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GRAFT COPOLYMERIZATION OF METHYL ACRYLATE ONTO CHITOSAN INITIATED BY POTASSIUM DIPERIODATONICKELATE (IV)

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ABSTRACT

A novel redox system, potassium diperiodatonickelate [Ni (IV)]–chitosan, was employed to initiate the graft copolymerization of methyl acrylate (MA) onto chitosan in alkali aqueous solution. The effects of reaction variables such as monomer concentration, initiator concentration, reaction time, pH and temperature were determined. By means of a series of copolymerization, the grafting conditions were optimized. The maximum grafting percentage obtained was 404.1% when 0.3 g chitosan was copolymerized with 1.8 mL monomer at 35°C for 5 hours with [Ni (IV)] = 9.4×10^{-4} M and the total volume was 20 mL. Ni (IV)-chitosan system is found to be an efficient redox initiator for this graft copolymerization. A single electron transfer mechanism is proposed to explain the formation of radicals and the initiation. The grafted copolymers were characterized by IR and X-ray diffraction diagrams. The thermal stability of chitosan and chitosan-g-PMA was studied by thermogravimetric analysis (TGA).

Key Words: Potassium diperiodatonickelate [Ni (IV)]; Chitosan; Methyl acrylate; Graft copolymerization

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INTRODUCTION

The basic theoretical research and application on supernormal valence transition-metal attract more and more attention in chemical fields nowadays. It is no doubt that its feasibility in the polymerization widens people's thinking. In recent years, some achievements have been obtained on vinyl monomer polymerization and graft copolymerization initiated by supernormal valence transition-metals, such as Ag (III), Cu (III) [1–3]. But there are no reports on graft copolymerization of vinyl monomer onto chitosan using Ni (IV) redox system as initiator. Normally, it is believed that the mechanism of oxidation of Ni (IV) is a two-electron-transfer process without radicals, and Ni (IV) cannot initiate polymerization of vinyl monomer [4–9]. However, under our experimental conditions, the results show that radical polymerization of monomers such as acrylamide, and acrylonitrile can be initiated by Ni (IV) redox system [10–11]. A two-step single electron transfer mechanism is proposed to explain the produce of radicals and the initiation.

Chitin, poly- β -(1,4)-Nacetyl-D-glucosamine, is the second most abundant natural polymer on earth after cellulose. It is found widely distributed in the exoskeletons of insects and aquatic arthropods such as lobsters, crabs and shrimp. Chitosan, which is obtained from chitin through deacetylation using strong aqueous alkali solution, is a more versatile form of this polysaccharide. Grafting of various monomers onto its backbone is a promising method for the preparation of new materials, because the potential and multiple applications of this versatile material can be increased and its chemical and physical properties can be improved greatly. To date, in spite of many papers having been published on this, whereas they mainly focus on the studying of the grafting methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), poly (vinyl alcohol) (PVA) onto chitosan, and the initiators used are those traditional redox systems such as ceric ammonium nitrate (CAN) [12–16] $K_2S_2O_8$ [17–20], $Fe^{2+}-H_2O_2$ [21–23], etc. The grafting of methyl acrylate, an industrially important monomer, onto chitosan has been rarely reported [18, 23] and Ni (IV)-chitosan as initiator in the grafting polymerization has not been reported.

In this paper, Ni (IV) was employed as oxidant and chitosan as reductant to make up the redox system to initiate the grafting polymerization of MA on chitosan backbone in alkali aqueous medium. The combined effects of the principal reaction variables on the copolymerization were investigated and the structures and properties of the grafted products were characterized by infrared spectroscopy (IR), thermogravimetric analysis (TGA) and X-ray diffraction. In comparison with other initiators, the results showed that Ni (IV)-chitosan was an efficient initiation system.



EXPERIMENTAL

Materials

The sample of pure chitosan was obtained as a gift from the Yuhuan County Chemical Plant, Zhejiang Province. Its degree of deacetylation is $\geq 82\%$ and the molecular weight $2.0 \times 10^5 - 3.0 \times 10^5$. According to the publication [24], chitosan was ground into powders (< 60 mesh) from flats and dried under vacuum at room temperature. MA from the Beijing Yili Company was washed successively with aqueous sodium hydroxide solution and distilled water in order to get rid of the inhibitor. Then, it was dried over anhydrous sodium sulfate and finally distilled under vacuum. The middle fraction was used. Ni (IV) was synthesized and measured according to the reported procedure [5]. The other solvents (analytical grade) were used without any further purification.

Graft Copolymerization and Treatment of Copolymer

Graft copolymerization was carried out in a 50 mL four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet. In a typical reaction, 0.3 g chitosan was added with constant stirring under nitrogen. The required amount of monomer was added, followed by Ni (IV) aqueous solution and the total volume was made up to 20 mL with distilled water. The graft copolymerization was performed on the conditions of different temperature, pH, monomer concentration, initiator concentration and time. After completion of reaction, the reactant was cooled and poured in aqueous hydrochloric acid solution. Then it was filtered through weighted sintered glass funnel and washed to neutral, then dried to a constant weight under vacuum at 60°C . The homopolymer of methyl acrylate (PMA) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 hours. The final copolymer was then dried to a constant weight under vacuum.

Measurements

Chitosan-g-PMA was characterized, after exhaustive Soxhlet extraction to remove PMA, by IR analysis using an FTS-40 spectrophotometer in the potassium bromide medium. X-ray diffraction of the graft copolymer was carried out with Yaa 900 X-ray diffraction. The TGA of chitosan (8.7 mg) and the copolymers (7.5 mg) were carried out on a Shimadzu apparatus DGC-40 DTA-TG in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.



RESULTS AND DISCUSSION

The grafting parameters, such as grafting percentage (P%), efficiency percentage (E%) and total conversion percentage (C%) were defined and calculated as follows:

$$C\% = (\text{total weight of PMA} / \text{weight of MA charged}) \times 100\%$$

$$P\% = (\text{weight of PMA grafted} / \text{weight of chitosan}) \times 100\%$$

$$E\% = (\text{weight of PMA grafted} / \text{total weight of PMA}) \times 100\%$$

Effect of Temperature

When the other reaction conditions were invariable, the grafting parameters at various temperatures are shown in Fig. 1. In accordance with the general rule of radical polymerization, E% changes gradually and then levels off slightly. This may be due to the chance of chain transfer reaction speeding up with the increase of temperature that results in the increase of homopolymerization of MA. Both C% and P% increase at first and then decrease rapidly. Lower temperatures are a benefit for the

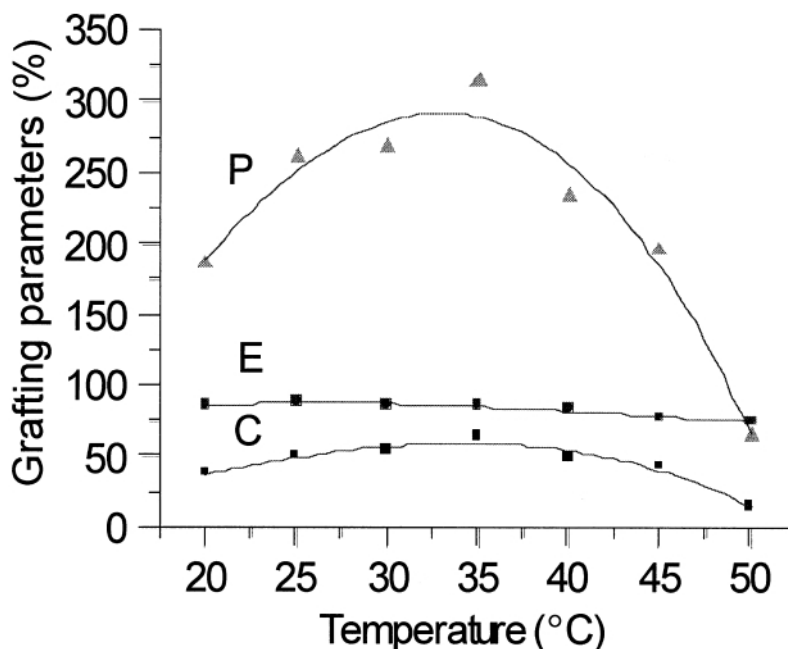


Figure 1. Effect of temperature on graft parameters. Chitosan: 0.3 g; MA: 2 mL; [Ni (IV)]: 4.9×10^{-4} M; 1 hour.



initiating reaction and the chain propagating. When the temperatures exceed 45°C, the termination reaction of Ni (IV) and radicals, as well as the chain transfer reaction speeds up, so the grafting parameters decrease at higher temperatures. The optimum temperature for maximum grafting is 35°C.

Effect of Monomer Concentration

By studying the influence of the amount of MA on the graft yields shown in Fig. 2, P% and C% reach a maximum when MA is added up to 2 mL and then fall gradually. This could be due to the fact that the concentration of Ni (IV) increases in aqueous phase relatively with the amount of MA increased due to the unchanged total volume. With an increasing Ni (IV) concentration, the number of free radicals on chitosan is augmented which initiates grafting polymerization of MA resulting in increased C% and P%. However, Ni (IV) not only reacts with reductant to produce radicals initiating polymerization of vinyl monomer, but also reacts with radicals terminating polymerization. Though the total weight of PMA increased, related to the MA charged, it is decreased. In addition, the more MA added,

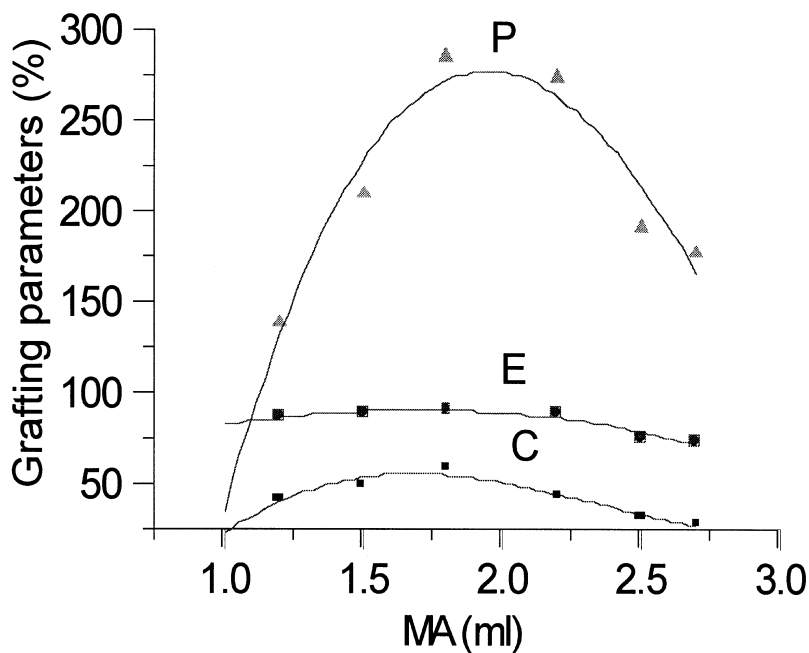


Figure 2. Effect of [MA] on graft parameters. chitosan: 0.3 g; [Ni (IV)]: 4.9×10^{-4} M; 37°C; 1 hour.

the more chance of chain transfer reaction to monomer. The increase of homopolymerization results in the decrease of P% and E%.

Effect of pH

The graft parameters were evaluated under conditions of different pH as shown in Fig. 3. The total volume 20 mL and the amount of Ni (IV) were kept unchanged and aqueous hydrochloric acid solution or aqueous potassium hydroxide solution was added in beakers to make up of solutions with different pH. pH was determined with acidimeter (PHS-3C). Then the required amount of aqueous hydrochloric acid solution or aqueous potassium hydroxide solution was added to the reaction system before Ni (IV) was injected to make pH varied, so that the graft copolymerization was carried out at different pH. The variation of pH causes the change of C% and P% because of the different complex forms of Ni (IV) at different pH. In alkali aqueous solution, the ratio of the concentration of $[\text{Ni}(\text{H}_3\text{IO}_6)_2(\text{OH})_2]^{2-}$ to $[\text{Ni}(\text{H}_2\text{IO}_6)_2(\text{OH})_2]^-$ changes with pH [25, 26], which directly influences the amount of radicals in the reaction system. The optimum pH for maximum grafting MA onto chitosan is between 12.5 and 13.0.

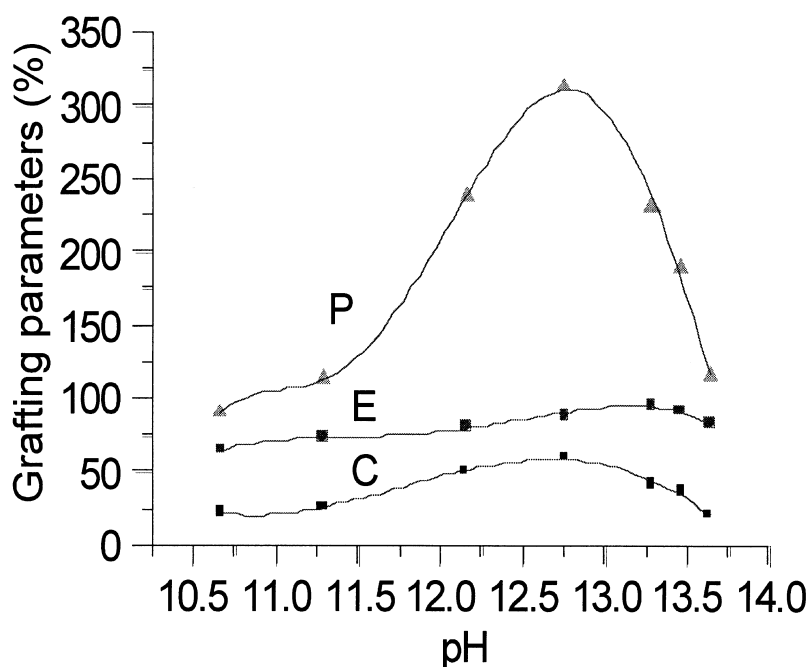


Figure 3. Effect of pH on graft parameters chitosan: 0.3 g; MA: 2 mL; [Ni (IV)]: 4.9×10^{-4} M; 1 hour; 37°C.

Effect of Initiator Concentration

The effect of Ni (IV) concentration on the extent of graft parameters is shown in Fig. 4. The concentration of Ni (IV) effects E% little, whereas the parameters P% and C% all show the tendency of increasing first with the increase of Ni (IV) concentration. This is because Ni (IV) attacks on the characteristic group ($-\text{NH}_2$) of chitosan backbone directly and so increasing macroradicals could be originated to initiate the polymerization of MA. As a result, C% and P% augment. However, an excess of the Ni (IV) concentration may accelerate the reaction of Ni (IV) and radical which terminates the chain propagating reaction. At the same time, the chance of chain transfer reaction to monomer is enhanced. Consequently, all these can cause the decrease of grafting parameters.

Effect of Reaction Time

Figure 5 illustrates the influence of the reaction time on graft parameters. Grafting percentage and total conversion percentage increases with the reaction time and P% and C% reached 404.1% and 86.2% after 5 hours respectively.

This may be the reason that Ni (IV) could keep its activity for a long reaction time. But E% changes little before 2 hours, and then it

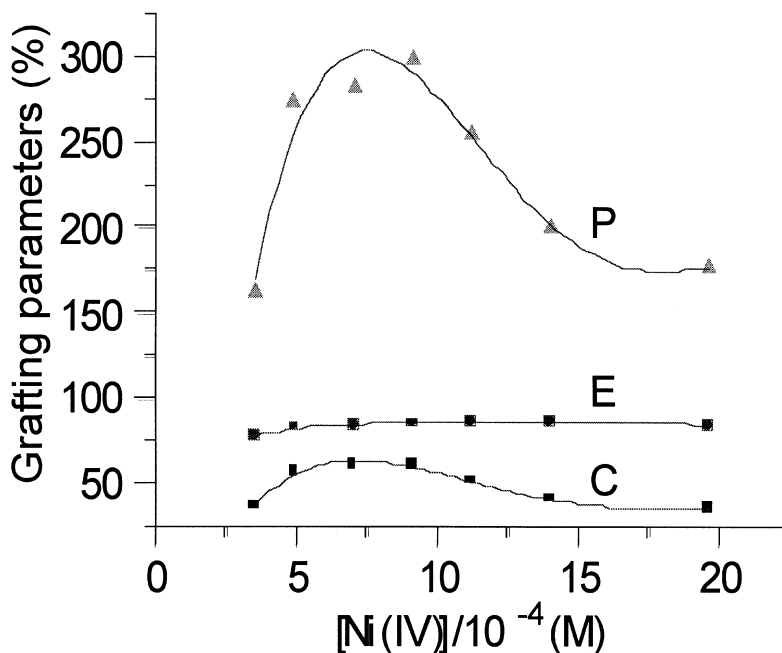


Figure 4. Effect of [Ni (IV)] on graft parameters. chitosan: 0.3 g; MA: 1.8 ml; 37°C; 1 hour.

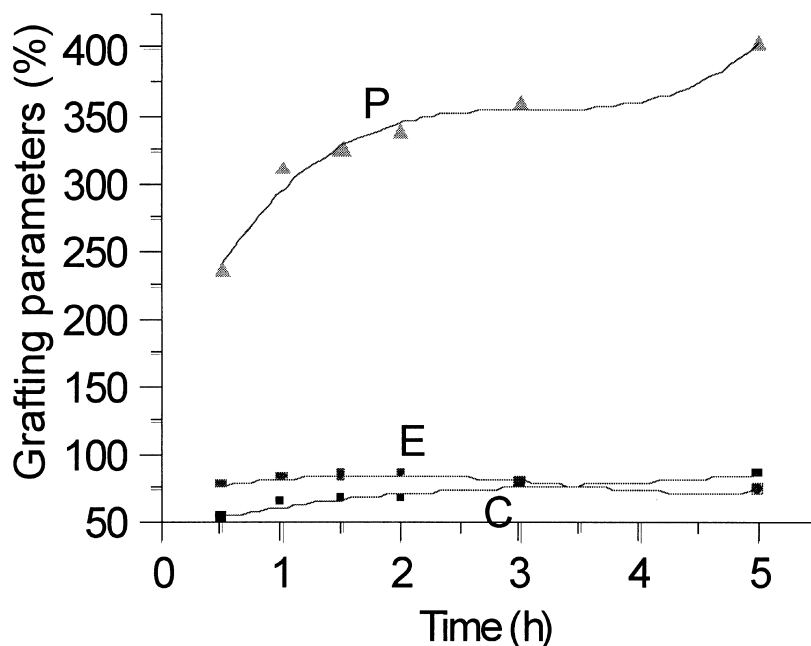


Figure 5. Effect of the reaction time on the graft parameters. Chitosan: 0.3 g; MA: 1.8 mL; [Ni (IV)]: 9.4×10^{-4} M; 35°C.

declines slightly. The chain transfer reaction is dominant after 2 hours, which results in the increase of homopolymerization of MA. Moreover, prolonging the reaction time could lead to the increase of hydrolysis of MA, which causes the pH to level off. These are the reasons why E% declines after 2 hours.

IR Spectroscopy

The grafting was confirmed by comparing the IR spectra of chitosan with that of the grafted product. The results obtained are shown in Fig. 6. The main difference observed is the appearance of a carbonyl absorption band at 1730 cm^{-1} corresponding to the carbonyl group of PMA chains. Absorption bands at 840 cm^{-1} and 752 cm^{-1} are observed due to the rocking absorption of methylene groups in PMA. All these bands are absent in the IR spectra of pure chitosan. Moreover, the N–H zigzag vibration bands of the copolymer at 1660 cm^{-1} (I), 1560 cm^{-1} (II) compared with that of pure chitosan become different. Due to the above results, it could be proposed that Ni (IV) reacts with amino group in chitosan to originate macroradicals first and then initiate MA grafting polymerization.



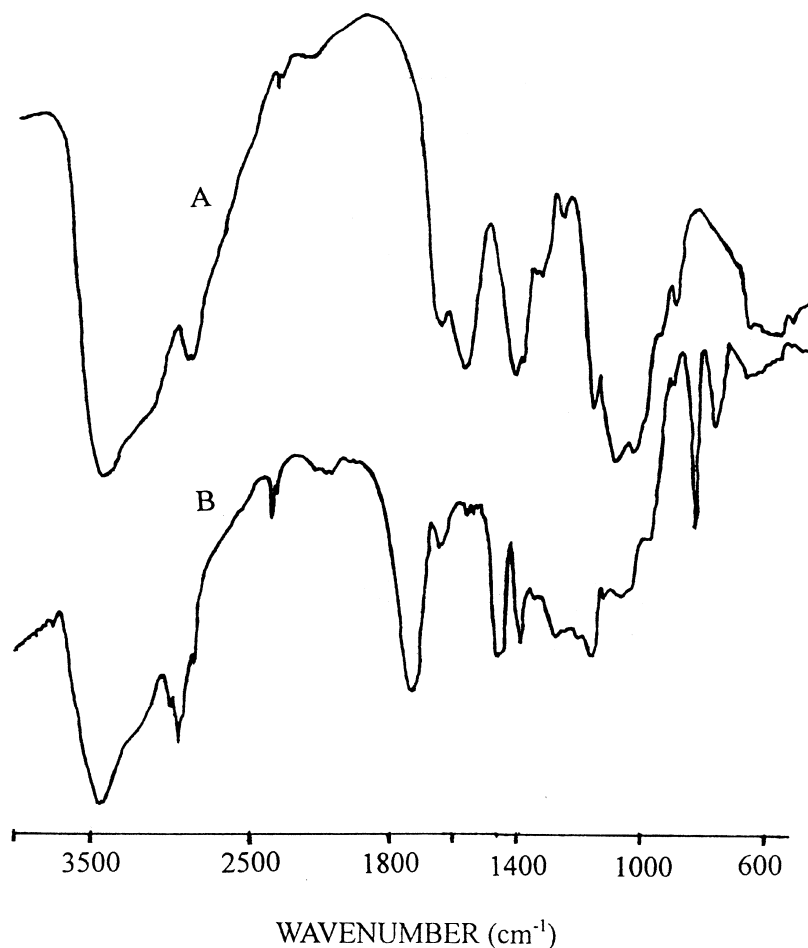


Figure 6. IR spectra of chitosan (A) and chitosan-g-PMA (B).

Thermal Analysis

Thermogravimetric analysis (TGA) of pure chitosan and the grafted copolymer is shown in Fig. 7. The TGA of chitosan shows a weight loss in two stages. The first stage ranges between 80°C and 120°C and shows about a 4.0% wt. loss. This may correspond to the loss of adsorbed and bound water. The second stage of wt. loss starts at 232°C and continues up to 341°C, during which there was 40.8% of wt. loss due to the degradation of chitosan. The TGA of the grafted product is different from it. It is observed the latter only has one stage of distinct wt. loss between 370°C and 442°C, with about 74.3% of the wt. loss that could be attributed to the grafted polymer.



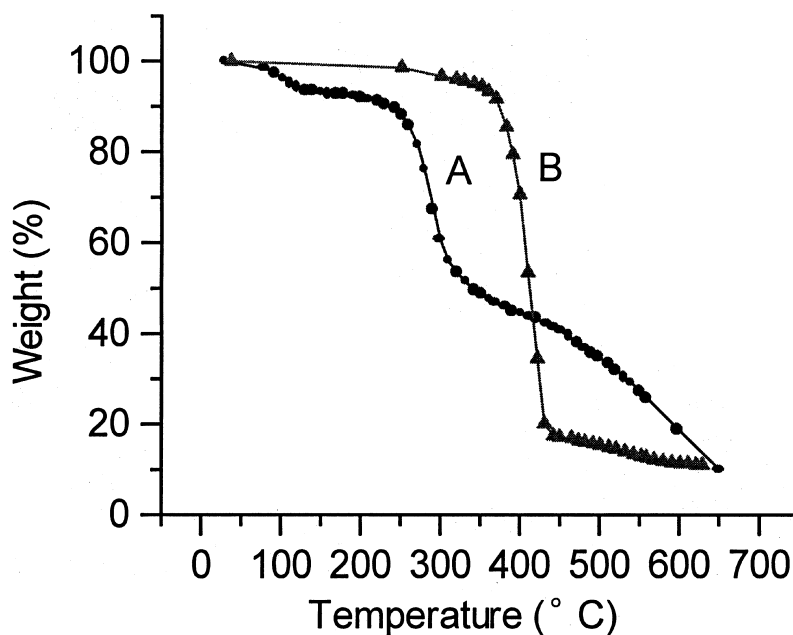


Figure 7. TGA curves of chitosan (A) and chitosan-g-PMA (B).

The decomposition temperatures of pure chitosan and chitosan-g-PMA at 50% wt. loss are 332°C and 410°C. It is evident that grafting MA onto chitosan could enhance the stability of pure chitosan at higher temperature.

X-Ray Diffraction Diagrams

The X-ray diffraction spectra of pure chitosan and chitosan-g-PMA were measured, which were shown in Fig. 8. The Figure of chitosan is more convex than that of copolymer. When the integrated angle range is at between 18.580° and 23.860°, the crystallinity of chitosan is 0.41 and that of chitosan-g-PMA is 0.14. The crystallinity of the graft copolymer decreased obviously.

Other Reactions

Besides the above experiment, experiments on grafting methyl methacrylate (MMA) and ethyl acrylate (EA) onto chitosan were carried out at the same time with Ni (IV) as initiator, respectively. When the condition is controlled at 35°C, $[\text{Ni (IV)}] = 9.4 \times 10^{-4} \text{ M}$ and the reaction time is 1 hour, P% of the graft copolymerization of MMA onto chitosan is 310.8% and that of EA onto chitosan is 298.6%.



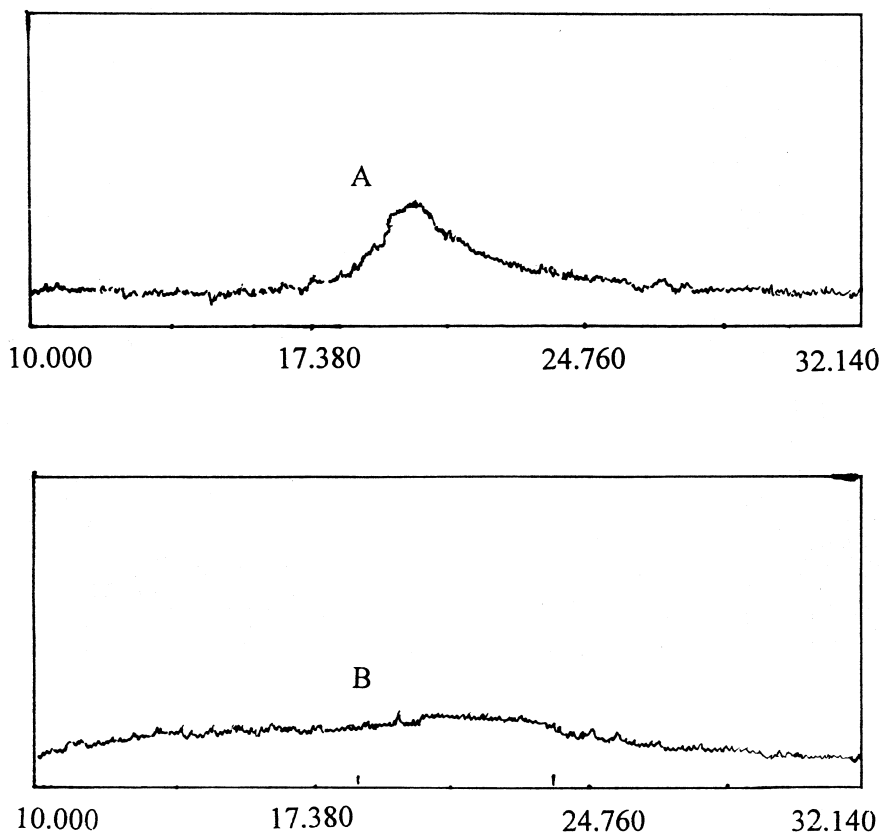


Figure 8. X-ray photograph of chitosan (A) and chitosan-g-PMA (B).

Solubility Test

The solubility test of chitosan-g-PMA is shown in Table 1. The grafted products are insoluble in solvents for either homopolymer. However, the graft copolymers swell in many solvents tested. This is probably due to partial crosslinking by radical coupling of PMA chain ends and/or intermolecular hydrogen bonding. In benzene, toluene, and chloroform, the copolymer became yellow and had loose particles because the grafted PMA may be dissolved.

The Initiation Mechanism of Grafting Reaction

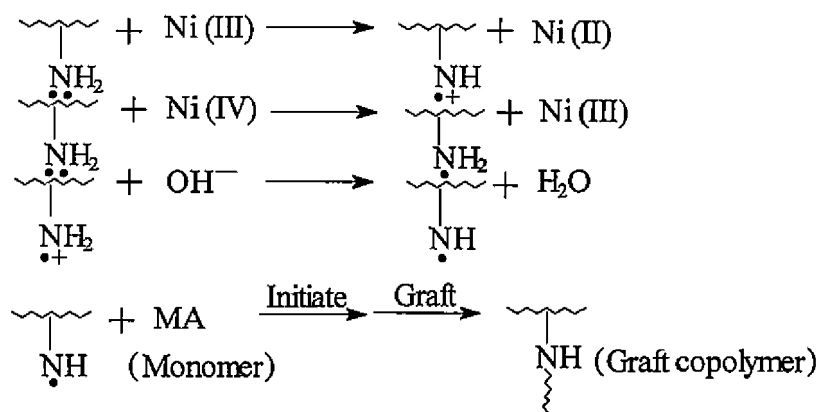
IR spectra, TGA, and X-ray diffraction diagrams illustrate that MA has been grafted onto chitosan. So, it could be concluded that the process $Ni(IV) \rightarrow Ni(II)$ belongs to the two-step single electron transfer mechanism.



Table 1. The Solubility of Chitosan-g-PMA

Solvent	Observation
1% acetic acid	White, swelling
Ethanol	Swelling
Glacial acetic acid: ethanol(1:1)	White, swelling
Glacial acetic acid: ethanol(1:2)	White, swelling
THF	Swelling
Acetone	Swelling
10% Tartaric acid	Swelling
Benzene	Yellow, insoluble
Toluene	Yellow, insoluble
Chloroform	Yellow, insoluble

The IR spectrum above has characterized the structure of graft copolymer chitosan-g-PMA. The initiation mechanism referring to the paper may be shown as follows:



CONCLUSION

The feasibility of grafting MA onto chitosan by using Ni (IV)-chitosan as the redox initiator has been demonstrated by this work. The crystallinity of the Chitosan-g-PMA sample levels off greatly and, due to the presence of PMA, the copolymer enhances hydrophobic character compared with pure chitosan. Moreover, grafted product shows augmented thermal stability and its solubility differs from that of unmodified chitosan.



It is commonly believed that the mechanism of oxidation by Ni (IV) is a two-electron-transfer process without radicals, and Ni (IV) cannot initiate polymerization of vinyl monomer. Under our experimental conditions, graft copolymer with high graft efficiency and grafting percentage using Ni (IV)-chitosan system as initiator has been obtained. Ni (IV)-chitosan is concluded to be an efficient redox initiator for the graft copolymerization. The two-step single electron transfer mechanism proposed in redox process is a modification to traditional mechanism. Moreover, because the activation energy of the reaction employing Ni (IV)-chitosan as initiator is low so that the graft copolymerization is able to be carried out at a mild temperature 35°C and in alkali aqueous medium, which is superior to other initiators. So, Ni (IV)-chitosan as initiator is thought to be practical and has a good foreground.

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GRAFT COPOLYMERIZATION OF METHYL ACRYLATE

143

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