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H. K. Das^a; N. C. Nayak^a; B. C. Singh^a

^a Post Graduate Department of Chemistry, Utkal University Vani Vihar, Bhubaneswar, Orissa, India

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EFFECT OF TOLUENE ON THE KINETICS OF Ce(IV)-ION-INITIATED GRAFTING OF METHYL METHACRYLATE ONTO CHEMICALLY MODIFIED JUTE FIBERS

H. K. DAS, N. C. NAYAK, and B. C. SINGH*

Post Graduate Department of Chemistry
Utkal University
Vani Vihar, Bhubaneswar 751004, Orissa, India

ABSTRACT

A study of the graft copolymerization of methyl methacrylate onto jute fiber using Ce(IV) and toluene has been carried out. The effects of concentration of monomer, Ce(IV), and toluene on graft yield have been studied. The effects of time, temperature, acid, amount of jute fiber, and some inorganic salts and organic solvents on graft yield have also been investigated. The investigation includes characterization of the grafted fiber by infrared and thermogravimetric studies. Grafting improves the thermal stability of jute fibers. More than 200% graft yield was achieved in the present investigation.

INTRODUCTION

Chemically modified jute can be graft copolymerized effectively by a free radical mechanism with methyl methacrylate (MMA). A lot of work [1–3] has been done on graft copolymerization of vinyl monomers onto

*To whom correspondence should be addressed.

similar cellulosic fibers. Trivedi and Mehta [4] reported the grafting of acrylonitrile onto defatted and bleached jute fibers with Ce(IV) ion as initiator. Graft copolymerization of both acrylonitrile (AN) and MMA onto delignified and bleached jute fibers using ceric ammonium sulfate as initiator has been reported by Ray [6] and Huque et al. [5]. These authors observed that the percentage of grafting is very low. Hence, it was felt necessary to improve the process of modification of jute fibers by chemical means. In this paper we report on a new technique which gives a significant increase in grafting and thermal stability of the grafted fibers.

In order to enhance the graft yield, many workers [7, 8] have carried out graft copolymerization on jute fibers by using various redox systems. In earlier studies [11] it was shown that toluene acts as a retarder in polymerization. We had intended to use toluene as a retarder in graft copolymerization, but to our surprise, we observed that the presence of toluene with Ce(IV) at low concentration (up to 0.05 mol/L) enhanced the percentage of grafting. Subsequently, on increasing the concentration of toluene, there was fall in percent grafting. The present investigation reports a kinetic study of Ce(IV)-toluene initiated graft copolymerization of MMA onto chemically modified jute fibers.

EXPERIMENTAL

The pretreatment of jute fibers was done as described earlier [7]. Monomer (MMA) was purified following a standard procedure [9]. All other chemicals, i.e., toluene, ammonium ceric sulfate, sulfuric acid, glacial acetic acid, etc., were (BDH) A.R. grade and were used without further purification.

The graft copolymerization reactions were carried out at the desired temperature in a constant temperature bath with an accuracy of $\pm 0.1^\circ\text{C}$. Before initiating the graft copolymerization reaction, the jute fibers were soaked with an appropriate quantity of monomer for about 5 to 10 min. The graft copolymerization was carried out in Pyrex vessels equipped with gas inlet and outlet tubes. Appropriate quantities of reaction mixture containing jute fibers (chemically modified), monomer, toluene, sulfuric acid, glacial acetic acid, and water were placed in the reaction vessel. The required amount of ammonium ceric sulfate solution was poured into vessels containing the reaction mixture. The reactions were carried out for specific times at three different temperatures: 40,

50, and 60°C. After a specific time interval, each reaction was quenched by immersing the vessel in ice-cold water. The homopolymer and the grafted jute fibers were filtered off, washed with ion-free water, and dried to constant weight. Finally, the fibers were refluxed with acetone repeatedly for about 12 h to dissolve all the homopolymers. The weight of the grafted fibers was considered to be the point at which they attained a constant value. The percentage of grafting was estimated as follows:

$$\% \text{ of graft yield} = \frac{\left[\text{dry weight of} \right] \text{ jute (grafted)} - \left[\text{dry weight of} \right] \text{ original jute}}{\left[\text{dry weight of original jute} \right]} \times 100$$

The thermogravimetric analysis (TGA) was done by using a Du Pont 1090 thermal analyzer.

The IR spectra of the grafted jute fibers were recorded on a Perkin-Elmer 337 spectrophotometer.

RESULT AND DISCUSSION

Figure 1 shows the percentage of grafting of MMA onto chemically modified jute fiber as a function of time at three different temperatures: 40, 50, and 60°C. It was observed that graft percent increases steadily with an increase in time up to 2 h. Beyond this, the rate of increase slowed. This may be attributed to the partial dissolution of the grafted fiber on prolonged exposure to heat. Thus, an optimum graft yield was obtained within 2 h.

The effect of variation of monomer concentration on the percentage of grafting at three different temperatures is shown in Fig. 2. With an increase in monomer concentration from 0.188 to 0.470 mol/L, the percentage of graft yield increases; above the latter, it decreases. This decrease is probably due to the competition between homopolymerization and grafting where the former prevails over the latter at higher MMA concentrations.

Figure 3 represents the effect of a variation of oxidant concentration on the percentage of grafting at different temperatures. The percentage of grafting increases with an increase of Ce(IV) concentration up to 0.035 mol/L; beyond that it levels off. This is different from the observation made earlier while studying the grafting of MMA onto jute by

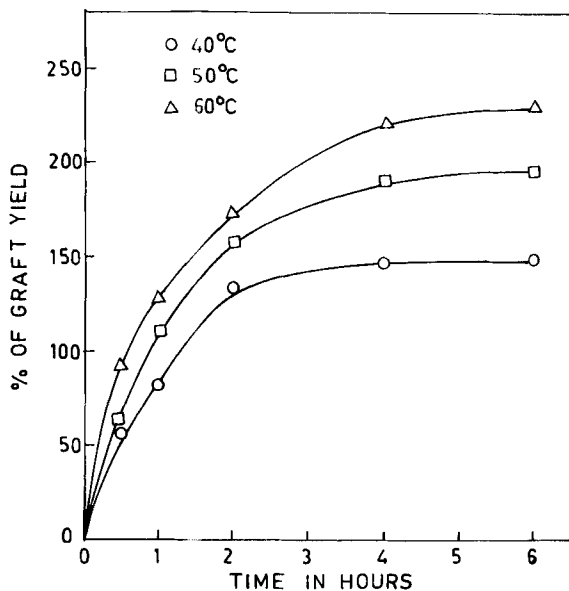


FIG. 1. Effect of variation of time. Jute = 0.1 g, [MMA] = 0.470 mol/L, [Ce(IV)] = 0.025 mol/L, [toluene] = 0.1 mol/L, [glacial HOAc] = 5.22 mol/L, [H₂SO₄] = 0.25 mol/L.

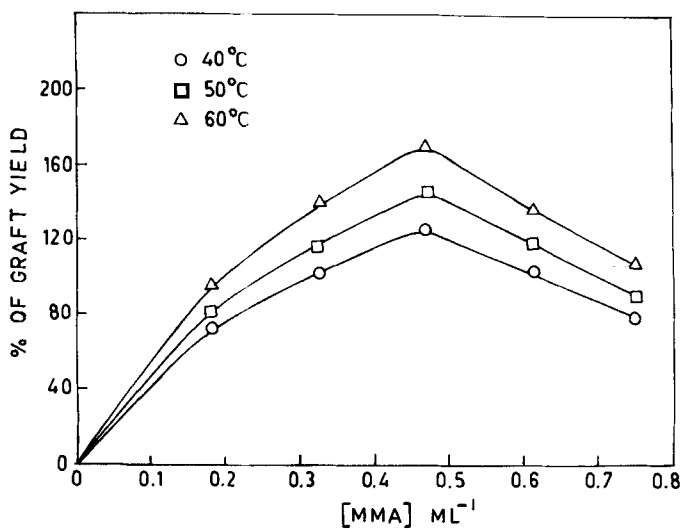


FIG. 2. Effect of variation of monomer. Jute = 0.1 g, [glacial HOAc] = 5.22 mol/L, [Ce(IV)] = 0.035 mol/L, [H₂SO₄] = 0.35 mol/L, [toluene] = 0.05 mol/L, time = 2 h.

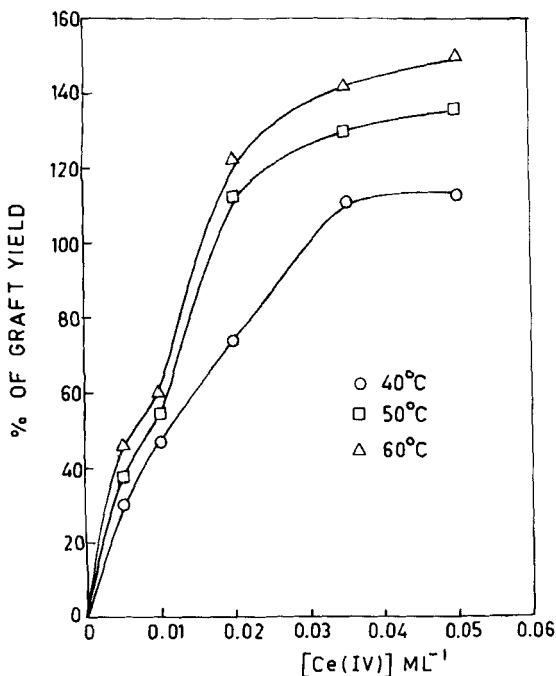


FIG. 3. Effect of variation of initiator (ammonium ceric sulfate). Jute = 0.1 g, [MMA] = 0.470 mol/L, [toluene] = 0.1 mol/L, [glacial HOAc] = 5.22 mol/L, [H₂SO₄] = 0.5 mol/L, time = 2 h.

using a peroxy-disulfate-thiourea initiating system [10] and a V(V)-cyclohexanol system [12] which showed a decrease in grafting beyond a certain concentration of initiator. In our system the increasing trend in percent grafting may be due to the formation of a greater number of grafting sites with an increase in oxidant concentration.

The effect of a variation of toluene concentration on the percent of grafting is shown in Fig. 4 at three different temperatures. At each of these temperatures, the percent grafting increases with an increase in toluene concentration from zero to 0.05 mol/L; above this concentration it decreases regularly. In our previous paper on the effect of toluene on the graft copolymerization of AN onto jute fibers, we reported that the presence of toluene enhances the rate of grafting up to a much higher concentration. It was concluded that toluene did not act as a retarder in graft copolymerization. However, in the present investigation the ability of toluene to retard was found to be more pronounced. The decreasing

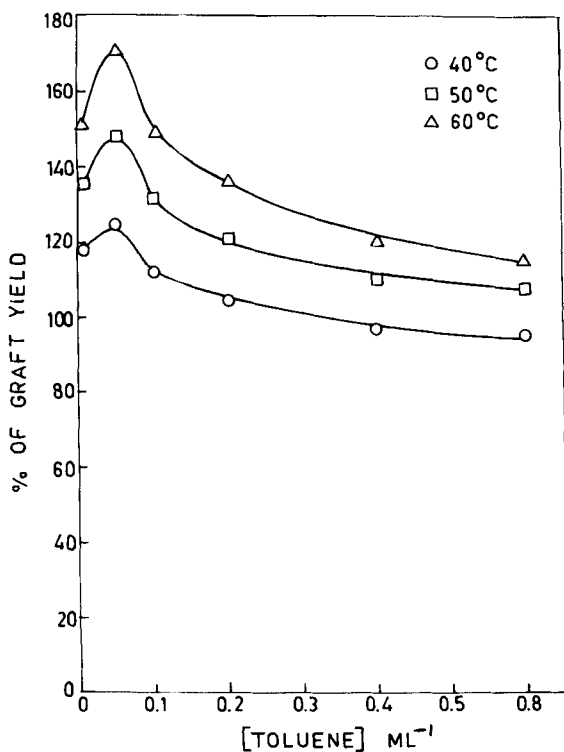


FIG. 4. Effect of variation of toluene. Jute = 0.1 g, [MMA] = 0.470 mol/L, [Ce(IV)] = 0.035 mol/L, [H₂SO₄] = 0.35 mol/L, [glacial HOAc] = 5.22 mol/L, time = 2 h.

trend in percent grafting is probably due to the fast rate of termination and/or the formation of radical scavengers at the higher concentration.

From the variation of temperature, it is seen that grafting of MMA onto jute fibers is nearly impossible below 40°C, which is unlike the situation for other natural fibers [9]. This may be due to the rigidity of the cellulosic structure of jute as compared to other fibers. The effects of temperature on percent grafting are illustrated in Figs. 1-4. Under the present reaction conditions, the percent grafting reaches a maximum at 60°C. The increase in graft yield with an increase in temperature can be attributed to the swellability of jute and the enhancement of the rate of diffusion of the monomer.

The reaction medium also plays an important role in the graft copoly-

TABLE 1. Effect of Variation of H_2SO_4 and Glacial HOAc on Graft Yield at 50°C . (Jute = 0.1 g, $[\text{MMA}] = 0.470$ mol/L, $[\text{toluene}] = 0.1$ mol/L, $[\text{glacial HOAc}] = 5.22$ mol/L, $[\text{Ce(IV)}] = 0.035$ mol/L, time = 2 h)

$[\text{H}_2\text{SO}_4]$, mol/L	$[\text{HOAc}]$, mol/L	$R_g \times 10^6$	Efficiency, %	Graft yield, %
0.35	5.22	9.22	14.13	133
0.40	5.22	8.80	13.41	127
0.45	5.22	7.77	11.90	112
0.55	5.22	7.28	11.15	105
0.65	5.22	6.58	10.09	95
0.35	1.74	8.46	12.96	122
0.35	3.48	8.94	13.70	129
0.35	6.09	9.71	14.87	140
0.35	8.7	3.74	5.73	54
0.35	10.44	1.11	1.70	16

merization reaction. The effects of sulfuric acid and glacial acetic acid concentrations on the percentage of graft yield have been studied at three different temperatures (40, 50, and 60°C). An increase in H_2SO_4 concentration from 0.35 to 0.65 mol/L decreases the percent of graft yield (Table 1). However, an increase in glacial acetic acid concentration from 1.74 to 6.09 mol/L increases the graft yield at all temperatures, and an additional increase in concentration depresses the percent grafting considerably (Table 1).

The graft yield tracks the following order of solvents when added in equal proportions (5% v/v): control > methyl alcohol > dioxane > acetone. All of these solvents depress the graft yield (Table 2). Similarly, the effect of some inorganic salts when added in equimolar concentrations follows the order: NaCl > control > K_2SO_4 > MnCO_3 > CuSO_4 (Table 2). This is in close agreement with observations made earlier [13]. The effect of organic solvents on the graft yield may be due to the termination of grafted radicals via chain transfer. The depression of the percentage of graft yield through the addition of some salts may be attributed to the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in premature termination of the growing chain.

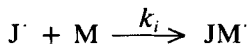
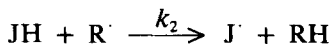
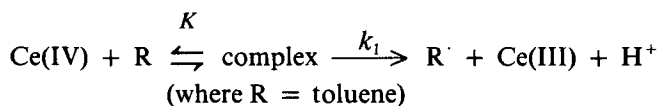
TABLE 2. Effect of Organic Solvent and Inorganic Salt at 50°C (jute = 0.1 g, [MMA] = 0.470 mol/L, [glacial HOAc] = 5.65 mol/L, [Ce(IV)] = 0.035 mol/L, [toluene] = 0.05 mol/L, [H₂SO₄] = 0.35 mol/L, time = 2 h)

Solvent, 5% v/v	Graft yield, %	[Salt], 0.01 mol/L	Graft yield, %
Control	160	Control	150
Methyl alcohol	139	CuSO ₄	73.5
Dioxane	57	MnCO ₃	93
Acetone	42	NaCl	171
		K ₂ SO ₄	114

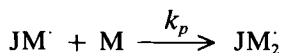
Reaction Mechanism

In a system containing ceric ammonium sulfate, methyl methacrylate, toluene, and jute fibers in sulfuric acid, Ce(IV) interacts with toluene to form a complex which dissociates to give a free radical. This free radical abstracts hydrogen from the jute molecule (JH), yielding a macroradical (J). The following scheme is an outline of the reaction mechanism.

Initiation:



Propagation:



⋮



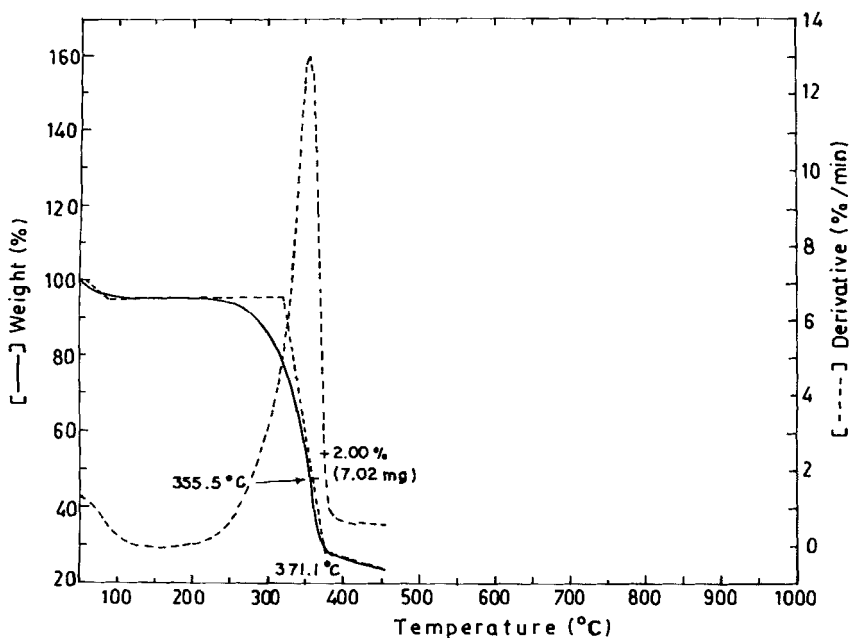
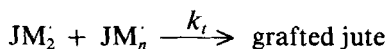
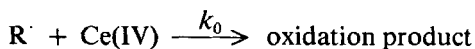


FIG. 5. TGA curve of chemically modified jute. $[T_D] = 355.5^\circ\text{C}$, rate of heating = $10^\circ\text{C}/\text{min}$.

Termination:



Oxidation:



where Ce(IV), JH, J, M, K, k_1 , k_2 , k_i , k_p , k_t , and k_0 are ceric ion, jute material, jute macroradical, monomer, equilibrium constants, and different rate constants, respectively.

The thermal behaviors of natural jute (chemically modified) and MMA grafted jute were examined through thermogravimetric analysis (TGA). The TGA curves of chemically modified jute (Fig. 5) and MMA grafted jute (Fig. 6), with their percentage of weight loss at various temperatures,

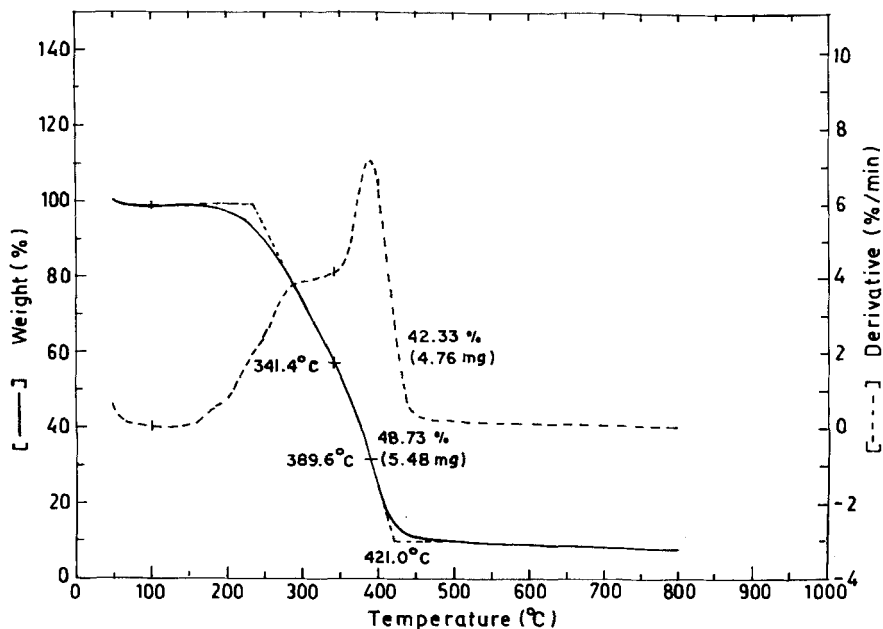


FIG. 6. TGA curve of MMA grafted jute fibers. Graft yield = 116%, $[T_D]$ = 389.6°C, rate of heating = 10°C/min.

were determined by means of a Du Pont 1090 thermal analyzer. It was found that the maximum weight loss in the case of MMA grafted jute (graft yield 116%) occurs at 389.6°C whereas decomposition occurs at 355.5°C in chemically modified pure jute. Hence, it is concluded that jute grafted with MMA is thermally more stable than chemically modified jute without grafting.

The IR spectra of natural jute (chemically modified) and of jute fibers grafted with MMA in the form of KBr pellets were recorded on a Perkin-Elmer 377 spectrophotometer and are shown in Fig. 7. It is observed that the natural, chemically modified jute shows the characteristic broad absorption of the hydroxyl group around 3400 cm^{-1} . However, the spectrum of MMA-grafted chemically modified jute shows an additional peak of the ester group at about 1715 cm^{-1} . This indicates the presence of a MMA unit in the grafted jute.

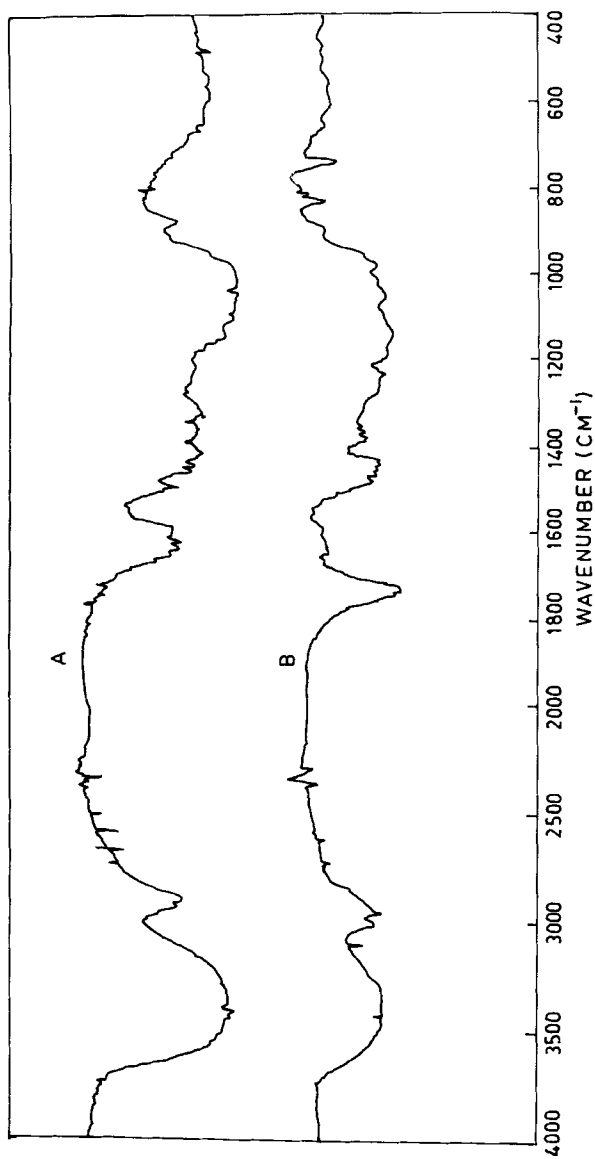


FIG. 7. (A) IR spectrum of chemically modified jute fibers. (B) IR spectrum of chemically modified jute grafted with MMA.

CONCLUSIONS

Our results are sufficient to establish the mechanism of the grafting reaction. Although toluene acts as a common retarder in vinyl polymerization, our results indicate that toluene does not retard grafting, at least at lower concentrations. On the basis of the effect of various additives, an optimum condition for the effective grafting has been determined: jute = 0.1 g, [MMA] = 0.470 mol/L, [glacial HOAc] = 5.65 mol/L, [Ce(IV)] = 0.035 mol/L, [toluene] = 0.05 mol/L, [H₂SO₄] = 0.35 mol/L, time = 2 h.

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