

Influence of Glycine on the Kinetics of the Graft Copolymerization of Acrylonitrile onto Jute Fibers Initiated by Ceric Ion

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SYNOPSIS

A study of the influence of glycine 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 glycine on graft yield have been studied. In addition, 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 qualitative reaction mechanism has been proposed and the optimum condition for effective grafting has been suggested.

INTRODUCTION

Ceric salts in aqueous acidic solutions either by themselves¹ or in combination with reducing agents²⁻⁴ are well-known initiators of vinyl polymerization and graft copolymerization of vinyl monomers onto various natural and synthetic fibers. A number of studies have been conducted in the past to deal with the mechanism and the kinetics of graft copolymerization involving different monomers and natural fibers. The reducing agents have been alcohols,⁴⁻⁶ aldehydes and ketones,⁷ and carboxylic acids.⁸ However, no attempt has so far been made to use amino acids as reducing agent.

Recently, kinetics of glycine oxidation by Ce⁴⁺ in H₂SO₄ medium⁹ and its subsequent use in the initiation of vinyl polymerization have been reported in detail.¹⁰ It has been found that the yield of homo polymer was significantly less than that found in other systems. This observation has prompted us to undertake the studies of graft copolymerization onto jute fibers. Very interesting results different from our earlier findings¹¹ have been obtained. This has resulted in a drastic change in the proposition of a slightly different mechanism of grafting reaction.

In this paper, we report the results on graft copolymerization of acrylonitrile onto delignified jute fibers using Ce⁴⁺ in the presence of glycine.

EXPERIMENTAL

Jute fibers (white jute, mesta variety) obtained from Konark Jute Mills Ltd., Orissa, India, were subjected to different chemical treatment as mentioned earlier.¹² Acrylonitrile (BDH, AnalaR) was washed with 5% NaOH, 3% orthophosphoric acid, and then washed thoroughly with conductivity water. Next, the washed acrylonitrile was dried over anhydrous calcium chloride and then stored in the refrigerator until use. All other chemicals used, i.e., glycine, ammonium ceric sulphate, sulfuric acid, etc., were of BDH or AnalaR grade and were used as such without further purification.

The graft copolymerization reactions were carried out at the desired temperatures 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_{24/29} standard joints equipped with gas inlet and outlet tubes. An appropriate quantity of reaction mixture containing jute fiber, monomer, glycine,

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sulfuric acid, and water were taken in the reaction vessel. Then, the required amount of ammonium ceric sulphate 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. This process has been repeated to check the reproducibility in the result. 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.¹³ The percentage of grafting was calculated on dry weight, determined by storing the materials in weighing bottles over P₂O₅ at room temperature in a vacuum desiccator until a constant weight was obtained. Percentage of graft yield, rate of grafting, and the percentage of efficiency were calculated as follows:

% graft yield (GY)

$$= \frac{\text{dry wt of grafted jute} - \text{dry wt of original jute}}{\text{dry wt of original jute}} \times 100$$

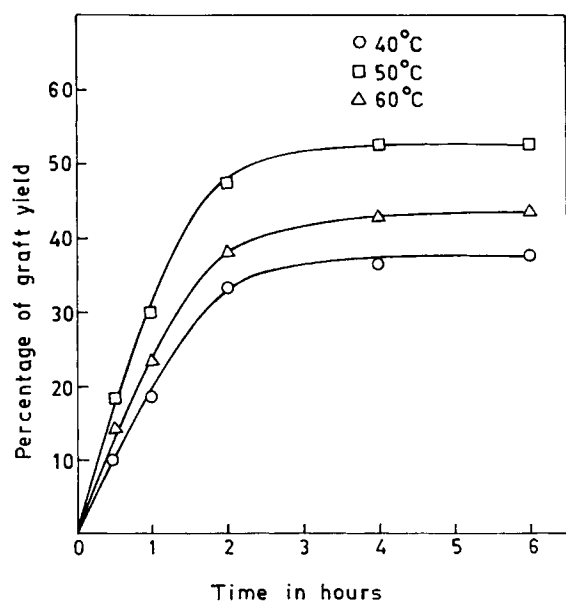


Figure 1 Effect of reaction time: jute = 0.1 g; [AN] = 0.759 mol L⁻¹; [H⁺] = 0.50 mol L⁻¹; [Ce⁴⁺] = 0.025 mol L⁻¹; [glycine] = 0.15 mol L⁻¹.

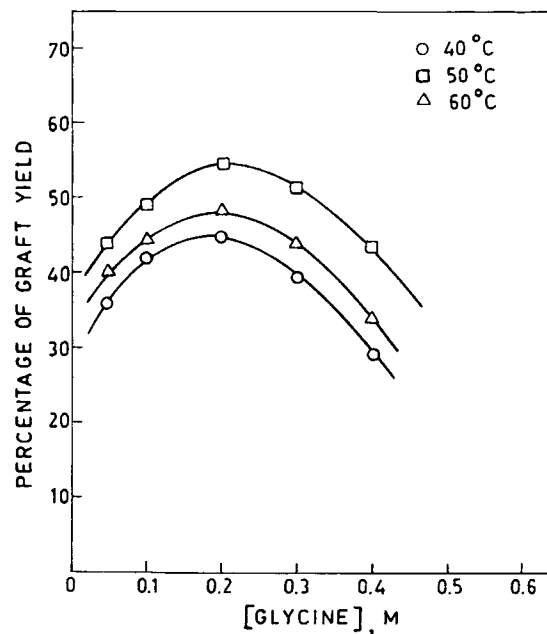


Figure 2 Effect of variation of glycine concentration: jute = 0.1 g; [AN] = 0.759 mol L⁻¹; [H⁺] = 0.50 mol L⁻¹; [Ce⁴⁺] = 0.035 mol L⁻¹; time = 2 h.

RESULTS AND DISCUSSION

Effect of Variation of Time on Graft Yield

The effect of variation of time (from 0.5 to 6 h), on graft yield at three different temperatures (40, 50, and 60°C) is shown 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 the graft yield levels off. Similar observations have also been reported earlier in the study of graft copolymerization of vinyl monomers onto jute fibers.¹⁴⁻¹⁷

Effect of Variation of Glycine Concentration

The effect of variation in glycine concentration on percentage of graft yield is shown in Figure 2. The concentration was varied from 0.05 to 0.4 mol L⁻¹. It is observed that with the increase of the concentration of glycine up to 0.2 mol L⁻¹ the percentage of graft yield increases at all temperatures, and beyond this concentration, there is a decrease in graft yield. The decrease of graft yield beyond a certain concentration of glycine may, therefore, be attributed to the formation of an increased amount of homopolymers.¹⁸

Effect of Variation of Ce⁴⁺ Concentration

Concentration of Ce⁴⁺ has been varied from 0.005 to 0.05 mol L⁻¹. Although the percentage of graft

yield has been found to increase with the concentration of Ce^{4+} up to 0.035 mol L^{-1} , there has been a fall in the graft yield at the concentration of 0.05 mol L^{-1} at all temperatures. Figure 3 shows the effect of Ce^{4+} concentration on the percentage of graft yield. This certainly indicates that at lower concentration of Ce^{4+} (below 0.035 mol L^{-1}) mutual termination of growing grafted radical chains prevails over the termination due to metal ion. However, beyond 0.035 mol L^{-1} , linear termination due to metal ion prevails. We have included mutual termination in the mechanism of graft copolymerization. This explains the increase in percentage of grafting at low Ce^{4+} concentration. Contrary to this observation, we have found that the percentage of homopolymerization consistently decreases with the increase of concentration of $Ce(IV)$.¹⁰

Effect of Variation of Monomer Concentration

The effect of variation in monomer concentration on percentage of graft yield at three different temperatures has been studied. It is observed that the percentage of graft yield increases with the increase of monomer concentration from 0.3036 to $0.7590 \text{ mol L}^{-1}$ and thereafter decreases. In the increasing region, the percentage of grafting was found to be proportional to the first power of monomer concentra-

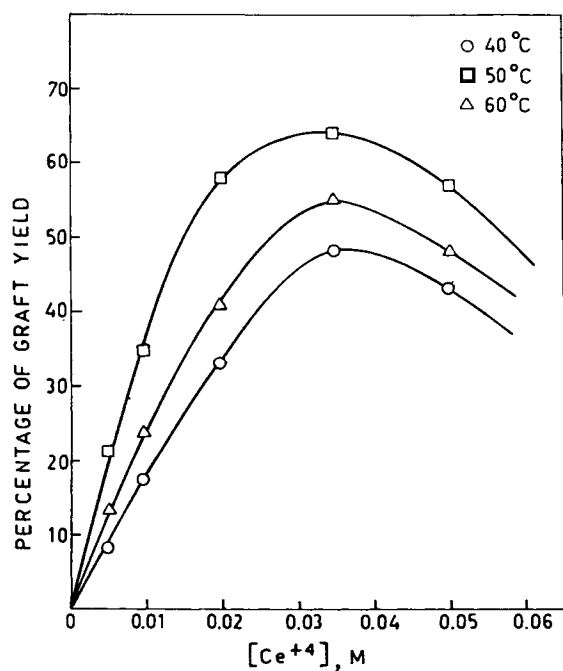


Figure 3 Effect of variation of ammonium ceric sulphate concentration: jute = 0.1 g; $[H^+] = 0.50 \text{ mol L}^{-1}$; $[AN] = 0.759 \text{ mol L}^{-1}$; $[glycine] = 0.15 \text{ mol L}^{-1}$; time = 2 h.

Table I Effect of Variation of Jute

Weight of Jute Fiber (g)	% Graft Yield		
	40°C	50°C	60°C
0.05	52.0	62.5	54.2
0.10	44.8	55.0	48.2
0.15	35.0	44.0	40.0
0.20	27.5	35.0	31.5
0.25	18.0	24.8	21.8

$[Ce^{4+}] = 0.035 \text{ mol L}^{-1}$; $[AN] = 0.759 \text{ mol L}^{-1}$; $[H_2SO_4] = 0.50 \text{ mol L}^{-1}$; $[glycine] = 0.2 \text{ mol L}^{-1}$; time = 2 h.

tion. The enhancement of grafting by increasing monomer concentration up to certain value could be ascribed to the availability of grafting sites of jute fiber under the present experimental conditions. However, the decreasing trend of percent graft yield after certain optimum concentration of AN is probably due to the competition between the homopolymerization and grafting, where the former prevails over the latter at higher AN concentration. Similar observations have also been reported earlier.¹⁸

Effect of Variation of Jute Fiber

The effect of variation of amount of jute fibers on percentage of graft yield at three different temperatures (40, 50, and 60°C) has been studied (Table I). It is observed that within the range studied the graft yield consistently decreased by increasing the amount of jute fiber in the graft copolymerization system. Increase in amount of jute fiber probably makes the termination rate faster than rate of initiation due to hydrogen abstraction. This finding is surprisingly different from our earlier work,¹⁹ where we had observed no definite trend.

Effect of Variation of Temperature

The graft copolymerization of acrylonitrile onto jute fibers has been studied at three different temperatures, i.e., 40, 50, and 60°C . The effect of temperature on percentage of graft yield is shown in Figures 1–3. It is observed that the percentage of graft yield increases with rise of temperature from 40 to 50°C . However, the graft yield decreases with a further increase in temperature. The increase in graft yield with increase in temperature can be attributed to the swellability of jute and the enhancement of rate of diffusion of monomer with increase in temperature. With a further increase in temperature, graft copolymerization occurs with poor selectivity and

various hydrogen abstraction and chain transfer reactions might be accelerated, leading to decrease in graft yield. In the study of influence of dimethyl sulphoxide on the kinetics of graft copolymerization, we have noticed that the percentage of grafting decreases consistently with increase in temperature.

Effect of Variation of Acid Concentration

The graft copolymerization of acrylonitrile on jute fibers has been carried out in aqueous sulfuric acid medium. The concentration of sulfuric acid was varied from 0.35 to 0.75 mol L⁻¹, keeping the concentration of all other reactants fixed (Table II). Although no consistent results have been obtained, there is a decreasing tendency on the graft yield with increasing concentration of the acid. The increase in concentration of acid is not only unfavorable to grafting, but it also destroys some of the useful properties of the fiber. Similar reports have also been made in our earlier papers.²⁰

Reaction Mechanism

In the present experimental conditions, the active species of Ce(IV) ion in sulfuric acid media interacts with glycine (NH₂CH₂COOH) 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.⁸ The reaction proceeds through the following steps:

Initiation

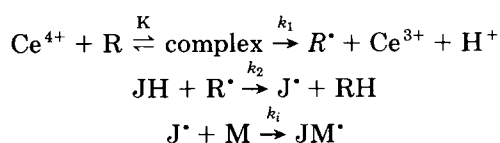


Table II Effect of Variation of Acid

[H ₂ SO ₄] mol L ⁻¹	% Graft Yield		
	40°C	50°C	60°C
0.35	48.4	55.2	50.0
0.45	45.0	54.1	46.0
0.55	42.4	53.0	44.0
0.65	43.4	48.4	45.2
0.75	43.4	48.0	43.8

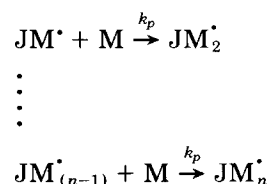
[Ce⁴⁺] = 0.035 mol L⁻¹; [AN] = 0.759 mol L⁻¹; [glycine] = 0.2 mol L⁻¹; jute = 0.1 g; time = 2 h.

Table III Effect of Solvents and Inorganic Salts

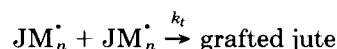
Solvent (5% v/v)	% GY	[Salt] 0.01 mol L ⁻¹	% GY
Control	55.0	Control	55.0
Dioxane	8.0	CuSO ₄	47.2
Acetone	18.5	MnCO ₃	32.5
Acetic acid	51.0	NaCl	52.0
Methyl alcohol	48.2	K ₂ SO ₄	45.1

Jute = 0.1 g; [AN] = 0.759 mol L⁻¹; [Ce⁴⁺] = 0.035 mol L⁻¹; [glycine] = 0.2 mol L⁻¹; time = 2 h, Temp = 50°C.

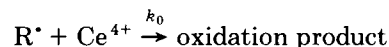
Propagation



Termination



Oxidation



where NH₂CH₂COOH is denoted as R and Ce⁴⁺, JH, J[·], M, K, k₁, k₂, k_i, k_p, and k_t are ceric ion, jute material, jute macro radical, monomer, and different rate constants, respectively. Rigorous kinetic analysis was not attempted since the process is complex and heterogeneous.

Effect of Reaction Medium

The graft yield follows the order with the solvents when added in equal proportions (5% v/v): control > acetic acid > methyl alcohol > acetone. The important feature in this trend is that all the solvents used depress the percent of grafting. Similarly, the effect of neutral salts when added in equal molar concentrations follows the order: control > NaCl > CuSO₄ > K₂SO₄ > MnCO₃. The above results are shown in Table III.

IR Spectra

It is observed that the ungrafted, i.e., chemically modified, jute shows the characteristic broad ab-

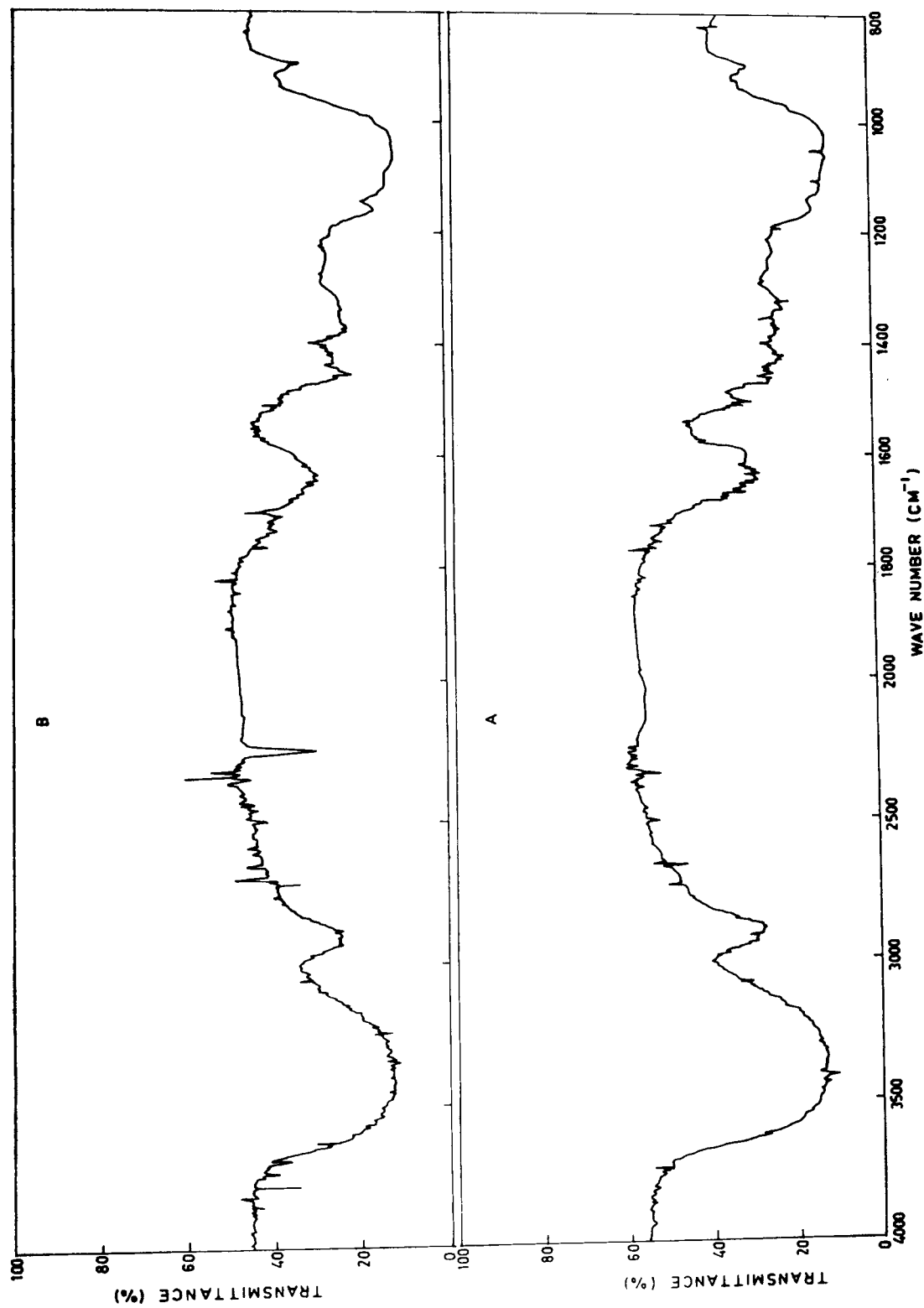


Figure 4 Infrared spectra: (A) jute fibers (chemically modified); (B) jute fibers grafted with acrylonitrile.

sorption band on the hydroxyl group around 3400 cm^{-1} in its IR spectrum. However, the spectrum of AN-grated jute shows an additional peak of the nitrile group at about 2250 cm^{-1} , thereby indicating the occurrence of grafting (Fig. 4). Similar observations have also been reported by Trivedi and Mehta.²¹

CONCLUDING REMARKS

In conclusion, it should be noted that our results are sufficient to establish the mechanism of the grafting reaction. Although the Ce(IV) ion has been shown to polymerize vinyl monomers under the influence of many organic substrates, it is not possible to carry out grafting onto jute fibers using all the redox couples. Competition between homopolymerization and grafting is the root cause for such failure. Therefore, study of grafting with the use of an effective redox system is highly essential so far as modification of fiber properties is concerned. Besides, from the effect of various additives, an optimum condition for the effective grafting has been found. The optimum condition for grafting reaction has been worked out as follows: $[\text{Ce}^{4+}] = 0.035 \text{ mol L}^{-1}$; $[\text{AN}] = 0.759 \text{ mol L}^{-1}$; $[\text{glycine}] = 0.2 \text{ mol L}^{-1}$; $\text{H}_2\text{SO}_4 = 0.5 \text{ mol L}^{-1}$; jute = 0.05 g.

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