

# Grafting Vinyl Monomers onto Cellulose. I. Graft Copolymerization of Methyl Methacrylate onto Cellulose using Quinquevalent Vanadium Ion

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## Synopsis

Graft copolymerization of methyl methacrylate on cellulosic materials with the use of quinquevalent vanadium as an initiator was studied. Increase of  $V^{5+}$  ion concentration up to 0.0025 mole/liter increases graft yield, and with further increase of the initiator the graft yield decreases. The graft yield increases with increase of monomer concentration. The increase of acid concentration is accompanied by decrease of graft yield. A measurable increase in graft yield was observed with increase in temperature from 65 to 75°C. The graft yield is medium and substrate dependent. A suitable kinetic scheme has been pictured and a rate equation has been derived.

## INTRODUCTION

Grafting of synthetic polymers to cellulose is an effective method for modifying its properties.<sup>1</sup> Grafting may be accomplished either by reacting a preformed polymer with cotton or by actually causing polymerization to take place at active sites on the cotton cellulose. Reaction with preformed polymers are of limited use since diffusion of the high molecular weight synthetic polymer limits the grafting reaction to the fiber surface. Various properties such as water proofing, improved rot resistance, flame proof, change in dye characteristics, and modifying physical properties such as abrasion resistance and stiffness could be imparted to cotton through graft copolymerization. Grafted celluloses are now finding various applications, i.e., in ion exchange resins, rot and mildew resistant materials, and in soil resistant garments.

Grafting vinyl monomers to a cellulose chain could be carried out by either ionic or free-radical initiation methods. The free radicals could be created at the backbone of the cellulose by various methods such as chain transfer,<sup>2</sup> high-energy irradiation,<sup>3-10</sup> low-energy irradiation in the presence of sensitizers,<sup>11,12</sup> mechanical degradation,<sup>13-15</sup> or by redox systems.<sup>16-19</sup>

Of all these methods, the redox systems have attracted attention in recent years.<sup>20-25</sup> Some of the redox systems which have been studied for the graft copolymerization of vinyl monomers onto cellulose include ceric salts,<sup>26-37</sup> ferrous salt-hydrogen peroxide,<sup>38</sup> sodium thiosulfate-potassium persulfate,<sup>39</sup> sodium periodate,<sup>40</sup> and manganic sulfate-sulfuric acid.<sup>41</sup>

Of the redox systems investigated so far, the tetravalent ceric ion has received considerable interest<sup>26-37</sup> because of its high grafting efficiency. Cumberbirch and Holker<sup>27</sup> devoted attention mainly to the mechanical properties (such as water retention, load at yield, dry and wet tenacity, and extension at break) of the grafted products.

Arthur et al.<sup>42</sup> reported an ESR study of cerium-oxidized cellulose and postulated cleavage of the C<sub>2</sub>-C<sub>3</sub> bond of anhydroglucose units with formation of free radicals at C<sub>2</sub>. Kulkarni and Meheta<sup>36</sup> made a detailed study of the mechanism of oxidation of cellulose with Ce<sup>4+</sup>. In a series of communications, Hebeish and co-workers<sup>43-47</sup> reported the graft copolymerization of vinyl monomers onto modified cotton using ceric ion as the initiator.

Most of the authors who have used the ceric ion as an initiator did not mention the large amount of homopolymer formed during the process of grafting. Since the oxidation potential of cerium is very high,<sup>48</sup> it can react very easily with vinyl monomer to initiate homopolymerization. Once the homopolymer is formed on the backbone of the fiber, it will be a difficult problem to completely remove it by the usual solvent extraction technique. The formation of homopolymer on the fiber surface sometimes destroys the basic properties of the fiber.

The main objective of the present investigation is to find a suitable method for, we used quinquevalent vanadium ion for grafting methyl methacrylate (MMA) onto cellulose.

## EXPERIMENTAL

Egyptian cotton slivers were purified by mild alkaline scouring (2% Na<sub>2</sub>CO<sub>3</sub>, 1.0% Na<sub>3</sub>PO<sub>4</sub>, and 0.2% wetting agent, per weight of material) for 5 hr at 110°C and 10-15 psi in the laboratory kier with a liquid ratio of 10.

Methyl methacrylate was washed with 5% NaOH solution, dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Ammonium metavanadate (AR), sulfuric acid (18M, AR BDH) were used. Water distilled twice over alkaline permanganate and deionized by passing through a column of biodeminrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. Nitrogen used to deaerate the experimental systems was freed from oxygen by passing through Fieser's solution.

The modified cellulose was prepared using standard procedures and reaction was carried out according to our previous methods.<sup>49-53</sup>

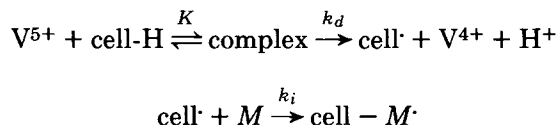
## RESULTS AND DISCUSSION

Cellulose is essentially a poly(1,4-*B-D*-anhydroglucopyranose) unit with primary and secondary hydroxyl groups on the backbone. The site of grafting in the metal ion redox systems in cellulose is still controversial. Some indications are that it may occur at hemiacetal oxygen (the polymeric link), and also at the adjacent hydroxyl unit, possibly by the oxidation of the —OH groups. In this connection, Iwakura and co-workers<sup>31</sup> have isolated both block and graft copolymers from a cellulose-styrene graft copolymer. They have further verified these reactions in a model system using various alcohols. Grafting on cellulose is also affected by the presence of carbonyl and aldehyde groups, particularly at low concentration of metal ions.

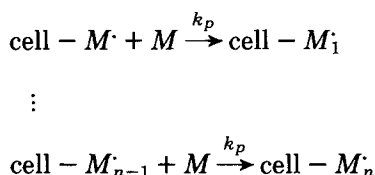
In the present study, the mechanism proposed for free radical formation on the cellulose backbone entails a V<sup>5+</sup>-cellulose complex of the chelate type, possibly through the C<sub>2</sub> and C<sub>3</sub> hydroxyl groups. A similar type of complexes has been pictured by Mino and Kizerman<sup>26</sup> in Ce<sup>4+</sup>-glycols, Ikada and co-workers<sup>56,57</sup>

in  $V^{5+}$ -PVA and  $Ce^{4+}$ -PVA, and by Nayak and co-workers<sup>58</sup> in  $V^{5+}$ -glycols. Dissociation of this complex occurs through a transfer of electrons from the cellulose molecule to  $V^{5+}$ , thereby causing its reduction to  $V^{4+}$ , breaking the glycol bond, and creating a free radical on the cellulose backbone for the sites of grafting. The mechanism is suggested below.

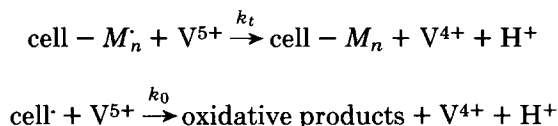
Initiation:



Propagation:



Termination:



Here cell-H denotes a reactive group in cellulose;  $M$  is the monomer;  $K$  is equilibrium constant; and  $k_i$ ,  $k_p$ ,  $k_t$ , and  $k_0$  are rate constants.

By applying steady-state conditions to the concentrations  $[\text{cell}\cdot]$  and  $[\text{cell-M}\cdot]$ , the overall rate of polymerization can be derived as follows:

$$d[\text{cell}\cdot]/dt = Kk_d[V^{5+}][\text{cell}] - k_i[\text{cell}\cdot][M] - k_0[\text{cell}\cdot][V^{5+}] = 0$$

or

$$[\text{cell}\cdot] = \frac{Kk_d[V^{5+}][\text{cell}]}{k_i[M] + k_0[V^{5+}]}$$

Again

$$d[\text{cell-M}\cdot]/dt = k_i[\text{cell}\cdot][M] - k_t[\text{cell-M}\cdot][V^{5+}] = 0$$

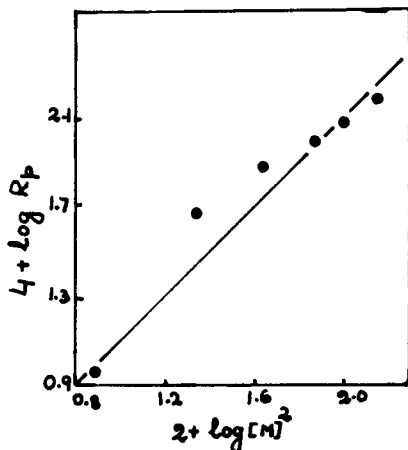
or

$$[\text{cell-M}\cdot] = k_i[\text{cell}\cdot][M]/k_t[V^{5+}]$$

Putting the value of  $[\text{cell}\cdot]$  in the above expression, we get

$$[\text{cell-M}\cdot] = \frac{Kk_d[\text{cell-H}][M]}{k_t[M] + (k_0/k_i)[V^{5+}]}$$

$$R_p = k_p [\text{cell-M}\cdot][M]$$

Fig. 1. Plot of  $\log R_p$  vs.  $\log[M]^2$ .

Putting the value of  $[\text{cell-M}\cdot]$  into the expression, we get

$$R_p = \frac{k_p}{k_t} [M]^2 \frac{Kk_d [\text{cell-H}]}{[M] + (k_0/k_i) [V^{5+}]}$$

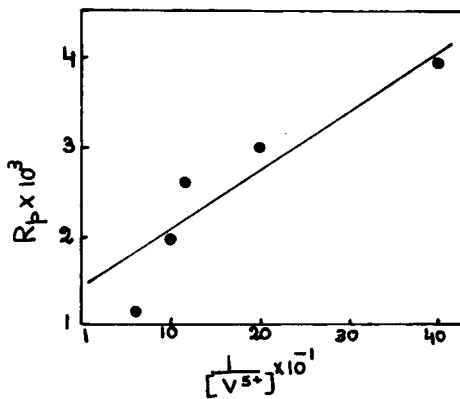
In their study of the ethylene glycol-acrylonitrile system, Katai and co-workers<sup>59</sup> estimated that  $k_0/k_i = 50$  and reported that the rate constant for the oxidation of radicals formed is considerably larger than the rate constant for the initiation. Assuming that  $(k_0/k_i)[V^{5+}] \gg [M]$ , the equation reduces to

$$R_p = Kk_p k_i k_d [\text{cell-H}] [M]^2 / k_0 k_t [V^{5+}]$$

and the number-average molecular weight of polymers is

$$1/\bar{P}_m = k_t [V^{5+}] / k_p [M]$$

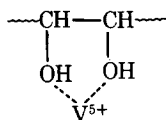
The above rate expression was verified by plotting  $\log R_p$  vs.  $\log[M]^2$  (Fig. 1) and  $R_p$  vs.  $1/[V^{5+}]$ , which were linear (Fig. 2).

Fig. 2. Plot of  $R_p$  vs.  $1/[V^{5+}]$ .

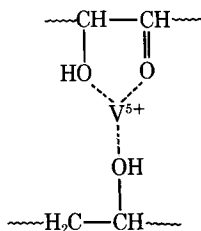
Effect of  $[V^{5+}]$  on Graft Yield

The effect of the concentration of the  $V^{5+}$  ion on the grafting of MMA onto cellulose is shown in Figure 3. The rate of grafting has been investigated by changing the  $V^{5+}$  concentration within the range of 0.00125 to 0.015 mole/liter. The data indicate that increasing  $V^{5+}$  up to 0.0025 is accompanied by a significant increase in graft yield, while further increase causes a marked fall in grafting. A possible explanation for this observation might be as follows.

In a recent paper, Ikada and co-workers<sup>56</sup> have pictured the chemistry of  $V^{5+}$  with PVA containing 1,2-glycol unit.  $V^{5+}$  initially complexes with 1,2-glycol unit of cellulose as represented by



This complex breaks in a unimolecular fashion to produce a free radical  $\sim\text{CH}_2-\text{CH}-\text{CH}-\dot{\text{O}}$  on the backbone of the cellulose which initiates grafting, but when the concentration of  $V^{5+}$  increases beyond 0.0025M, it oxidizes the free radical, forming keto alcohol and thereby decreasing its population on the backbone of cellulose, reducing grafting. Further, this keto alcohol might complex with  $V^{5+}$  with a neighboring  $-\text{OH}$  group as presented by



This phenomenon might block some of the  $-\text{OH}$  groups so that the free radicals

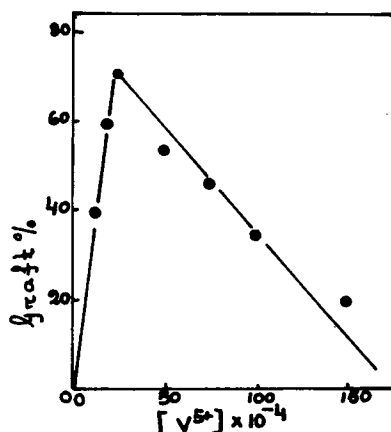


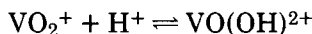
Fig. 3. Effect of  $[V^{5+}]$  on graft yield:  $[\text{MMA}] = 0.4694$  mole/liter;  $[\text{H}_2\text{SO}_4] = 0.45$  mole/liter; temperature:  $70^\circ\text{C}$ ; time: 5 hr;  $M:L = 1:100$ .

are not formed at these centers. With increasing  $V^{5+}$  concentration, the termination process may also become very fast, which reduces the percentage of grafting.

### Effect of Acid Concentration on Graft Yield

The grafting reaction has been carried out by varying the sulfuric acid concentration from 0.075 to 0.45 mole/liter. A perusal of the result indicates that percentage graft-on decreases with increasing acid concentration (Fig. 4).

Jones and Waters<sup>60</sup> have suggested that  $VO_2^+$  and  $VO(OH)^{2+}$  are the active species of quinquivalent vanadium ion. This species are in equilibrium with each other as shown below.



Of the two active species  $VO_2^+$  and  $VO(OH)^{2+}$ , the latter is definitely a stronger oxidizing agent than the former. As the concentrations of acid increases, the probability of the formation of most active species of  $VO(OH)^{2+}$  will be more, which could interact with the radicals on the backbone of the cellulose, producing oxidation products and thereby decreasing grafting. At higher concentration of acid, the cellulose molecule is degraded through hydrolytic splitting of the  $\beta$ -glucoside linkages between the structural units of the cellulose chain.

### Effect of [MMA] on Graft Yield

The effect of monomer (methyl methacrylate) concentration on the rate of grafting is depicted in Figure 5 from which it is clear that with increase of monomer concentration from 27.98 to 122 ( $\times 10^{-2}$ ) mole/liter the graft yield increases. The probable explanation for the above findings might be due to the following: (1) The complexation of cellulose with monomer which is favored with increase of monomer concentration. (2) Gel effect,<sup>61</sup> i.e., increase in viscosity of the medium owing to the solubility of poly(methyl methacrylate) (PMMA) in its own monomer, which could be more pronounced with increase of monomer concentration. This hinders termination, particularly by coupling

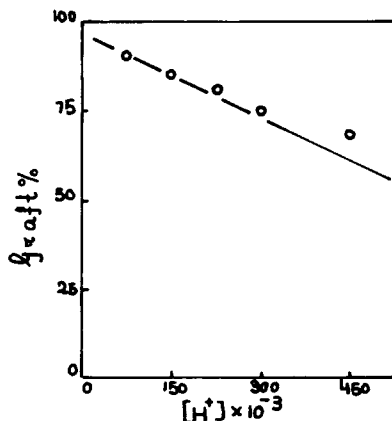


Fig. 4. Effect of  $[H_2SO_4]$  on graft yield:  $[V^{5+}] = 0.0025$  mole/liter;  $[MMA] = 0.4694$  mole/liter; temperature:  $70^\circ C$ ;  $M:L = 1:100$ ; time: 5 hr.

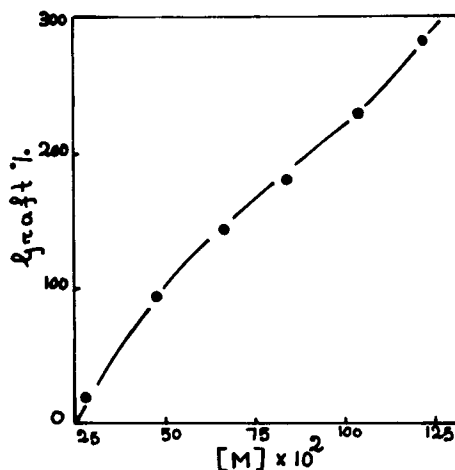


Fig. 5. Effect of [MMA] on graft yield:  $[V^{5+}] = 0.0025$  mole/liter;  $[H_2SO_4] = 0.075$  mole/liter; temperature:  $70^\circ C$ ;  $M:L = 1:100$ ; time = 5 hr.

of growing polymer chains. The gel effect also causes swelling of cellulose, thus facilitating the diffusion of monomer to growing chains and active sites on the backbone, thereby enhancing grafting. (3) The monomer molecule might form some type of charge transfer complex with the oxidant which favors grafting.

#### Effect of Temperature on Graft Yield

The graft copolymerization reaction was carried out at different temperatures ranging from  $65$  to  $75^\circ C$ . The graft yield increases significantly with the increase of temperature (Fig. 6). The dependence of the rate of grafting on temperature could be ascribed to the greater activation energy. Again, the swellability of cellulose, solubility of monomer, and its diffusion rates are enhanced by increasing the temperature, and as a result the graft yield increases.

From the Arrhenius plot of  $\log R_p$  vs.  $1/T$  the overall activation energy was found to be  $16.10$  kcal/mole (Fig. 7). Using the value of  $E_p - \frac{1}{2}E_t = 4-5$  kcal/mole

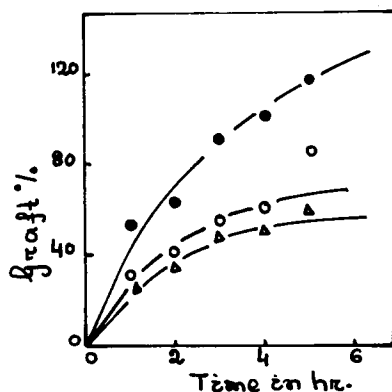


Fig. 6. Effect of temperature on graft yield:  $[V^{5+}] = 0.0025$  mole/liter;  $[H_2SO_4] = 0.075$  mole/liter;  $[MMA] = 0.4694$  mole/liter;  $M:L = 1:100$ . ( $\Delta$ ) Temperature:  $65^\circ C$ ; ( $O$ ): temperature:  $70^\circ C$ ; ( $\bullet$ ): temperature:  $75^\circ C$ .

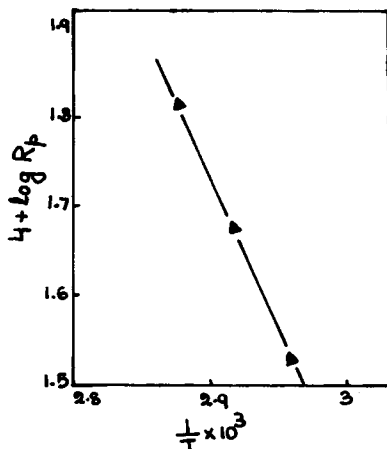


Fig. 7. Arrhenius plot of  $\log R_p$  vs.  $1/T$ .

given by Tobolsky,<sup>62</sup> where  $E_p$  and  $E_t$  are energies of propagation and termination, respectively, the activation energy of initiation  $E_d$  can be calculated from these values as follows:

$$E_d = 2E_a - (2E_p - E_t)$$

where  $E_a$  is the overall activation energy, and  $E_d = 23.2$  kcal/mole for total conversion reaction of MMA to PMMA.

### Nature of Substrate

Figure 8 shows graft yields obtained with various cellulosic materials grafted with MMA. The cellulosic materials examined include purified cotton, cotton treated with aqueous NaOH, crosslinked cotton, and periodate oxidized cotton. The grafting reaction exhibits the same trend with respect to all substrates, but for a given reaction time, the graft yield follows the order

cotton treated with 6N NaOH > untreated cellulose  
> periodate oxidized cellulose > crosslinked cellulose

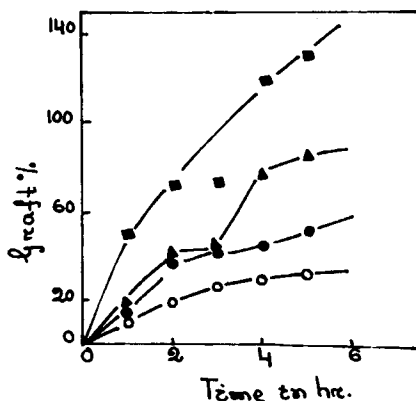


Fig. 8. Effect of substrates on graft yield:  $[V^{5+}] = 0.0025$  mole/liter;  $[MMA] = 0.4694$  mole/liter;  $[H_2SO_4] = 0.075$  mole/liter; temp. =  $70^\circ C$ ;  $M:L = 1:100$ . (○) Crosslinked cellulose; (●) periodate oxidized cellulose; (▲) untreated cellulose; (■) NaOH-treated cellulose.



Graft yield for NaOH-treated cotton is substantially higher than that for native cotton. This is expected since NaOH-treated cotton has greater accessibility than native cotton. Periodate ion is a well-known reagent which attacks the glycols, converting these to either aldehyde or ketones. When cellulose is treated with periodate, it attacks the 1,2-glycol units converting them to aldehyde groups, thereby destroying the grafting sites for which the graft yield decreases. It is not worthy to point out that crosslinking the cellulose decreases the extent of grafting, because crosslinking affects diffusion of monomer and initiator adversely and reduces the number of grafting sites on the cellulose backbone, thereby lowering the graft yield.

### Effect of Solvents

Grafting of MMA onto the cellulose was investigated in the presence of different alcohols. The graft yield follows the order



The decrease in graft yield from methanol to pentanol is due to decrease in the swelling of cellulose by the alcohols. The difference in capability of these solvents as terminator for the graft polymer radical and the cellulose macroradical via chain transfer cannot also be ruled out.

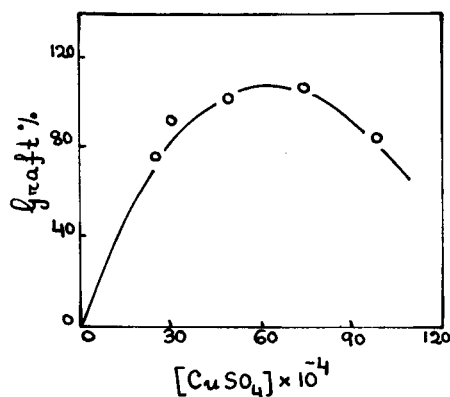


Fig. 9. Effect of  $[\text{CuSO}_4]$  on graft yield:  $[\text{V}^{5+}] = 0.0025$  mole/liter;  $[\text{H}_2\text{SO}_4] = 0.075$  mole/liter;  $[\text{MMA}] = 0.4694$  mole/liter; temperature:  $70^\circ\text{C}$ ;  $M:L = 1:100$ ; time: 5 hr.

TABLE I  
Molecular Weight and Degree of Polymerization of the Grafted Cellulose

Graft %	$\bar{M} \times 10^{-5}$	$DP \times 10^{-3}$
57.45	13.96	13.94
70.95	14.65	14.63
83.45	16.11	16.09
181.55	52.45	52.43

### Effect of [CuSO<sub>4</sub>] on Graft Yield

The effect of copper sulphate concentration on graft yield has been studied by varying CuSO<sub>4</sub> concentration from  $25 \times 10^{-4}$  to  $100 \times 10^{-4}$  mole/liter. A perusal of the result indicates that the graft yield increases up to  $75 \times 10^{-4}$  mole/liter and thereafter it decreases (Fig. 9). The initial increase in graft yield might be due to the creation of free radical species under the influence of Cu<sup>2+</sup> ions which could be in the proximity of cellulose, thus assisting the formation of cellulose macroradicals. The drop of graft yield beyond  $75 \times 10^{-4}$  mole/liter of copper sulfate concentration might be due to (1) the termination of free radicals in solution on polymer and/or on cellulose; the Cu<sup>2+</sup> ions seem to act as radical trap; and (2) a particular concentration of Cu<sup>2+</sup> ions which favors complexation of monomer with cellulose and perturbs such complexation beyond this concentration of Cu<sup>2+</sup> ions.

### Molecular Weight Determination

The intrinsic viscosity was calculated by using a single-point-method for poly(methyl methacrylate) by Valles et al.<sup>63</sup> The molecular weight was obtained from

$$\eta = 9.6 \times 10^{-5} M^{0.69}$$

The result indicates that the average molecular weight as well as the degree of polymerization increases with an increase in percentage of grafting (Table I).

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