Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2010, 2(5):541-547

Ag(I) catalysed grafting of acrylonitrile onto Polyvinyl alcohol with Cerium in H_2SO_4 medium

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ABSTRACT

Grafting of Acrylonitrile(AN) onto water soluble polymers like Polyvinyl alcohol(PVA), was carried in the presence of Ag(I) using Ce(IV) as an initiator in H_2SO_4 *medium at 313K .The rate of oxidation* (R_{oxi}) *was determined for catalysed and uncatalysed oxidation. The rate of grafting (Rg) and grafting efficiency(GE) were determined for [Ag(I)] catalysis. The rate of grafting was found to increase with increase in [PVA], [AN] and [Ag(I)] and the orders were 0.72, 1.43 and 0.41 respectively.. A probable mechanism involving the formation of Ag(I) - polymer adduct followed by its oxidation with Ce(IV) to Ag(II) - polymer adduct which decomposes to give initiating radicals is proposed to explain the results.*

Key words: oxidation, graft copolymerization, kinetics, catalysis, polyvinyl alcohol, acrylonitrile.

INTRODUCTION

The water soluble polymers have wide application in industries due to its unique properties[1]. Since they are biodegradable, their utilization is restricted. Chemical modification of conventional polymers can provide a potential route for significantly altering their physical and chemical properties. The modification is brought about by graft copolymerization technique.[2] Grafting techniques are successful in modifying some of the properties of natural[3] and synthetic polymers. Various initiators are employed for grafting technique.[4,5] The graft polymerization occurs either through abstraction of hydrogen atom from the backbone polymer containing a hydroxyl group or an amino group.[6,7]

The Ce(IV) ion is known to be one of the versatile water soluble initiator for grafting of vinyl monomers onto natural and synthetic polymers like starch[8,9,10], cellulose[11,12], sodium alginate[13,14], carboxymethyl cellulose etc.[15,16,17,18] In all these cases graft copolymers were formed along with homopolymer and which is very difficult to separate. In view of this we thought it is worthwhile to search for effective initiator systems to prepare exclusive graft copolymers without contamination of homopolymer. We have carried out the grafting of acrylonitrile onto water soluble polymers like PVA in presence of Ag(I) in order to get pure exclusively graft copolymers with greater efficiency without contamination of homopolymer.

EXPERIMENTAL SECTION

All the chemicals used were of the BDH AR grade .The monomer AN was purified by distilling at low pressure under N_2 atmosphere after washing with 5% NaOH 3%H_3PO_4 and water. The graft copolymerization were conducted in dark under N_2 atmosphere to prevent any photochemical reaction and inhibition by atmospheric oxygen. Time average kinetics were followed and assumed as steady state kinetics. The rate of grafting (R_g), rate of oxidation (R_{oxi}) and grafting efficiency was calculated as follows

$$R_g = \frac{-d[\text{monomer}]}{dt} = \frac{1000 \text{ x wt of copolymer}}{\text{Volume x time x mol weight}}$$

$$R_{oxi} = \frac{-d[\text{Ce(IV)}]}{dt} = \frac{\text{Volume of Ce(IV)x concentration}}{\text{time}}$$

$$GE = \frac{\text{wt. of copolymer-wt.of polymer(PVA) x 100}}{\text{Wt of monomer}}$$

The concentration of the total Ce(IV) ion in the reaction mixtures was estimated volumetrically by ferrous ammonium sulphate, using ferrous o-phenanthroline (ferroin) as indicator.

RESULTS AND DISCUSSION

Rate of Ce(IV) disappearance:

Oxidation of PVA was carried out with Ce(IV) in the presence and absence of Ag(I) at 313 K in H_2SO_4 medium. The orders in [PVA] was 0.38 in [Ag(I)] catalysed and 0.55 in uncatalysed oxidation. The orders in Ce(IV) were found to be unity in the presence and absence of [Ag(I)]. The rate of oxidation was studied by varying the [Ag(I)] in the range of $5x10^{-2}$ to $25x10^{-2}$ M and the order in Ag(I) is 0.36..The increase in R_{oxi} with increase in Ag(I) is due to the formation of Ag(I)-(PVA) polymer adduct which is oxidized by Ce(IV) to form radicals at a faster rate .

Mechanism of oxidation in absence of Ag(I)

$$\text{Ce(IV)} + \text{PVA} \xrightarrow{k} \text{PVA}^* + \text{Ce(III)} + H^+$$

$$\text{PVA}^* + \text{Ce(IV)} \xrightarrow{k_0} \text{Products}$$

The rate law is given as-----

$$\frac{-d[Ce(IV)]}{dt} = k_0[Ce(IV)]\,[PVA]$$

Table I-Effect of [Ag(I)] , [PVA] on the Rate of oxidation
Temp 313K, $[H_2SO_4]$

$[Ag(I)] \times 10^2$	$[Ce(IV)] \times 10^2$	$[PVA] \times 10^2$	$R_{oxi} \times 10^5$
0.50	5.00	1.00	9.25
1.00	5.00	1.00	15.0
1.50	5.00	1.00	15.8
2.00	5.00	1.00	17.5
2.50	5.00	1.00	19.8
1.00	5.00	0.50	12.0
1.00	5.00	1.00	15.0
1.00	5.00	1.50	18.0
1.00	5.00	2.00	20.0
1.00	5.00	2.50	21.3
1.00	5.00	1.00	12.5
1.00	5.00	1.00	15.0
1.00	5.00	1.00	17.0
1.00	5.00	1.00	18.8
1.00	5.00	1.00	20.0
0.00	5.00	0.50	7.25
0.00	5.00	1.00	12.5
0.00	5.00	1.50	15.8
0.00	5.00	2.00	16.3
0.00	5.00	2.50	17.3

Mechanism of oxidation in the presence of Ag(I)

$$PVA + Ag(I) \overset{K}{\rightleftarrows} Ag(I)\text{-adduct}$$

$$Ag(I)\text{-adduct} + Ce(IV) \xrightarrow{k_1} Ag(II)\text{-adduct} + Ce(III)$$

$$Ag(II)\text{-adduct} \xrightarrow{k_2} PVA^* + Ag(I) + H^+$$

$$PVA^* + Ce(IV) \xrightarrow{k_0} \text{Products .}$$

The rate law is given as-----

$$\frac{-d[Ce(IV)]}{dt} = \frac{k_1K[PVA]\,[Ag(I)]\,[Ce(IV)]}{1+K[PVA]+K[Ag(I)]}$$

The observations from the Table I suggest that,

1. The rate of oxidation of PVA is found to be more in the presence of catalyst
2. The rate of oxidation of PVA is comparatively less but no homopolymer of AN is formed in the presence of Ag(I) with Ce(IV) in reaction conditions.

The observations indicate that the polymer obtained under experimental conditions is purely a graft copolymer. Ag(I) exclusively catalyzes the graft copolymerization.

In view of this we have carried out the grafting of AN onto water soluble polymer PVA, using Ce(IV) in the presence of Ag(I) to understand its role in the mechanism of graft copolymerization.

Rate of monomer disappearance in the presence of Ag(I)

Grafting of AN onto PVA was carried in the presence of Ag(I) by Ce(IV) in H_2SO_4 medium at 313K under identical conditions as above. The grafting efficiency and R_g was found to be high in the presence of Ag(I).

Effect of [Ag(I)] on grafting:-

The rate of graft copolymerization and grafting efficiency increased significantly with increase in [Ag(I)] in the range of $5.0x10^{-2}$- $25.0x10^{-2}$. The order in Ag(I) was found to be 0.41 as evident from the slope of plot 5+log Rg Vs2+ log[Ag(I)].(Fig-1). The catalytic activity of Ag(I) is probably due to the facile reaction path through the intermediacy of a new redox system formed by added Ag(I) ions. Ag(I) ions are known to form colorless adducts with oxygen containing compounds like alcohols, acids, etc.. In the present case Ag(I) may form an adduct with polymers like PVA in the initial step followed by its oxidation with Ce(IV) to form an Ag(II) adduct which subsequently undergoes internal oxidation to provide grafting sites at a faster rate compared to polymer alone. Thus the increase in rate of graft copolymerisation with Ag(I) could be explained as due to the production of more number of initiating radicals. It is also possible that the Ag(II) intermediate can directly initiate the reaction ,since it is known to be a more powerful oxidizing agent. Similar observations were also made in Ce(IV)-isopropyl alcohol redox system initiated polymerization of AN in the presence of Ag(I) ions[19].

Effect of[Ce(IV)] on grafting

In the presence of Ag(I), R_g and grafting efficiency were determined for the concentration range of $2.5x10^{-3}$ –$12.5x10^{-3}$ M.. An induction period was noticed and this period increased with increase in concentration of Ce(IV). The grafting efficiency and rate of grafting was higher in the presence of catalyst . The decrease in Rg with increase in [Ce(IV)] was explained by assuming the participation of Ce(IV) in the initiation and termination steps .

Effect of [PVA] on grafting

Increasing the percentage of polymer (w/v), the rate of grafting as well as grafting efficiency was increased The order in [PVA] in the presence of Ag(I) was found to be 0.72 as evident from the plot 5+log Rg Vs 2+log[PVA] .The deviation from unit order is due to the complexation of polymer with Ag(I).The order thus leads to linear termination of grafted polymer chains.

Effect of [AN] on grafting

The rate of graft copolymerization and grafting efficiency increased with increase in [AN] in the presence of Ag(I) and the order in [AN] was 1.43 .It is well known that order in [monomer] can be explained by linear terminations of polymer grafted chains.

From the above results and discussion , it is concluded that the grafting is initiated by the primary radicals as well as the Ag(II)-adduct and the termination by Ce(IV) is linear.

Fig1-Effect of [Ag(I)] on Rate of grafting(Rg)
Plot of 5+logRg vs 2+log [Ag(I)]
[PVA]= $10x10^{-2}$%(w/v) , [AN]=$4.00x10^{-2}$ M , Temp=313 K
[H_2SO_4]=0.1M , [(Ce(IV)]=$5.00x10^{-3}$ M

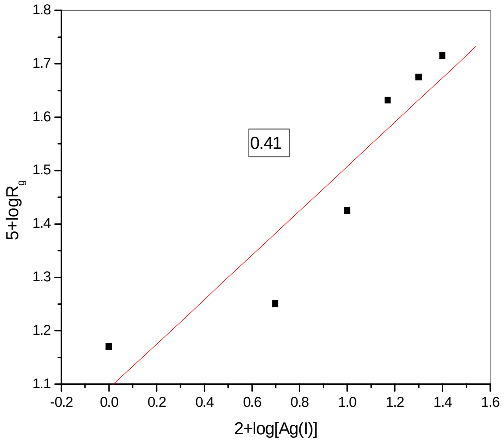


Fig2-Effect of [Polyvinyl alcohol] on Rate of grafting (Rg)
Plot of 5+logRg vs 2+log[PVA] in presence of Ag(I)
[(Ce(IV)]=$5.00x10^{-3}$M , [AN]=$4.00x10^{-2}$ M , Temp=313 K
[H_2SO_4]=0.1M , [Ag(I)]=$1.00x10^{-2}$ M

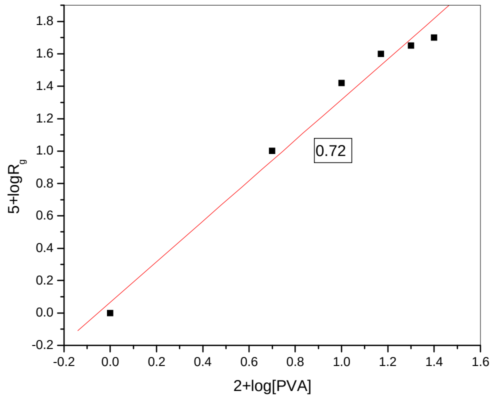
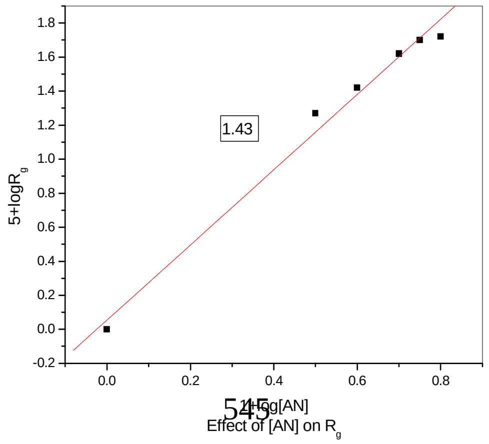


Fig3-Effect of [Acrylonitrile] on Rate of grafting (Rg)
Plot of 5+logRg vs 2+log[AN] in presence of Ag(I)
[(Ce(IV)]=$5.00x10^{-3}$M , [PVA]=$10x10^{-2}$ M , Temp=313 K
[H_2SO_4]=0.1M , [Ag(I)]=$1.00x10^{-2}$ M



Mechanism in presence of Ag(I).

1)Production of initiating species

$PVA + Ag(I) \overset{K}{\rightleftharpoons} Ag(I) - adduct$

$Ag(I)\text{-}adduct + Ce(IV) \xrightarrow{k_1} Ag(II) - adduct + Ce(III)$

$Ag(II)\text{-}adduct \xrightarrow{k_2} PVA^* + Ag(I) + H^+$

2)Initiation of graft copolymerisation

$PVA^* + M \xrightarrow{k_i} PVA\text{-}M^*$

$Ag(II)\text{-}adduct + M \xrightarrow{k_i'} PVA\text{-}M^* + Ag(I) + H^+$

M=monomer(AN)

3)Propagation

$PVA\text{-}M^* + M \xrightarrow{k_p} PVA\text{-}M^*_2$

$PVA\text{-}M_{n-1} + M \rightarrow PVA\text{-}M^*_n$

4)Termination of polymerization

$PVA\text{-}M^*_n + PVA\text{-}M^*_m \xrightarrow{k_t} PVA\text{-}M_{n+m}$ (Graft polymer)

5)Consumption of PVA by Ce(IV)

$PVA^* + Ce(IV) \xrightarrow{k_o} Products$

Applying steady state principle ,the rate law derived for graft copolymerisation is

$$R_g == \frac{k_0 k_i k_p[Ag(I)][M]^2[PVA]}{k_i\{k_0[Ce(IV)]+k_i[M]\}(1+K[Ag(I)]+K[PVA]}$$

CONCLUSION

A novel approach of synthesis has been proposed with the aim of preparing graft copolymers without any homopolymer. The adopted methodology is to initiate polymerization by polymer radicals formed due to interaction of Ce(IV) with polymer. Ce(IV) participates in the initiation and termination steps of polymerization. The grafting was carried out in acidic medium by varying concentration of monomer(acrylonitrile), polymer(PVA) and Ag(I) and the grafting yields were found to be higher in the presence of Ag(I).The grafting mechanism has been explained satisfactorily by linear termination of grafted polymers.

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