



Graft copolymerization of methyl acrylate onto pullulan using ceric ammonium nitrate as initiator

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ABSTRACT

Water absorption resins of pullulan graft methyl acrylate (PU-g-MA) using ceric ammonium nitrate (CAN) as an initiator has been investigated under nitrogen atmosphere in aqueous medium. The percentage grafting (%PG) is favoured by increasing reaction time but is affected by higher concentration of initiator and monomer, and high temperature. Experiments showed that the optimal conditions for grafting were: [CAN] = 0.004 mol/l which was added in 1 mol/l nitric acid; [MA] = 0.0465 mol/l; reaction time; 180 min and temperature, 40 °C. The graft copolymer was analyzed by infrared spectroscopy. The water absorption capacity of the resins decreased significantly with the increase in %PG.

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1. Introduction

Pullulan, an exocellular homopolysaccharide produced by *Aureobasidium pullulans*, is a linear mixed linkage α -D-glucan consisting mainly of maltotriose units interconnected via α -(1 → 6) linkages (Saha & Zeikus, 1989). The regular alternation of α -(1 → 4) and α -(1 → 6) bonds results in structural flexibility and enhanced solubility (Leathers, 1993). Pullulan can form thin films which are transparent, oil resistant and impermeable to oxygen. It may be used as a coating and packaging material, sizing agent for paper or starch replacer in low-calorie food formulations, cosmetic emulsions and other industrial applications (Deshpande, Rale, & Lynch, 1992).

Chemically modified pullulans with improved properties are gaining interests mainly because the polysaccharide portion of the product is flexible in structure, water soluble and biodegradable. Their applications may relate to agriculture, industry, medical treatment and sanitation, and so on. This may be achieved by treating pullulan with a crosslinking agent, ester agent, and other agent, or grafting various monomers onto pullulan.

Grafting copolymerization of varying monomers onto pullulan is one of the most effective methods to incorporate desirable properties into it without sacrificing its nature. For the last

few decades, a number of monomers grafted onto pullulan by copolymerization are as follows: *N*-isopropylacrylamide (Masci, Bontempo, & Crescenzi, 2002); ethylenic compound (Seizo, Kozo, Nobuhiro, & Fumio, 1975); lactide (Ohya, Maruhashi, & Ouchi, 1998); ethylene glycol (Jiao, Fu, & Jiang, 2004); butyl acrylate (Tian, Gao, Yu, & Duan, 1992); *p*-hydroxystyrene (Chen, Oshima, & Kumanotani, 1985).

In this paper, we present the results of a study on grafting of methyl acrylate (MA) onto pullulan in terms of effect of initiator and monomer concentration, reaction time and temperature using ceric ammonium nitrate (CAN) as an initiator. Further, we have examined the main factors (the percentage grafting (%PG) and grafting efficiency (%GE)) of influencing the water absorption capacity of pullulan graft methyl acrylate (PU-g-MA).

2. Experimental

2.1. Materials

Pullulan (Pharmacopoeia, Japan) was dried at 105 °C to a constant weight. Ceric ammonium nitrate (CAN) (Fuchen Co, Tianjin, China) was dried in the same way as pullulan. Dried pullulan and CAN were then stored over anhydrous CaCl_2 in a desiccator. Methyl acrylate (Fuchen Co, Tianjin, China) was freed from inhibitor, dried over anhydrous CaCl_2 , and stored in a refrigerator.

The reactor was a four-necked round bottom flask equipped with a stirrer, thermometer, nitrogen gas inlet and condenser.

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2.2. Graft copolymerization

Dried pullulan (2 g) and 70 ml of distilled water were added to the reactor. A predetermined quantity of CAN was added to the solution in the reactor and treated for 10 min to facilitate the free radical formation on pullulan (Fernandez, Casinos, & Guaman, 1990; Trimnell, Fanta, & Salch, 1996). This treatment was followed by the addition of different amount of monomer (methyl acrylate), and the total volume of the reaction system was made to 100 ml with distilled water. The copolymerization was carried out under N_2 atmosphere at different temperatures and time. The controlled reactions were carried out with 2 g pullulan under identical experimental conditions with various initial concentration of added monomer for each reaction. Upon completion of the reaction time, the reaction mixture with prepared PU-g-MA was precipitated with ethanol. The precipitate was washed with acetone to remove unreacted monomer and then dried at 40 °C. The dried residue was made free from homopolymer (methyl acrylate polymer) employing soxhlet extraction with *N,N'*-dimethyl formamide and then dried at 80 °C to a constant weight.

2.3. Hydrolytic degradation of PU-g-MA

An amount of graft copolymer was refluxed in 1 mol HCl aqueous at about 105 °C for 12 h to remove the grafted side chain from the backbone. The precipitates were washed with distilled water, and dried at 80 °C to a constant weight.

The %PG and %GE were calculated from the Eq. (1) and Eq. (2) (Athawale & Lele, 1998; Eromosele, 1994; Shukla & Sharma, 1987).

$$\%PG = 100W_2/W_1 \quad (1)$$

$$\%PG = 100W_2/(W_2 + W_3) \quad (2)$$

where W_1 , W_2 and W_3 are the weights of PU-g-MA, grafted side chain and homomonomer, respectively.

2.4. Infrared (IR) spectral analysis

The IR spectra of representative grafted and ungrafted pullulan were run as KBr pellets on Nicolet Nexus FTIR 470 spectrophotometer in the frequency ranges of 400–4000 cm^{-1} .

2.5. Measurement of water absorption

Water absorption was measured in terms of Eq. (3)

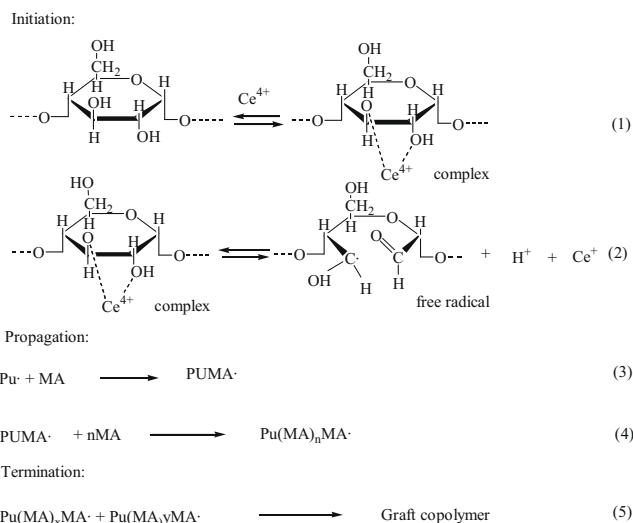
$$C_{WA}(g/g) = (W_1 + W_2)/W_1 \quad (3)$$

where C_{WA} is water absorption capacity, W_1 and W_2 are the masses of dried powered sample and amount of water absorbed, respectively.

3. Results and discussion

3.1. Synthesis of PU-g-MA

The mechanism of the graft copolymerization was expected according to the Scheme 1 (Mehrotra & Ranby, 1977). All graft copolymerization samples were milkiness and hard. They only swelled, but did not dissolve in water, DMSO and *N,N'*-dimethyl formamide, which are good solvents for pure pullulan. The insolubility of these copolymers may be the result of cross-linking due to chain combination of the growing ends of grafted chains and hydrophobicity of the grafted side chains.



Scheme 1. The synthetic route of PU-g-MA.

3.2. Evidence of grafting

The graft copolymer samples were followed gravimetrically. The increase in weight of the residue for each sample, over that of the corresponding control, indicates possible grafting.

The IR spectra of pullulan and a representative graft copolymer sample, contained a broad band at 3400–3500 cm^{-1} due to –OH stretching frequency of anhydroglucose units (Fig. 1). The grafted sample showed an additional band at 1735 cm^{-1} due to C=O stretching vibration of the –COOCH₃ group, indicating the occurrence of grafting of MA on to pullulan.

3.3. Effect of initiator concentration

Fig. 2 exhibits the effect of [CAN] on the grafting of MA onto pullulan. It should be noted that graft copolymerization did not occur when [CAN] was below 0.001 mol/l, indicating that copolymerization needs at least a certain amount of CAN. The %PG and %GE initially increased steadily with the increase in [CAN] from 0.001 to 0.004 mol/l. However, they decreased with further rise in concentration of CAN. The initial increase in %PG and %GE can be due to the increasing number of free radical sites on the pullulan backbone at which the monomer can be grafted. The decrease in %PG and %GE may be attributed to (i) the termination of the growing grafted chains (Shukla & Sharma, 1987), (ii) primary radical termination by excess ceric ions.

3.4. Effect of monomer concentration

Fig. 3 shows the effect of monomer concentration on the grafting parameters. The %PG and %GE increased sharply with the increase in monomer concentration from 0.0116 to 0.465 mol/l. However, further increase in monomer concentration did not improve %PG further and decreased %GE. It is well known that the rate of grafting reaction depends on the rate of supply of monomer to substrate (Vazquez, Goni, Gurruchaga, Valero, & Guzman, 1992). The initial increase in the grafting reaction was due to increasing supply of monomers to pullulan macroradicals, however, the decline in %GE at higher concentration of MA could be ascribed to the chain transfer to excess monomer molecules in the vicinity of growing ends of grafted chains (Gao, Tian, Yu, & Duan, 1994). Experimental results indicated that the optimum concentration of MA was found to be 0.0465 mol/l.

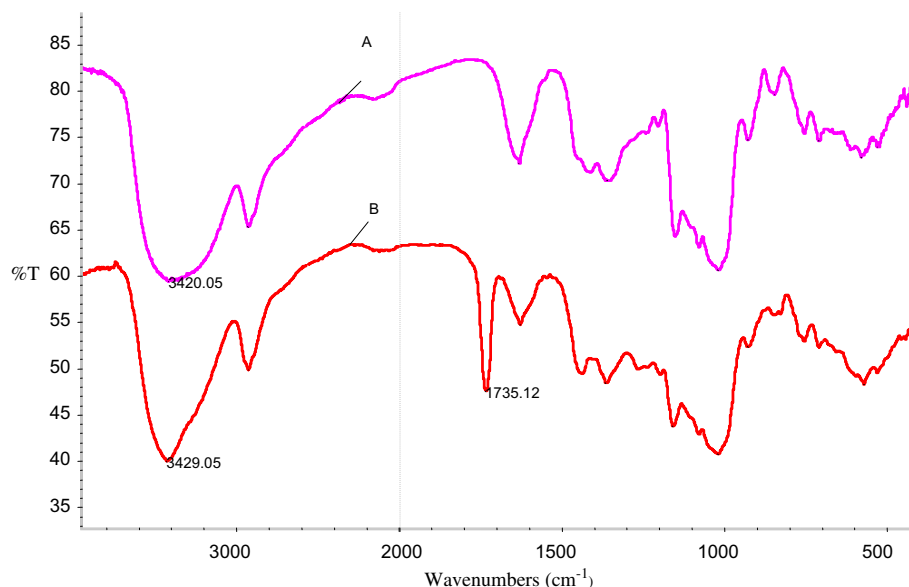


Fig. 1. Infrared spectra of (A) pullulan and (B) grafted pullulan.

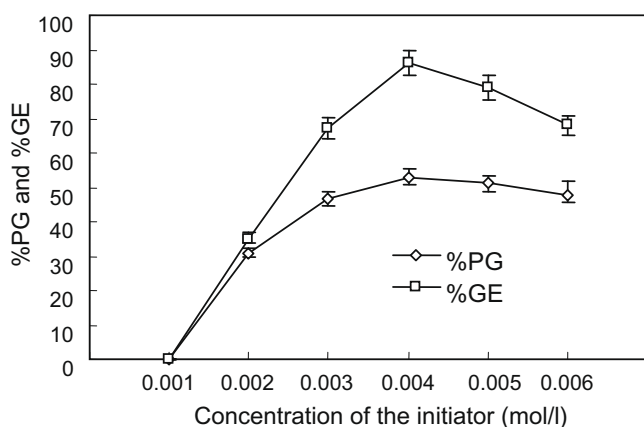


Fig. 2. Effect of initiator (ceric ammonium nitrate) concentration on the percentage grafting (%PG) and grafting efficiency (%GE) (reaction conditions: pullulan, 2.0 g; methyl acrylate, 0.0348 mol/l; temperature, 40 °C; time, 180 min).

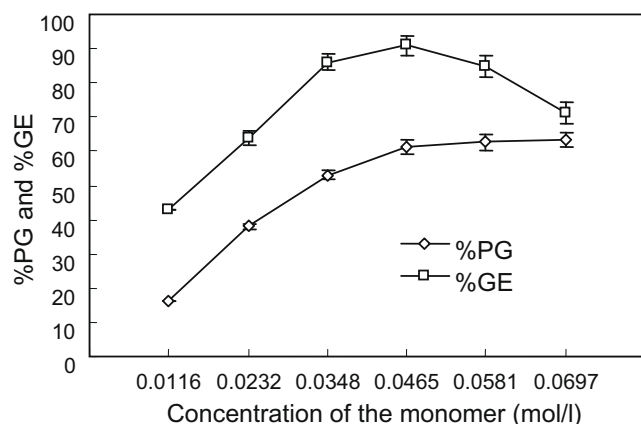


Fig. 3. Effect of monomer (methyl acrylate) concentration on the percentage grafting (%PG) and grafting efficiency (%GE) (reaction conditions: pullulan, 2.0 g; ceric ammonium nitrate, 0.0040 mol/l; temperature, 40 °C; time, 180 min).

3.5. Effect of polymerization time

The reaction time course studies on %PG and %GE were made for a period of 360 min. As shown in Fig. 4, both %PG and %GE increased sharply with time, reaching an optimum %PG of 61.3% and %GE of 91% within 180 min and then did not increase further. The leveling off of the grafting rate can be rationalized on the basis of progressive consumption of pullulan, the monomer and initiator with time (Shukla & Sharma, 1987). Therefore, the optimal copolymerization time was 180 min.

3.6. Effect of reaction temperature

The effect of reaction temperature on the grafting parameters was summarized in Fig. 5. The %PG and %GE increased with increase in temperature up to 40 °C probably due to the enhanced diffusion of monomer molecules to the macroradical sites. However, further increasing the temperature resulted in decrease in %PG and %GE. This is expected as the chain transfer reactions with higher activation energy were favoured at high temperature and in most of the cases they contributed nothing to the grafting (Mishra,

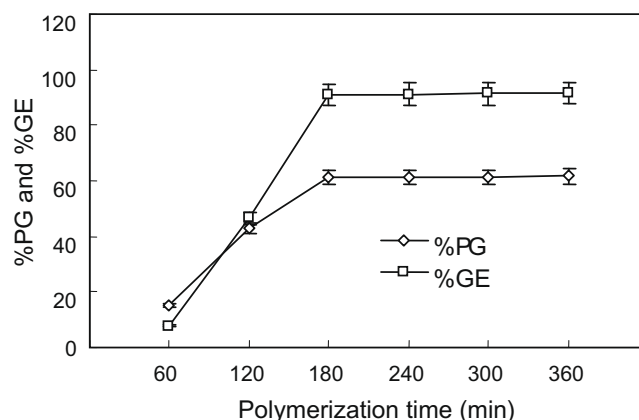


Fig. 4. Effect of polymerization time on the percentage grafting (%PG) and grafting efficiency (%GE) (reaction conditions: pullulan, 2.0 g; ceric ammonium nitrate, 0.0040 mol/l; methyl acrylate, 0.0465 mol/l; temperature, 40 °C).

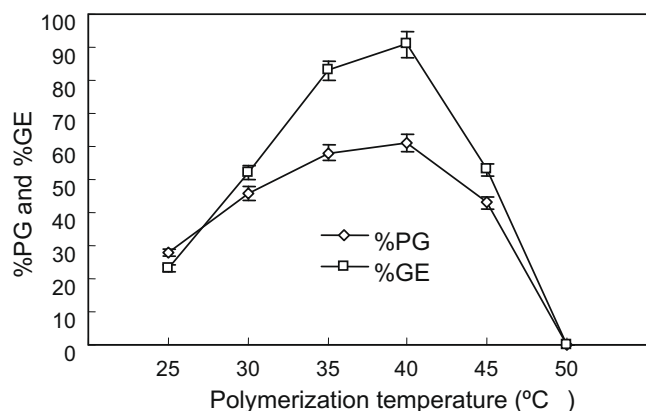


Fig. 5. Effect of reaction temperature on the percentage grafting (%PG) and grafting efficiency (%GE) (reaction conditions: pullulan, 2.0 g; ceric ammonium nitrate, 0.0040 mol/l; methyl acrylate, 0.0465 mol/l; time, 180 min).

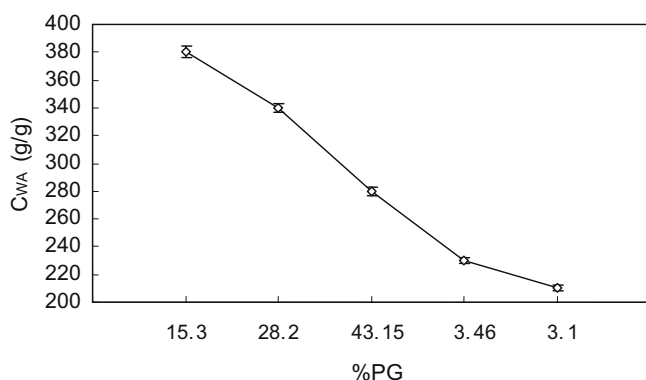


Fig. 6. Relationship of the water absorption capacity with the percentage grafting (%PG).

Dogra, Kaur, & Sood, 1980). It is also likely that at higher temperature there is an increase in the rate of oxidation of pullulan.

3.7. Water absorption capacity of PU-g-MA

The water absorption capacity of PU-g-MA decreased with the increase of %PG due to the increase of the number of the hydrophobic monomer (Fig. 6). The copolymer is made up of two parts: hydrophobic grafted side chains and hydrophilic polysaccharide backbones and therefore, it shows a similar characteristic of surfactants. It can absorb more water when the rate of polysaccharide part increases, and vice versa. It is likely that the copolymer can absolutely dissolve in water if the rate of the hydrophobic side chains is low enough.

4. Conclusions

The %PG and %GE can be adjusted by [CAN], [MA], reaction time and reaction temperature. The optimum conditions carried out on the basis of present work are as follows:

[CAN] = 0.004 mol/l; [MA] = 0.0465 mol/l; reaction time, 180 min; reaction temperature, 40 °C.

The water absorption capacity of the reins decreased significantly with the increase in %PG.

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