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CERIC ION-INITIATED GRAFTING OF POLY(METHYL ACRYLATE) ONTO CHITIN

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ABSTRACT

Poly(methyl acrylate) was grafted onto chitin in an aqueous medium by using the ceric ion as a redox initiator in the presence of 10^{-4} M nitric acid and oxygen from the atmosphere. The grafting percentage turned out to be dependent on reaction temperature, time, and initiator concentration, but it was found to be independent of monomer concentration. In the course of the grafting reaction, homopolymerization of methyl acrylate occurs. The percentage of homopolymer was found to depend only on the reaction temperature. The apparent activation energy for the grafting reaction was estimated to be 11 kcal/mol. The grafted chitin is insoluble in solvents for chitin but shows enhanced swelling in some organic solvents.

INTRODUCTION

Cellulose-like biopolymers such as chitin (poly- β (1 \rightarrow 4)-*N*-acetyl-D-glucosamine) is distributed widely in nature where it forms the principal constituent of the shell of crustacea such as crabs, lobsters, prawn, antarctic krill, etc. Chitin is structurally analogous to cellulose, containing an acetamido group instead of the C-2 hydroxyl group [1–3]. However, the chemical and physical properties of chitin are quite different from those of cellulose. Chitin has been subjected to numerous modifications, and several applications, predominantly in medicine, have been re-

ported in the literature [3–14]. Recently there has been a growing interest in the study of grafting of vinyl monomers onto this biopolymer [15–23]. The chemical combination of natural and synthetic polymers by grafting technique yields new materials which could have desirable properties for new applications such as flocculants, ion exchangers, etc. Graft copolymerizations of methyl methacrylate (MMA) onto chitin using tributylborane as initiator [15], styrene onto chitin using γ -ray irradiation [16, 17], MMA onto chitin film using a ceric salt [18], γ -methyl-L-glutamate NCA onto chitin and water-soluble chitin [19, 20], MMA onto chitin and oxchitin by a noncatalytic photoinduced and photosensitized method [21], and MMA [22], acrylamide, and acrylic acid [23] onto chitin using ceric ammonium nitrate as redox initiator have been reported in the literature. It has been shown that ceric salts are very efficient in grafting vinyl monomers onto a number of polysaccharides [24–31].

The purpose of the present work was to determine the feasibility of grafting poly(methyl acrylate) onto chitin by using ceric ion in dilute nitric acid as a redox initiator. The effect of reaction time and temperature as well as the monomer and initiator concentrations were extensively investigated. This was done in order to optimize the grafting process.

EXPERIMENTAL

Materials and Methods

Chitin was obtained from lobster by the method of Hackmann [32] and purified by extraction with acetone in a Soxhlet apparatus for 24 h, washed with methanol and then with diethyl ether, and finally dried under reduced pressure at room temperature. Methyl acrylate (MA) from Fluka was washed with 5% NaOH, then with distilled water, dried over CaCl_2 , and finally distilled under vacuum. Ceric ammonium nitrate (CAN) from Merck was used as received.

Graft Copolymerization

Into a reaction tube were placed given amounts of pulverized and dried chitin (<100 mesh) and freshly prepared CAN solution in nitric acid (10^{-4} M). The reaction tube was then closed and placed in a thermostated bath at the desired reaction temperature and was shaken for 1 minute. Methyl acrylate was then added with stirring. Graft copolymerizations were carried out at 50, 60, and 70°C in the presence of atmospheric oxygen. At the end of the polymerization, the grafted chitin was separated from unreacted monomer by filtration, washed with plenty of warm water, and dried under vacuum to constant weight. The copolymer obtained was freed from poly(methyl acrylate) as homopolymer by extraction with acetone in a Soxhlet for 24 h, and the remaining product after drying to constant weight was considered to be a graft copolymer. The increase in weight of the extracted copolymer samples, compared with that of the original unreacted chitin and the weight of the extracted homopolymer, was used to calculate the grafting parameters as follows:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

$$\% \text{ grafting efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

$$\% \text{ homopolymer} = \frac{W_4 - W_2}{W_3} \times 100$$

$$\% \text{ total conversion} = \frac{W_4 - W_1}{W_3} \times 100$$

where W_1 , W_2 , W_3 , and W_4 denote the weights of chitin, grafted chitin after acetone extraction, methyl acrylate, and grafted chitin before acetone extraction, respectively.

RESULTS AND DISCUSSION

Evidence of Grafting

The increase in weight of the extracted copolymer samples, as compared with that of the initial chitin and their infrared (IR) spectra, were used as evidence of grafting. The IR spectra of chitin and grafted chitin are shown in Fig. 1. It can be seen that a band at $5.8 \mu\text{m}$ arises from carbonyl absorption of chitin and a new band appears at $6.1 \mu\text{m}$ which corresponds to the carbonyl absorption of grafted PMA chains. Two other new bands in the IR spectrum of grafted chitin, at 12.1

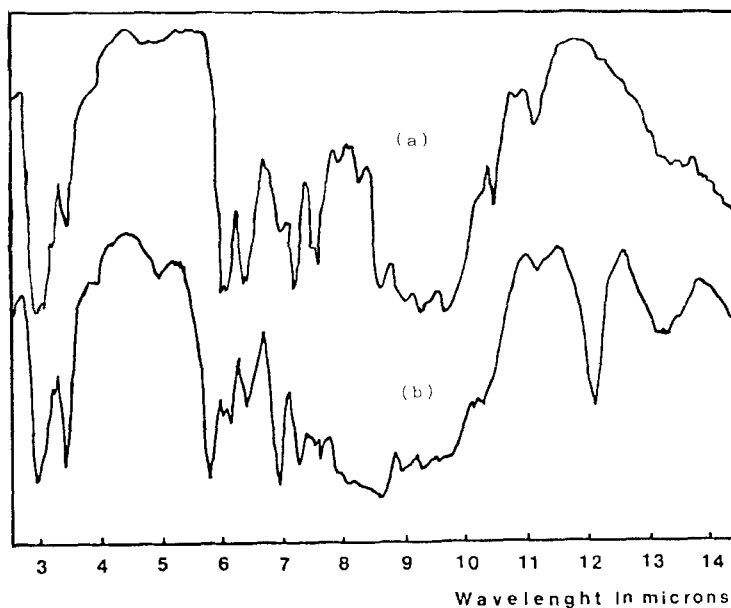


FIG. 1. IR spectra of chitin (a) and grafted chitin with PMA (b).

and 13.2 μm , are also observed. They are assigned to rocking absorption of $-\text{CH}_2$ groups contained in PMA chains.

Grafting Sites and the Copolymerization Reaction

To our knowledge the mechanism of graft copolymerization of vinyl monomers onto chitin with ceric ion has not been established. Lee et al. [22] found that the presence of water was essential for grafting when they carried out grafting of MMA onto chitin by ceric ion. They proposed that water is responsible for the rupture of intermolecular hydrogen bonds between chitin molecules so that MMA could diffuse readily into them. The grafting was assumed to proceed via free radical mechanism in three steps by cooperative interaction of water to chitin, formation of the complex from solvated chitin and ceric ion, and graft initiation by free radicals from the complex. On the other hand, Takahashi et al. [21] in their study of grafting MMA onto oxychitin by a noncatalytic photoinduced and photosensitized method suggested that free radicals were produced on the chitin backbone by the scission of the C2–N bond since the C–N bond has the lowest of all the chemical bond energies of chitin. We think that free radicals could also form on the C2 of anhydroglucosamine rings when the ceric ion is used to initiate grafting. These free radicals can be expected to be relatively stable due to the presence of acetamido groups. Therefore, these should be capable of initiating the graft copolymerization of MA onto chitin. A somewhat different reaction mechanism has been suggested by a number of investigators [33–39] for the case of cellulose where the ceric ion (Ce^{IV}) in acidic solutions forms a chelate with the cellulose molecule, probably by reaction through the hydroxyl groups and carbon C2–C3 of the anhydroglucose ring. Electron transfer from cellulose to the Ce^{IV} ion reduces this to Ce^{III} , followed by the release of Ce^{III} ions and anhydroglucose ring cleavage at the C2–C3 bond with the formation, on the cellulose backbone, of a free radical which is capable of initiating graft copolymerization.

Effect of the Initiator Concentration on Grafting

Table 1 shows the effect of CAN concentration on polymer add-on. The highest grafting yield was observed when the initiator concentration is 0.06 mol/L. For higher concentrations of the initiator, an increase in the percentage of grafting and, consequently, total conversion and grafting efficiency were not observed. As can be seen from Table 1, the percentage of grafting begins to level off when the concentration of the initiator is greater than 0.06 mol/L. The increase in grafting percentage with increasing CAN concentration could be due to the greater number of active sites formed on the chitin backbone which are initially involved in the grafting reaction. However, the leveling off of the grafting yield observed at higher initiator concentrations could probably be attributed to the limited number of radical sites that can only form on the surface of chitin. The decay of free radicals could also occur by transfer and termination processes.

In the case of cellulose, the decay of free radicals on the cellulose molecule by Ce^{IV} ion interaction has been observed [35]. These authors attribute this to the possible reaction of Ce^{IV} ion with the free radical to yield Ce^{III} ion and oxidized

TABLE 1. Influence of CAN Concentration on the Grafting of MA on Chitin^a

Sample	(CAN) × 10 ³	% Grafting	% Grafting efficiency	% Homo- polymer	% Total conversion
1	3	1.1	0.1	0.8	0.9
2	6	14.0	1.5	1.7	3.2
3	9	257.9	27.0	18.8	45.8
4	30	449.4	47.0	51.1	98.1
5	60	488.3	51.1	44.7	95.8
6	90	492.5	51.5	48.0	99.6

^aReaction conditions: Chitin, 0.3 g; MA, 2.87 g; HNO₃, 10⁻⁴ M (8 mL); temperature, 60°C; reaction time, 45 min.

products of cellulose. On the other hand, Terasaki et al. [32] proposed that the reaction of a solvent, usually water, with the free radical could also terminate the radical.

The homopolymer formation could be the result of the high oxidation potential of ceric ion. The percentage of homopolymer formed during graft copolymerization increases with CAN concentration up to 0.03 mol/L and then remains almost constant with any further increase in initiator concentration. This can be explained by taking into account that the reaction of the oxidant cations with monomer molecules at higher concentrations of the initiator is also favored until a point is reached where the excess cations take part in a chain termination process.

Effect of Monomer Concentration on Grafting

The influence of monomer concentration on grafting yield obtained with chitin is shown in Table 2. The percentage of grafting is independent of the monomer concentration. This can be due to the heterogeneous nature of the reaction which results only in surface grafting of the chitin particles, where only a limited number of active sites could be formed by a determined amount of the initiator, which in

TABLE 2. Influence of MA Concentration on the Grafting of MA on Chitin^a

Sample	MA, mL	% Grafting	% Grafting efficiency	% Homo- polymer	% Total conversion
7	1	171.9	53.9	10.9	64.8
8	2	183.1	28.7	6.0	34.7
9	3	186.2	19.5	0.3	19.8
10	4	187.2	14.7	1.3	16.0
11	5	186.2	11.7	0.2	11.9
12	6	186.2	9.7	2.1	11.8

^aReaction conditions: Chitin, 0.3 g; CAN, 10⁻² M; HNO₃, 10⁻⁴ M (8 mL); temperature, 60°C; reaction time, 45 min.

this case is kept constant. From this result it seems that the chain lengths of the grafted poly(methyl acrylate) does not increase with an increase in the amount of monomer.

In relation with the amount of homopolymer that forms during grafting, it can be seen from Table 2 that the highest homopolymer percentage corresponds to the lowest amount of monomer used. This indicates that the reaction between initiator and monomer is somewhat favored in relation to the generation of macro-radicals and/or the growing of the grafted polymer chains in this case. We think that the diffusion-controlled nature of the reactions could induce, at lower monomer concentrations, a comparative scarcity of monomer in the proximity of the surface of chitin during the grafting reaction. However, the mass of homopolymer obtained in all experiments in comparison with the mass of grafted chitin is not very different, varying between -0.01 and 0.12 g.

Influence of Reaction Time and Temperature on Grafting

The results obtained from the study of the effect of the variation of reaction time from 15 to 210 minutes and of temperature from 50 to 70°C on the extent of MA grafting onto chitin are presented in Table 3. For grafting reactions performed at 50°C, the percentage of polymer add-on increases with an increase in reaction time. The amount of grafting obtained at 60 and 70°C also increases with reaction

TABLE 3. Influence of Reaction Time and Temperature^a

Sample	<i>t</i> , min	<i>T</i> , °C	% Grafting	% Grafting efficiency	% Homo-polymer	% Total conversion
13	15	50	13.6	1.4	6.1	6.1
14	15	60	23.4	2.4	4.3	17.2
15	15	70	136.7	14.3	10.4	35.2
16	30	50	23.4	2.4	6.4	6.4
17	30	60	103.4	10.8	10.5	31.8
18	30	70	301.1	31.5	15.4	57.3
19	60	50	182.7	19.1	7.1	40.1
20	60	60	298.2	31.2	8.0	49.7
21	60	70	599.6	62.8	13.4	86.5
22	90	50	506.9	53.1	5.2	68.7
23	90	60	614.7	64.3	15.7	90.5
24	90	70	661.2	69.2	14.6	94.3
25	150	50	526.5	55.1	5.7	71.3
26	150	60	734.9	76.9	12.1	99.4
27	150	70	688.0	72.0	9.0	91.4
28	210	50	646.6	67.7	15.1	93.2
29	210	60	653.0	68.4	12.7	91.5
30	210	70	664.4	69.5	16.6	96.6

^aReaction conditions: Chitin, 0.3 g; MA, 2.87 g; CAN, 10^{-2} M; HNO₃, 10^{-4} M (8 mL).

TABLE 4. Rate of Grafting (RG) Dependence on Temperature

T, K	RG
323	3.80
333	6.16
343	10.24

time up to 150 minutes; thereafter, there is a nearly constant value. It was observed that by increasing the reaction temperature in the range studied, the maximum percentage of grafting that could be reached was roughly constant. As expected, the rate of grafting reaction increases with temperature, and consequently the time required to reach a predetermined grafting percentage is less for a higher temperature. The observed homopolymer percentage tends to increase slightly with reaction temperature, probably due to a contribution from the thermal polymerization of MA.

The apparent activation energy for the grafting reaction was estimated from the usual Arrhenius plot of the rate versus the polymerization temperature. The values of the rate of the grafting reaction (RG) are presented in Table 4. The RG values were calculated from the slopes of the initial portions of the curves obtained by plotting the values of the grafting percentages at different temperatures, shown in Table 3, against the reaction time. The effect of the reaction temperature on RG is shown in Fig. 2. From this plot, the apparent activation energy for the grafting reaction was estimated to be about 11 kcal/mol. This value is considerably lower than that reported by Kojima et al. [15] (22.8 kcal/mol) in the case of grafting of MMA onto chitin by using tributylborane as the initiator where the grafting maximum reached was only about 25%.

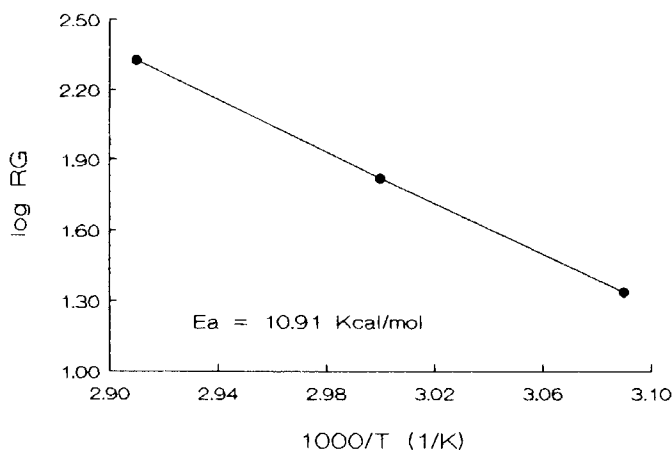


FIG. 2. Relation between the rate of grafting (RG) and polymerization temperature.

CONCLUSIONS

From the results obtained in this study, it is concluded that MA can be successfully grafted onto chitin by using Ce^{IV} ion in dilute nitric acid as the redox initiator. It was found that the percentage of grafting depends on the reaction time, temperature, and Ce^{IV} concentration but is independent of the monomer concentration. MA homopolymerizes during grafting, and its amount increases with the reaction temperature. The optimum conditions for the grafting reaction are established.

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