

# Graft Copolymerization with New Class of Acidic Peroxo Salts as Initiators. I. Grafting of Acrylamide onto Cotton–Cellulose Using Potassium Monopersulfate, Catalyzed by Co(II)

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## Synopsis

Graft copolymerization of acrylamide (AM) onto cotton–cellulose has been studied using a new class of acidic peroxy-salt “potassium monopersulfate” as initiator catalyzed by Co(II). It is observed that the graft yield is influenced by the reaction time, temperature, and concentrations of the monomer, catalyst, initiator, at fixed weight of the polymer. Maximum graft yield (30.8%) is obtained at 40°C under nitrogen atmosphere for the concentrations of monomer 1.2M; initiator  $4.83 \times 10^{-3}M$ ; Co(II)  $5 \times 10^{-4}M$  for 4 h of reaction time. The graft copolymers after proper purification have been subjected to IR analysis, testing of their water-retention properties, rot resistance, tensile properties, and behavior towards acids and alkalis. The results of such analysis are compared with the base. Suitable mechanism for the graft copolymerization is suggested and grafting rate has been evaluated.

## INTRODUCTION

Grafting reactions provide a potential route for significantly altering the physical and mechanical properties of a substrate polymer to specific end uses. Graft copolymerization of vinyl monomers onto cellulose fibers has been the subject of extensive studies since 1950. There has been intense research and development activity in the field since those early days,<sup>1-3</sup> and many hundreds of papers and patents have been published. A systematic approach on various methods of graft copolymerization onto cellulose has been recently reviewed by Samal and co-workers.<sup>4</sup> The purpose of grafting vinyl monomers onto cellulosic fibers in most of the reports was to produce fibers like synthetic fibers such as nylon, polyesters,<sup>5-8</sup> etc. and other industrially important materials like ion exchangers<sup>9,10</sup> using cheap fibers as starting materials. However, irrespective of skillful chemical experiments and use of ideal initiation systems, no improvement of the wrinkle recovery angle of the modified fibers was observed, and loss of tenacity of the fibers was remarkable. The probable reasons for these anomalies may be attributed to the concurrent formation of homopolymers in most of the cases which are extremely difficult

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to be separated by the conventional extraction method using suitable solvents and the oxidative chain cleavage of cellulose backbone, thereby limiting the grafting process. The latter phenomenon is noticed mostly with V(V), Ce(IV), Mn(III),  $S_2O_8^{2-}$ ,  $P_2O_8^{4-}$ , etc., due to their high oxidation potential. However, potassium monopersulfate ( $KHSO_5$ ) with oxidation potential of  $-1.44$  V does not cleave the cellulose backbone either alone or in the presence of metal salt, but is capable of generating cellulosic radical to effect graft copolymerization. In addition the formation of homopolymer is negligible. We have therefore been interested in grafting vinyl monomers like acrylamide using  $KHSO_5$  under the catalytic influence of Co(II).

### EXPERIMENTAL

Cotton cellulose was purified according to our previous method.<sup>11</sup> Acrylamide (E. Merck) was purified by recrystallization from acetone and dried at room temperature under vacuum. A 4M stock solution of the monomer in triple-distilled water was used.

Potassium monopersulfate ( $KHSO_5$ ) was a gift from DuPont Co. and was used without further purification. A stock solution, 0.2M of the initiator, was used for all experiments. The strength of the stock solution was determined by iodometry. All other reagents were of BDH (AR) grade and were used after purification by standard methods.

Graft copolymerization was carried out in a specially designed reaction vessel carrying outlet and inlet systems for deaeration. The method adopted was identical to our previous report.<sup>11</sup> The graft copolymer after separation from the homopolymer was repeatedly extracted with warm water for removal of the occluded homopolymers and finally allowed to dry at 40°C to constant weight. From the weight of the graft copolymer and base polymer the percent grafting and grafting efficiency were calculated using the following formula.

$$\text{percent grafting} = \frac{X - Y}{Y} \times 100$$

$$\text{grafting efficiency} = \frac{X - Y}{X - Y + Z} \times 100$$

where  $X$  = weight of the grafted sample,  $Y$  = weight of original dry sample, and  $Z$  = weight of the homopolymer. The graft copolymers were subjected to IR analysis, the evaluation of their water retention, rot resistance, and tensile properties.

### RESULTS AND DISCUSSION

Recently we have studied the spectrophotometrical and kinetic aspects of the course of decomposition of potassium monopersulfate in solution alone and under the catalytic action of a number of metal salts. We have observed that  $KHSO_5$  alone in solution undergoes feeble or negligible decomposition, even at 50°C and above, whereas, in the presence of trace of metal salt like  $CoSO_4$ ,  $MnSO_4$ ,  $Cr_2(SO_4)_3$ ,  $AgNO_3$ , etc., it suffers facile homolysis of the peroxolinkage resulting in the formation of various free-radical species. The

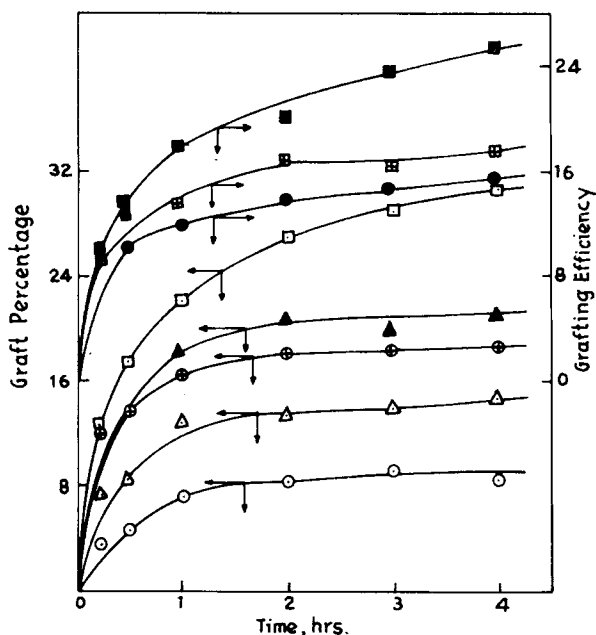


Fig. 1. (a) Variation of % grafting with time; effect of acrylamide:  $[\text{CoSO}_4] = 5 \times 10^{-4}M$ ;  $[\text{KHSO}_5] = 4.83 \times 10^{-3}M$ ; cellulose = 0.2 g; temp =  $40^\circ\text{C}$ . Plots: (○)  $[\text{AM}] = 0.4M$ ; (△)  $[\text{AM}] = 0.6M$ ; (⊕)  $[\text{AM}] = 0.8M$ ; (□)  $[\text{AM}] = 1.2M$ ; (▲)  $[\text{AM}] = 1.4M$ . (b) Variation of grafting efficiency with time; effect of acrylamide. Plots: (●)  $[\text{AM}] = 0.8M$ ; (■)  $[\text{AM}] = 1.2M$ ; (⊗)  $[\text{AM}] = 1.4M$ .

generated free-radicals cause high rate of initiation in vinyl polymerization.<sup>12-16</sup> Further the metal salt catalysis becomes more significant in the presence of complexing agents and preformed polymers, where the primary radicals attack the polymer to generate polymer radical that initiates grafting. In such grafting reaction the negligible formation of homopolymer is noticed. We have therefore used  $\text{KHSO}_5/\text{Co(II)}$  couple in the study of graft copolymerization of acrylamide onto cotton-cellulose, at varying reaction conditions.

### Effect of Monomer Concentration

The effect of monomer concentration on grafting is shown in Figure 1. The graft percentage increases on increasing the concentration of acrylamide (AM) from  $0.4M$  to  $1.2M$ , beyond which it decreases. This increase of grafting with an increase of the monomer concentration may be attributed to increase of the monomer concentration at the reaction site and complexation of cellulose with AM enhancing the reactivity of AM owing to the formation of a donor-acceptor complex in which the uncomplexed AM, though initially an electron acceptor, behaves as donor relative to the complexed AM, which is converted to a strong acceptor. Similar explanations for enhancement in grafting have been suggested by Gaylord<sup>17</sup> and Hebeish et al.<sup>18</sup> The grafting efficiency was also calculated and is plotted in Figure 1.

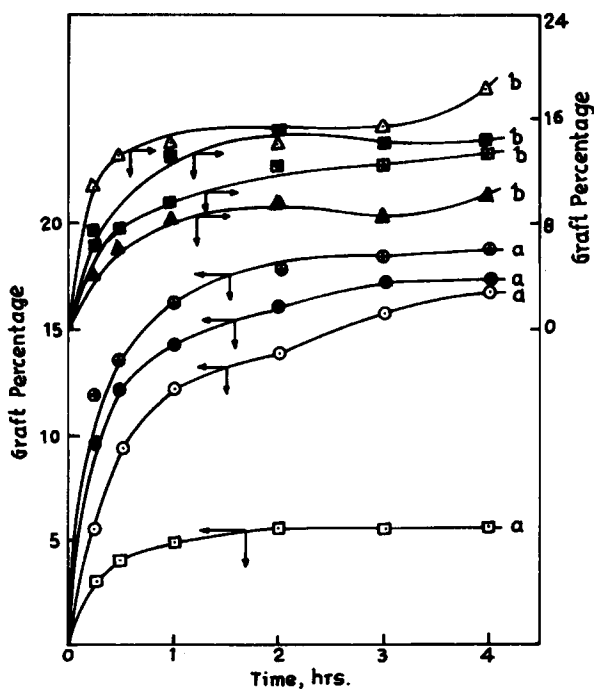


Fig. 2. (a) Variation of % grafting with time: effect of  $\text{KHSO}_5$ :  $[\text{CoSO}_4] = 5 \times 10^{-4}M$ ;  $[\text{AM}] = 0.8M$ , Cell = 0.2 g; temp =  $40^\circ\text{C}$ . Plots: ( $\square$ )  $[\text{KHSO}_5] = 1.6 \times 10^{-3}M$ ; ( $\circ$ )  $[\text{KHSO}_5] = 3.22 \times 10^{-3}M$ ; ( $\oplus$ )  $[\text{KHSO}_5] = 4.83 \times 10^{-3}M$ ; ( $\bullet$ )  $[\text{KHSO}_5] = 6.45 \times 10^{-3}M$ . (b) Variation of % grafting with time; effect of  $\text{CoSO}_4$ :  $[\text{KHSO}_5] = 9.67 \times 10^{-3}M$ ;  $[\text{AM}] = 0.08M$ ; Cell = 0.2 g; temp =  $40^\circ\text{C}$ . Plots: ( $\blacktriangle$ )  $[\text{CoSO}_4] = 2.5 \times 10^{-4}M$ ; ( $\triangle$ )  $[\text{CoSO}_4] = 5 \times 10^{-4}M$ ; ( $\blacksquare$ )  $[\text{CoSO}_4] = 7.5 \times 10^{-4}M$ ; ( $\square$ )  $[\text{CoSO}_4] = 25 \times 10^{-4}M$ .

### Effect of Initiator Concentration

The percent grafting and grafting efficiency increases on increasing the concentration of  $\text{KHSO}_5$  from  $1.61 \times 10^{-3}M$  to  $4.84 \times 10^{-3}M$ , beyond which it decreases (Fig. 2). The increase of graft percentage in the present use may be due to an increase in the number of active sites on the cellulosic backbone, arising from the attack of the diffused  $\text{KHSO}_5$  molecules into the fiber matrix. The decrease of rate at higher  $\text{KHSO}_5$  concentration ( $> 4.8 \times 10^{-3}M$ ) arises from (i) the predominancy of homopolymerization over grafting and (ii) termination of growing grafted chains by unstable  $\text{Co(III)}$  ions produced upon oxidation of  $\text{Co(II)}$ .

### Effect of Catalyst Concentration

Increase in the concentration of  $\text{Co(II) SO}_4$  from  $2.5 \times 10^{-4}M$  to  $5.0 \times 10^{-4}M$  increases percent grafting and grafting efficiency, after which the rate decreases (Fig. 2).

The increase of percent grafting with increase in  $\text{Co(II)}$  concentration within the mentioned range may be due to an increase in the concentration of free radicals and highly reactive unstable  $\text{Co(III)}$  ions, which increase the number of active free-radical sites on the cellulose backbone. The increase in

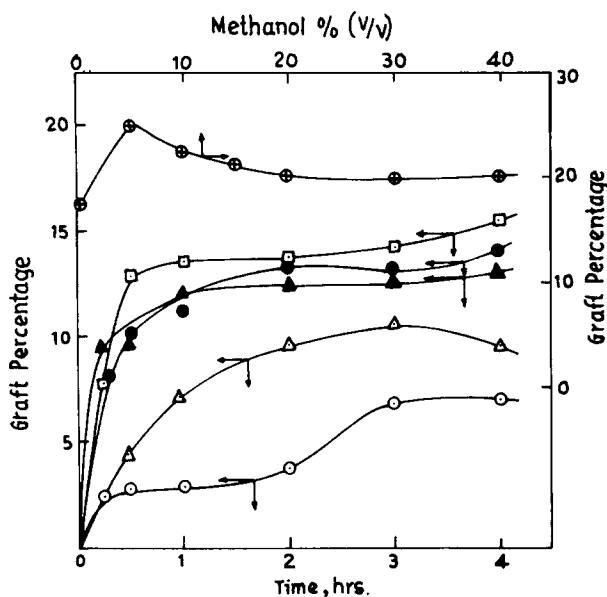


Fig. 3. (a) Variation of % grafting with time; effect of temperature:  $[\text{KHSO}_5] = 9.67 \times 10^{-3}M$ ;  $[\text{AM}] = 0.8M$ ;  $[\text{CoSO}_4] = 12.5 \times 10^{-4}M$ ; Cell = 0.2 g. Plots: (○) 30°C; (△) 35°C; (□) 40°C; (●) 45°C; (▲) 50°C. (b) Effect of solvent composition on % grafting:  $[\text{KHSO}_5] = 4.83 \times 10^{-3}M$ ;  $[\text{AM}] = 0.8M$ ;  $[\text{CoSO}_4] = 5 \times 10^{-4}M$ ; temp = 40°C. Plot: (⊕)  $\text{CH}_3\text{OH}$ .

the concentration of the intermediate species may be due to an increase in the rate of interaction of bridged peroxo orbitals of  $\text{KHSO}_5$  with vacant  $d^7$ -orbital of  $\text{Co(II)}$  ions. Initiation of vinyl polymerization<sup>19,20</sup> and graft copolymerization<sup>21</sup> onto cellulose by  $\text{Co(III)}$  ions has been reported.

### Effect of Temperature

Increase of reaction temperature up to 40°C increases percent grafting at fixed concentration of the monomer (0.8M) and  $\text{KHSO}_5$  ( $9.06 \times 10^{-3}M$ ). A further increase of temperature decreases percent grafting. The results are plotted in Figure 3. The increase of percent grafting up to 40°C may be attributed to: (i) increase in the rate of production of active free radicals, which, in turn, increase the number of grafting sites at a higher rate (the rate of graft initiation by the macrocellulosic radical is thereby increased); (ii) increase of temperature increases the rate of diffusion of acrylamide into the fiber matrix, where grafting is also initiated at the complexed monomers. Similar phenomena were noticed by Samal et al.<sup>22,23</sup> in the grafting of acrylamide onto nylon-6 and silk fibers.

Further, the depression of percent grafting beyond 40°C may be due to (i) increase in the rate of homopolymer formation and (ii) premature termination of the growing grafted chains by unstable  $\text{Co(III)}$  ions produced upon oxidation of  $\text{Co(II)}$ . Premature termination of growing polymer chains by higher valency transition metal ions has been observed by Bamford et al.<sup>24</sup> and Samal et al.<sup>25</sup>

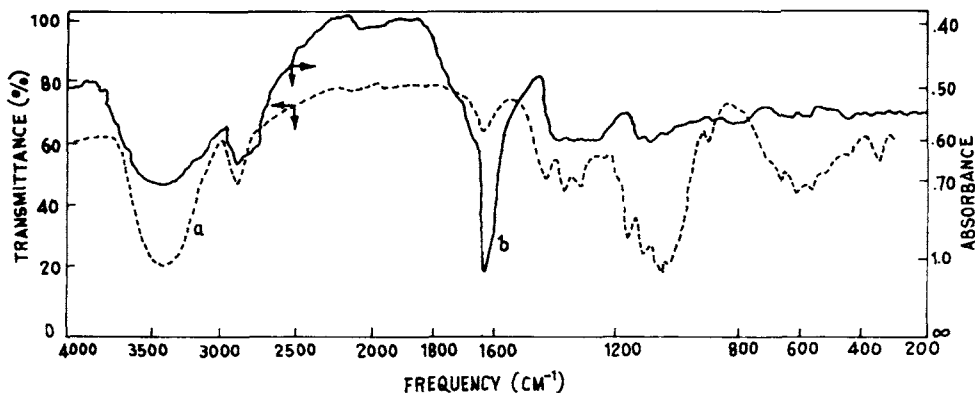


Fig. 4 (a) IR spectrum of cellulose,  
(b) IR spectrum of the graft copolymer.

Fig. 4.

### Effect of Solvent Composition

Grafting reaction was carried out in the presence of water-soluble organic solvents such as acetic acid, formic acid, and methanol of various compositions (5 : 95 to 40 : 60) at fixed concentration of  $\text{KHSO}_5$  ( $4.83 \times 10^{-3}M$ ), AM ( $1.2M$ ),  $\text{CoSO}_4$  ( $5 \times 10^{-4}M$ ) cellulose (1 g) at  $40^\circ\text{C}$ . It is observed that the graft percentage and grafting efficiency are not significantly affected by acetic acid and formic acid of various compositions. The grafting of 17.9% for the control set for 3 h of reaction time remains unaltered. On the other hand, the percent grafting increased up to 25% at the methanol : water ratio of 5 : 95, and on further increase up to 40 : 60 the value decreased but not below the control (Fig. 3). Similar behavior of methanol was noticed in our previous communication.<sup>11</sup> The increase of graft percentage at the solvent : water composition of 5 : 95 may be attributed to: (i) swelling of fibers resulting in diffusion of monomers more towards the grafting site, (ii) formation of solvent radicals and/or hydrogen or hydroxyl radicals from water under the influence of primary radical species, and (iii) formation of solvent-water cage via intermolecular hydrogen bonding that protects the free-radical sites on the cellulose backbone from side reactions like oxidation, dimerization, etc., thereby favors monomer addition onto it.

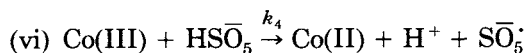
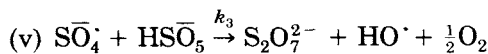
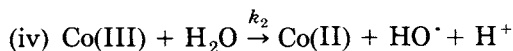
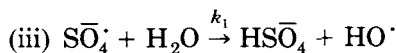
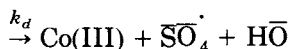
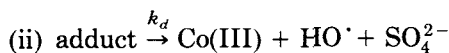
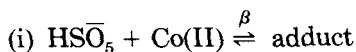
The slow depletion of grafting from 25 to 20% with increasing methanol proportion in the reaction medium may be due to massive reaction of the initiator radical with solvent molecules which decreases the number of active free-radical sites on the cellulose molecule.

### MECHANISM

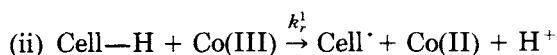
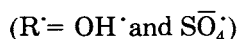
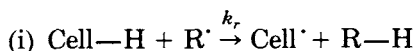
The mechanism of graft copolymerization may be pictured as involving generation of macrocellulosic radicals, resulting from the attack of various free-radical species ( $\text{OH}^\cdot$ ;  $\text{SO}_4^{\cdot-}$ ) and to some extent by Co(III) ions on cellulose. The free-radical species and Co(III) ions are produced from the redox reaction between  $\text{KHSO}_5$  and Co(II). The macrocellulosic radical subsequently attacks

the monomer resulting in chain initiation. This is then followed by propagation and finally the termination of the growing grafted chain is affected by Co(III) and mutual combination.

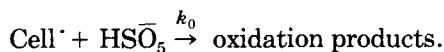
### 1. Primary Radicals and Co(III) Production.



### 2. Formation of Macrocellulosic Radical.

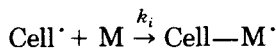


### 3. Oxidation.



### 4. Initiation.

(i) *Graft copolymerization:*



(ii) *Homopolymerization:*

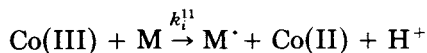
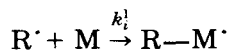






TABLE I  
Water Retention Values of Acrylamide-Grafted Samples with Various Percent  
Using the Method of Ranby and Gadda.<sup>26</sup>

Percent grafting	Water retention (g/g)
Base	2
12.2	8
17.5	12
22.0	19
26.8	23
28.0	25
30.8	28

Co(III); verification of the evolution of O<sub>2</sub> and experimental verification of eq. (2).

### PROPERTIES OF THE GRAFT COPOLYMERS

Cellulose-*g*-polyacrylamide copolymers with varying graft percentage were subjected to screening of their improved physical and chemical behavior.

#### IR Analysis

The IR spectra of the purified graft copolymer was carried out in a Beckman Model spectrophotometer. The grafted samples exhibited new peaks at about 1650 cm<sup>-1</sup> (characteristics of amide carboxyl) ascertaining the hanging of amide groups on the grafted chains (Fig. 4).

#### Effect of Percent Grafting on Water Retention of the Grafted Samples

The water retention of the dry cellulose-*g*-polyacrylamide samples were determined using the methods as reported by Ranby and Gadda.<sup>26</sup> The results are recorded in Table I. The water retention increases on increasing the percent grafting. Further the samples showed enhanced water retention property when hydrolyzed with dil. NaOH.

#### Effect of Percent Graft on Rot Resistance of Cotton

The rot resistance of the grafted samples were determined as per Mino et al.<sup>27</sup> Acrylamide-grafted cotton cellulose does not significantly improve the fabric properties as observed from their rot and mildew resistance behavior. The result of a 2-week soil burial test on fabric are recorded in Table II. The results show that cotton cellulose grafted with varying percentage of polyacrylamide afforded comparatively little protection to bacterial attack of the fiber.

#### Behavior towards Acids and Alkalies

Acrylamide-grafted cotton cellulose showed higher affinity to alkalies with respect to the base fiber, probably due to hydrolysis of the amide groups on the grafted chain. Moderate resistance to the action of acids at room temperature was observed. However, at elevated condition, hydrolysis of the gluco-

TABLE II

% (Grafting)	Initial tensile strength (dyn/cm <sup>2</sup> )	Tensile strength after 2 weeks of burial (dyn/cm <sup>2</sup> )	Percent strength retain
Base	41	0	0
12.2	41	1	2
17.5	42	2	4.7
22.2	45	3	6.6
26.8	47	3	6.4
28.0	48	4	8.3
30.8	49	4	8.0

pyranose units of the backbone of the fiber was noticed. The grafted fibers are still under the test for their thermal behavior and dye uptake ability. The details of thermal analysis data and dye uptake ability will be reported in a separate communication.

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