Polymer Bulletin 49, 47-54 (2002)

Polymer Bulletin

Graft-copolymerization of methylacrylic acid onto hydroxypropyl chitosan

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Received: 25 Febuary 2002/Revised version: 7 July 2002/Accepted: 12 July 2002

Summary

In order to study the graft modification of chitosan derivatives, hydroxypropyl chitosan (HPCTS) was prepared and characterized by FTIR, ^{1}H NMR, and elemental analysis. Methylacrylic acid (MAA) was grafted onto HPCTS in an aqueous solution using ammonium persulfate (APS) as an initiator. Evidence of grafting was obtained by comparison of FTIR spectra of HPCTS and the grafted copolymer as well as solubility characteristics of the products. Variations of grafting percentage and grafting efficiency with reaction time, temperature, concentration of initiator and monomer had been investigated.

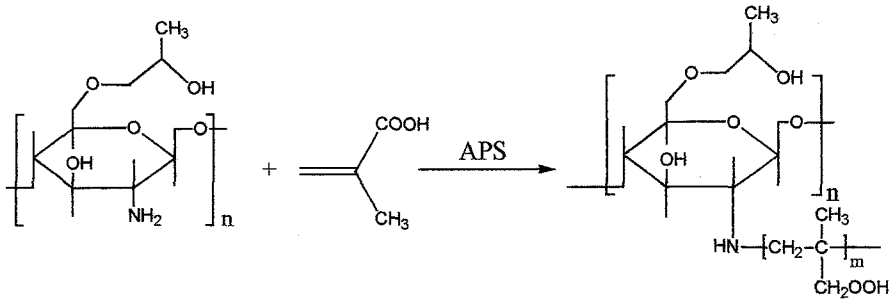
Introduction

Chitosan, the product of deacetylation of chitin, is one of the most important natural polysaccharides. Because of its special properties in structure and biodegradation, chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membranes and flocculation. However, chitosan can only solve in few dilute acid solution, which limits its wide applications. Recently, there has been a growing interest in chemical modification of chitosan to improve its solubility and widen its applications [1-7]. Among various methods, graft copolymerization is most attractive because it is a useful technique for modifying the chemical and physical properties of natural polymers.

Many investigations have been carried out on the graft copolymerization of chitin or chitosan [9-23]. However, the properties of grafted chitosan have been improved but not so much because of its regular structure and the strong intermolecular and intramolecular hydrogen bonds. Compared with chitosan, its derivative obtained from etherification has higher reactivity for the graft copolymerization [30]. But reports on the studies of graft copolymerization of chitosan derivatives are very limited [24-27]. Interestingly, recent researches showed that after primary derivation then followed by graft modification, chitosan would obtain much improved water solubility and bioactivities such as antibacterial and antioxidant activities [28-30].

It is very important to study the graft copolymerization of chitosan derivatives in view of preparing polysaccharide-based advanced materials with unique bioactivities and thus widening their applications in biomedicine. The present paper describes graft copolymerization of methylacrylic acid onto hydropropyl chitosan using APS as an initiator (Scheme 1). Effects of copolymerization conditions on

grafting are discussed in detail.



HPCTS HPCTS-g-MAA

Scheme 1 Reaction principal of graft copolymerization of hydropropyl chitosan

Experimental

Materials

Chitosan, a white powder of about 60 meshes, was supplied by Zhejiang Yuhuan Biochemical Co. Ltd. (China). Its degree of deacetylation was 97 % calculated from ^{1}H NMR, and average molecular weight was 8.8×10^5 determined by viscosity in the mixture solution of 0.2 N NaCl and 0.1 N HAc. It was purified before use as following: dissolved and precipitated several times, then extracted in a Soxhlet apparatus by refluxing in alcohol for 24 h, and dried at 60 °C under vacuum for 48 h. Ammonium persulfate (APS) was an analytical grade reagent and used as an initiator. Methylacrylic acid (MAA) was redistilled under reduced pressure prior to use. All other reagents were used as supplied by the company.

Preparation of hydropropyl chitosan

In order to increase the reactivity for graft copolymerization and obtain advance materials with multifunctions, hydropropyl chitosan was prepared before graft modification. Purified chitosan (8.0 g) was added into 50 wt% NaOH solution, swelled enough under room temperature, then put into a refrigerator at -18 °C for alkalization. Alkali chitosan and isopropyl alcohol (80.0 mL) were charged into a 250 mL three necked round-bottomed flask, and stirred for 1 h at 40 °C, then 80.0 mL propylene epoxide was added, and refluxed 2 h at 60 °C with continuous stirring. The reaction mixture was adjusted to pH 7.0 by adding 1/1 (v/v) HCl solution, filtrated, and the obtained product was repeatedly washed by acetone, absolute alcohol and 75% (v/v) alcohol, then dried under vacuum at 60 °C for 48 h.

Graft copolymerization

A 100 mL three necked round-bottomed flask, filled with a stirrer in a temperature-controlled water-bath, was used for the reaction. HPCTS, a desired quality of MAA, and deionized water were mixed with constant stirring and bubbling of a slow stream of nitrogen gas for about 30 min. Ammonium persulfate dissolved in moderate deionized water was slowly added into the flask to initiate the graft copolymerization. After the desired time interval, the reaction was stopped by letting air into the reactor and cooling the flask. The reaction mixture was adjusted to pH 7.0 by adding dilute NaOH

solution slowly. The products were precipitated by pouring the reaction mixture into alcohol/water mixture. The precipitate was filtrated, washed thoroughly by acetone, alcohol, and alcohol/water mixture, alternatively, and dried under vacuum at 60 °C for 48 h. The grafting parameters were calculated as:

$$\text{Grafting percentage}\,(GP/\%) = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

$$\text{Grafting efficiency}\,(GE/\%) = \frac{W_1 - W_0}{W_2} \times 100\% \quad (2)$$

where W_0, W_1, and W_2 denote the weight of HPCTS, graft copolymer, and monomer charged, respectively.

Characterization

IR spectra of chitosan derivatives were recorded with a NICOLET NEXUS 670 Fourier-transform infrared (FTIR) spectrometer in the range 4000-400 cm^{-1} using KBr pellets. Elemental analysis was performed in a CE instruments apparatus Mod. EA 1110 (ThermoQuest Italia S. P. A). ^{1}H NMR spectrum was measured on a Bruker DMX 500 spectrometer at 70 °C. HPCTS was dissolved in D_2O, which contained a small amount of CF_3COOH. ^{1}H chemical shifts were expressed in ppm downfield from the signal for sodium 4, 4-dimethyl-4-silapenture sulfonate (DSS) as an internal reference.
Water solubility was carried out as following: 0.10 g graft copolymers were dissolved in 20 mL deionized water under stirring for 48 h.

Results and Discussion

Characterization of chitosan derivatives

Structure changes of chitosan and its derivatives were confirmed by FTIR spectroscopy (figure 1).

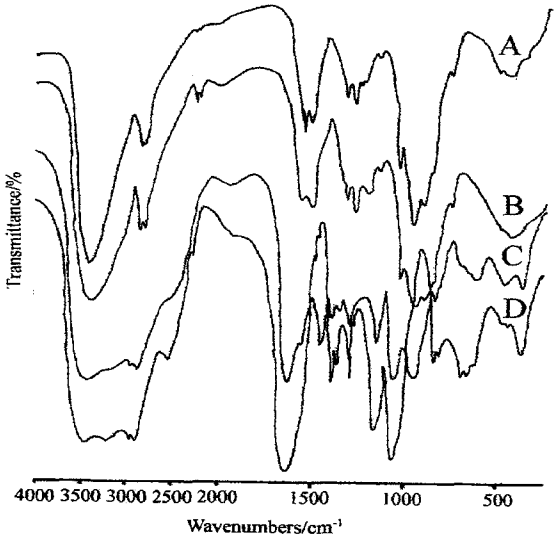


Fig. 1 FTIR of CTS (A), HPCTS (B), HPCTS-g-MAA (C) and PMAA (D)

The IR spectrum of chitosan showed three strong peaks at 1030 cm^{-1}, 1080 cm^{-1}, and 1150 cm^{-1}, which were characteristic peaks of saccharide structure. The much strong peak at around 3420 cm^{-1} should be assigned to the stretching vibration of O-H, extension vibration of N-H, and intermolecular hydrogen bonds of polysaccharide. There were weak absorption peaks of amide at 1650 cm^{-1}, 1550 cm^{-1} and a middle strong peak of 1599 cm^{-1}, which indicated that chitosan had very high deacetylation degree. Compared with chitosan, HPCTS had a different IR spectrum. Some peaks became stronger such as the stretching vibration of $-CH_2-$ and $-CH_3$ at 2850-2960 cm^{-1}, and the bending vibration of $-CH_2-$ and $-CH_3$ at 1380 cm^{-1} and 1460 cm^{-1}, respectively. The absorption of primary hydroxyl group at 1040 cm^{-1} became relatively weak, and the peak of secondary hydroxyl group of 1150 cm^{-1} became stronger. The deforming vibration of $-NH_2$ at 1599 cm^{-1} was very clear. The above results indicated that the substitution of hydroxyl propyl group mainly occurred at C_6 position. In the IR spectrum of HPCTS-g-MAA, there was a characteristic absorption peak at 1083 cm^{-1}, and characteristic peaks of PMAA at 1707, 1483, 1389, 1260, and 1179 cm^{-1}.

The degree of substitution of HPCTS was 0.25, which was calculated from the elemental analysis data: Anal. C, 43.90; N, 7.59; H, 7.37; Found. C, 43.89; N, 7.57; H, 7.04. The ^{1}H NMR spectrum for HPCTS showed the proton peaks of hydroxypropyl were found successively at δ=3.10 ppm, 5.05 ppm and 3.80 ppm, respectively.

Proof of grafting

As shown in the figure 1, the grafted copolymer HPCTS-g-MAA had both characteristic peaks of poly (methylacrylic acid) and saccharide unit of chitosan and its derivatives, which could be an effective evidence of grafting. There are some reports about that persulfate and fatty amine can combine a redox system to initiate the copolymerization of vinyl monomers [31-33]. Chitosan can act as a weak reducing reagent because of the amino groups in the polymer chains. Persulfate has been used to initiate the graft copolymerization of chitosan [14, 20-21, 27]. A conclusion has been drawn that the amino groups of chitosan took part in the initiation process when potassium persulfate was used as an initiator by comparing the graft copolymerization of chitosan with different deacetylation degrees. According to the above results, we can indicate that the initiator of APS and NH_2 group in HPCTS combined a redox system and initiated the copolymerization by generating free radicals in the macromolecules. This is, the graft copolymerization occurred at the NH_2 position, which can be proved by the fact that the absorption peak of NH_2 disappeared in the FTIR spectra of the graft copolymers.

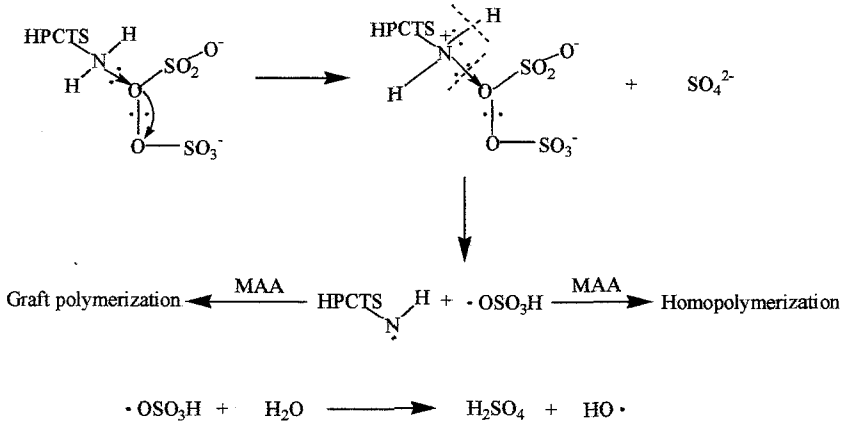
Chitosan and HPCTS with low substitution degree both have poor water solubility. All grafted copolymers have much improved water solubility, which could be another evidence of grafting.

Effect of initiator concentration

Redox initiator is often an efficient method for graft copolymerization. It usually results in grafting with a minimum of homopolymerization since only the polymer radical is formed. APS was selected as an initiator because it can combine with the free NH_2 group of HPCTS to form an effective redox system (Scheme 2) [14].

This kind of redox system will be helpful to the formation of macromolecules radicals on HPCTS. To study the effect of initiator concentration, graft copolymerization was studied at various APS concentrations by keeping all other reaction variables constant. It can be observed from figure 2 that GP% and GE% increased initially on increasing the initiator concentration up to 4 mmol/L, thereafter

decreased to a low value. The increase of GP% with increasing initiator concentration may be ascribed to the increase of the active sites on the saccharide unit of HPCTS arising from the attack of APS. With the increase of initiator concentration, the chance of redox reaction increased, more HPCTS macroradicals generated, thus more sites of HPCTS can react with MAA, and initiated the propagation reaction of MAA. This resulted in the increase of GP%. On the other hand, the increase of chance of redox reaction increased the amount of $\cdot OSO_3H$ and $\cdot OH$ radicals, and thus the collision chance with MAA to be helpful to the copolymerization of MAA. This resulted in the decrease of GP% and GE%.



Scheme 2 Redox mechanism of graft copolymerization of hydropropyl chitosan

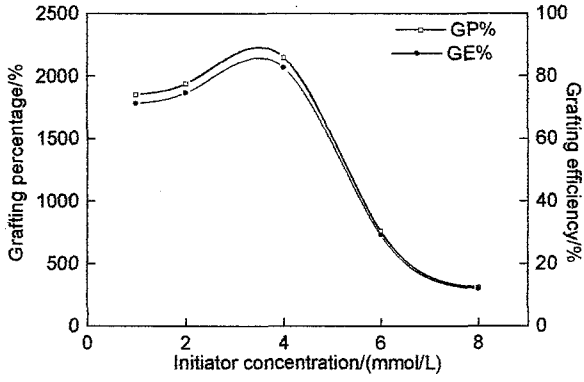


Fig. 2 Effect of concentration of the initiator on grafting percentage and grafting efficiency
Reaction conditions: HPCTS: 8 g/L; MAA: 1.2 mol/L; Time: 120 min; Temperature: 70 °C

Effect of concentration of MAA

The effect of monomer concentration on grafting is shown in figure 3. The GP% and GE% reached the maximum at the monomer concentration of 1.2 mol/L. With the further increase of amount of monomer, the GP% and GE% decreased greatly. As shown in the figure, GP% and GE% were very low

when the concentration of monomer reached 2.4 mol/L, which indicated homopolymerization was overwhelmingly predominated. As the MAA concentration increased, the collision chance of MAA molecules with HPCTS increased, leading to a higher GP%. When the amount of monomer was further increased, the $\cdot OSO_3H$ and $\cdot OH$ radicals generated from the redox reaction had more chance to interact with MAA, leading to the happening of homopolymerization, and decrease of GP% and GE%.

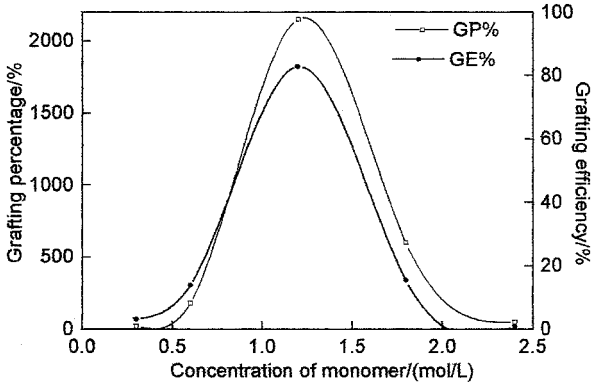


Fig. 3 Effect of concentration of monomer on grafting percentage and grafting efficiency
Reaction conditions: HPCTS: 8 g/L; APS: 4 mmol/L; Time: 120 min; Temperature: 70 °C

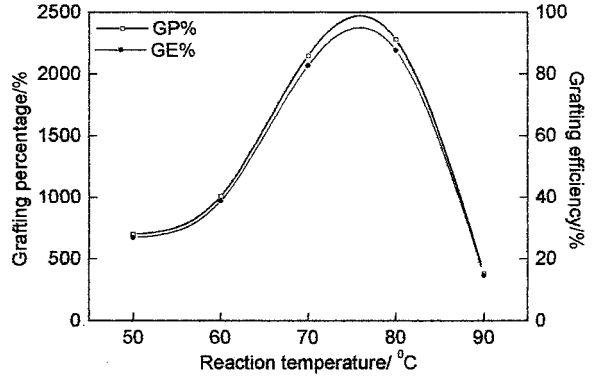


Fig. 4 Effect of reaction temperature on grafting percentage and grafting efficiency
Reaction conditions: HPCTS: 8 g/L; APS: 4 mmol/L; MAA: 1.2 mol/L; Time: 120 min

Effect of reaction temperature

The influence of reaction temperature is shown in figure 4. As can be seen, at the temperature of 70-80 °C, maximum grafting percentage was achievable. Both lower and higher temperatures than 70-80 °C were unfavorable. At lower temperatures, the decomposing rate of initiators was low. When the temperature was raised to 90 °C, the chain transfer and termination rate of polymerization was higher,

both resulting in a decrease of the values of W_1, GP% and GE%.

Effect of reaction time

Grafting of HPCTS was carried out by changing copolymerization times (30-150min.) and keeping other reaction conditions constant, as shown in figure 5. The GP% and GE% increased with increase in the reaction time, and level off after 90 min., reaching saturation grafting value. The leveling off of grafting may be attributed to the saturation of active HPCTS backbone by MAA.

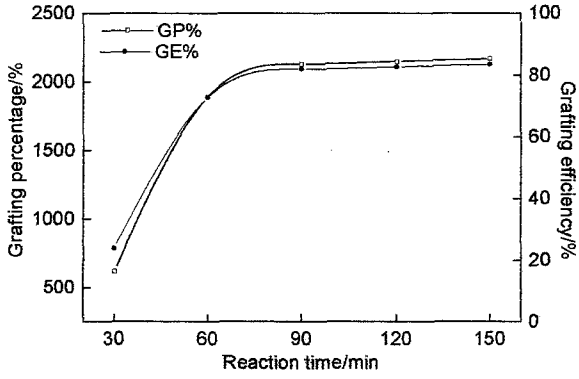


Fig. 5 Effect of reaction time on grafting percentage and grafting efficiency
Reaction conditions: HPCTS: 8 g/L; APS: 4 mmol/L; MAA: 1.2 mol/L; Temperature: 70 °C

Conclusions

MAA can be easily graft copolymerized onto HPCTS using an initiator APS in an aqueous medium. The reaction variables such as initiator concentration, monomer concentration, temperature and time played an important role in the grafting copolymerization of MAA on HPCTS. All the grafting copolymers have good water-solubility. The study of graft copolymerization of chitosan derivatives is very helpful to prepare polysaccharide-base advance materials with multifunctions and widen their applications.

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