

Grafting of Acrylonitrile onto Cellulose Initiated by Ceric Ion

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Synopsis

Acrylonitrile was grafted onto cellulose with the use of ceric salt as initiator and the grafting was found to be maximum at 0.6*N* acid concentration. The effect of monomer and initiator concentration on the extent of grafting was studied. A new method for quantitative estimation of extent of grafting on cellulose was developed and its validity was established. The grafted samples with 20% increase in weight were found to be highly resistant to microorganisms.

INTRODUCTION

The graft polymerization of vinyl monomers onto cotton cellulose and related substances by ceric ion as initiator has been studied in detail.¹⁻⁹ It is well known that incorporation of a few graft side chains of a vinyl polymer such as polyacrylonitrile, polyacrylamide etc., considerably modifies the properties of cellulose,^{1,2} such as resistance to chemical attack and microorganisms, abrasion resistance, tensile strength, etc. It is generally observed that the accurate determination of the extent of grafting is rendered difficult owing to the unsatisfactory removal of the ungrafted homopolymer. In the present work, polymerization of acrylonitrile onto cellulose fiber using Ce^{4+} in nitric acid medium has been studied and optimum reaction conditions to obtain maximum degree of grafting without affecting the desirable properties of cellulose are established. A procedure for quantitative estimation of the degree of grafting of acrylonitrile is proposed and its validity is established. The effect of reaction conditions on the properties of grafted cellulose, i.e., resistance to microorganisms and tensile strength was studied.

EXPERIMENTAL

Materials

Scoured and bleached cotton hanks (28s count) were used. Acrylonitrile was B.D.H. reagent grade, free from inhibitor and distilled before use. Analar-grade ceric sulfate (supplied by Bhabha Atomic Research Centre, Trombay, Bombay), was used. Dimethyl formamide (DMF) was purified by standard procedure.

Grafting Reaction

Dried cotton hanks (1.8 g) were immersed in a solution consisting of nitric acid (0.25–1.0*N*) and acrylonitrile (0.1 – 1.0 m/l) at 30°C. Ceric sulfate was added to the reaction mixture with stirring such that $[Ce^{4+}]$ varied from 0.007 to 0.03 mole/l. The material: liquor ratio was 1:70 and the reaction time varied from 1 to 6 hr. After the grafting reaction, the cotton hanks were first washed with distilled water and then twice with 100-ml portions of nitric acid (1.0*N*) (to remove adhering ceric hydroxide formed during the reaction), followed by distilled water, methanol, and acetone washing and drying at room temperature.

Removal of Polyacrylonitrile

The grafted fibers were shaken with successive quantities of dimethyl formamide (each 100 ml) in a well-stoppered flask for about 8 to 10 days at room temperature till the washings did not give any turbidity with excess methanol, indicating the absence of polyacrylonitrile. The samples were then washed thoroughly with water and dried at 40°C at 20 mm Hg.

Estimation of Percentage of Grafting

TABLE I
Comparison of the Degree of Grafting as Estimated by Gravimetric, Volumetric, and Nitrogen (Kjeldahl) Analyses^a

Initiator concentration, mole/l.	Percentage grafting estimated by		
	Gravimetric method	Volumetric method	Nitrogen analysis
0.0156	58.35	58.04	57.85
0.0195	64.49	64.21	64.02
0.0216	65.83	65.49	65.08
0.0234	68.58	68.13	67.76
0.0250	70.08	69.63	69.21
0.0273	70.82	70.36	69.85
0.0312	72.47	71.92	71.31

^a Monomer concentration = 0.950*M*; acid concentration = 0.60*N*; total volume = 128 ml; temperature = 30°C; time = 4 hr; weight of cotton hank = 1.817 ± 0.017 g.

Gravimetric Method. The percentage grafting was computed from the increase in weight of the sample after the grafting reaction.

Saponification Method. The grafted cellulose (0.5 g) after removal of loosely held polyacrylonitrile was gently boiled with a 10% solution of sodium hydroxide (20 ml) for about 20 min, followed by washing successively with 10% sodium hydroxide solution, sulfuric acid (1%), and distilled water. The sample was dried at 40°C and 20 mm Hg and agitated with 0.1*N* sodium hydroxide solution (50 ml) for 10 min. A 10-ml portion of the aliquot was titrated against standard sulfuric acid (0.1*N*). From the

amount of alkali consumed, the carboxyl content and hence the weight of grafted acrylonitrile was computed.

Nitrogen Estimation. The nitrogen content of the grafted samples was estimated by Kjeldahl's method and the percentage grafting was determined.

Properties of Grafted Samples: Microbial Resistance and Tensile Strength

The resistance of the grafted cotton hanks along with the unreacted cotton hanks to different microorganisms, (1) *Pencilium* SP, (2) *Aspergillus fumigatus*, (3) *Aspergillus niger*, (4) *Chaetomium globosum*, (5) *Memnoiella chinata*, and (6) *Rhizopus* SP, was tested by Defence Research Laboratory (Materials), Kanpur (Table II).

The grafted and untreated cotton hanks were conditioned at 70°F and 65% R.H. for three days before testing. The breaking strength of the samples was measured on a Zweigle machine (Table II).

RESULTS AND DISCUSSION

Effect of Reaction Conditions on Percentage Grafting

The extent of grafting was studied at various nitric acid concentrations

TABLE II
Effect of Reaction Conditions on Resistance of the Grafted Sample to Microorganisms^e

Untreated sample	Percentage grafting	Fungal growth	Increase or decrease in tensile strength, %
Acid conc. ^a		Profuse	
0.7 N	60.12	slight	+4.37
0.8 N	51.99	slight	-11.88
0.9 N	49.65	slight	-26.25
1.0 N	49.62	moderate	-43.75
Time, hr ^b			
4	70.08	none	+18.75
5	72.61	slight	-5.00
6	72.65	moderate	-39.06
Time, hr ^c			
6	71.53	moderate	36.02
Monomer conc., mole/l. ^d			
0.1185	1.047	slight	0.0
0.2370	4.035	very slight	+2.50
0.3555	9.137	very slight	+5.31
0.5925	25.300	none	+9.69

^a Initiator conc. = 0.025M, monomer conc. = 0.950 M, time = 4 hr.

^b Initiator conc. = 0.025 M, monomer conc. = 0.95M, acid conc. = 0.60N.

^c Initiator conc. = 0.0262M, monomer conc. = 0.950M, Acid conc. = 0.50N.

^d Initiator conc. = 0.0195M, acid conc. = 0.60M, time = 4 hr.

^e Weight of cotton hank = 1.817 ± 0.017 g; Tensile strength of untreated hank (count 28s) = 320 g; total volume = 128 ml; temperature = 30°C.

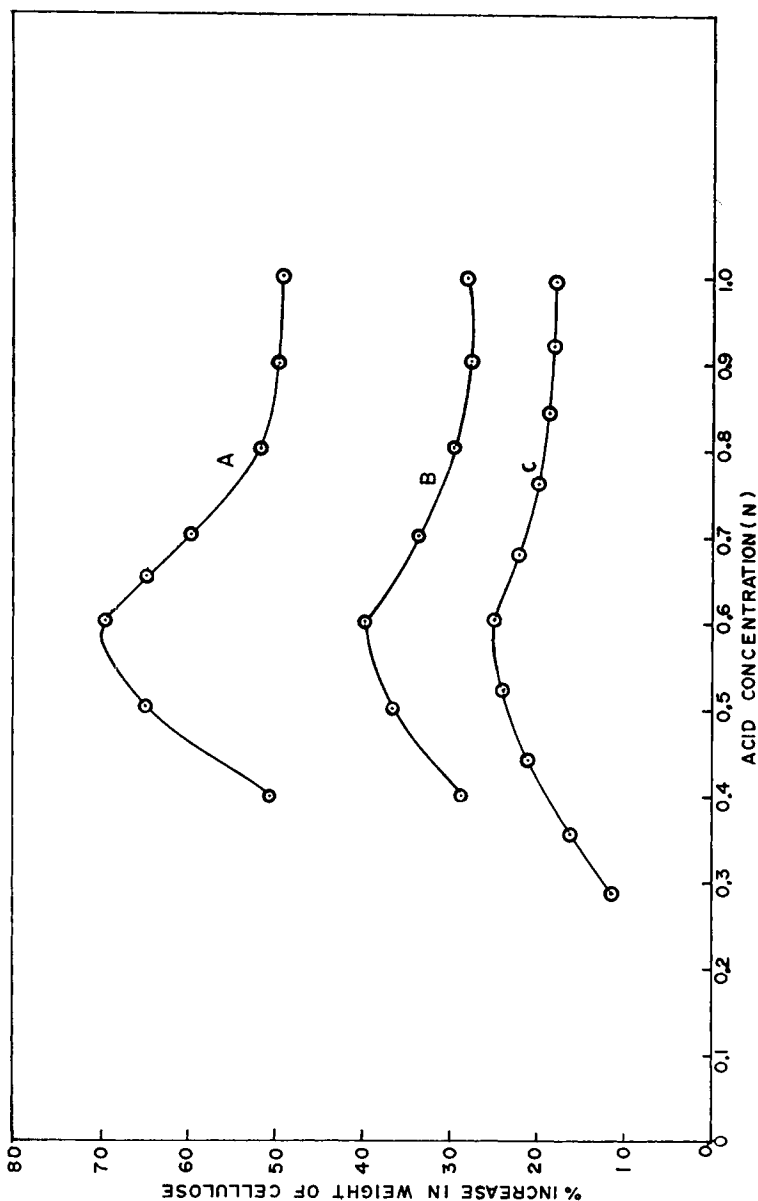


Fig. 1. Percentage increase in weight of cellulose versus HNO_3 concentration. (Time = 4 hr, total volume = 128 ml, temperature = 30°C): (A) [initiator] = $0.025M$, [monomer] = $0.95M$; (B) [initiator] = $0.025M$, [monomer] = $0.711M$; (C) [initiator] = $0.0195M$, [monomer] = $0.5925M$.

between 0.28 and $1.0N$. Excessive precipitation of ceric hydroxide was noticed below $0.4N$ nitric acid. It was found that the extent of grafting increased between 0.40 and $0.60N$ HNO_3 and then decreased between 0.60 and $1.0N$ HNO_3 . Maximum grafting occurred at $0.60N$ HNO_3 (Fig. 1).

It is generally known that ceric ion forms various species with anions depending upon acid concentration.¹⁰⁻¹³ Mino and Kaizerman¹⁴ pointed out that ceric salts form very effective redox systems in the presence of

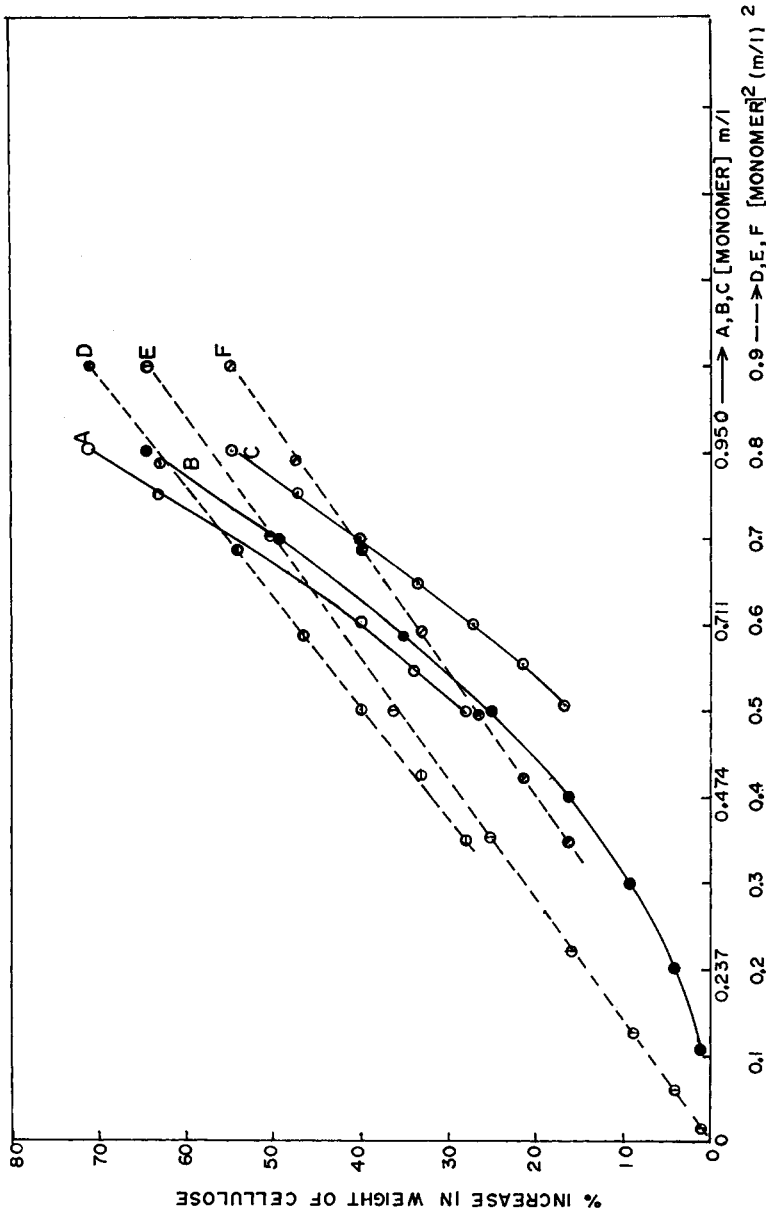
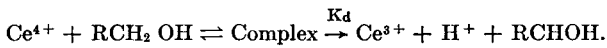


Fig. 2. Percentage increase in weight of cellulose versus monomer concentration and the square of the monomer concentration: (A) and (D) [initiator] = 0.0262M, [HNO₃] = 0.5N, time = 4 hr; (B) and (E) [initiator] = 0.0195M, [HNO₃] = 0.6N, time = 4 hr; (C) and (F) [initiator] = 0.0262M, [HNO₃] = 0.5N, time = 3.5 hr.

organic reducing agents such as alcohols, the resulting complex dissociating into a free radical capable of initiating polymerization, as follows:



Hence the observed maximum in the percentage grafting presumably indicates greater complex formation between ceric ions and the cellulose backbone at 0.6N HNO₃.

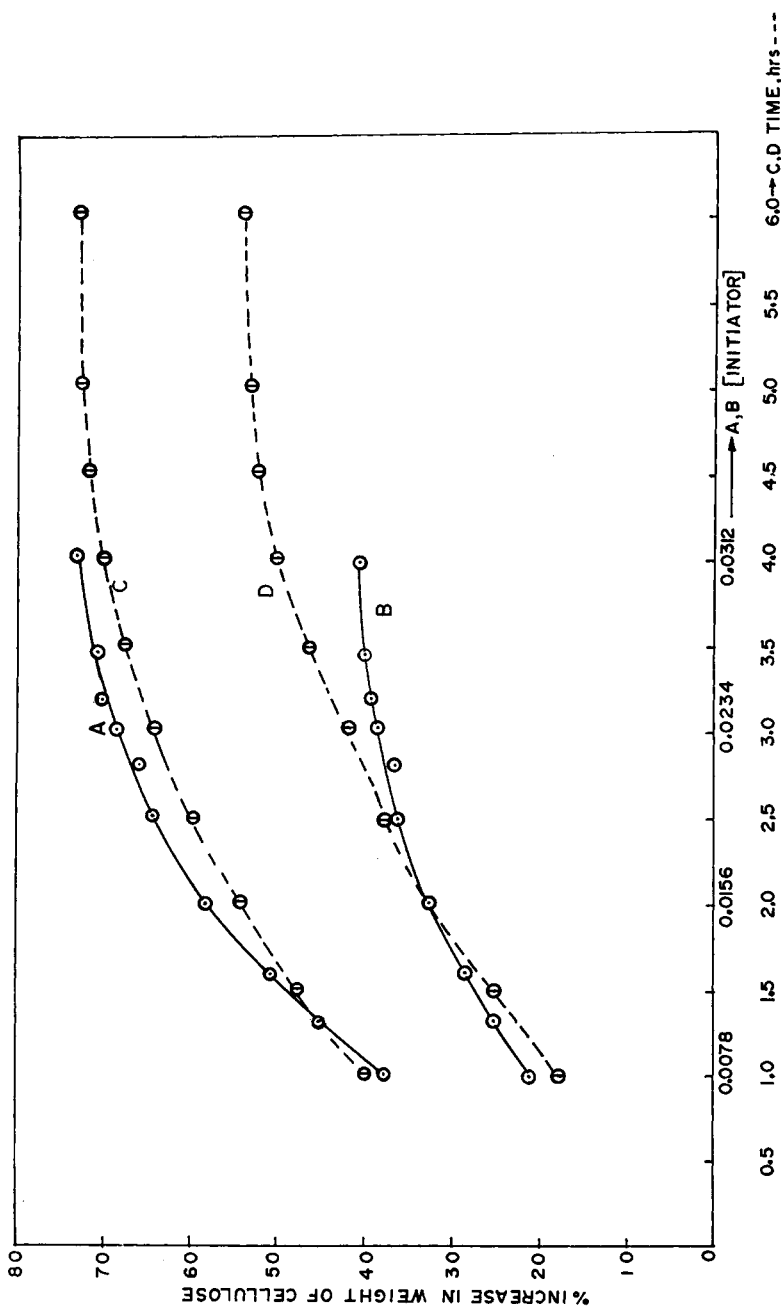


Fig. 3. Percentage increase in weight of cellulose versus initiator concentration and time. (Total volume = 128 ml, temperature = 30°C): (A) $[\text{HNO}_3] = 0.6N$, $[\text{monomer}] = 0.950M$, time = 4 hr; (B) $[\text{HNO}_3] = 0.6N$, $[\text{monomer}] = 0.711M$, time = 4 hr; (C) $[\text{initiator}] = 0.025M$, $[\text{HNO}_3] = 0.6N$, $[\text{monomer}] = 0.950M$; (D) $[\text{initiator}] = 0.025M$, $[\text{HNO}_3] = 0.4N$, $[\text{monomer}] = 0.95M$.

It was found that the percentage grafting was proportional to the square of the monomer concentration (Fig. 2). Grafting increased with $[\text{Ce}^{4+}]$ in the range 0.007–0.025 mole/l. and started decreasing at higher concentrations (Fig. 3), obviously due to the predominance of termination of growing

graft chains by Ce^{4+} . As expected, percentage grafting registered an increase with time (Fig. 3) but no significant increase of grafting was noticed for time intervals of more than 4 hr.

Extent of Grafting

Cellulose fibers after grafting contain chemically bound as well as free polyacrylonitrile. For accurate estimation of the percentage of grafting, complete removal of occluded and loosely held homopolymer is necessary. It has been observed¹⁵ that the removal of occluded polyacrylonitrile by extraction of the grafted fibers with dimethyl formamide in the cold is incomplete if the extraction is carried out for a short time. For a satisfactory removal of the occluded polyacrylonitrile, it was necessary to carry out the extraction with dimethyl formamide for 8–10 days. The fibers, after washing and drying, were weighed and the percentage of grafting was computed from the increase in weight.

It was noticed that while the ungrafted sample was completely soluble in cuprammonium hydroxide solution, the samples containing more than 15% polyacrylonitrile were insoluble. However, when the percentage grafting was less than 10%, partial solubility (about 10%) in cuprammonium hydroxide solution was noticed. Since part of the ungrafted polyacrylonitrile still remains occluded to the fiber in spite of extraction with dimethyl formamide, it is rather difficult to compute the degree of grafting based on the solubility in cuprammonium hydroxide.

We find that a very reliable method of estimation of the percentage grafting consists in the saponification of the grafted cellulose (along with occluded polyacrylonitrile) with 10% sodium hydroxide (see experimental procedure). Cellulose swells in sodium hydroxide to a considerable extent, thereby facilitating the hydrolysis of both the grafted and the occluded polyacrylonitrile. Thus the free and occluded polymer is extracted completely from the fiber in the form of poly(sodium acrylate) by the alkali, and pure cellulose-grafted poly(acrylic acid) is obtained in the form of the sodium salt. This is converted into the acid form by treatment with mineral acids and the acrylic acid content is estimated volumetrically. The polyacrylonitrile content in the original sample is then easily computed from the amount of poly(acrylic acid) present in the sample after saponification.

The values of the percentage grafting computed by (a) gravimetric method, after prolonged extraction of the grafted fibers with dimethyl formamide, (b) saponification of polyacrylonitrile, and (c) nitrogen estimation by the Kjeldahl method are compared (see Table I). It is concluded that the saponification procedure may be conveniently employed to determine the percentage grafting, since complete removal of occluded homopolymer is ensured. This method is quite simple and easy compared to the laborious solvent extraction procedure and it can also be extended to other cellulose-acrylic graft systems.

Microbial Resistance and Tensile Strength

The resistance of the cotton hanks to microorganisms is considerably improved by grafting with acrylonitrile and tensile strength is also apparently increased (Table II). Thus with a low degree of grafting (10%) the microbial resistance is good. However, the strength of the fiber is quite sensitive to the experimental conditions also, especially to the acid concentration and the reaction time. Acid concentrations above 0.6*N* and reaction times beyond 4 hr are deleterious to the strength of the fiber as shown by a fall in tensile strength; and thus the microbial resistance is also diminished.

CONCLUSIONS

About 70% grafting may be obtained by maintaining the following reaction conditions: $[\text{Ce}^{4+}] = 0.025$ mole/l., [acrylonitrile] = 0.950*M*, $[\text{HNO}_3] = 0.60$ *N* time = 4.0 hr, material:liquor ratio = 1:70, and temperature = 30°C.

The ungrafted polyacrylonitrile is quantitatively removed from the grafted cotton hanks by prolonged extraction with dimethyl formamide (8–10 days) at room temperature. The percentage grafting may be accurately determined by the saponification of the grafted hanks with sodium hydroxide and subsequent removal of the free poly(sodium acrylate).

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