

Article

Graft Copolymerization of Acrylonitrile on Biopolymer Chitin Using Ce^{4+} as the Redox Initiator

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A extração do polissacarídeo quitina [β -(1-4)-2-acetamido-2-desoxi-D-glicana] foi realizada a partir de cascas de camarão. O enxerto foi estudado em meio aquoso usando sulfato cérico como iniciador redox. Evidências de enxerto foram obtidas por espectroscopia infravermelho e pela eficiência da N,N-dimetilformamida na extração do homopolímero da mistura física de quitina e PAN. As percentagens de enxerto e de eficiência do processo foram calculadas em função das concentrações do iniciador e do monômero, do tempo de reação e da temperatura. A partir dessas dependências sobre os parâmetros de enxerto, foi sugerido um provável mecanismo para o enxerto envolvendo as participações dos radicais iniciador, monômero, quitina e quitina enxertada. Os melhores resultados obtidos foram com 109,30% de enxerto e com eficiência de 74,14%, e contribuem para a compreensão do mecanismo de copolimerização de enxerto do monômero vinílico acrilonitrila sobre quitina.

Polysaccharide chitin [β -(1-4)-2-acetamido-2-deoxy-D-glucan] was extracted from shrimp shells. The grafting of acrylonitrile on chitin was studied using ceric sulfate as the redox initiator in aqueous media. Infrared spectroscopy and the complete removal of the homopolymer from the physical mixture of chitin and PAN by N,N-dimethylformamide extraction were used as evidence of grafting. The percentages of grafting and the efficiency of the process were calculated as a function of the concentration of initiator and monomer, the reaction time and the temperature. From these dependencies on grafting parameters a plausible mechanism for grafting involving the participation of initiator radical, monomer radical, chitin radical and chitin graft radical is suggested. Maximum grafting occurred with a percentage grafting of 109.30% and a percentage efficiency of 74.14% and contributing to an understanding of the mechanism of the graft copolymerization of vinyl monomers on chitin.

Keywords: *chitin, graft copolymerization, polyacrylonitrile, ceric sulfate*

Introduction

Chitin, a biopolymer which forms the exoskeleton of insects and crustaceans, and consists mainly of β -(1,4)-2-acetamido-2-deoxy-D-glucose units, is the second most abundant polysaccharide occurring in nature, after cellulose^{1,2}.

Graft copolymerization reactions of vinyl monomers on chitin, using a redox initiator, have recently been explored as an interesting alternative chemical modification required

for the development of new natural / synthetic polymer hybrid materials³.

Extensive studies on the preparation, properties and applications of polysaccharide graft copolymers have been carried out, mainly on cellulose and its derivatives⁴⁻¹¹. Graft copolymerization on chitin and chitosan has been studied to a lesser extent¹²⁻¹⁶.

Chitin and chitosan graft copolymers, involving vinyl monomer grafted side chains, are promising as new materials for a number of applications, such as ion exchangers, chelating agents, modified electrodes, bactericides, mem-

branes for a number of separation procedures, binders for enzymes, and coatings for papers^{1,15,17-23}.

The present paper describes the grafting of acrylonitrile on chitin, **1**, using ceric sulfate as the redox initiator in aqueous media. In order to obtain an understanding of the mechanism of the grafting reaction, the effects of variation in reaction time, monomer concentration, initiator concentration and temperature on the grafting parameters were studied.

Experimental

Materials and methods

Chitin was extracted from shrimp shells, according to Ramachandram *et al.*, by alkali and acid treatment²⁴.

Acrylonitrile (Riedel) was extracted with an aqueous solution of 5% NaOH/20% NaCl to remove the hydroquinone stabilizer. The monomer was distilled and the middle fractions were used. Inhibitor-free acrylonitrile (Fluka puriss) was also used.

Reagent-grade ceric sulfate supplied by Merck was used to prepare the initiator solution, and was used without further purification. Other reagents were of analytical grade and were used without further treatment.

The infrared spectra were obtained from using a pastille of KBr on an Infrared Perkin-Elmer 781 spectrophotometer.

Graft copolymerization

The chitin powder sample was dispersed in a definite volume of deaerated distilled water, in a thermostated reaction flask at 60 °C for 60 min. The ceric sulfate in 0.5 M sulfuric acid solution was then loaded into the reactor under continuous stirring. Then, a known weight of acrylonitrile was also injected into the reactor. The reaction was assumed to have started at the moment the monomer was injected.

Graft copolymerization was carried out at room temperature under constant stirring in nitrogen atmosphere for 3 h. At the end of the graft copolymerization, the reaction mixture was neutralized with a 1 M NaOH solution, and the reaction products (graft copolymer and homopolymer) were filtered and thoroughly washed with distilled water, and then dried to a constant weight. The homopolymer was

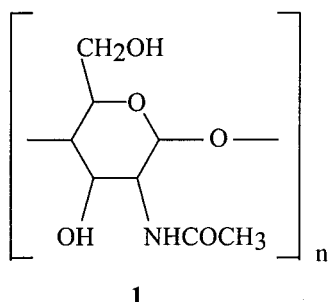


Figure 1. Structure of the chitin.

subsequently removed by extraction with N,N-dimethylformamide for 6 h. The remaining product, after drying to a constant weight, was considered to be a graft copolymer.

Grafting percentage (%G), which designates the amount of polymer grafted on the substrate backbone (chitin), and grafting efficiency (%E), which indicates the efficiency of conversion of the initial acrylonitrile to the grafted PAN, were calculated from the increase in weight of the chitin after graft copolymerization in the following manner:

$$\% G = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (1)$$

$$\% E = \frac{(W_2 - W_1)}{W_3} \times 100 \quad (2)$$

where W_1 , W_2 and W_3 represent the weights of the original chitin, the graft copolymer after N,N-dimethylformamide extraction, and the monomer, respectively.

Evidence of grafting

The infrared IR spectrum of the grafted chitin showed an absorption band at 2250 cm^{-1} , which was assigned to the axial deformation of the -CN bond of grafted PAN; no such band was present in the IR spectrum of the original chitin. These IR spectra were used as evidence of grafting, supporting the previous Differential Scanning Calorimetry studies¹⁶.

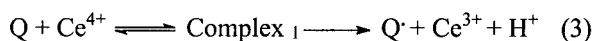
A physical mixture of chitin (1.00 g) and polyacrylonitrile (PAN) (0.50 g) in N,N-dimethylformamide was stirred at room temperature for 6 h. The mixture was filtered, and the residue was extracted with N,N-dimethylformamide for 6 h, at which time all the homopolymer was completely removed, and 0.90 g of chitin was recovered. Thus, the complete removal of homopolymer from the physical mixture by N,N-dimethylformamide extraction can also be a evidence for the grafting copolymerization of acrylonitrile on chitin.

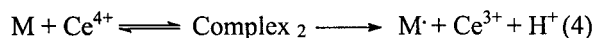
Results and Discussion

The graft copolymerization mechanism initiated by ceric ion, and the influence of certain factors on the grafting efficiency, such as the monomer and initiator concentrations, the temperature and the reaction time, are generally understood^{5,7,8-11}.

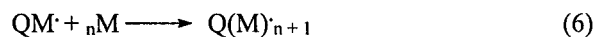
The following mechanism (Eqs. 3-10), which may be suggested to explain the grafting of vinyl monomers on polysaccharides such as cellulose, starch and wool, can also be assumed for the graft copolymerization of acrylonitrile on chitin initiated by ceric sulfate^{9,15,16}.

Initiation:

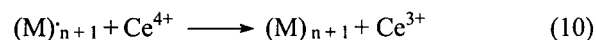
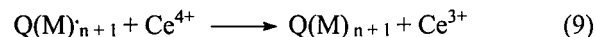
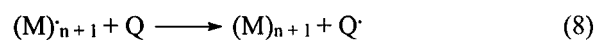




Propagation:



Termination:



where Q, M, $Q(M)_{n+1}$, and $(M)_{n+1}$ represent chitin, acrylonitrile, the graft copolymer and the homopolymer, respectively.

The effect of initiator concentration

Table 1 shows the effect of the concentration of the initiator Ce^{4+} on grafting acrylonitrile. It was observed that the maximum percentage of grafting occurred at 5.79×10^{-3} M. A further increase in the Ce^{4+} concentration leads to a decrease in the grafting percentage of acrylonitrile. This could be explained by the fact that ceric ion at a higher concentration causes the termination of grafted polymeric chains growth^{5,7,8}. Another factor which could contribute to a decrease in the grafting percentage at higher concentrations of initiator is the increase in the homopolymer formation, which competes with the grafting reaction for the available monomer^{7,11}.

The effect of monomer concentration

The effect of the acrylonitrile concentration on the graft yields obtained with chitin is shown in Table 2. An increase in the monomer concentration is accompanied by a significant increase in grafting up to 0.75 M. However, with a further increase in the concentration of the monomer, grafting is found to decrease. This could be ascribed to the substantial amount of polymer grafted on the substrate backbone, which inhibits the diffusion of Ce^{4+} and the monomer into chitin for further grafting⁷.

Table 1. The effect of redox initiator concentration on the grafting of acrylonitrile onto chitin^a.

N ^o	Chitin (g)	$[Ce^{4+}] \times 10^3$ (M)	%G	%E
1	4.03	3.94	50.62	34.91
2	4.07	5.79	109.30	74.14
3	4.07	7.58	43.07	25.24
4	4.00	9.30	44.44	29.65

^a acrylonitrile 6.00 g; temperature of 25 °C; reaction time of 180 min.

Table 2. The effect of monomer concentration on the grafting of acrylonitrile onto chitin^a.

N ^o	Chitin(g)	Acrylonitrile (g)	%G	%E
1	2.02	0.50	-	-
2	2.00	1.00	3.01	1.49
3	2.02	2.00	69.33	68.63
4	2.10	3.00	10.50	7.35

^a $[Ce^{4+}] = 3.90 \times 10^{-3}$ M; temperature of 25 °C; reaction time of 180 min.

The effect of temperature

The dependence of the grafting yields on temperature in the range of 25-52 °C is shown in Table 3. The maximum grafting of acrylonitrile occurs at 35 °C within 180 min. A further increase in temperature reduces the percentage of grafting. This is to be expected, since at higher temperatures various chain transfer reactions are accelerated, which leads to a decrease in the percentage of grafting, or in other words, the formation of more homopolymer⁸.

The effect of time

The effect of the reaction time on the percentage of grafting and the grafting efficiency is shown in Table 4. The percentage of grafting was found to increase linearly with time, and then remained approximately constant. The initial increase in the rate is due to the increase in the number of grafting sites, but this number remains constant with further increases in time^{7,11}.

Table 3. The effect of temperature on the grafting of acrylonitrile on the chitin^a.

N ^o	Chitin (g)	T (°C)	%G	%E
1	2.10	25	10.50	7.35
2	2.04	35	54.41	36.82
3	2.04	42	4.14	2.81
4	2.05	52	-	-

^a $[Ce^{4+}] = 3.90 \times 10^{-3}$ M; acrylonitrile = 3.00 g; reaction time 180 min.

Table 4. The effect of time on the grafting of acrylonitrile onto chitin^a.

time	%G	%E
30	2.24	1.53
60	3.02	2.05
90	3.84	2.61
150	3.80	2.58

^a $[Ce^{4+}] = 3.90 \times 10^{-3}$ M; chitin = 2.00 g; acrylonitrile = 3.00 g; reaction temperature of 25 °C.

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