NOTE

Ceric Ion-Initiated Grafting of Acrylonitrile onto Hydrolyzed Cotton

INTRODUCTION

Graft polymerization of vinyl monomers onto cellulose or chemically modified celluloses using ceric ion as initiator has gained considerable importance in recent years. The ceric ion method has been used for vinyl graft polymerization onto cellulose,[1,2] hemicellulose,[3,4] starch,[5,6] lignocellulose,[7] partially carboxymethylated cellulose,[8] acrylamidomethylated cellulose,[9] acetylated cellulose,[10] crosslinked cellulose,[11] oxidized cellulose,[12-16] and polyester fibers.[17] Grafting vinyl monomers to cellulose and its derivative are now finding various applications, i.e., in ion exchange resins, rot and mildew resistant material, flame proof, change in dye characteristics, and resistance to microorganisms.[18] The grafting of vinyl monomers onto hydrocellulose using ceric ion as initiator and the study of its resistance to different microorganisms have not clearly been elucidated. The present work deals with the graft polymerization of acrylonitrile onto hydrocellulose using ceric ion as initiator for the purpose of finding (1) the optimum reaction conditions to obtain maximum degree of grafting; (2) the factors affecting the magnitude, efficiency, and conversion of polymerization; (3) the effect of reaction conditions on the homopolymerization; and (4) the resistance of grafted and ungrafted samples to different microorganisms.

EXPERIMENTAL

Preparation of Hydrocellulose

Egyptian cotton linters were purified by a mild alkaline pulping (2% sodium hydroxide solution). This was followed by hypochlorite bleaching with 2.5% active chlorine. Hydrolysis of the cellulose was carried out on one portion with $0.8N$ sulfuric acid at 100°C for 2 h and other portion with $4N$ sulfuric acid under the same conditions.

Purification of Monomer

Acrylonitrile was purified by washing with 5% sodium hydroxide solution to remove the inhibitor. After this treat-

ment, the monomer was washed with distilled water and dried overnight over anhydrous calcium chloride. The monomer was then distilled under reduced pressure in nitrogen and stored in a refrigerator.

Preparation of Initiator Stock Solution

$0.1M$ stock solution of the initiator was prepared by dissolving the required amount of cerium ammonium nitrate in a $1M$ nitric acid solution. During the course of the experiments, it was observed that the activity of the initiator appeared to decrease with time. Therefore, stock solutions that were stored for more than 4 d were discarded and fresh solutions prepared.

Grafting Procedure

One g pure hydrocellulose powder (which hydrolyzed with $0.8N$ sulfuric acid) was dispersed in deaerated water in a three-necked flask and maintained at the reaction temperature. The reaction flask was purged with purified nitrogen for 20 min. A weighed amount of ceric nitrate was added to the reaction mixture and followed with a required amount of acrylonitrile under stirring by a magnetic stirrer. The material : liquor ratio was 1 : 50 and the reaction was allowed to proceed for the required amount of time. After the grafting reaction, the grafted cellulose was taken out and washed with distilled water and acetone to remove excess monomer and initiator. It was then ovendried at 60°C under vacuum to constant weight.

Removal of Polyacrylonitrile

The grafted samples were extracted in a Soxhlet extraction apparatus with dimethyl formamide for 72 h at room temperature. The samples were then washed thoroughly with water. Finally, the samples were dried and weighed. The calculations were carried out according to the following equations:

Grafting %

$$= \frac{\text{wt of grafted cellulose} - \text{wt of cellulose}}{\text{wt of cellulose}} \times 100$$
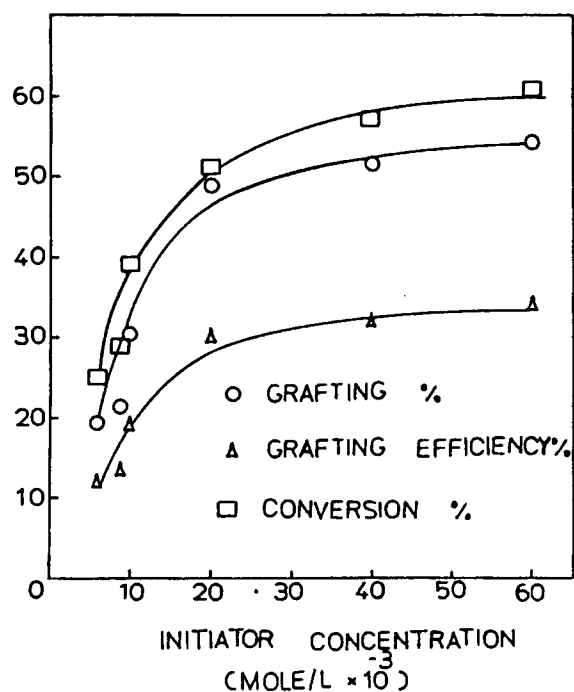
Figure 1 Effect of ceric ion concentration on the percent of graft yield, grafting efficiency, and conversion.

Grafting efficiency %

$$= \frac{\text{wt of grafted cellulose} - \text{wt of cellulose}}{\text{wt of monomer}} \times 100$$

Conversion %

$$= \frac{\text{wt of vinyl polymer} - \text{wt of cellulose}}{\text{wt of monomer}} \times 100$$

Homopolymer extracted % $= \dfrac{\text{wt of homopolymer}}{\text{wt of monomer}} \times 100.$

All calculations are based on a moisture-free cellulose weight basis.

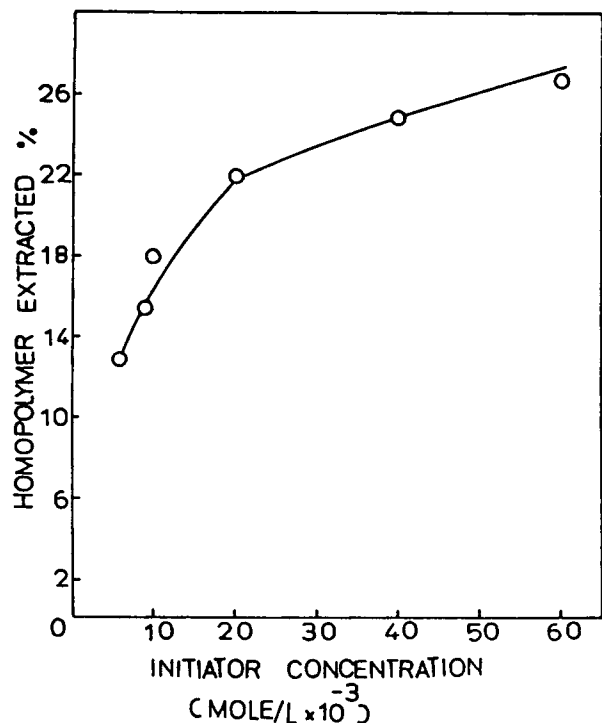## Microbiological Resistance Measurement

The resistance of the grafted and ungrafted samples to the following microorganisms: (1) *Trichoderma Sp.,* (2) *Aspergillus Niger,* and (3) *Penicillium Citrinum* were examined by Laboratory of Microbial Ecology. The samples were incubated at 28°C for 14 d.

RESULTS AND DISCUSSION

Grafting of acrylonitrile onto hydrocellulose using ceric ion as initiator was carried out under various conditions to investigate the optimal conditions for grafting polymerization. Variables studied included ceric ion concentration, acrylonitrile concentration, polymerization temperature, and reaction time, and the percentage of grafting, conversion, and homopolymer extracted were determined. In addition, the effect of the resistance of grafted and ungrafted samples to different microorganisms was studied.

EFFECT OF CERIC ION CONCENTRATION

Figure 1 shows the effect of ceric ion concentration on the percent of graft yield, grafting efficiency, and conversion obtained with hydrocellulose using acrylonitrile as a monomer. The concentration range studied is from 6 $\times 10^{-3}$ to 60×10^{-3} mol/L. It is seen that increasing ceric ion concentration is accompanied by a significant increase in the graft yield, graft efficiency, and conversion percent even at higher concentration of initiator (Table I). This could be ascribed to the facts that the hydrolysis of cellulose with 0.8 N sulfuric acid at 100°C for 2 h results in

Table I Effect of Initiator Concentration on the Graft Polymerization of Acrylonitrile onto Hydrocellulose

IV Ce (mol/L)	Grafting %	Grafting Efficiency %	Conversion %	Homopolymer Extracted %
0.006	19.35	12.09	24.93	12.83
0.009	21.45	13.41	28.78	15.38
0.010	30.48	19.05	38.06	18.04
0.020	47.90	29.94	52.06	22.13
0.040	51.46	32.16	57.01	24.85
0.060	54.44	34.03	60.81	26.79

Grafting temperature, 50°C; grafting time, 120 min. 0.603 mol/L concentration of monomer used. 1 g amount of dry wt hydrocellulose used. Material : liquor ratio 1 : 50.

Figure 2 Homopolymer extracted percent as a function of initiator concentration.

the formation of new hydroxyl groups in the anhydroglucose units of cellulose macromolecules and the grafting on cellulose is affected by the presence of these reducing groups. Figure 2 shows the homopolymer extracted percent as a function of initiator concentration. It is clear that the homopolymer percent increased continuously by increasing the initiator concentration, and the maximum homopolymer extracted percent are shown at concentration 0.06 mol/L. This could be attributed to the higher oxidation of the growing radicals with ceric ions.
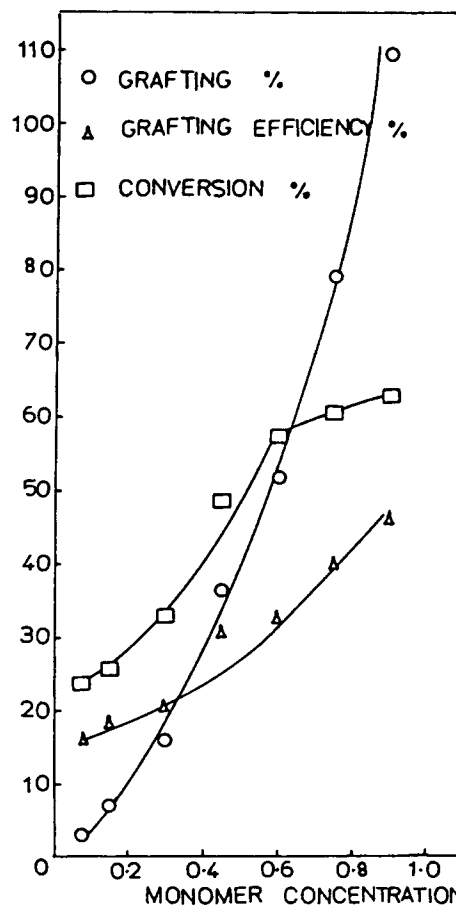
Figure 3 Effect of acrylonitrile concentration on the percent of grafting, grafting efficiency, and conversion.

Effect of Monomer Concentration

The effect of acrylonitrile concentration on the percent of grafting, grafting efficiency, and conversion is depicted in Figure 3, from which it is clear that when increasing

Table II Effect of Monomer Concentration on the Graft Polymerization of Acrylonitrile onto Hydrocellulose

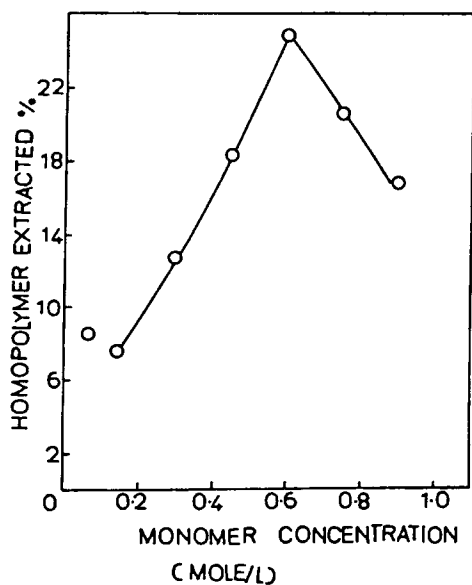| Acrylonitrile (mol/L)	Grafting %	Grafting Efficiency %	Conversion %	Homopolymer Extracted %
0.0754	3.16	15.80	24.30	8.50
0.1508	7.14	17.85	25.35	7.50
0.3015	16.07	20.09	32.79	12.70
0.4523	36.20	30.17	48.39	18.23
0.6030	51.46	32.16	57.01	24.85
0.7538	79.08	39.54	60.14	20.60
0.9046	109.59	45.66	62.48	16.81

Grafting temperature, 50°C; Grafting time, 120 min. 0.04 mol/L concentration of initiator used. 1 g amount of dry wt hydrocellulose used. Material : liquor ratio 1 : 50.

Table III   Effect of Time on the Graft Polymerization of Acrylonitrile onto Hydrocellulose

Time (min)	Grafting %	Grafting Efficiency %	Conversion %	Homopolymer Extraction %
30	40.61	25.38	40.05	15.29
60	43.55	27.22	44.96	17.74
90	45.43	28.39	50.31	21.92
120	51.46	32.16	57.01	24.85
150	52.60	32.88	59.95	27.08
180	52.32	32.70	56.56	23.86

Grafting temperature, 50°C. 0.04 concentration of initiator used. 0.603 mol/L concentration of monomer used. 1 g amount of dry wt hydrocellulose used. Material : liquor ratio 1 : 50.

the monomer concentration from 0.0754 to 0.9046 mol/ L the graft yield, graft efficiency, and conversion percent increase. This might be due to the complexation of hydrocellulose with monomer to increase its reactivity, which is favored with increase of monomer concentration. On the other hand, at higher monomer concentration the monomer molecules associated in close vicinity of the cellulose; consequently, there is a significant increase in the graft yield and graft efficiency by increasing the monomer concentration (Table II). It is apparent from Figure 4 that the percent of extracted homopolymer increases by increasing the concentration of monomer until certain limit of concentration 0.7538 mol/L. Further increase in the monomer concentration lowered the amount of homopolymer extracted. This could be attributed to that the homopolymer produced from the reactions of the ceric ion

with the monomer themselves until concentration 0.7538 mol/L of acrylonitrile; after this concentration (at 0.9046 mol/L), the rate of diffusion of monomer to growing chains and active sites on the hydrocellulose increased and consequently the graft yield continuously increased, while the percent of extracted homopolymer decreased.

Effect of Reaction Time

The effect of graft yield as a function of reaction time is shown in Figure 5. It is noticed that the reaction increased

Figure 4   Homopolymer extracted percent as a function of monomer concentration.
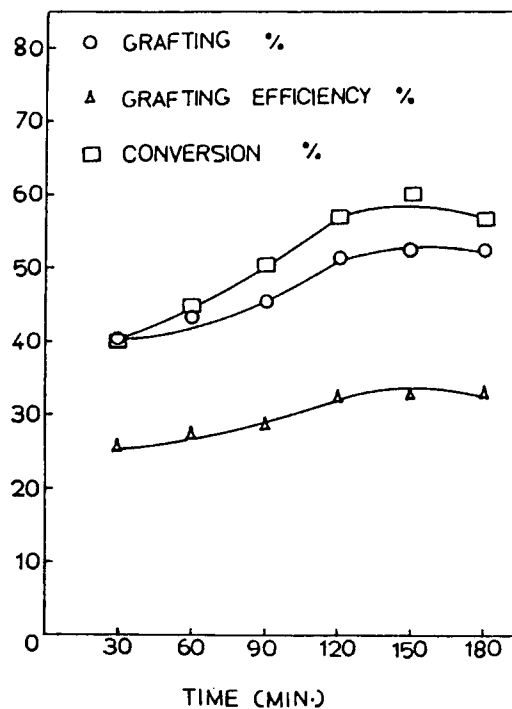
Figure 5   Effect of reaction time on the percent of grafting, grafting efficiency, and conversion.
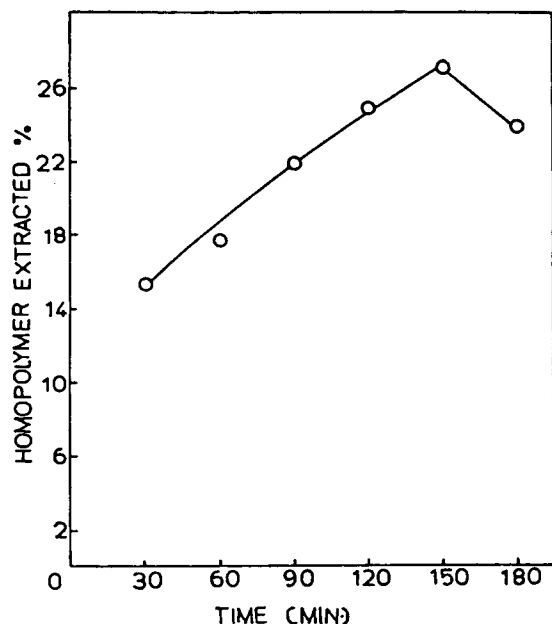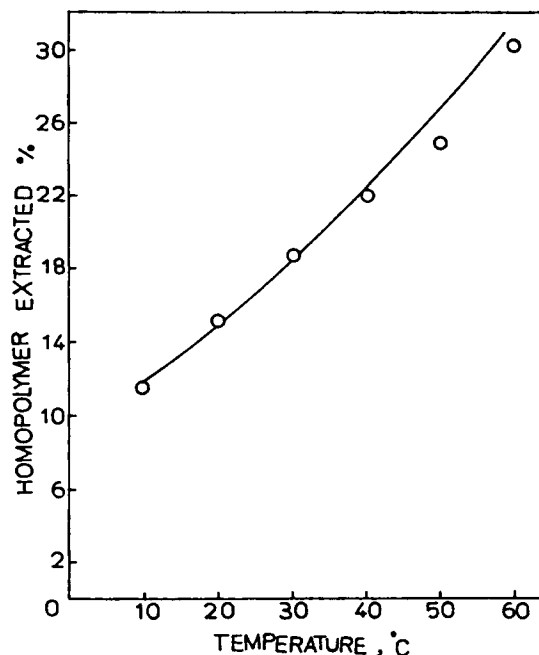
Figure 6 Homopolymer extracted percent as a function of reaction time.

steadily up to 120 min; then the grafting curve leveled off with prolonging the duration of polymerization. This could be explained by the depletion in initiator and monomer concentration. It is also observed from Figure 5 that the
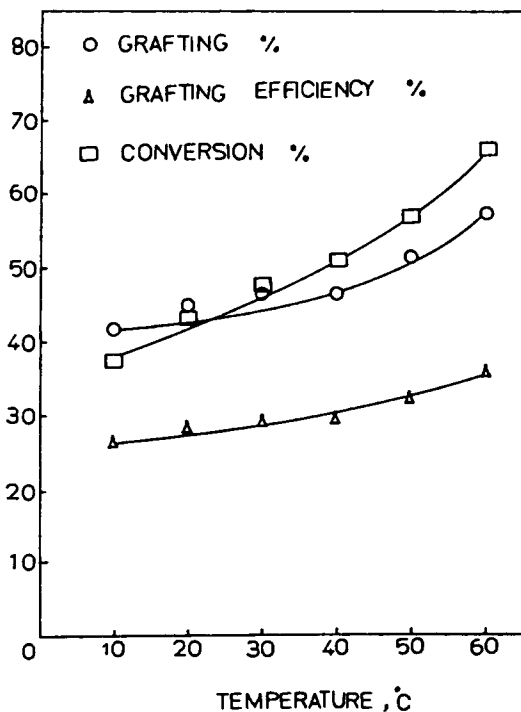
Figure 7 Effect of polymerization temperature on the percent of grafting, grafting efficiency, and conversion.

Figure 8 Homopolymer extracted percent as a function of polymerization temperature.

conversion percent decreases at 3 h polymerization due to consumption of the monomer at this period of polymerization; consequently, there is no new monomer units added to the growing monomer radical leading to lower the conversion percent. It is obvious from Figure 6 that the maximum homopolymer percent formed during grafting at 2.5 h then falls upon further prolonging the duration of polymerization.

Polymerization Temperature

The graft polymerization was carried out at different temperatures ranging from 10–60°C. The relation between graft yield and polymerization temperature is illustrated in Figure 7. It is seen that the effect of raising the polymerization temperature to 60°C is to bring about a significant increment in grafting, grafting efficiency, and conversion percent. This might be attributed to the increased mobility and the diffusion rate of acrylonitrile monomer at radical sites of the hydrocellulose by raising the reaction temperature. It is clear from Figure 8 that the homopolymer percent increases with the increase of temperature and the maximum homopolymer extracted during grafting are shown at 60°C (Table IV). This could be due to higher temperatures leading to the reaction of growing radicals with each other through coupling, which increases the homopolymerization.

Resistance to Microorganisms

It was noticed from Table V that the microbial resistance of the ungrafted hydrocellulose depends upon acid con-

Table IV   Effect of Temperature on the Graft Polymerization of Acrylonitrile onto Hydrocellulose

Temperature (°C)	Grafting %	Grafting Efficiency %	Conversion %	Homopolymer Extracted %
10	41.83	26.14	37.58	11.44
20	44.98	28.11	43.24	15.13
30	46.40	29.00	47.65	18.65
40	46.42	29.01	51.05	22.04
50	51.46	32.16	57.01	24.85
60	57.33	35.83	66.09	30.26

Grafting time, 120 min. 0.04 concentration of initiator used. 0.603 mol/L concentration of monomer used. 1 g amount of dry wt hydrocellulose used. Material : liquor ratio 1 : 50.

Table V   Microbial Resistance of the Ungrafted and Grafted Hydrocellulose

	Condition	Grafting %	Fungal Growth
0.8N sulfric acid hydrolysis	Ungrafted hydrocellulose	—	Heavy
4N sulfric acid hydrolysis	Ungrafted hydrocellulose	—	Slight
Initiator (mol/L)	0.006	19.35	Slight
	0.009	21.45	Slight
	0.010	30.48	Slight
	0.020	47.90	None
	0.040	51.46	None
	0.060	54.44	Slight
Time (min)	30	40.61	Slight
	60	43.55	None
	90	45.43	Traces
	150	52.60	Moderate
	180	52.32	Slight
Temperature (°C)	10	41.83	Traces
	20	44.98	Slight
	30	46.40	Traces
	40	46.42	Slight
	60	57.33	Slight
Monomer (mol/L)	0.0754	3.16	Slight
	0.1508	7.14	Traces
	0.3015	16.07	Slight
	0.4523	36.20	None
	0.7538	79.08	None
	0.9046	109.59	None

centration used in hydrolysis of cellulose, i.e., the microbial resistance of the ungrafted hydrocellulose prepared by hydrolysis of cellulose with 4N sulfuric acid was much higher as compared with ungrafted hydrocellulose prepared by hydrolysis of cellulose with 0.8N sulfuric acid. Moreover, it was found that the cellulose hydrolyzed with 0.8N sulfuric acid is highly resistant to microorganisms after grafting with acrylonitrile under the conditions used in this work.

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