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Ceric Ammonium Nitrate 개시제를 사용한 Chitosan 과 Acrylamide 의 Graft 공중합

김 경 호·김 공 수·신 재 섭*
충북대학교 화학공학과, *충북대학교 화학과
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Graft Copolymerization of Chitosan and Acrylamide by using Ceric Ammonium Nitrate Initiator

Kyoung-Ho Kim, Kong-Soo Kim, and Jae-Sup Shin*
Dept. of Chem. Eng., Chungbuk National Univ., Cheongju, Chungbuk 310, Korea
**Dept. of Chemistry, Chungbuk National Univ., Cheongju, Chungbuk 310, Korea*
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Abstract : The grafting of acrylamide onto chitosan initiated by ceric ammonium nitrate (CAN) was investigated at 30~50℃. The graft polymerization was found to proceed predominantly in the presence of dilute acetic acid solution. The optimum conditions on the weight increase and the percentage of grafting were determinded by varing initiator concentration, monomer concentration and reaction time. Activation energy for initial reaction was estimated to be about 5.49 kcal/mole.

INTRODUCTION

Chitin, a polysaccharide consisting of β-2-acetoamino-2-deoxy-D-glucose units is one of the principal ingredients of bone of the Cuttlefish and shell of the Crustacea such as crabs, lobsters, prawn and shrimps. This polysaccharide, therefore, can be regarded as an analogue of cellulose which has an acetylamino group instead of the C-2 hydroxyl group.

Since the total production of all the Crustacea in nature is estimated to be on the order of several billion tons, the utilization of chitin is believed to be of importance for the welfare of mankind.

Chitin exists in three difference polymorphic forms, depicted as a α-chitin, β-chitin and γ-chitin depending upon the crystalline structure.[1] α-chitin is the most abundant and most stable natural polymorphic form, but during the process of isolation it is converted into the other forms.[2]

In spite of the similarity in their chemical structures, the chemical or physical properties of chitins are quite different from those of celluloses. For instance, chitin is considerably more resistant to chemical reagents because of its strong micelle structure and hence research on chitin is limitted ; 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.[3] Chitin has been found suitable as a biodegradable pharmaceutical carrier,[4] a blood anticoagulant.[5] Chitosan membranes have also been proposed

as artificial organ membranes because of their sutable permeability and high tensile strength[6].

Despite these applications, chitin as a natural resource is still underutilized in comparison with other polysaccharides such as cellulose and starch.

There are many well-known methods of grafting for vinylmonomers onto natural products, such as starch[7], dextran[8], amylose[9] at ordinary temperature.

We applied a method using ceric ammonium nitrate as an initiator to the modification of chitosan of chitin derivative.

EXPERIMENTAL

Materials

Chitosan was prepared from chitin which have been isloated from bone of the cuttlefish by Hackman's method[10]. Chitin was treated with an aqueous solution of sodium hydroxide at 95℃ for 4 hours[11].

The acrylamide monomer supplied by Hayashi pure chemical Co. was recrystallized two times from methanol and dried thoroughly under vacuum before use.

The initiator solution was prepared by dissolving 5.77 g of ceric ammonium nitrate (Wako Co.) in 100ml of 1N-nitric acid.

Other chemicals of reagent grade were obtained from Wako pure chemical Co. and used without further purification.

Graft Copolymerization

Into 250ml, four-necked flask equipped with purge tube, thermometer, stirrer and condenser were added chitosan, acrylamide, 150ml of 15 wt. % acetic acid solution. The compound was then heated to 30℃ and stirred for one hour while being purged with nitrogen. The ceric ammonium nitrate initiator was then added. The initiator was a 0.1 N-ceric ammonium nitrate in 1N nitric acid solution. The reaction mixture was stirred for planned reaction times at constant temperature.

The polymer was diluted to 5 percent solid with water and precipitates were filtered and washed with acetone and dried at 50℃ in vacuum to constant weight. The dried products were extracted with acetone-water (volume ratio=40 : 60) mixture for 8 hours to remove the homopolymer of acrylamide. The homopolymer was reprecipitated in acetone but was not produced. This result agreed to study of Hea Ya[7]. The graft copolymers were dried at 50℃ in vacuum to constant weight.

Calculation

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

$$\Delta W = \frac{W_p - W_o}{W_o} \times 100$$

$$\varphi_\alpha = \frac{W_{pa}}{W_a} \times 100$$

$$\varphi_c = \frac{W_{pa}}{W_o} \times 100$$

where ΔW is the weight increase(%), W_p is the weight of product, W_o is the original weight of chitosan, φ_α is the percentage of grafting, W_{pa} is the weight of polyacrylamide grafted, W_a is the weight of acrylamide charged, φ_c is the degree of grafting %.

Viscosity Measurement

The intrinsic viscosity of the chitosan and the graft copolymer were determined at 25℃ by using a suspended type Ubbelohde viscometer in the mixed solution of the equal volume of 0.2 M-acetic acid, 0.1 M-sodium chloride, and 4 M-urea. And the viscosity average molecular weights were estimated from the following equation[12].

$$[\eta] = 8.93 \times 10^{-4} \bar{M}_v^{0.71} \quad (dl/g,\ 25℃)$$

IR Spectra and Scanning Electron Microscope

IR spectra of the backbone polymer of chitosan, polyacrylamide and grafted chitosan were determined from film by Perkin Elmer 298.

Also mophologies were studied for the polyacrylamide, grafted chitosan and chitosan by scanning electron microscope Hitachi X-650.

RESULTS AND DISCUSSION

Fig.1 presents the IR spectra of polyacrylamide,

chitosan and grafted chitosan. The IR spectrum of grafted chitosan showed a strong absorption at 1650 cm^{-1} attributed to C=O of poly acrylamide, which shows a weak absorption in the IR spectrum of pure chitosan.

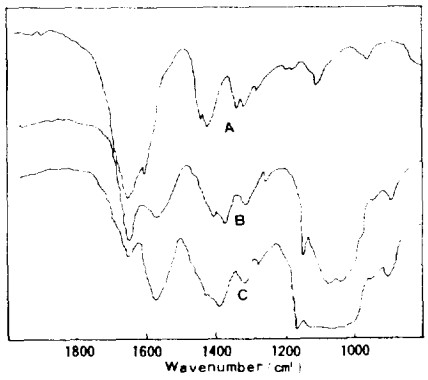
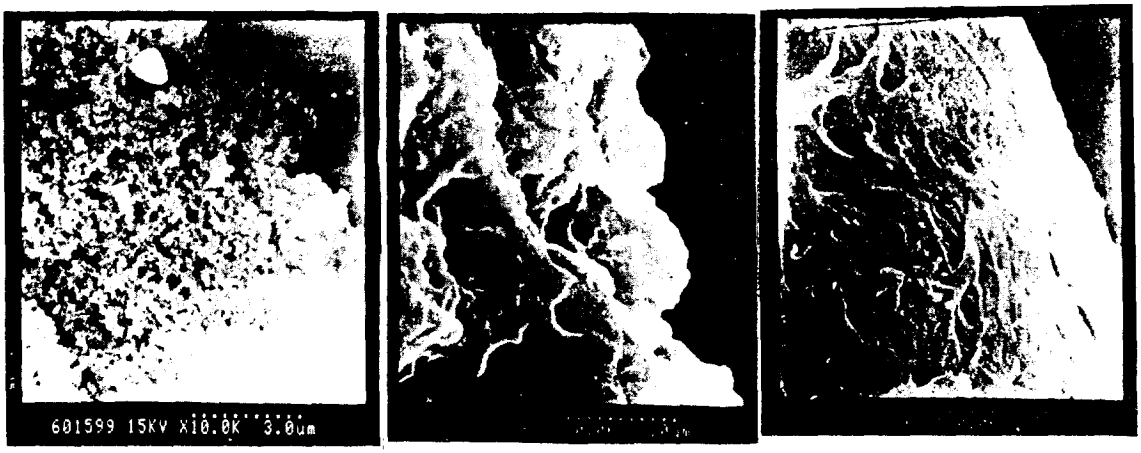


Fig. 1. IR spectra of polyacrylamide(A), grafted chitosan(B) and chitosan(C).

Also, the scanning electron microscope of polyacrylamide, grafted chitosan and chitosan is shown in Fig.2.

When viewed in a scanning electron microscope, the grafted chitosan powder appears to have a different structure from the homopolyacrylamide and chitosan powder. Therefore, we think that acrylamide appears chemically to be bonded to the surface of chitosan powder.

Table 1 and Fig.3 show the effect of the ceric ammonium nitrate initiator concentration. The weight increase and the percentage of grafting increased untill 2.36×10^{-5} mole/l of ceric ammonium nitrate concentration, but reached constant above this concentration. These tendencies have



(A) (B) (C)

Fig. 2. The scanning electron micrographs of polyacrylamide(A), grafted chitosan(B) and chitosan(C).

Table 1. Graft Copolymerization of Chitosan and Acrylamide at Various Ceric Ammonium Nitrate Concentration (chitosan=2 g, [acrylamide]=8.44×10^{-3}M, 15 wt.%-acetic acid solution=150ml, reaction temp.=30℃, swelling time=1hr., reaction time=3hr)

Sample code	[CAN]$\times10^{5}$M	Weight of grafted acrylamide (g)	Weight increase (%)	Percentage of grafting (%)	Degree of grafting (%)
C-1.0	1.58	0.310	15.50	7.75	15.50
C-1.5	2.36	0.535	26.75	13.38	26.75
C-2.0	3.15	0.550	27.50	13.75	27.50
C-2.5	3.93	0.564	28.20	14.10	28.20
C-5.0	7.87	0.575	28.75	14.38	28.75
C-10	15.73	0.534	26.70	13.55	26.70

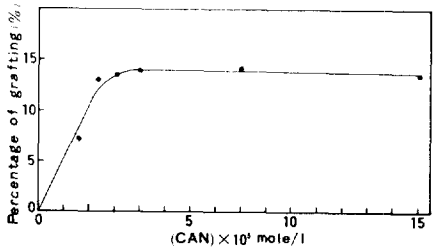


Fig. 3. Relation between percentage of grafting and ceric ammonium nitrate concentration at 30℃ (chitosan=2g, [acrylamide]=8.44×10^{-3}M, 15 wt.%-acetic acid solution 150ml, swelling time=1 hr., reaction time=3hr.).

been considered that initiator concentration does not affect to the formation of radical site onto backbone polymer in the above of 2.36×10^{-5} mole/l of ceric ammonium nitrate. Particularly, no grafting occurred in the usual organic solvent. It seems that the grafting sites on chitosan are formed by a reaction between chitosan, ceric ammonium nitrate and water. The grafting was assumed to proceed via redox mechanism in three steps : (1) solvation of water to chitosan (2) formation of the complex from solvated chitosan and ceric ion (3) graft initiation by free radicals

Table 2. Graft Copolymerization of Chitosan and Acrylamide at Various Acrylamide Concentration (chitosan=2 g, [CAN]=7.87×10^{-5}M, 15 wt.%-acetic acid solution=150ml, reaction temp.=30℃, swelling time=1hr., reaction time=3hr.)

Sample code	[Acrylamide] $\times10^{-3}$M	Weight of grafted acrylamide (g)	Weight increase(%)	Percetage of grafting(%)	Degree of grafting(%)	$\overline{M}_v\times10^{-6}$
A-1	2.11	0.095	4.75	9.50	4.75	3.48
A-2	4.22	0.235	11.75	11.75	11.75	3.68
A-4	8.44	0.575	28.75	14.38	28.75	4.12
A-6	12.66	0.765	38.25	12.75	38.25	4.17
A-8	16.88	0.709	35.45	8.86	35.45	4.16

Table 3. Graft Copolymerization of Chitosan and Acrylamide at Various Reaction Time (chitosan=2 g, [acrylamide]=8.44×10^{-3}M [CAN]=7.87×10^{-5}M, 30~50℃, swelling time=1hr.)

Reaction temp(℃)	Sample code	Reaction time(hr.)	Weight of grafted acrylamide(g)	Weight increase(%)	Percentage of grafting(%)	Degree of grafting(%)
30	T-30-0.5	0.5	0.083	4.16	2.08	4.16
	T-30-1.0	1.0	0.092	4.60	2.30	4.60
	T-30-2.0	2.0	0.380	19.00	9.50	19.00
	T-30-3.0	3.0	0.575	28.75	14.38	28.75
	T-30-4.0	4.0	0.596	29.80	14.90	29.80
	T-30-6.0	6.0	0.652	32.60	16.30	32.60
40	T-40-0.5	0.5	0.083	4.16	2.08	4.16
	T-40-1.0	1.0	0.108	5.38	2.69	5.38
	T-40-2.0	2.0	0.402	20.10	10.05	20.10
	T-40-3.0	3.0	0.739	36.96	18.48	36.96
	T-40-4.0	4.0	0.800	40.02	20.01	40.02
	T-40-6.0	6.0	0.781	39.06	19.53	39.06
50	T-50-0.5	0.5	0.084	4.20	2.10	4.20
	T-50-1.0	1.0	0.111	5.56	2.78	5.56
	T-50-2.0	2.0	0.602	30.10	15.05	30.10
	T-50-3.0	3.0	0.947	47.36	23.68	47.36
	T-50-4.0	4.0	0.940	47.00	23.50	47.00
	T-50-6.0	6.0	0.946	47.30	23.65	47.30

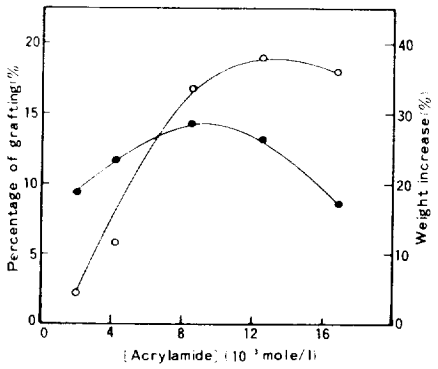


Fig. 4. Relation between percentage of grafting and weight increase on the various acrylamide concentration at 30℃. (chitosan=2g, [CAN] $=7.87\times10^{-5}$mole/l, 15 wt.%-acetic acid solution=150ml,swelling time=1hr.reaction time= 3 hr.) ● ; percentage of grafting, ○ : weight increase.

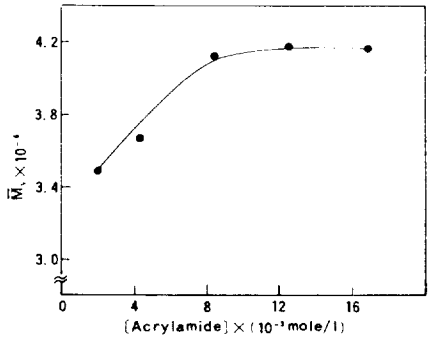


Fig. 5. Effect on the acrylamide concentration on the average molecular weight at 30℃ (chitosan=2g, [CAN]=7.87×10^{-5}M, 15 wt.% -acetic acid solution=150ml, swelling time= 1hr., reaction time= 3hr.).

from the complex.

Table 2 and Fig.4 illustrate the dependence of the grafting on the monomer concentration. The percentage of grafting decreased at high monomer concentration after having had a maximum at 8.44×10^{-3}mole/l. Also, the weight increased rapidly untill 8.44×10^{-3}mole/l of acrylamide concentration and then reached a plateau.

Fig.5 shows the effect of the acrylamide concentration against the viscosity average molecular weight. The viscosity average molecular weight reached a plateau at the above monomer con-

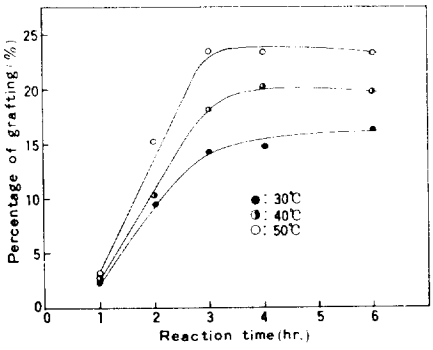


Fig. 6. Graft copolymerization of chitosan and acrylamide at various reaction time. (chitosan= 2g, [acrylamide]=8.44×10^{-3}M, [CAN]= 7.87×10^{-5}M, 30~50℃, swelling time=1hr.).

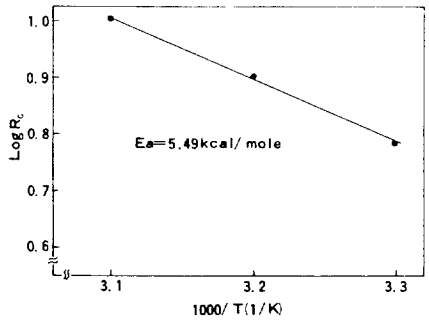


Fig. 7. Relation between the rate of grafting and polymerization temperature. (chitosan=2g, [acrylamide]=8.44×10^{-3}M, [CAN]=7.87×10^{-5}M).

centration after having had a maximum at 8.44×10^{-3}mole/l.

Table 3 and Fig.6 present the relationship between reaction time and the percentage of grafting at 30~50℃. As the reaction time became longer, the percentage of grafting increased initially, but after about 3 hours it reached plateaux for all reaction temperature. These results indicate that the propagation predominantly occurred in the initial stage but the termination rate may be considerably higher than the propagation rate with increasing reaction time.

As Fig.7 shows, the reaction temperature influenced the rate of grafting. The rate of grafting increased as the reaction temperature was raised.

Activation energy for initial reaction (≃3hrs) was estimated to be 5.49 Kcal/mole in the graft copolymerization of chitosan and acrylamide monomer.

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