]$ is complex. The percentage of grafting had a maximum at the sulfuric acid concentration of 0.01 mol/L, while grafting efficiency decreased within the $[\text{H}^+]$ range we discussed.

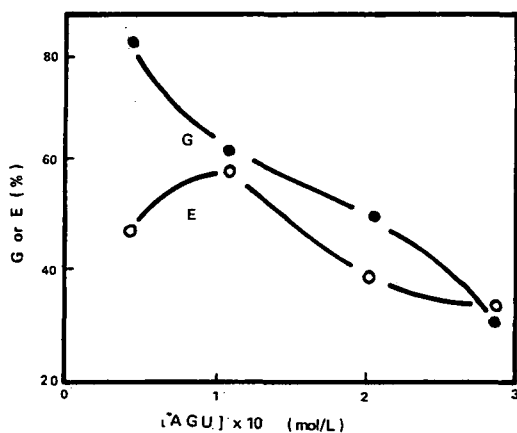


Figure 3 Effect of [AGU] on grafting. $[\text{BA}] = 0.23$ mol/L; $[\text{Mn(III)}] = 2 \times 10^{-3}$; $[\text{H}_2\text{SO}_4] = 0.05$ mol/L; 30°C , time = 3 h.

Table I Effect of Sulfuric Acid

$[\text{H}_2\text{SO}_4]$ mol/L	10^{-3}	10^{-2}	10^{-1}
P	67	77	75
G	52	44	40

$[\text{Mn(III)}] = 3 \times 10^{-3}$ mol/L; $[\text{AGU}] = 0.12$ mol/L; $[\text{BA}] = 0.14$ mol/L, 30°C , time = 3 h.

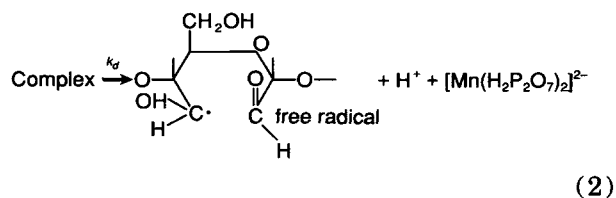
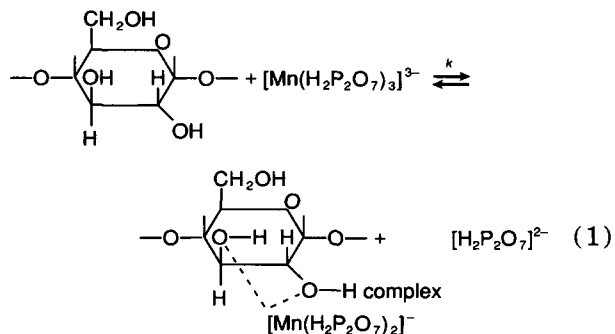
Effect of Reaction Time

The effect of reaction time on percentage of grafting P in different reaction parameters are shown in Figures 4–6. It indicated that with the reaction time, the P increased rapidly initially and then tended to a constant. These results are similar to the grafting of butyl acrylate onto gelatin with ceric ion as initiator.³

Mechanism and Rate

The mechanism of this graft copolymerization was expected to proceed according to the following scheme:¹⁰

Initiation:



Propagation



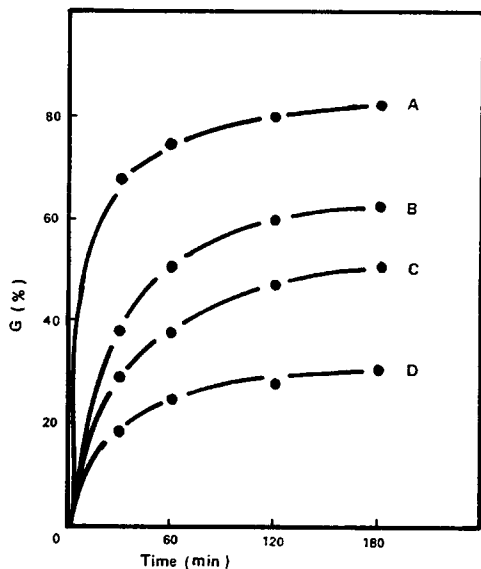
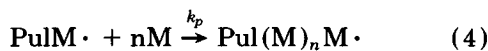
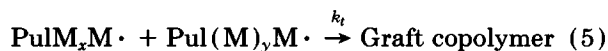


Figure 4 Effect of time on grafting. $[AB] = 0.23$ mol/L; $[AGU] = 0.12$ mol/L; $[H_2SO_4] = 0.05$ mol/L; $30^\circ C$. (a) $[Mn(III)] = 6 \times 10^{-3}$ mol/L; (b) $[Mn(III)] = 4 \times 10^{-3}$ mol/L; (c) $[Mn(III)] = 2 \times 10^{-3}$ mol/L; (d) $[Mn(III)] = 1 \times 10^{-3}$ mol/L.



Termination



Taking into account the above reaction scheme

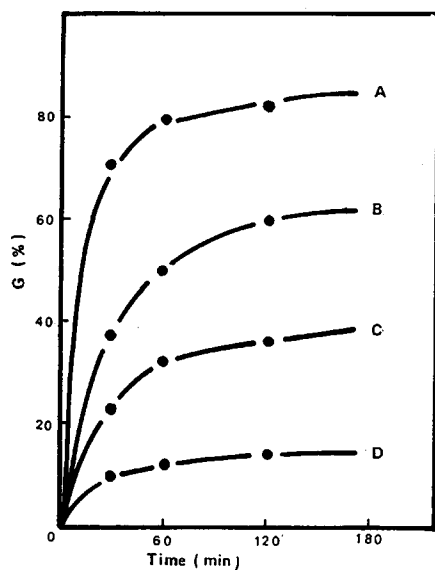


Figure 5 Effect of time on grafting. $[Mn(III)] = 2 \times 10^{-3}$ mol/L; $[AGU] = 0.12$ mol/L; $[H_2SO_4] = 0.05$ mol/L; $30^\circ C$. (a) $[BA] = 0.37$ mol/L; (b) $[BA] = 0.23$ mol/L; (c) $[BA] = 0.14$ mol/L; (d) $[BA] = 0.047$ mol/L.

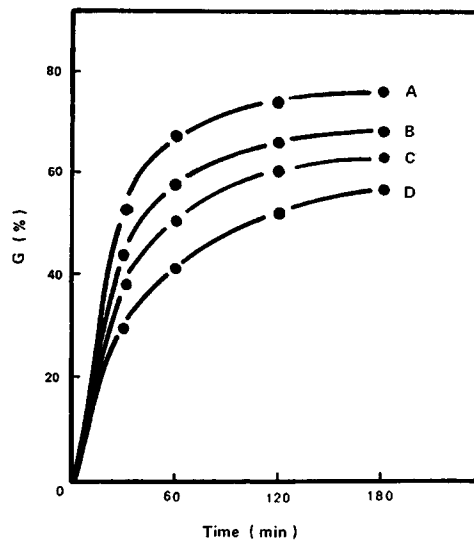


Figure 6 Effect of time on grafting. $[AB] = 0.23$ mol/L; $[Mn(III)] = 2 \times 10^{-3}$ mol/L; $[H_2SO_4] = 0.05$ mol/L; $30^\circ C$. (a) $[AGU] = 0.04$ mol/L; (b) $[AGU] = 0.12$ mol/L; (c) $[AGU] = 0.21$ mol/L; (d) $[AGU] = 0.29$ mol/L.

and three basic hypotheses in free-radical polymerization, the following expressions were derived:

$$\frac{d[Pul\cdot]}{dt} = Kk_d[Pul][Mn(III)] - k_i[Pul\cdot][M]$$

$$[Pul\cdot] = \frac{Kk_d[Pul][Mn(III)]}{k_i[M]} \quad (6)$$

$$\frac{d[PulM\cdot]}{dt} = k_i[Pul\cdot][Mn(III)] - k_t[PulM\cdot]$$

$$[PulM\cdot] = \left(\frac{Kk_d[Pul][Mn(III)]}{k_t} \right)^{1/2} \quad (7)$$

$$\begin{aligned} R_g &= k_p[PulM\cdot][M] \\ &= k_p \left(\frac{Kk_d}{k_t} \right)^{1/2} [Pul]^{1/2}[M][Mn(III)]^{1/2} \quad (8) \end{aligned}$$

Where M and Mn(III) represent monomer BA and initiator $[Mn(H_2P_2O_7)_3]^{3-}$.

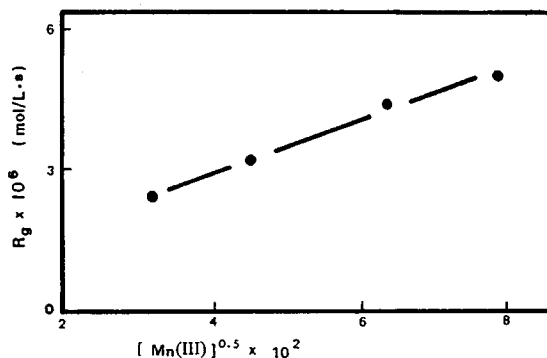


Figure 7 Plot of R_g vs. $[Mn(III)]^{1/2}$. Conditions as in Fig. 1.

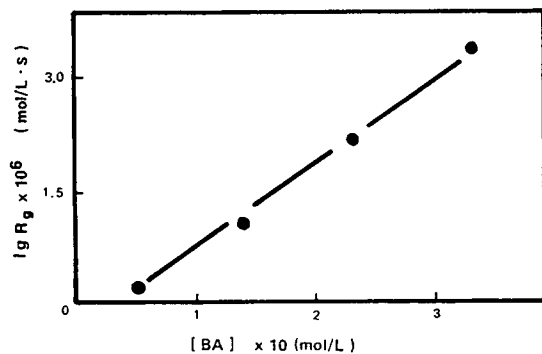


Figure 8 Plot of R_g vs. $[BA]$. Conditions as in Fig. 2.

The above relationship between R_g and the concentration of pullulan $[Pul]$ (in practice replaced by $[AGU]$), monomer butyl acrylate $[M]$, as well as initiator manganic pyrophosphate $[Mn(III)]$ could be illustrated in Figures 7–9. The plot of R_g vs. $[Mn(III)]$ (Fig. 7) and R_g vs. $[BA]$ (Fig. 8) are all linear, which was in accord with that derived from the scheme and favored the mechanism. Figure 9 shows the relationship between R_g and the concentration of pullulan $[AGU]$. It indicates that R_g is almost independent of $[AGU]$, which is not in agreement with the relationship in Eq. (7). This difference is not clear and may be due to the fact that the concentrations of pullulan used in experiments were exceeding and could be considered as a constant. Thus R_g had nothing to do with $[AGU]$.

Proof of Graft

IR spectroscopy has been found to be a valuable method used in the proof of graft copolymer. IR spectra of graft copolymer [Fig. 10(c)] showed the characteristic absorption of carbonyl-group [of PBA Fig. 10(b)] at 1730 cm^{-1} , in addition to the hydroxy peak [of pullulan Fig. 10(a)] at $3600\text{--}3800\text{ cm}^{-1}$. This confirmed the formation of graft copolymer.

Besides, the insolubility of the grafted pullulan in water compared with pure pullulan, which was soluble in water, also provided a proof for grafting.

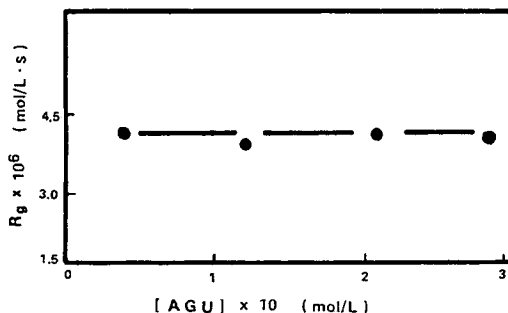


Figure 9 Plot of R_g vs. $[AGU]$. Conditions as in Fig. 3.

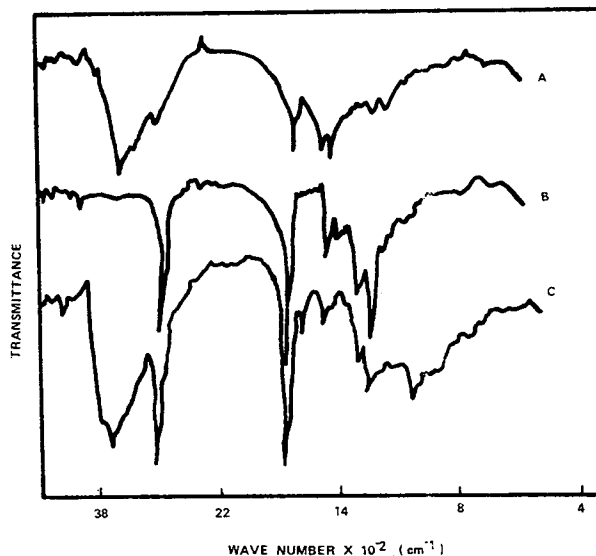


Figure 10 IR spectra of (a) pullulan, (b) homo-PBA, and (c) pullulan-*g*-PBA.

CONCLUSION

1. Manganic pyrophosphate can effectively initiate the graft copolymerization of BA onto pullulan under a wide range of experimental conditions.
2. The percentage of grafting and the grafting efficiency can be adjusted by varying the concentration of monomer, initiator, pullulan, or acid.

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