



Rate of Polymerisation of Methylacrylate Initiated by Ce(IV) in β -CD

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ABSTRACT

The kinetics of methylacrylate (MA) polymerization initiated by Ce(IV) – Lactic acid redox system in the presence of β -cyclodextrin (β -CD) in aqueous sulphuric acid medium have been studied for the temperature 30 °C and 35 °C. The rate of polymerization R_p (obs) as well as the rate of Ce(IV) consumption, R_{Ce} , were found under various concentration of MA, Ce(IV), H^+ and β -CD. Polymerization was done in both presence and absence of β -CD, and the results were compared. The β -CD complexation of oxidant and monomer decreases the rate of polymerization due to its cavity.

1. Introduction

A chemical compound containing one or more polymerizable structural units is known as monomer. The process by which the monomer molecules are bonded together to form a macro size molecule (polymer) called polymerization. The macromolecules consisting of identical monomers are called homopolymers. When different types of monomers are used, the resulting polymer is called copolymer or mixed polymer. Metal ions such as Cr^{3+} , V^{5+} , Ce^{4+} , Co^{3+} , Mn^{3+} , etc. reacted with certain organic compounds like alcohols [1], aldehydes [2], ketones [3], amines [4], etc. were useful redox system for initiating vinyl polymerization. $KMnO_4$ and ceric salts – reducing agent systems in acid – aqueous medium were used for the preparation of graft co-polymer of vinyl monomers such as acrylonitrile, methylmethacrylate, acrylic acid or acrylamide [5–8]. Umayavalli et al. [9] reported cyclopolymerisation of N, N-methylenebisacrylamide (MBA) with a redox pair of Mn(VII)-tetramethylene-diamine in a homogeneous gel free state under varying conditions of concentration, temperature, ionic strength and pH. The rate of polymerization was found to be independent of ionic strength and pH. R_p increases with increase in temperature and it is independent of [Mn(VII)] and [tetramethylene-diamine]. Yagci and Yildiz [10] reported decrease in rate of polymerization of MMA on increasing the concentration of Ce(IV) and MMA. In redox systems, oxidant forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization. Numerous redox pairs containing organic and inorganic components as polymerization initiator have been used successively. Commonly used oxidants include peroxides, persulfates, permanganates, etc. the salts of transition metals. These oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, ketones, amines, amides, acids, thiols, etc. for the aqueous polymerization of vinyl monomers. Ce(IV) ion has been used for the oxidation of many organic compounds, in the form of Ce(IV) ammonium nitrate, Ce(IV) ammonium sulfate, Ce(IV) sulfate and ceric perchlorate. Cyclodextrins are well-known host molecules that find extensive use in complexation due to its well defined cavities and small size [11]. In the present investigation the polymerization of methylacrylate initiated by lactic acid- Ce(IV) redox system in the presence of β -CD was carried out. Ce(IV) was chosen as the

oxidizing agent because it has been found to be an active oxidant in vinyl polymerization. Polymerization will be done both in the absence and in the presence of β -CD at 30 °C and 35 °C temperatures and the results were compared. The rates of polymerization in the presence and in the absence of β -CD at various temperatures, various concentrations of monomer, oxidant were compared.

2. Experimental Methods

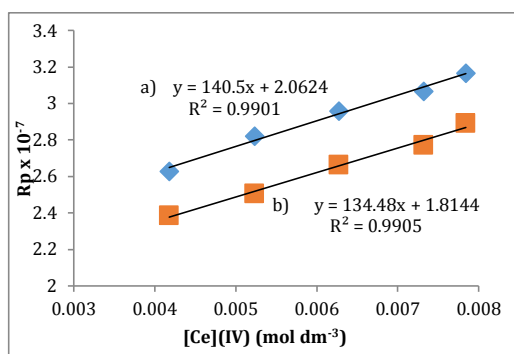
Methylacrylate (Merck) was distilled under reduced pressure. Lactic acid (Fluka) was also distilled under reduced pressure, β -CD (Aldrich) was used as such. Sulphuric acid (Nice) and sodium bi sulphate (Nice) were of analar grade and used as such. The reaction tubes used for the experiments were pyrex glass tubes. The nitrogen gas used to deaerate the experimental system, was free from oxygen by passing through several columns of Fiesher's solution. A solution containing the required amount of monomer, reducing agent, sulfuric acid, $NaHSO_4$ (to maintain the ionic strength), was taken in the reaction vessel and made up to the fixed volume (20 mL) with distilled water. The solution was then de-aerated for 20 minutes with nitrogen gas. The tube was thermostated at the appropriate temperature in thermostat. After 20 minutes, required amount of ceric ammonium sulfate solution was added into the polymer tube through a micro funnel. Passage of nitrogen gas was continued for 5 more minutes. The inlet and outlet tubes were closed to maintain the nitrogen atmosphere till the end of the fixed reaction time. Ferrous ammonium sulfate solution was then added and air was bubbled into the reaction tube to arrest the reaction. The concentration of the monomer was determined by the method of addition of bromine to the double bond. To 10 mL of 0.2 M Winkler's solution in an Erlenmeyer flask, 3 ml of stock monomer solution and 20 mL of 2.0 M H_2SO_4 were added. This tightly stoppered flask was kept in dark for about 20 minutes with intermittent shaking to allow the liberated bromine to add on to the double bonds in the monomer. KI was then added to the mixture and the iodine liberated by the excess bromine was titrated against std. $NaHSO_4$ using starch as an indicator. A blank titration was also made with 10 ml of Winkler's solution as before and the difference in the time value was used to estimate the monomer concentration.

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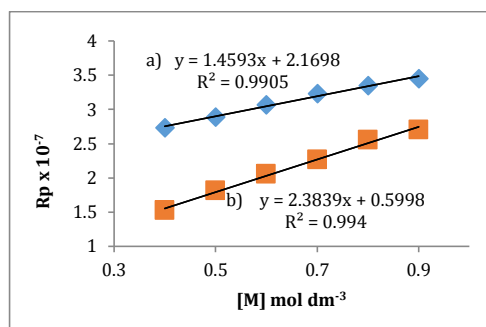
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Table 1 Comparison of R_p at different oxidant concentration. ($[LA] = 0.02 \text{ mol dm}^{-3}$, $\mu = 1.1 \text{ mol dm}^{-3}$, $[H_2SO_4] = 5 \text{ mol dm}^{-3}$, Temperature = 35°C)

$Ce(IV) \times 10^{-3} (\text{mol dm}^{-3})$	$R_p \times 10^{-7}$	
	Without β -CD	with β -CD
0.00418	2.6292	2.3858
0.00523	2.8205	2.5062
0.00627	2.9601	2.6644
0.00732	3.0682	2.7713
0.00784	3.1672	2.8918

**Fig. 1** Rate of polymerisations at different oxidant concentrations a) without β -CD and b) with β -CD.**Table 2** Comparison of R_p at different monomer concentration. ($[LA] = 0.02 \text{ mol dm}^{-3}$, $\mu = 1.1 \text{ mol dm}^{-3}$, $[H_2SO_4] = 5 \text{ mol dm}^{-3}$, Temperature = 35°C)

$[M] (\text{mol dm}^{-3})$	$R_p \times 10^{-7}$	
	Without β -CD	with β -CD
0.4	2.7317	1.5218
0.5	2.8901	1.8074
0.6	3.0682	2.0484
0.7	3.2662	2.2652
0.8	3.3456	2.5544
0.9	3.4483	2.699

**Fig. 2** Rate of polymerisations at different monomer concentrations a) without β -CD and b) with β -CD.

3. Results and Discussion

3.1 Variation of Oxidant

On increasing the concentration of β -CD in the reaction mixture the rate of polymerization R_p as well as percentage of methylacrylate conversion was found to be decreased (Fig. 1). As β -CD cavity holds smaller

percentage of reductant lactic acid, oxidant $Ce(IV)$ and the monomer in small entity and more and more molecules are outside the cavity it decreases the rate of polymerization and thereby decrease in the chain of polymerization. More and more monomers were away from the cyclodextrin cavity, which decreases the R_p . On increasing the MA concentration (0.1 – 0.2 M) in the mixture, R_p was found to be decrease. Now the availability of MA at CD cavity increases with its concentrations leads to rate decreased. Such type of rate dependent was reported [4, 9] which concludes the polymerization undergoes linear termination. Decrease in the rate of polymerization was observed on increasing the concentration of $Ce(IV)$ from 0.004 to 0.007 (Table 1) in reaction mixture in the presence of 0.2 M of β -CD. The $Ce(IV)$ has the capacity of influencing through the polymer chain. On increasing the concentration of β -CD (0.2 to 0.6 M), the rate of polymerization was decreased (Fig. 1). This will show more and more molecules of MA away from CD cavity which decreases the chain length and thereby the rate was decreased.

3.2 Variation of Monomer

In the variation of monomer concentration from 0.4 to 0.9 M, the R_p was calculated with and without β -CD at 35°C . When we compare the R_p , it always decreases in the presence of β -CD and the values are shown in Table 2 and Fig. 2. This is also due to β -CD cavity which separates the monomer and oxidant.

4. Conclusion

The polymerization rate decreases due to hydrophobic interaction of β -CD which holds the monomer, oxidant and reductant in its cavity which slows down the polymerization reaction.

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