

# Role of 1,10-Phenanthroline and Ortho Phosphoric acid on Graft Polymerization of Vinyl Monomers from Poly (Vinyl Alcohol) in the Presence of Fenton's Reagent

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**ABSTRACT:** The effect and role of 1,10-phenanthroline (*o*-phen) and ortho phosphoric acid on graft polymerization of vinyl monomers from poly (vinyl alcohol) (PVA) in the presence of Fenton's reagent have been studied. Reaction conditions were optimized. Fourier transform infrared (FT-IR) spectra were used for confirmation of grafting. A probable mechanism of grafting to elucidate the role of phenan-

throline and phosphoric has been suggested. Thermal properties of the grafted polymer were studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2335–2339, 2005

**Key words:** poly (vinyl alcohol); grafting; Fenton's reagent; vinyl monomers

## INTRODUCTION

Graft modified poly (vinyl alcohol) (PVA) possesses great potential as a unique polymeric material for several applications, such as biomedicine, adhesive, painting, packaging, and others.<sup>1</sup> Most of the grafting reactions have been implemented in aqueous media, and they are initiated mainly by Ce (IV),<sup>2–9</sup> Cu(II),<sup>10–13</sup> S<sub>2</sub>O<sub>8</sub><sup>2-</sup>,<sup>14–16</sup> potassium diperiodatonickalate (IV),<sup>17</sup> and gamma rays.<sup>18</sup> Grafting efficiencies of these initiators except Ce (IV) are very low, due to homo polymerization. Although Ce (IV) is superior in its efficiency, it is expensive. Very little work has been done on vinyl grafting from PVA using Fe(II) and Fe(III). Mishra et al.<sup>19</sup> and Sanjay et al.<sup>13</sup> used Fe(II) and Fe(III), respectively, along with hydrogen peroxide as an initiator. Ferrous/Ferric inter conversion is a single step one electron transfer process and produces free radicals (HO·) in the presence of hydrogen peroxide and vinyl monomer. The produced free radicals thus preferably lead to vinyl polymerization, rather than vinyl graft polymerization. However, the presence of phosphoric acid and phenanthroline (complex forming reagents) may change the activity of the Fenton's reagent (Fe<sup>2+</sup> + H<sub>2</sub>O<sub>2</sub>) towards vinyl grafting. H<sub>3</sub>PO<sub>4</sub> form a stable complex with Fe<sup>3+</sup>, while 1,10-phenanthroline (*o*-phen) with Fe<sup>2+</sup>. The presence of these complex form-

ing agents thus alters the redox potential of the systems containing iron metal ions.

The present investigation involves studies on the effect and role of H<sub>3</sub>PO<sub>4</sub> and *o*-phen towards graft co polymerization of vinyl monomers from PVA, initiated by Fenton's reagent.

## EXPERIMENTAL

### Materials

Poly (vinyl alcohol) (Burgoyne Burbidges, India; Viscosity average molecular weight = 1610, Degree of hydrolysis = 98.5–99.0 mol %, Viscosity = 26–31 cps) was used. Methyl methacrylate (Merck, Schuchardt) was purified before use. Hydrogen peroxide (Qualigens, LR, India), ferrous ammonium sulfate (Merck, India), 1,10-phenanthroline hydrate (BDH, UK), and phosphoric acid (Aldrich) were used as received. All other chemicals and solvents were analytical grade and used without further purification.

### Graft polymerization

Graft polymerization was carried out in a two-necked round bottomed flask that was kept in a constant temperature bath maintained at the required temperature. A definite amount of PVA was soaked with a requisite quantity of MMA monomer for 15 min before graft polymerization started. Water, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, and ferrous ammonium sulfate (FAS) and complex forming agents were then added. Nitrogen atmosphere was then maintained throughout the entire reaction period. After the specific time interval, the

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reaction was arrested by quenching with hydroquinone. To remove homopolymer, the sample was precipitated with acetone. Finally, the sample was extracted with acetone in a Soxhlet apparatus for 4 h to dissolve all the homopolymers. The colorless product was dried under vacuum at 50°C for > 24 h to a constant weight.

### Determination of graft level

The grafting ratio (GR), grafting efficiency (GE), percentage of homopolymer (H), and average rate of grafting ( $R_g$ ) were determined by the following formulas, respectively<sup>20</sup>:

$$GR = (w_2 - w_1)/w_1 \quad (1)$$

$$GE(\%) = 100(w_2 - w_1)/w_3 \quad (2)$$

$$H(\%) = 100(w_4 - w_2)/w_4 \quad (3)$$

$$R_g(\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-3}) = (w_2 - w_1)/M\cdot t\cdot v \quad (4)$$

where  $w_1$  is the weight of the original PVA taken,  $w_2$  is the weight of the grafted product after Soxhlet extraction (homopolymer free),  $w_3$  is the weight of the monomer charged, and  $w_4$  is that of the product before extraction (grafted product + homopolymer).  $M$  is the molecular weight of the monomer,  $t$  is the reaction time in seconds, and  $v$  is the volume in  $\text{m}^3$  of the reaction mixture.

### Characterization

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer Spectrum RX FTIR system in the range of 4000–400  $\text{cm}^{-1}$ . Thermo-gravimetric analysis (TGA) was conducted using a Stanton Redcraft Thermal Analyzer (STA 780) in air at a rate of 10°C/min. pH of the solution was measured by a pH meter (Elico, India, LI 120). Flow time of the grafted polymer in dimethyl sulfoxide solution was measured by an Ubbelohde viscometer.

TABLE I  
FTIR Spectral Data

Stretching vibration ( $\text{cm}^{-1}$ )	PVA	PMMA	PMMA-g-PVA
3500–2950	Intense broad band	Weak band	Broad band
1730–1735	-	Strong band	Sharp band
1150–1155	Weak peak, sharp	Sharp peak	Sharp peak

TABLE II  
Thermo-Gravimetric Analysis (TGA)

Temp. range (°C)	% weight loss of PVA	% weight loss of PMMA	% weight loss of PVA-g-PMMA
49.9–130.1	07.50	—	—
130.1–349.2	13.10	—	—
349.2–452.5	94.64	—	—
452.5–600.7	04.51	—	—
120.6–192.3	—	10.30	—
192.3–590.4	—	93.20	—
590.4–987.8	—	04.27	—
102.6–171.3	—	—	11.20
171.3–462.3	—	—	60.75
462.3–576.4	—	—	80.12
576.4–977.8	—	—	03.62

## RESULTS AND DISCUSSION

### Evidence of grafting by FTIR spectroscopy

The presence of PMMA on the PVA molecules was verified by the FTIR spectra of PVA, PMMA, and PMMA-g-PVA. (Spectral data is given in Table I.) Both the spectra of PVA and the grafted polymer show a characteristic broad absorption band of the hydroxyl group around 3500–2952  $\text{cm}^{-1}$ . This is attributed to the O-H bond stretching vibration<sup>21,22</sup> of PVA. The spectrum of PMMA-g-PVA exhibits a strong absorption band at 1730  $\text{cm}^{-1}$ , which is absent in the spectrum of PVA. The peak near 1730  $\text{cm}^{-1}$  could be associated with the C=O stretching vibration of an ester group<sup>20,23</sup> from MMA. The appearance of a new peak at 1730  $\text{cm}^{-1}$  in the resulted copolymer provides strong evidence of grafting.

### Thermal properties of the grafted polymer

Thermal properties of the grafted polymer were studied with the help of comparative TGA data (Table II) of PVA, PMMA, and grafted PVA. The TG curves indicate the better thermal stability of the grafted polymer with respect to pure PVA. Both PVA and g-PVA showed four-stage degradation, while PMMA exhibited three-stage decomposition. About 94.64% weight loss was observed in the temperature 349.2–452.5°C in the case of PVA. However, the synthesized grafted polymer showed 60.75% and 80.12% weight loss in the temperature range 171.3–462.3 and 462.3–576.4°C, respectively. This two-stage weight loss probably indicates the graft polymerization. The TG curve of PVA (not shown) shows a weak inflection at 110°C that is absent in the curve of the grafted polymer. The inflection at 110°C is due to the removal of absorbed moisture.<sup>6</sup> This suggests that the moisture absorbance capacity of the grafted polymer is lower than that of PVA itself.

**TABLE III**  
Effect of Phenanthroline and Phosphoric acid; PVA = 0.1 g, MMA = 28.2 m mol, H<sub>2</sub>O<sub>2</sub> = 0.022 mol, FAS = 0.397 m mol, H<sub>2</sub>SO<sub>4</sub> = 0.184 mol, T = 50° C, t = 3.5 h, Total volume = 100 mL

Reagent	GR	GE (%)	R <sub>g</sub> × 10 <sup>3</sup> (mol · s <sup>-1</sup> · m <sup>-3</sup> )
—	3.88	13.6	3.1
1,10-Phenanthroline (0.1 %, w/v)	20.32	72.06	16.1
H <sub>3</sub> PO <sub>4</sub> (5%, v/v)	1.89	6.70	1.50

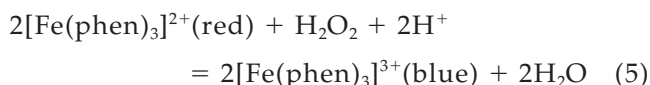
### Effect of 1,10-phenanthroline and phosphoric acid

Table III shows the effect of phenanthroline and phosphoric acid towards grafting of MMA from PVA in the presence of Fenton's reagent. The presence of phenanthroline increases GR, GE, and R<sub>g</sub> to a considerable extent with respect to the system having no complex forming agent. On the other hand, introduction of H<sub>3</sub>PO<sub>4</sub> decreases the grafting level compared to the system without a complex forming agent.

The above observation may be explained on the basis of the generally accepted concept of the effect of complex formation on the standard reduction potential. Phenanthroline forms a more stable complex with Fe<sup>2+</sup> than Fe<sup>3+</sup>.<sup>24</sup> As a result, the reduction potential of Fe<sup>3+</sup>/Fe<sup>2+</sup> increases<sup>24</sup> ([Fe(phen)<sub>3</sub>]<sup>3+</sup> + e = [Fe(phen)<sub>3</sub>]<sup>2+</sup>; E<sup>0</sup> = 1.12 V at 25°C), and this increase is significant at the temperature of polymerization. The increase in the reduction potential is probably responsible for the higher grafting efficiency of the Fenton's reagent. Phosphoric acid, on the other hand, forms a stable complex with Fe<sup>3+</sup> and none with Fe<sup>2+</sup> at room temperature. This difference in complex formation ability reduces the oxidizing power of Fe<sup>3+</sup> ([Fe(HPO<sub>4</sub>)<sub>4</sub>]<sup>+</sup> + e = Fe<sup>2+</sup> + HPO<sub>4</sub><sup>2-</sup>; E<sup>0</sup> = 0.67 V at 25°C).<sup>24</sup> Thus, it may be concluded that the presence of H<sub>3</sub>PO<sub>4</sub> deactivates the Fenton's reagent towards grafting.

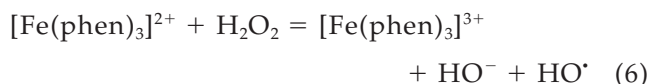
### Fixing of optimum [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] mole ratio

The results obtained by changing the [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] mole ratio (from 0.5 to 90.9) on the grafting ratio, rate, and efficiency are shown in Table IV. At the mole ratio 0.5, no polymer (either homopolymer or grafted polymer) is formed. There was a color change of the solution from red to blue, indicating the formation of ferric phenanthroline complex from ferrous phenanthroline complex (eq. (5)):

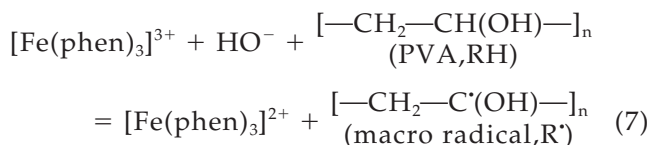


At the mole ratio 1.0, only 5.1% homopolymer is formed (no grafted polymer). The formation of ho-

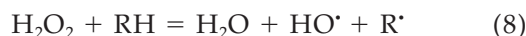
mopolymer may be explained with the help of the generally accepted reaction (eq. (6))<sup>25</sup>:



The produced HO<sup>·</sup> free radicals then lead to the formation of homopolymers through the free radical mechanism. At the mole ratio beyond 1.0, both homopolymer and grafted polymer are produced. The formation of the grafted polymers may be accounted for by chemical eq. (7), given below:



The produced PVA macro radical<sup>26</sup> induces graft polymerization. A small amount of acid is required to resist the hydrolysis of iron salt. However, excess acid diminishes the formation of graft polymer by withdrawing HO<sup>-</sup> from the system. The extent of grafting increased sharply with the increase of mole ratio up to 55.5 and beyond this, the increase was marginal. This increase of grafting level may be attributed to the formation of a larger amount of PVA radical with the addition of more H<sub>2</sub>O<sub>2</sub>. The optimum mole ratio of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] was found to be 55.5, which indicates that the catalytic amount of Fe<sup>2+</sup> is required for grafting purposes. Eqs. (6) and (7) clearly explain the catalytic activity of Fe<sup>2+</sup>. Eqs. 6 and 7 ultimately lead to eq. (8).

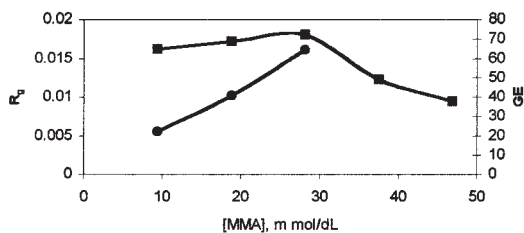


### Graft mechanism

The rate of graft polymerization is largely dependent on the concentration of monomer and initiator at fixed levels of acid and PVA. The relationship between (a) R<sub>g</sub> and [MMA] and (b) R<sub>g</sub> and [H<sub>2</sub>O<sub>2</sub>]<sup>1/2</sup> (Figs. 1 and 2,

**TABLE IV**  
Effect of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] Mole Ratio; PVA = 0.1 g, MMA = 28.2 m mol, H<sub>2</sub>SO<sub>4</sub> = 0.184 mol, 1,10-Phenanthroline = 0.1 g, T = 50°C, t = 3.5 h, Total volume = 100 mL

Mole ratio	GR	GE (%)	H (%)	R <sub>g</sub> × 10 <sup>2</sup> (mol · s <sup>-1</sup> · m <sup>-3</sup> )
0.5	—	—	—	—
1.0	—	—	5.10	—
10.0	7.05	25.00	15.21	0.56
22.7	14.29	50.67	10.06	1.13
55.5	20.32	72.06	14.72	1.61
90.9	20.34	72.10	16.43	1.62



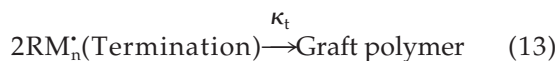
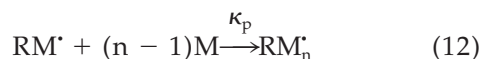
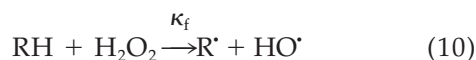
**Figure 1** Monomer concentration vs. grafting rate and efficiency: [PVA] = 0.1 g/dL, [H<sub>2</sub>O<sub>2</sub>] = 0.22 mol/dL, [FAS] = 0.397 m mol/dL, [H<sub>2</sub>SO<sub>4</sub>] = 0.184 mol/dL, T = 323 K, t = 3.5 h.

respectively) are linear, indicating graft polymerization is first order with respect to monomer and half order to initiator concentration. Therefore, the following rate equation is established:

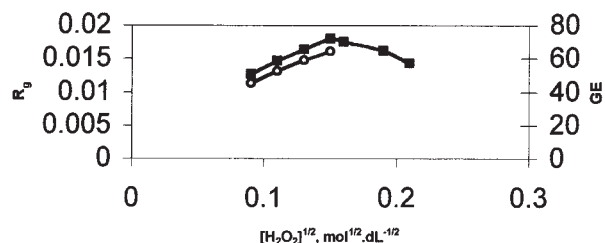
$$R_g = k \cdot [\text{MMA}] \cdot [\text{H}_2\text{O}_2]^{1/2} \quad (9)$$

where  $k$  is the rate constant of the graft polymerization.

The mechanism of grafting is suggested as follows:



RH and M represent poly (vinyl alcohol) and monomer, respectively. The following rate expressions are derived on the basis of the reaction shown in eqs.



**Figure 2** Initiator vs. grafting rate and efficiency: [PVA] = 0.1 g/dL, [MMA] = 28.2 m mol/dL, [FAS] = 0.393 m mol/dL, [H<sub>2</sub>SO<sub>4</sub>] = 0.184 mol/dL, T = 323 K, t = 3.5 h.

**TABLE V**  
Variation of Time; [PVA] = 0.1g, [FAS] = 0.397 m mol, [H<sub>2</sub>O<sub>2</sub>] = 0.022 mol, [MMA] = 28.2 m mol, [H<sub>2</sub>SO<sub>4</sub>] = 0.184 mol, T = 323 K, Phenanthroline = 0.1 g, Total volume = 100 mL

Time, min.	GR	GE (%)	H (%)	Flow time(s)	PH
45	09.86	34.96	10.98	37.80	1.58
90	13.10	46.45	11.88	38.70	1.58
135	17.90	63.48	12.50	41.40	1.58
180	18.64	66.10	14.61	42.00	1.58
210	20.32	72.06	14.72	42.30	1.58
225	20.40	72.34	14.74	42.35	1.58

(10)–(13) and steady state assumption for the free radicals R and RM<sub>n</sub><sup>\*</sup>:

$$d[\text{R}^*]/dt = \kappa_f[\text{RH}] \cdot [\text{H}_2\text{O}_2] - \kappa_i[\text{R}^*][\text{M}] = 0 \quad (14)$$

$$[\text{R}^*] = \kappa_f[\text{H}_2\text{O}_2] \cdot [\text{RH}] / \kappa_i[\text{M}] \quad (15)$$

$$d[\text{RM}'_n]/dt = \kappa_i[\text{R}^*][\text{M}] - \kappa_t[\text{RM}'_n]^2 = 0 \quad (16)$$

$$[\text{RM}'_n] = (\kappa_i / \kappa_t)^{1/2} \cdot [\text{H}_2\text{O}_2]^{1/2} \cdot [\text{RH}]^{1/2} \quad (17)$$

$$\begin{aligned} R_g &= \kappa_p \cdot [\text{RM}'_n][\text{M}] \\ &= \kappa_p \cdot (\kappa_i / \kappa_t)^{1/2} \cdot [\text{H}_2\text{O}_2]^{1/2} \cdot [\text{M}] \cdot [\text{RH}]^{1/2} \quad (18) \end{aligned}$$

At a fixed level of poly (vinyl alcohol), eq. (18) becomes

$$R_g = \text{Constant} \cdot [\text{M}] \cdot [\text{H}_2\text{O}_2]^{1/2} \quad (19)$$

Eq. (19) is identical with eq. (9), established from experiment.

### Effect of time on grafting

The GR and GE of MMA onto PVA following different reaction periods are shown in Table V. The GR and GE increase with the reaction period. However, it should be noted that after 210 min, the increase in grafting level is marginal. The effect of time on grafting can be explained as follows: it is obvious that the longer the contact time of monomer molecules with PVA macro radical sites, the greater will be the extent of grafting. The leveling of GR and GE after a certain time (210 min) can be attributed to the depletion of the initiator and monomer concentration with the progress of reaction. The pH of the reaction mixture did not change through the reaction period, indicating the grafting process was not involved with the production of H<sup>+</sup> or OH<sup>-</sup>. Flow time increases with time gradually. Probably it is due to the increase of molecular weight of the grafted polymer with time.

## CONCLUSION

1,10-phenanthroline plays an important role in the graft copolymerization of vinyl monomers onto PVA using Fenton's reagent. This reagent along with 0.1% phenanthroline may be considered as a substitute for ceric ion in its activity. The optimum mole ratio of  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  is 55.5. The poly (vinyl alcohol) grafted with poly(methyl methacrylate) has better thermal stability than by itself. The pH of the reaction mixture did not change during graft polymerization.

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