

Ceric염 개시제를 사용한 Chitin에 대한 Methyl Methacrylate의 그라프트 공중합

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Graft Polymerization of Methyl Methacrylate onto Chitin Initiated by Ceric Salt

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요 약 : Ceric ammonium nitrate (CAN)을 개시제로 하여 chitin에 methyl methacrylate (MMA)를 그라프트 공중합하였다. 그라프트 공중합체의 확인은 IR 스펙트럼과 전자현미경으로 행하였다. Formic acid, methanol과 같은 유기 용매를 사용하였을 경우에는 그라프트 공중합체가 형성되지 않았고, 물이 그라프트 공중합에 있어서 필수적인 용매임을 알 수 있었다. 중량 증가율, 그라프트율 등에 대한 반응 온도, 반응 시간, 단량체의 농도, 개시제의 농도 등의 최적 조건을 구하였다.

Abstract : The graft polymerization of methyl methacrylate (MMA) onto chitin initiated by ceric ammonium nitrate (CAN) was investigated. The grafted-polymer was identified by using IR spectroscopy and electron micrographs. No grafting was observed in the usual organic solvents such as formic acid and methanol. It was found that water was essential to the grafting. The optimum conditions on the weight increase, the percentage of grafting, and the degree of grafting were determined by varying media, reaction temperature, reaction time, monomer concentration, and initiator concentration.

INTRODUCTION

Chitin, a principal component of the supporting structure of several living organisms such as fungi and anthropods, is one of the mucopolysaccharides having the repeating structural unit of 2-acetamido-2-deoxy- β -D-glucose. This polysaccharide, therefore can be regarded as an analogue of cellulose with an acetylamino group instead of the C-2 hydroxyl group. However, the chemical and physical properties of chitin are quite different from those of cellulose despite the similarity in chemical structures. For instance, chitin is considerably more resistant to chemical reagents because of its strong micelle structure, and hence, research on chitin is limited; it has not yet been regarded as a useful natural resource compared with other polysaccharides such as cellulose or starch.

Chitin and chitin derivatives have been reported to have some useful medical application. For example, chitin administration to animals attacked by certain bacteria and fungi has proved very useful as a highly effective antigen.¹ Chitin has been found suitable as a biodegradable pharmaceutical carrier² and a blood anticoagulant.³ Chitosan membranes have also been proposed as artificial organ membranes because of their suitable permeability and high tensile strength.

Graft polymerization onto cellulose has been extensively studied, while very few works on the graft polymerization onto chitin and chitosan have been reported. Slagel reported a patent for making paper products with improved dry strength by grafting on chitosan.⁵ Kojima reported the graft polymerization of methyl methacrylate onto chitin using tributylborane as an initiator.⁶ Shigeno reported the graft polymerization of styrene onto chitin and chitosan initiated by γ -ray irradiation.⁷

We applied a method using ceric ammonium nitrate as an initiator to modify chitin. Ceric salts show a high reactivity in aqueous media,^{8,9} and they were used either alone¹⁰ or in combination with reducing agents¹¹ as initiators of vinyl polymerization.

EXPERIMENTAL

Materials

Chitin has been isolated from bone of the cuttlefish by the method of Hackman.¹² Chitin was extracted in a Soxhlet extractor with methanol, water, petroleum ether, and acetone in that order, each for 24hr. Methyl methacrylate (MMA) was washed with 5% NaOH solution and then with water to remove the inhibitor, dried over anhydrous calcium chloride, distilled under reduced pressure, and stored at 5°C. Reagent-grade ceric ammonium nitrate (CAN) was used without further purification. Anhydrous formic acid was obtained by direct fractional distillation under reduced pressure.

Graft Polymerization

A mixture of 0.3g of chitin and 5.75ml of water was placed in a 60ml tube with a stopper and was stirred by magnetic bar at room temperature for 20hr. This was added 1.17 M of MMA and stirred for 2hr. This was heated to 27°C, and then the CAN initiator was added. The initiator solution was prepared by dissolving CAN in 2 ml of 1 N nitric acid. The reaction mixture was stirred for polymerization. The grafting was stopped pouring the mixture into 100ml of methanol. The precipitates were filtered, washed with methanol, and dried at 70°C in vacuum to constant weight. The dried precipitates were extracted with acetone in a soxhlet apparatus for 48hr to remove the homopolymer of MMA. The residue was dried at 70°C in vacuum to constant weight.

Calculation

The increase of weight, the percentage of grafting, and the degree of grafting were calculated as follows:

$$\Delta W = \frac{W_P - W_0}{W_0} \times 100$$

$$G_m = \frac{W_{Pm}}{W_m} \times 100$$

$$G_c = \frac{W_{Pm}}{W_0} \times 100$$

where ΔW is the weight increase (%), W_P is

the weight of product, W_0 is the original weight of chitin, G_m is the percentage of grafting (%), W_{pm} is the weight of poly-MMA grafted, W_m is the weight of MMA charged, G_c is the degree of grafting (%).

RESULTS AND DISCUSSION

IR Spectra and Scanning Electron Micrograph

IR spectra of the backbone polymer of chitin and grafted chitin are shown in Fig. 1. The IR spectrum of grafted chitin showed a absorption at 1730cm^{-1} attributed to ester groups of poly-MMA. Also, the scanning electron micrographs of chitin, poly-MMA, and grafted chitin are shown in Fig. 2. The grafted chitin appeared to have a different structure from the ordinary chitin in the pictures of a scanning electron microscope.

Reaction Conditions

Table 1 shows the dependence of grafting on the type of medium. Grafting was found to occur

only in the cases that the reaction was performed in water or the water-methanol system. In the latter case the degree of grafting was substantially low and the formation of homopoly-MMA was slightly high. These results indicate that the presence of water is essential to the grafting. Chitin is known to have a crystalline structure, and the molecular chains of chitin are well arranged in piles or sheets linked by hydrogen bonding through

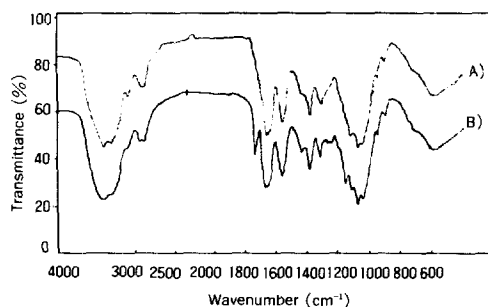


Fig. 1. IR spectra of chitin (A) and grafted chitin (B).

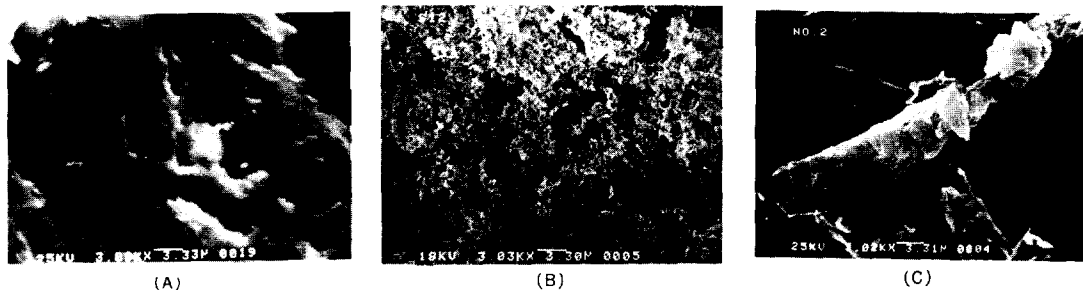


Fig. 2. Scanning electron micrographs of chitin(A), poly-MMA(B), and grafted chitin(C).^a

Table 1. Effects of Media in Graft Polymerization of Chitin

Medium	Product (g)	Grafted Chitin(g)	The Weight Increase(%)	The Percentage of Grafting(%)	The Degree of Grafting(%)
Formic Acid	0.2687	—	—	—	—
Methanol	0.2785	—	—	—	—
H ₂ O	0.6542	0.3934	118.1	7.983	31.13
1 : 1	1.0104	0.3934	236.8	7.983	31.13
H ₂ O : MeOH 1 : 2	0.7595	0.3764	153.2	6.530	25.47
2 : 1	1.0047	0.3321	234.9	2.743	10.70

Chitin (0.300g) : Medium (5.75ml) : MMA (1.17M) : CAN ($1.86 \times 10^{-2}\text{M}$) : Temp. (27°C) : Time (3hr) : Total Solution (10.0ml).

amide groups. In the grafting onto chitin, it appears, therefore, that the presence of water would be responsible for the rupture of intermolecular hydrogen bonds between chitin molecules so that MMA molecules diffuse readily into them.

Fig. 3 shows the dependence of reaction temperature on grafting from 20°C to 40°C. The weight increase increased as the polymerization temperature was raised. But the percentage of grafting and the degree of grafting reached maximum at 25°C.

Fig. 4 presents the relationship between reaction time and the grafting. As the reaction time became longer, the grafting increased to 3-4hr, but after about 3-4hr it reached plateaus.

Fig. 5 shows the dependence of the grafting on the monomer concentration. The weight increase and the degree of grafting reached maximum at 0.14 of the mole fraction of MMA and water.

Fig. 6 shows the effect of initiator concentration on the grafting. The percentage of grafting and the degree of grafting reached maximum at 2×10^{-2} M of the initiator concentration.

Reaction Mechanism

It is well known that the radical polymerization

of vinyl monomers is initiated by the redox system of ceric ion and polymer having hydroxyl groups to give a grafted polymer.¹³ The grafting mechanism is assumed to involve free radical. This assumption

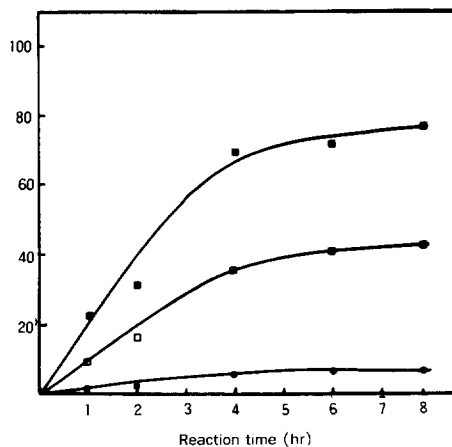


Fig. 4. Effect of reaction time, chitin (0.300g):water (5.00ml):MMA (1.86m):CAN (1.86×10^{-2} M):temp. (27°C):total solution(10.0 ml):■:weight increase (%), ●:percentage of grafting(%), □:degree of grafting(%).

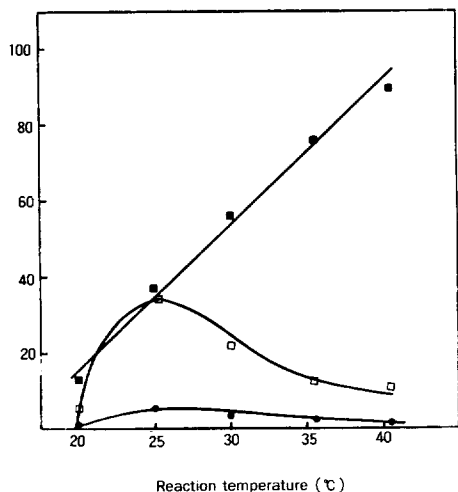


Fig. 3. Effect of reaction temperature, chitin(0.300g):water(5.00ml):MMA(1.86M):CAN(1.86×10^{-2} M):time(3hr):total solution(10.0ml):■:weight increase (%), ●:percentage of grafting(%), □:degree of grafting(%).

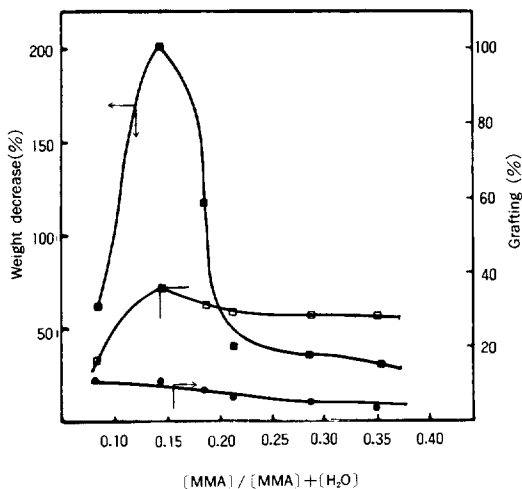


Fig. 5. Effect of MMA concentration, chitin(0.300 g):MMA+H₂O(7.00ml):CAN(1.86×10^{-2} M): time (3hr):temp.(27°C):total solution(10.0ml):■:weight increase(%), ●:percentage of grafting(%), □:degree of grafting(%).

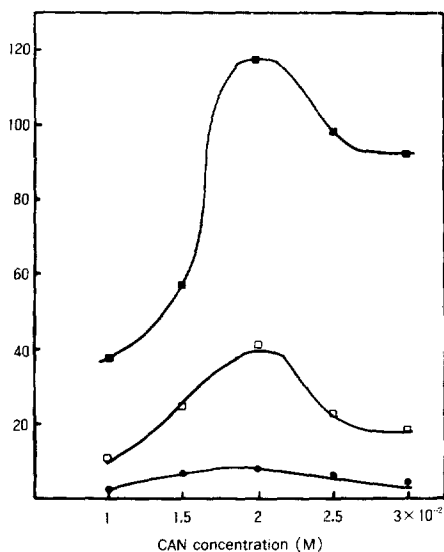


Fig. 6. Effect of CAN concentration, chitin(0.300g): water(5.75ml): MMA(1.17M): time(3hr) : temp.(27 °C): total solution(10.0ml): ■: weight increase(%), ●: percentage of grafting(%), □: degree of grafting (%).

is supported by the fact that free radical polymerization is less sensitive to water than ionic polymerization. The presence of water is essential to the grafting. No grafting occurred in the usual organic solvents, although CAN can initiate polymerization of MMA in these organic solvents. Therefore we think that the grafting sites on chitin are formed by a reaction among CAN, chitin, and water. The grafting was assumed to proceed via free radical mechanism in three steps (1) cooperative interaction of water to

chitin, (2) formation of the complex from solvated chitin and CAN, (3) graft initiation by free radicals from the complex.

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