

# Influence of Dimethyl Sulfoxide on the Kinetics of the Graft Copolymerization of Acrylonitrile onto the Jute Fibers Initiated by Ceric Ion

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## Synopsis

A study of the influence of dimethyl sulfoxide (DMSO) on the graft copolymerization of acrylonitrile (AN) onto jute fiber using ceric ion has been made. The effect of concentrations of monomer, Ce(IV) and DMSO on graft yield have been studied. Besides, the effect of time, temperature, acid, and the amount of jute fiber on graft yield has been investigated. On the basis of experimental findings, a reaction mechanism has been proposed and optimum condition for effective grafting has been suggested.

## INTRODUCTION

Chemical methods have been extensively used in the study of graft copolymerization of acrylic monomers and various natural and synthetic fibers.<sup>1</sup> Kaizerman et al.,<sup>2</sup> Negishi and co-workers,<sup>3</sup> Hebeish and Mehta<sup>4</sup> have grafted vinyl monomers onto cellulose using ceric ions as initiator. Although a lot of work has been done on graft copolymerization of vinyl monomers onto cellulosic and other textile fibers,<sup>5-7</sup> much less has been reported on grafting of vinyl monomers onto jute fibers. Trivedi and Mehta<sup>8</sup> have reported grafting of acrylonitrile onto defatted and bleached jute fibers with ceric ion initiation. In this paper we have clearly demonstrated how the choice of a suitable substrate coupled with ceric ion could bring about higher percentage of grafting and radical change in some of the useful properties than those obtained in the absence of the substrate.

## EXPERIMENTAL

Jute fibers (white jute, mesta variety) as obtained from Konark Jute Mills Ltd., Orissa, India, were subjected to different chemical treatments as mentioned earlier.<sup>9</sup> Acrylonitrile (BDH, Anala R) was washed with 5% NaOH, 3% orthophosphoric acid, and washed thoroughly with conductivity water. Then the washed acrylonitrile was dried over anhydrous calcium chloride, filtered, and stored in the refrigerator for use. All other chemicals used, i.e., dimethyl sulfoxide, ammonium ceric sulfate, sulfuric acid, etc. were of BDH or AnalaR grade and were used as such without further purification.

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The graft copolymerization reactions were carried out at the desired temperature, in a constant temperature bath with an accuracy of  $\pm 1^\circ\text{C}$ . Before initiating the graft copolymerization reaction, the jute fibers were soaked with an appropriate quantity of monomer for about 10 min. The graft copolymerization reactions were carried out in Pyrex vessels with B<sub>24/29</sub> standard joints equipped with gas inlet and outlet tubes. Appropriate quantity of reaction mixture containing jute fiber, monomer, dimethylsulfoxide, sulfuric acid, and water were taken in the reaction vessel. Then the required amount of ammonium ceric sulfate solution was poured into the vessels containing the reaction mixture and the time was noted. The reactions were carried out at three different temperatures, i.e., 40, 50, and 60°C. After the specific time intervals, each reaction was arrested by quenching the vessel with ice cold water. Then the grafted samples were washed well with water, given a mild soaping to remove the loosely adhering polymer, washed, and air-dried. It was also observed that, on further extraction with DMF (as polyacrylonitrile is soluble in DMF) for about 24 h at 30°C, the grafted samples showed a negligible weight loss. This type of observation has also been reported by Hebeish and Mehta.<sup>4</sup> The percentage of grafting was calculated on dry weight, determined by storing the materials in weighing bottles over P<sub>2</sub>O<sub>5</sub> at room temperature in a vacuum desiccator until a constant weight is obtained. Percentage of graft yield, rate of grafting, and the percentage efficiency were calculated as follows:

$$\% \text{ graft yield (GY)} = \frac{(\text{dry wt grafted jute} - \text{dry wt original jute})}{\text{dry wt original jute}} \times 100$$

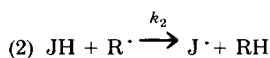
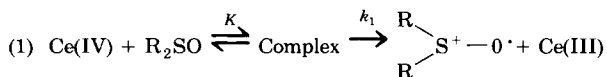
$$\text{Rate of grafting (} R_g \text{)} = \frac{1000 \times W}{V \times t \times M}$$

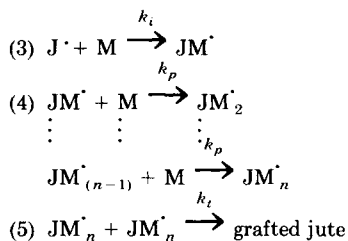
where  $W$  = weight of grafted jute - weight of original jute,  $V$  = volume of reaction mixture,  $t$  = time of reaction in seconds, and  $M$  = molecular weight of the monomer;

$$\% \text{ efficiency (} E \text{)} = \frac{(\text{wt grafted jute} - \text{wt original jute})}{\text{wt monomer}} \times 100$$

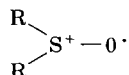
### REACTION MECHANISM

In the present experimental conditions the active species of Ce(IV) ion in sulfuric acid media interacts with dimethyl sulfoxide (DMSO) to form a complex. Subsequently, the complex dissociates in a slow step and generation of a free radical takes place by the abstraction of a hydrogen atom from the protonated complex.<sup>10</sup> The reaction proceeds through the following steps:





where



is denoted as  $R^\cdot$

and  $Ce(IV)$ ,  $JH$ ,  $J^\cdot$ ,  $M$ ,  $K$ ,  $k_1$ ,  $k_2$ ,  $k_i$ ,  $k_p$ , and  $k_t$  are ceric ion, jute molecule, jute macroradical, monomer, and different rate constants, respectively.

Taking into account the above reaction scheme and applying the steady state principle to all kinds of radicals involved, the following expression for the rate of grafting ( $R_g$ ) has been derived:

$$\frac{d[R^\cdot]}{dt} = k_1K [Ce(IV)][R] - k_2[JH][R^\cdot] = 0$$

or

$$k_1K [Ce(IV)][R] = k_2[JH][R^\cdot]$$

or

$$[R^\cdot] = \frac{k_1K [Ce(IV)][R]}{k_2[JH]} \quad (1)$$

$$\frac{d[J^\cdot]}{dt} = k_2[JH][R^\cdot] - k_i[J^\cdot][M] = 0$$

or

$$[J^\cdot] = \frac{k_2[JH][R^\cdot]}{k_i[M]}$$

Replacing the value of  $[R^\cdot]$  from eq. (1),

$$[J^\cdot] = \frac{k_1K [Ce(IV)][R]}{k_i[M]} \quad (2)$$

$$\frac{d[JM_n^\cdot]}{dt} = k_i[J^\cdot][M] - k_t[JM_n^\cdot]^2 = 0$$

or

$$[JM_n^\cdot] = \left( \frac{k_i[J^\cdot][M]}{k_t} \right)^{1/2}$$

Replacing the value of  $[J^*]$  from eq. (2),

$$[JM_n^*] = \left( \frac{k_1 K [Ce(IV)][R]}{k_t} \right)^{1/2} \quad (3)$$

$$R_g = k_p [JM_n^*][M]$$

Replacing the value of  $[JM_n^*]$  from eq. (3),

$$R_g = k_p [M] \left( \frac{k_1 K}{k_t} [Ce(IV)][R] \right)^{1/2}$$

The experimental results are in good agreement with the proposed mechanism.

## RESULTS

Although grafting of acrylonitrile onto jute fibers has been attempted earlier with the use of Ce(IV) ion alone,<sup>8,9</sup> we decided to carry out the work on grafting with the use of Ce(IV) ion coupled with dimethyl sulfoxide (DMSO). Better results, with respect to higher percentage of grafting, were obtained by working with such a system.

The effect of variation of time on graft yield at three different temperatures (40, 50, and 60°C) is presented in Figure 1. In all these cases the graft yield has been found to increase steadily with increase of time up to 2 h, after which there is little variation in graft yields. For all practical purposes steady state has been achieved at or around 2 h time.

The effect of variation of Ce(IV) ion concentration on the percentage of graft yield has been shown in Figure 2. It is observed that with the increase of Ce(IV) ion concentration from 0.005 to 0.035 ML<sup>-1</sup> the percentage of graft yield increases at all the temperatures studied. However, the increase of Ce(IV) ion concentration beyond 0.035 ML<sup>-1</sup> results in a decrease in graft yield.

DMSO coupled with Ce(IV) ion forms the initiating system. Figure 3 shows the effect of variation of DMSO concentration on the percentage of graft yield at three different temperatures, keeping the concentration of all other reagents constant. The percentage of graft yield increases with the increase of DMSO from 0.05 to 0.30 ML<sup>-1</sup> and thereafter it decreases.

The effect of variation in monomer concentration on percentage of graft yield at three different temperatures has been studied. The percentage of grafting increases with the increase in monomer concentration from 0.3036 to 0.9867 ML<sup>-1</sup> and thereafter decreases. In the increasing region the rate of grafting was found to be proportional to the first power of monomer concentration.

The graft copolymerization was carried out at three different temperatures between 40 and 60°C. A perusal of the result indicates that the percentage of grafting decreases with increase in temperature.

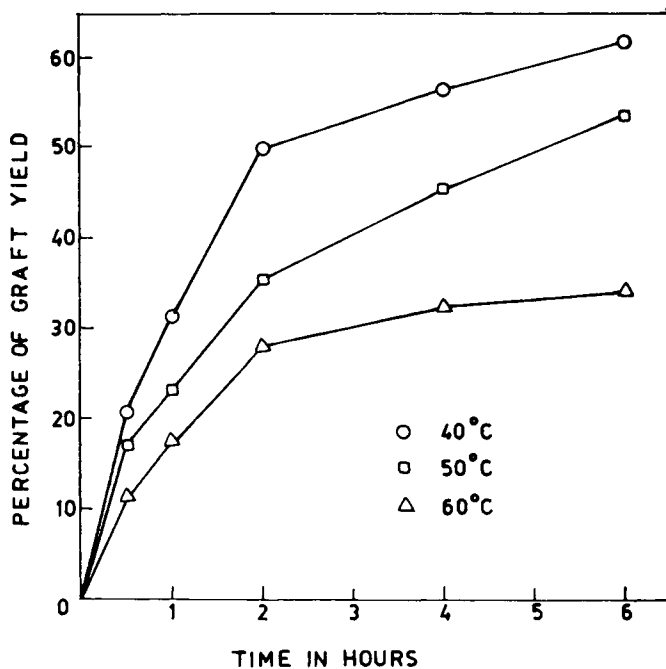


Fig. 1. Effect of reaction time: jute, 0.1 g; AN, 0.759M;  $H^+$ , 0.50M;  $Ce^{+4}$ , 0.025M; DMSO, 0.25M.

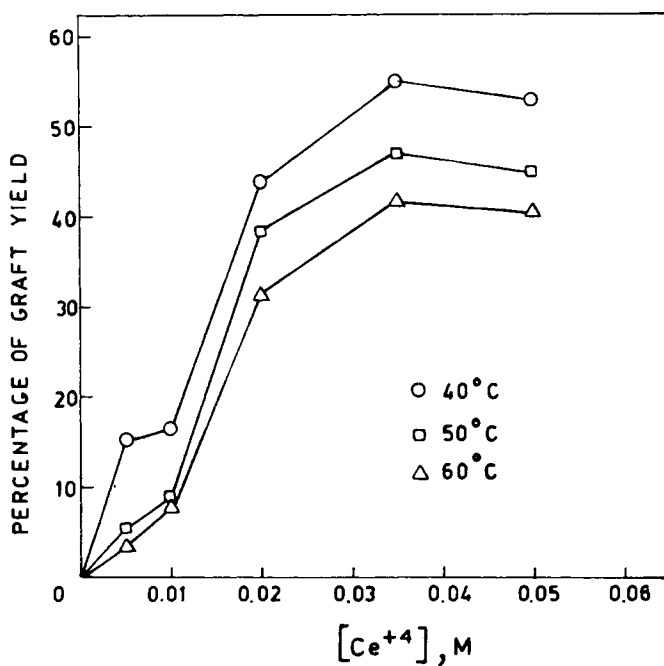


Fig. 2. Effect of ammonium ceric sulphate: jute, 0.1 g; AN, 0.759M;  $H^+$ , 0.50M; DMSO, 0.25M; time, 2 h.

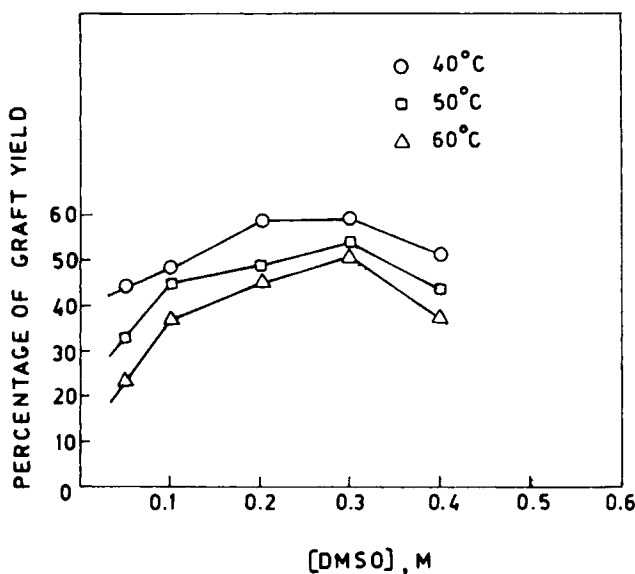


Fig. 3. Effect of dimethyl sulfoxide: jute, 0.1 g; AN, 0.759M;  $H^+$ , 0.50M;  $Ce^{+4}$ , 0.035M; time, 2 h.

TABLE I  
Effect of Sulfuric Acid<sup>a</sup>

[H <sub>2</sub> SO <sub>4</sub> ](ML <sup>-1</sup> )	40°C			50°C			60°C		
	GY(%)	$R_g \times 10^6$	E(%)	GY(%)	$R_g \times 10^6$	E(%)	GY(%)	$R_g \times 10^6$	E(%)
0.35	59.4	7.8	7.37	50.8	6.6	6.3	37.1	4.8	4.6
0.4	53.9	7.0	6.69	47.7	6.2	5.92	31.5	4.1	3.91
0.45	48.7	6.3	6.04	42.5	5.5	5.27	27.9	3.6	3.46
0.55	43.8	5.7	5.44	37.0	4.8	4.59	20.4	2.6	2.53
0.65	22.0	2.8	2.73	18.0	2.3	2.23	14.7	1.9	1.82

<sup>a</sup>Jute = 0.1 g, [AN] = 0.7590 ML<sup>-1</sup> [DMSO] = 0.30 ML<sup>-1</sup>, [Ce(IV)] = 0.035 ML<sup>-1</sup>, time = 2 h.

The grafting reaction has been carried out in varying acid concentrations from 0.35 to 0.65 ML<sup>-1</sup> (Table I). It is observed that with the increase of acid concentration the percentage of grafting decreases.

The effect of variation of the amount of jute fibers on the percentage of graft yield and the rate of grafting ( $R_g$ ) has been studied at three different temperatures. Surprisingly it was found that no definite trend could be observed. This suggests that probably the rate of grafting is independent of the amount of jute.

## DISCUSSION

In order to explain various experimental results in the present investigation, several possibilities were considered. In the initial stages of graft copolymerization reaction, the Ce(IV) ion initiates large number of growing polyacrylonitrile branches. This is reflected by steady increase in the grafting percentage up to 2 h. With grafting time greater than this, grafting percentage remains more or less constant.

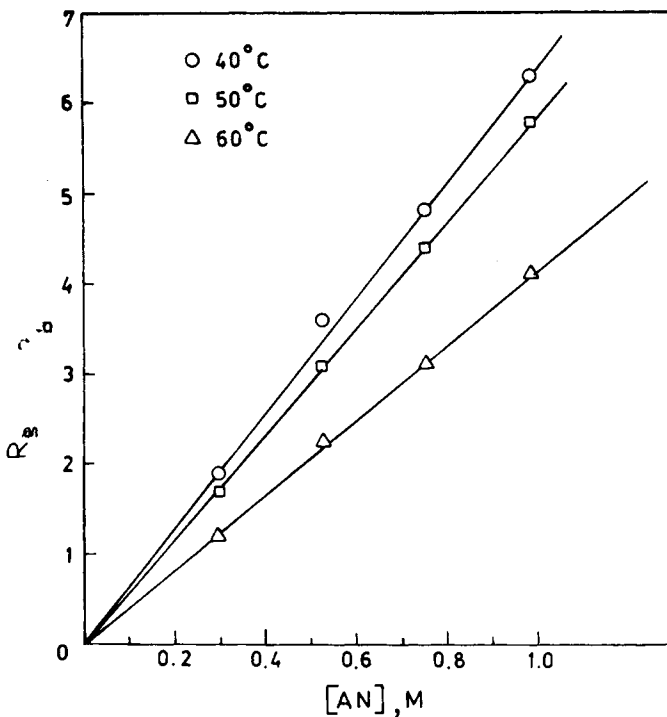


Fig. 4. Effect of monomer: jute, 0.1 g;  $Ce^{+4}$ , 0.035M;  $H^+$ , 0.50M; DMSO, 0.30M; time, 2 h.

A significant increase in grafting with increase of Ce(IV) ion concentration suggests that greater number of grafting sites are created by the Ce(IV) ion. However, at higher concentration of the Ce(IV) ion, the degree of grafting decreases considerably. Two types of termination mechanism are suggested for the polymerization and grafting initiated by metal ions. Although, at lower concentration of the Ce(IV) ion, mutual termination predominates over linear termination, at higher concentration linear termination may probably be prevalent over the mutual one, leading to shorter grafted chains. In the present investigation, since all the reactions have been carried out, under low and optimum concentration of the Ce(IV) ion, we have proposed mutual termination in the kinetic scheme.

The derivation of rate expression shows that the rate of grafting is directly proportional to the first power of monomer concentration. This has been reflected in Figure 4, where the plot of  $R_g$  vs.  $[AN]$  was found to be linear, passing through the origin. The decreasing trend in the percentage of grafting, after a certain optimum concentration of acrylonitrile, is probably due to the competition between the homopolymerization and grafting where the former prevails over the latter at higher monomer concentration.

It is observed that graft yield remains more or less unaffected by increasing the amount of jute fibers in the grafting system. This observation is at variance with other systems we have reported from this laboratory.<sup>11,12</sup>

The effect of DMSO on the percentage of grafting has been clearly demonstrated in Figure 3. Although at zero concentration of DMSO a very low percentage of grafting has been obtained, there is remarkable increase in graft

yield by increasing the concentration of DMSO. This corresponds to our reaction scheme and the expression for the rate of grafting. The decrease in graft yield beyond a certain concentration of DMSO might be due to the primary radical termination along with mutual termination.

The increase of temperature and concentration of sulfuric acid adversely affects the rate of grafting. It was reported earlier that grafting onto jute fibers hardly became possible below 50°C<sup>11</sup> and also below a certain minimum concentration of sulfuric acid.<sup>11</sup> Almost all the figures given in this paper depict the effect of temperature. Therefore, the present investigation is quite significant in the sense that grafting could be carried out at a low temperature and low acid concentration.

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