

Graft Copolymerization of Vinyl Monomers onto Chitin with Cerium (IV) Ion

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SYNOPSIS

Graft copolymerization of vinyl compounds onto chitin was studied, and an efficient and reproducible procedure has been established, cerium (IV) being used as the initiator. The reactions with acrylamide and acrylic acid onto powdery chitin were carried out under various conditions to elucidate the polymerization behavior in terms of grafting percentage. The amount of cerium (IV) affected the polymerization most strikingly, and grafting percentages showed maxima with suitable amounts of initiator for both the monomers. As a solvent water proved to be superior to aqueous nitric acid except the reaction with a small amount of initiator. Under appropriate conditions, around 240 and 200% grafting percentages were achieved for acrylamide and acrylic acid, respectively. The resulting graft copolymers showed much improved affinity for solvents and hygroscopicity compared to the original chitin.

INTRODUCTION

Although chitin is structurally similar to cellulose and the second most abundant organic resource on the earth next to cellulose, much less attention has been paid to chitin than cellulose due primarily to its intractable nature, and it has remained as an almost unutilized but quite attractive organic resource. Chemical modifications may become a breakthrough to promote utilization,¹ and, among them, graft copolymerization is anticipated to be a promising approach allowing a wide variety of molecular design. We recently reported a procedure for graft copolymerization of an amino acid NCA onto chitin, resulting in the formation of chitin/polypeptide hybrid materials.² Efficient graft copolymerization of vinyl compounds is also of importance in view of industrial applications, since it would easily impart desirable properties by choice of various types of side chains. It has, however, not attracted attention until quite recently, and only several papers on graft copolymerization onto chitosan have been published including those by AIBN,^{3,4} iron (II)-hydrogen peroxide,⁵ and cerium (IV).⁶ Graft

copolymerization onto chitin has been studied even to a lesser extent, and only those by tributylborane⁷ and γ -ray irradiation⁸ were reported. Basic studies are thus required to develop graft copolymerization procedures giving new chitin/synthetic polymer hybrid materials.

We have examined the influences of various factors on the grafting extent to develop and generalize the graft copolymerization onto powdery chitin, cerium (IV) being used as the suitable initiator, since it generally gives scarce amounts of homopolymers and is readily applicable to industrial purposes. As monomers, acrylamide and acrylic acid were chosen because of the potential applications of the graft copolymers as water absorbents, chelating agents, ion exchangers, and other uses.

EXPERIMENTAL

Materials

Chitin was isolated from shrimp (*Penaeus japonicus*) shells⁹ and powdered (100-mesh pass). The degree of deacetylation was 10% as determined by IR spectroscopy.¹⁰ Vinyl monomers and solvents were purified by recrystallization or distillation in usual manners before use. Ceric ammonium nitrate

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(Kanto Chemical Co.) was used as received. Water was purified by deionization followed by distillation.

Graft Copolymerization

Into a flask were placed given amounts of pulverized chitin, vinyl monomer, solvent, and ceric ammonium nitrate, and the atmosphere was replaced with nitrogen by repeating a degassing-purging procedure five times. The mixture was heated at 60°C for a given time with stirring and then poured into 200 mL of water. The product was collected on a glass filter and washed with water until the filtrate became neutral. It was further treated with water at 60°C for 30 min two times. To the suspension in water was added aqueous sodium hydroxide to make the pH around 12, and the mixture was stirred for 30 min. The product was filtered, washed with water until neutral and then with acetone, and dried under reduced pressure.

Grafting percentages were calculated by the following equation:

grafting (%)

$$= \frac{\text{graft copolymer (g)} - \text{chitin (g)}}{\text{chitin (g)}} \times 100$$

Hygroscopicity

The graft copolymers were kept in a desiccator of saturated water vapor at room temperature and

weighed at proper time intervals to calculate the amounts of absorbed water.

RESULTS AND DISCUSSION

Graft Copolymerization of Acrylamide

The graft copolymerization of acrylamide was carried out on powdered chitin dispersed in water under heterogeneous conditions, giving rise to chitin-*g*-polyacrylamides. The influence of the amount of cerium (IV) was first examined in the polymerization of 0.30 g (4.2 mmol) of acrylamide onto 0.10 g of chitin in 10 mL of water at 60°C for 2 h. Water had to be carefully purified to obtain reproducible results and high grafting efficiencies. The resulting graft copolymers were isolated by pouring the reaction mixtures into water and washed thoroughly with water to ensure the removal of homopolymers. They were also treated with aqueous alkali to remove acidic residues possibly attached to the free amino groups of chitin.

As summarized in Table I, the pH value of the mixture dropped markedly on addition of ceric ammonium nitrate and then decreased gradually with an increase in the amount of initiator. The grafting percentage increased with the amount of initiator, reaching a maximum at 1.6 mmol, and then decreased as illustrated in Figure 1. The graft copolymerization proceeded reproducibly under these conditions, and the grafting of as high as about 240% could be attained.

Table I Graft Copolymerization of Acrylamide onto Chitin with Cerium (IV)^a

Initiator [g (mmol) ^b]	Solvent ^c	pH ^d	Yield (g)	Grafting (%)
0	H ₂ O	7.04	0.10	0
0.11 (0.2)	H ₂ O	1.50	0.115	15
0.22 (0.4)	H ₂ O	1.21	0.166	66
0.44 (0.8)	H ₂ O	1.00	0.249	149
0.66 (1.2)	H ₂ O	0.86	0.341	241
0.88 (1.6)	H ₂ O	0.76	0.343	243
0.99 (1.8)	H ₂ O	0.72	0.324	224
1.37 (2.5)	H ₂ O	0.62	0.222	122
0	HNO ₃	1.19	0.10	0
0.11 (0.2)	HNO ₃	1.06	0.143	43
0.22 (0.4)	HNO ₃	0.94	0.165	65
0.44 (0.8)	HNO ₃	0.82	0.203	103
0.88 (1.6)	HNO ₃	0.67	0.202	102

^a Chitin 0.10 g (corresponding to 0.50 mmol of pyranose rings); acrylamide 0.30 g (4.2 mmol); temperature 60°C; time 2 h.

^b Ceric ammonium nitrate.

^c Solvent: 10 mL of water or 0.1 mol L⁻¹ nitric acid.

^d pH values of the mixtures before starting the graft copolymerization.

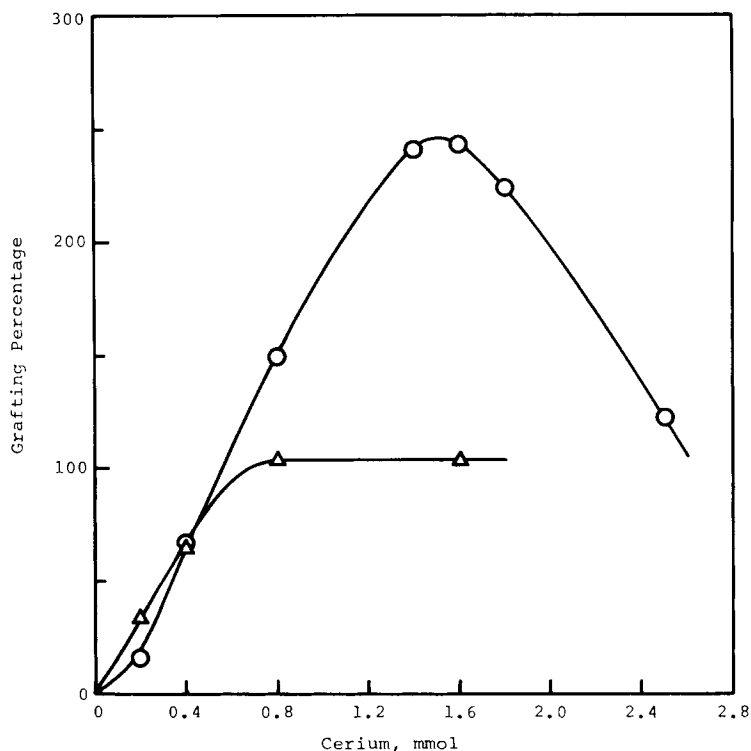


Figure 1 Graft copolymerization of acrylamide onto chitin with various amounts of cerium (IV) (chitin 0.1 g; acrylamide 0.3 g; solvent 10 mL; temperature 60°C; time 2 h). Solvent: (○) water; (Δ) 0.1 mol L⁻¹ nitric acid.

The graft copolymerization behavior was also examined in dilute nitric acid as suggested by the favorable effects generally recognized in the graft copolymerization onto cellulose. The reaction was conducted in 0.1 mol L⁻¹ nitric acid instead of water. The grafting was improved with a small amount of cerium (IV), but, with larger amounts, lower graftings were observed than in pure water as evident in Figure 1. These results indicate that the graft copolymerization is sensitively dependent on the reaction conditions, and optimum conditions proved to be determined by a combination of the amount of initiator and the pH value of the mixture.

The effects of reaction time on the grafting were then examined under the optimum conditions obtained above, and the results are shown in Figure 2. The grafting percentage increased in the initial stage and leveled off, 2 h being confirmed to be sufficient.

The amount of acrylamide was increased from 4.2 mmol to 8.5 and 12.7 mmol. As shown in Figure 3, the grafting was, however, not enhanced, and almost the same grafting percentages were attained even with increased amounts of monomer.

The resulting graft copolymers were obtained as white to off-white powdery materials. The IR spectra showed bands ascribable to polyacrylamide in ad-

dition to those characteristic of chitin. The amide I and II bands at 1640 and 1540 cm⁻¹ became strong and pyranose bands between 1050 and 1200 cm⁻¹ became relatively weak as the grafting percentage increased. Figure 4 shows a typical example of the IR spectra of the graft copolymers along with that of chitin.

The qualitative solubilities of the graft copolymers were examined in excess solvents at room temperature. Although they were not soluble in ordinary solvents, they showed somewhat improved affinity for solvents and swelled in dichloroacetic acid and 0.1 mol L⁻¹ sodium hydroxide.

Graft Copolymerization of Acrylic Acid

Acrylic acid was similarly subjected to graft copolymerization onto powdery chitin. The graft copolymerization was first carried out with 0.10 g of chitin, 0.43 g (6.1 mmol) of acrylic acid, 10 mL of water, and varying amounts of ceric ammonium nitrate at 60°C for 2 h. After the polymerization, the products were washed with water thoroughly to dissolve homopolymers and then with aqueous sodium hydroxide to remove acidic residues of the initiator. As a result, the side chain carboxyl groups were trans-

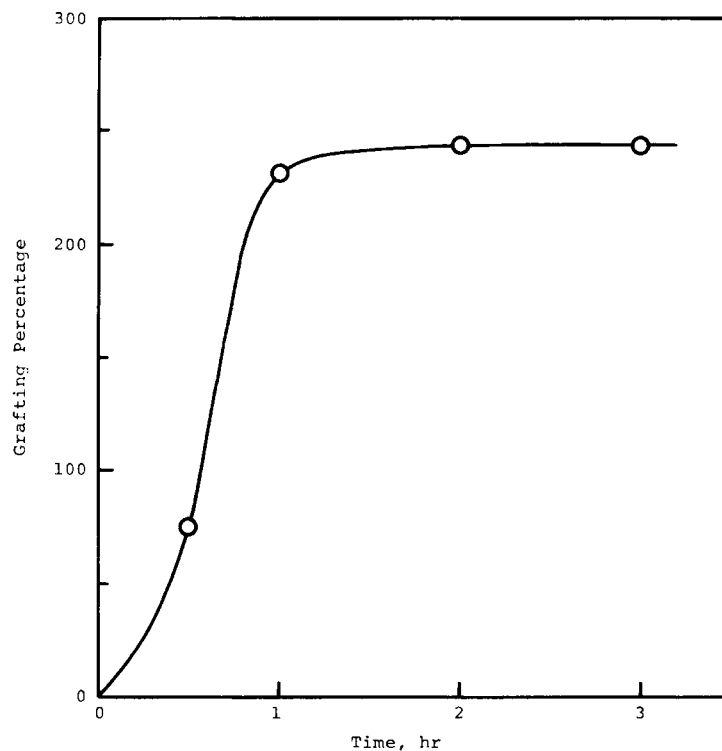


Figure 2 Influence of reaction time on the grafting of acrylamide (chitin 0.1 g; acrylamide 0.3 g; water 10 mL; cerium (IV) 1.6 mmol; temperature 60°C).

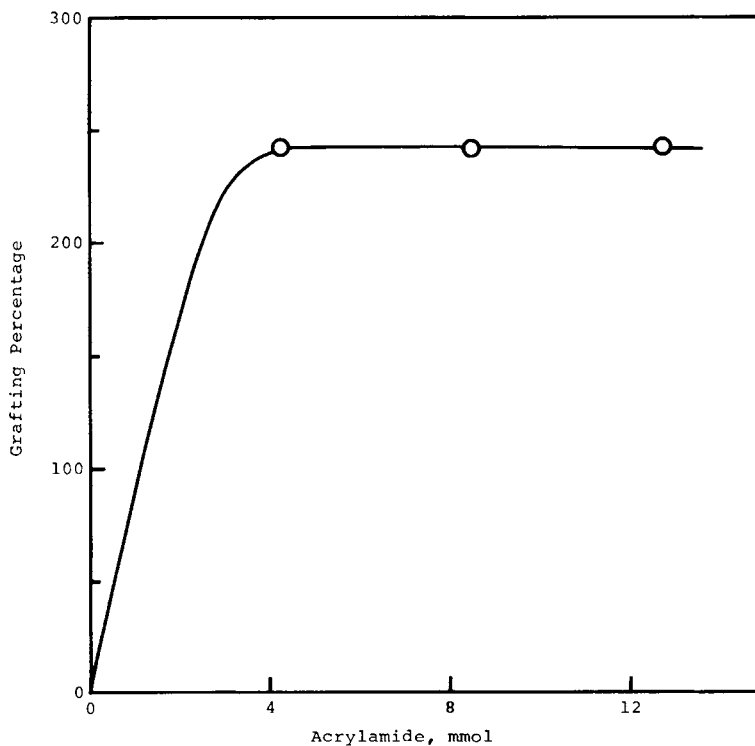


Figure 3 Effects of the amount of acrylamide on the grafting (chitin 0.1 g; water 10 mL; cerium (IV) 1.6 mmol; temperature 60°C; time 2 h).

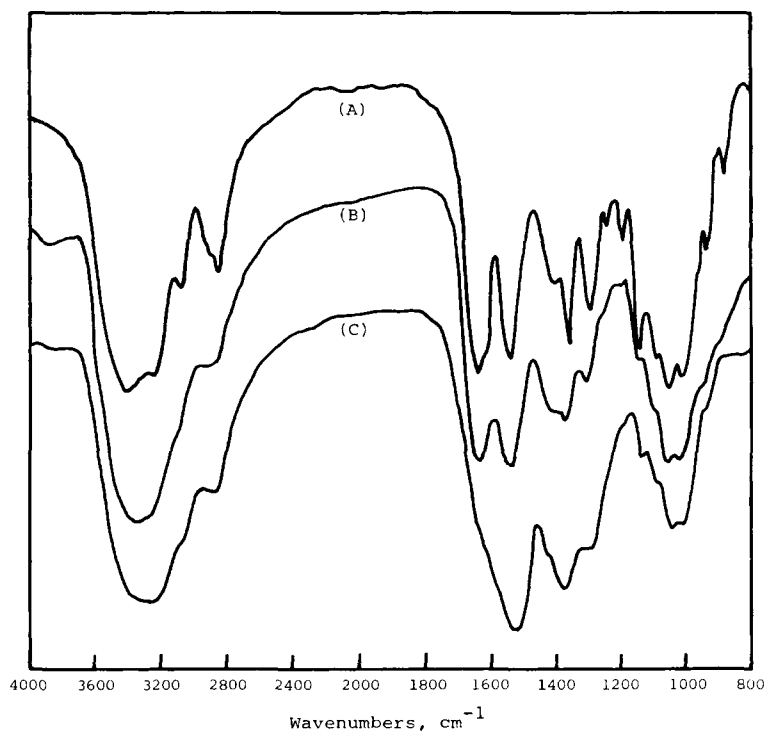


Figure 4 IR spectra of (A) chitin, (B) chitin-*g*-polyacrylamide (grafting 240%), and (C) chitin-*g*-poly(sodium acrylate) (grafting 190%).

formed into carboxylate groups, and chitin-*g*-poly(sodium acrylate)s were obtained. The grafting, as shown in Figure 5, increased with the amount of cerium (IV), and a maximum of 152% was achieved with 0.8 mmol of the initiator. It gradually decreased as in the case of acrylamide.

The reaction time also affected the grafting, and 2 h polymerization turned out almost suffice as indicated by the curve in Figure 6. When the amount of monomer was increased, the grafting increased initially (Fig. 7), but almost leveled off at around 200%. A slight reduction in grafting was observed

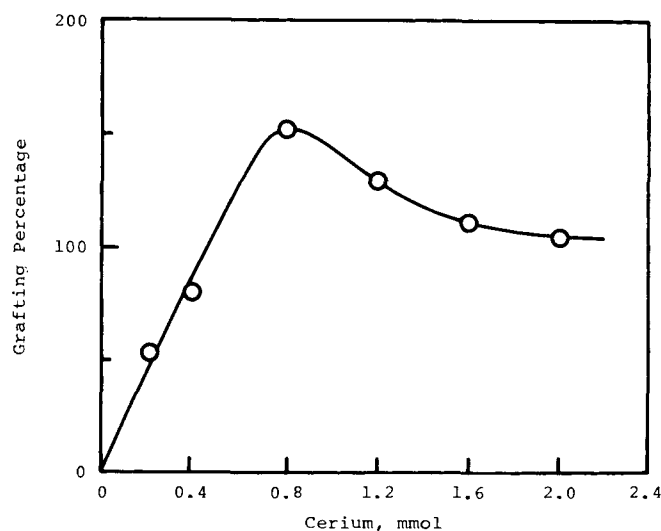


Figure 5 Graft copolymerization of acrylic acid with various amounts of cerium (IV) (chitin 0.1 g; acrylic acid 0.43 g; water 10 mL; temperature 60°C; time 2 h).

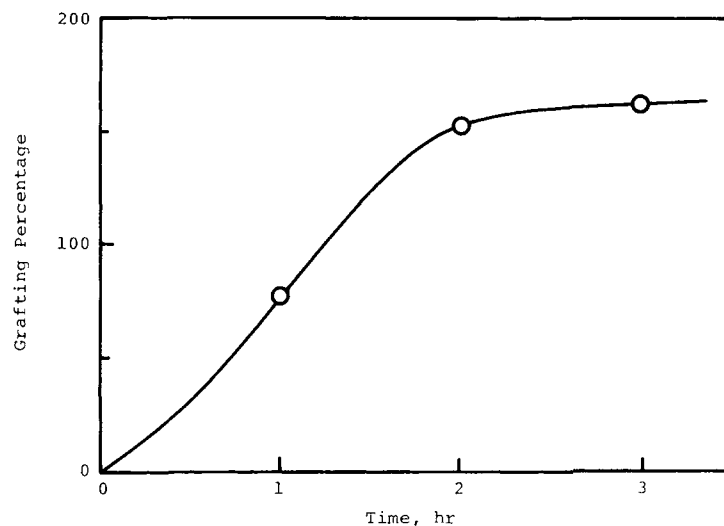


Figure 6 Time dependence of the graft copolymerization of acrylic acid (chitin 0.1 g; acrylic acid 0.43 g; cerium (IV) 0.8 mmol; water 10 mL; temperature 60°C).

as the amount of monomer increased over 11.7 mmol.

In the IR spectra of the copolymers, a characteristic absorption band of carboxylate was found at 1530 cm^{-1} , which became strong as the grafting increased. A typical example of the spectra is included in Figure 4. The solubility was improved considerably by graft copolymerization; they were readily soluble in dichloroacetic acid and swelled fairly in aqueous sodium hydroxide.

Hygroscopicity of the Graft Copolymers

Absorption of water vapor by the resulting graft copolymers as well as chitin was examined at room temperature in an atmosphere of saturated water vapor. The weight increases owing to water absorption are illustrated in Figure 8. As anticipated, introduction of polyacrylamide side chains into chitin brought about high hydrophilicity to chitin. Much improved hydrophilicity was, however, achieved by

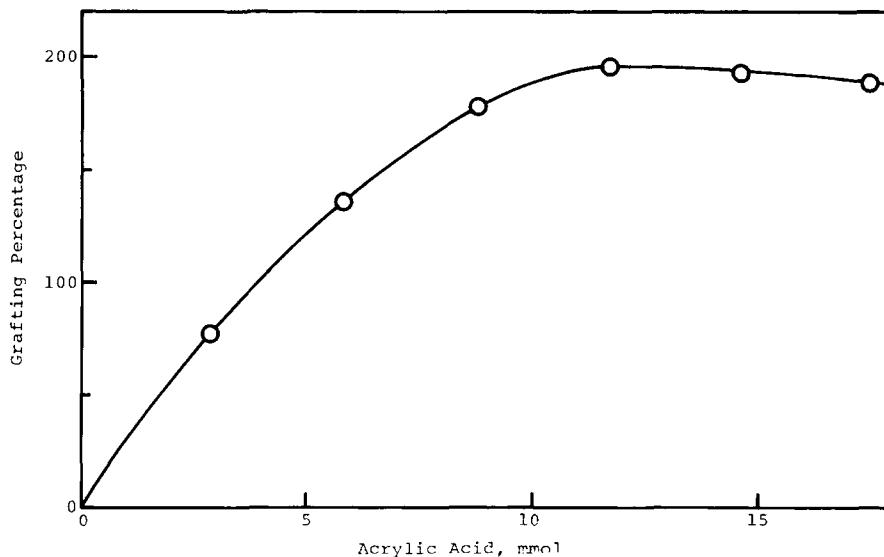


Figure 7 Influence of the amount of acrylic acid on the graft copolymerization (chitin 0.1 g; cerium (IV) 0.8 mmol; water 10 mL; temperature 60°C; time 2 h).

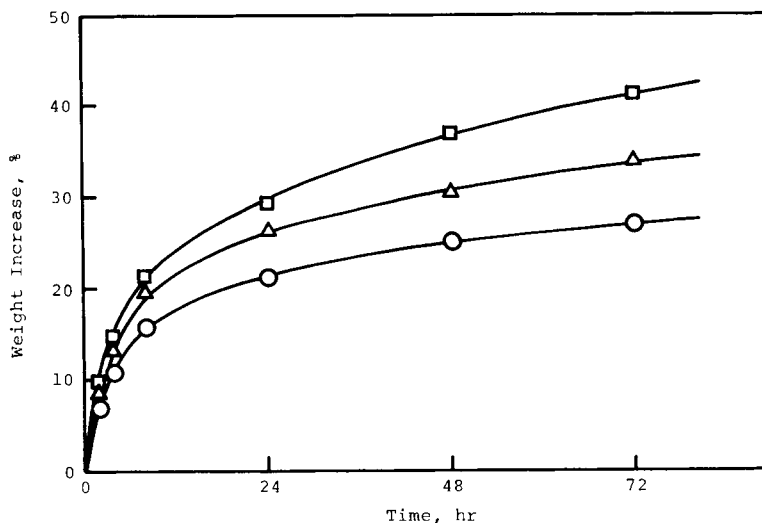


Figure 8 Water vapor absorption by (○) chitin, (△) chitin-*g*-polyacrylamide (grafting 240%), and (□) chitin-*g*-poly(sodium acrylate) (grafting 190%).

the graft copolymerization of acrylic acid; namely, chitin-*g*-poly(sodium acrylate) showed higher hygroscopicity than chitin-*g*-polyacrylamide.

CONCLUSIONS

A procedure for efficient and reproducible graft copolymerization of acrylamide and acrylic acid onto powdery chitin was established in the presence of cerium (IV). High grafting percentages were achieved under appropriate conditions in spite of the heterogeneous reaction. The resulting graft copolymers showed improved affinity for solvents and hygroscopicity compared to the original chitin, indicating graft copolymerization to be effective for chitin modifications.

This work was supported in part by a grant from the Science Research Promotion Fund, the Japan Private School Promotion Foundation, and also a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparations, and Control—, the Ministry of Education, Science, and Culture (#63604584).

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Received June 23, 1989

Accepted October 5, 1990