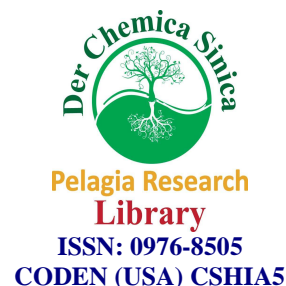




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Synthesis of block polymer of Acrylonitrile and Polyethylene glycol with Cerium in Acidic medium. Kinetic study

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ABSTRACT

Polyethylene glycol(PEG) block Acrylonitrile(AN) (PEG-b-AN) copolymer was synthesized in the presence of Ag(I) using Ce(IV) as an initiator in H_2SO_4 medium at 313K. The rate of oxidation was determined in the presence and absence of catalyst. and the orders were 0.25 in [Ag(I)], 0.22 in [PEG] in the presence of catalyst. The rate of copolymerization (R_p) and efficiency were determined for [Ag(I)] catalysis. The rate of copolymerization was found to increase with increase in [PEG], [AN] and [Ag(I)] and the orders were 0.50, 1.50 and 0.58 respectively.. A probable mechanism involving the formation of Ag(I) - polymer adduct followed by its oxidation with ceric to Ag(II) - polymer adduct which decomposes to give initiating radicals is proposed to explain the results.

Key words: oxidation, block copolymerization, kinetics, catalysis

INTRODUCTION

The water soluble polymers have wide application in industries due to its unique properties. 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. Multiphase polymer systems have received widespread attention in recent years, especially since the rate of appearance of new polymer types has diminished considerably. The new multiphase materials may be obtained in the form of blends, block and graft copolymers or interpenetrating networks all of which are characterized by the presence of polymeric phases in the solid state.

Block copolymers are linear copolymeric structures consisting of repeating units of a certain block copolymer of type (A -b-B); where A and B are macromolecular chains of low molecular weights . Many approaches have been reported in the literature on the block polymer synthesis

such as emulsion polymerization (1, 2) , atom transfer radical polymerization (3), photo induced polymerization(4) ,redox polymerization (5,6,7,8,9,10) etc(11).The most suitable method was through redox process initiation. Various redox systems like manganese, copper, iron, vanadium ion, hydrogen peroxide cerium were employed for the synthesis of block copolymers through redox methods. The Ce(IV) ion is known to be one of the versatile water soluble initiator for copolymerization of vinyl monomers with natural and synthetic polymers. In general copolymers are formed along with homopolymer which is very difficult to separate. In view of this we thought it is worthwhile to search for effective initiator systems to prepare exclusive copolymers without contamination of homopolymer. We have carried out the copolymerisation of acrylonitrile and water soluble polymers like PEG in presence of Ag(I) in order to get exclusively pure copolymers with greater efficiency without contamination of homopolymer.

MATERIALS AND METHODS

All the chemicals used were of the BDH AR grade. The monomer acrylonitrile was purified by distilling at low pressure under N₂ atmosphere after washing with 5% NaOH 3% H₃PO₄ and water. The block copolymerization were conducted in dark under N₂ 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 polymerisation(R_p), rate of oxidation (R_{oxi}) and efficiency was calculated as follows

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

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

$$\text{Efficiency} = \frac{\text{wt. of copolymer} - \text{wt. of polymer(PEG)} \times 100}{\text{Wt of monomer}}$$

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.

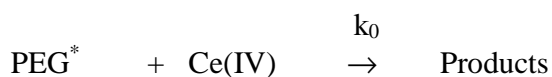
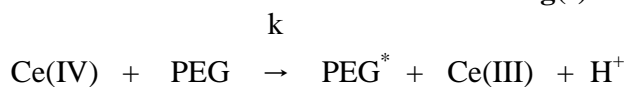
RESULTS AND DISCUSSION

Rate of Ce(IV) disappearance:

Oxidation of Polyethylene glycol (PEG) was carried out with Ce(IV) in the presence and absence of Ag(I) at 313 K in H₂SO₄ medium. The orders in [PEG] in the presence and absence of Ag(I) were found to be 0.19 and 0.22 respectively. 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 0.25. The increase in R_{oxi} with increase in Ag(I) is due to the formation of Ag(I)-Polyethylene glycol(PEG) polymer adduct which is oxidized by Ce(IV) to form radicals at a quite a fast rate.

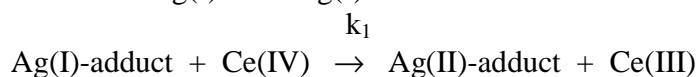
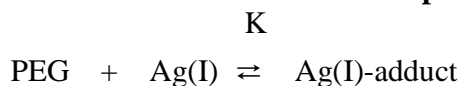
Table I: Effect of [Ag(I)], [Ce(IV)] , [PEG] on R_{oxi}

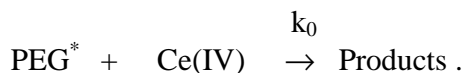
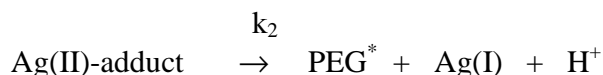
[Ag(I)] $\times 10^2$	[Ce(IV)] $\times 10^2$	[PEG] $\times 10^2$	$R_{\text{oxi}} \times 10^4$
0.50	5.00	1.00	12.3
1.00	5.00	1.00	14.0
1.50	5.00	1.00	15.3
2.00	5.00	1.00	16.3
2.50	5.00	1.00	18.0
1.00	5.00	0.50	12.5
1.00	5.00	1.00	14.0
1.00	5.00	1.50	14.8
1.00	5.00	2.00	16.0
1.00	5.00	2.50	17.3
1.00	0.50	1.00	9.75
1.00	1.00	1.00	13.5
1.00	1.50	1.00	14.8
1.00	2.00	1.00	17.0
1.00	2.50	1.00	12.8
0.00	5.00	0.50	11.8
0.00	5.00	1.00	12.5
0.00	5.00	1.50	13.3
0.00	5.00	2.00	14.5
0.00	5.00	2.50	15.5
0.00	0.50	1.00	8.75
0.00	1.00	1.00	12.0
0.00	1.50	1.00	13.0
0.00	2.00	1.00	14.7
0.00	2.50	1.00	11.7

Mechanism of oxidation in absence of Ag(I)

The rate law is given as-----

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

Mechanism of oxidation in the presence of Ag(I)



The rate law is given as-----

$$-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_1 K [\text{PEG}] [\text{Ag(I)}] [\text{Ce(IV)}]}{1 + K [\text{PEG}] + K [\text{Ag(I)}]}$$

The observations from the above table-1 are compiled as follows--

- 1) The rate of oxidation of PEG is found to be more in the presence of Ag(I).
- 2) The rate of oxidation of AN is comparatively less but no homopolymer of AN is formed either in the presence or absence of Ag(I) with Ce(IV) in reaction conditions.
- 3) In the presence of Ag(I) the rate of oxidation of PEG-AN (R_{oxi}) is slightly higher but R_p was significantly higher.

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

In view of this we have carried out the copolymerization of AN and PEG, using Ce(IV) in the presence of Ag(I) to understand its role in the mechanism of copolymerization.

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

Block copolymerisation of AN and PEG was carried in the presence of Ag(I) by Ce(IV) in H_2SO_4 medium at 313K under identical conditions as above. The R_p and efficiency was found to be high in the presence of Ag(I) .

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

The rate of copolymerization and efficiency increased significantly with increase in [Ag(I)] in the range of 5.0×10^{-2} - 25.0×10^{-2} (Table II). The order in Ag(I) was found to be 0.54 . 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 colourless adducts with oxygen containing compounds like alcohols, acids, etc. In the present case Ag(I) may form an adduct with polymers like PEG in the initial step followed by its oxidation with Ce(IV) to form an Ag(II) adduct which subsequently undergoes internal oxidation to provide active sites at a faster rate compared to polymer alone. Thus the increase in rate of 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 acrylonitrile in the presence of Ag(I) ions.

Effect of [Ce(IV)] on copolymerisation.

In the presence of Ag(I), R_p and efficiency were determined for the concentration range of 2.5×10^{-3} - 12.5×10^{-3} M. The copolymer appeared at an induction period and this period increased

with increase in concentration of Ce(IV). The efficiency and rate of copolymerization was determined in the presence of catalyst. The decrease in R_p with increase in $[Ce(IV)]$ was explained by assuming the participation of Ce(IV) in the initiation and termination steps.

Effect of [AN] on copolymerisation

The order in [AN] in presence of Ag(I) was 1.50. It is well known that order in [monomer] can be explained either by linear or mixed terminations of polymer chains.

Effect of [PEG] on copolymerisation

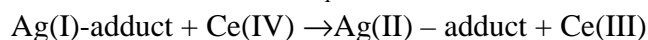
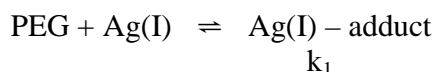
Increasing the percentage of polymer (w/v), the rate of copolymerization as well as efficiency was increased. The order in [PEG] in the presence of Ag(I) was found to be 0.90. The deviation from unit order is due to the complexation of polymer with Ag(I). The order thus leads to linear termination of copolymer chains.

From the above results and discussion, it is concluded that the copolymerisation is initiated by the formation of primary radicals. A suitable mechanism is proposed to explain the results.

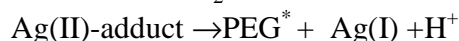
Mechanism in presence of Ag(I)

Production of initiating species

K

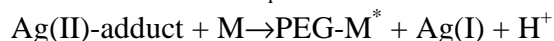
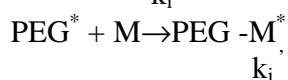


k_2



Initiation of copolymerisation

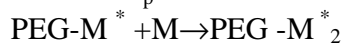
k_i



M=monomer(AN)

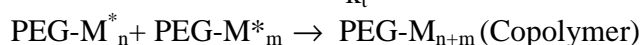
Propagation

k_p



Termination of polymerization

k_t



Consumption of PEG by Ce(IV)

k_0

$\text{PEG}^* + \text{Ce(IV)} \rightarrow \text{Products}$

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

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

Table II

[Ag(I)] x10 ²	[Ce(IV)]x10 ²	[PEG]x 10 ²	[AN]x10	R _p x 10 ⁵	Efficiency
0.50	5.00	1.00	4.00	15.3	38.4
1.00	5.00	1.00	4.00	28.8	45.7
1.50	5.00	1.00	4.00	33.7	53.5
2.00	5.00	1.00	4.00	43.3	68.7
2.50	5.00	1.00	4.00	46.1	73.1
1.00	0.50	1.00	4.00	16.3	25.8
1.00	1.00	1.00	4.00	28.8	45.0
1.00	1.50	1.00	4.00	33.0	52.5
1.00	2.00	1.00	4.00	29.3	47.5
1.00	2.50	1.00	4.00	25.1	40.0
1.00	5.00	0.50	4.00	16.9	20.0
1.00	5.00	1.00	4.00	28.8	45.0
1.00	5.00	1.50	4.00	31.4	50.0
1.00	5.00	2.00	4.00	34.6	55.0
1.00	5.00	2.50	4.00	37.7	60.0
1.00	5.00	1.00	3.20	15.8	31.2
1.00	5.00	1.00	4.00	28.8	45.0
1.00	5.00	1.00	4.80	33.0	44.0
1.00	5.00	1.00	5.60	40.9	46.0
1.00	5.00	1.00	6.40	48.0	48.0

CONCLUSION

A novel approach of synthesis has been proposed with the aim of preparing copolymers containing zero proportion of 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. In the presence of catalyst, Ag(I) interacts with the polymer resulting in the formation of polymer-adduct which dissociates to form polymer radical. The copolymerisation was carried out in acidic medium by varying concentration of monomer, polymer Ag(I). The mechanism has been explained satisfactorily by linear termination of copolymers.

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