

Ce(IV) INITIATED POLYMERISATION OF ACRYLAMIDE IN PRESENCE OF β - CYCLODEXTRIN

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ABSTRACT

The kinetics of polymerization of acrylamide initiated by Ce(IV) – Lactic acid redox system in the presence of β -cyclodextrin (β -CD) have been studied for the temperature 30°C and 35°C in dilute sulphuric acid medium. The rate of polymerization $R_p(\text{obs})$ as well as the rate of Ce(IV) consumption, R_{ce} , were found under various concentration of monomer (acrylamide), lactic acid(reductant), Ce(IV)(oxidant), and H^+ (acid), etc. both for the temperature 30°C and 35°C in the presence of β -cyclodextrin (β -CD) and in the absence of β -CD and the results were compared. As the temperature increases rate of polymerization R_p increases. Due to the presence of cavity in β -cyclodextrin the rate of polymerization decreases. The cavity enhances the complexation of oxidant, reductant and monomer, etc.

KEYWORDS: acrylamide, redox system, β -cyclodextrin, rate of polymerization, cavity.

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 $[\text{Mn(VII)}]$ and [tetramethylene-diamine]. Cigdem Yagci, Ufuk 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 acrylamide 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 concentrations of monomer, oxidant, reductant etc. were compared.

MATERIALS AND METHODS

Experimental methodology

The monomer acrylamide was distilled under reduced pressure. Reductant lactic acid was also distilled under reduced pressure, β -CD was used as such. Sulphuric acid which is used as acid medium and sodium bi sulphate which is used as ionic substance 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. The concentration of the monomer was determined by the method of addition of bromine to the double bond. To 10 ml of 0.2M Winkler's solution in an Erlenmeyer flask, 3 ml of stock monomer solution and 20 ml of 2M H₂SO₄ were added. The contents of the flask were tightly stoppered and 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. NaHSO₄ 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. The rate of disappearance of ceric ion was also calculated by this method. From this the consumed ceric ion amount and the weight of polymer formed were also calculated. From the weight of polymer formed, the rate of polymerization R_p was calculated by using the following formula.

$$R_p = \text{wt. of polymer} / \text{mol. wt. of monomer} \times 1000 / \text{vol. taken} \times 1 / \text{time in sec.}$$

RESULT AND DISCUSSION

Variation of oxidant

The increasing concentration of β-CD in the reaction mixture decreases the rate of polymerization R_p as well as percentage of acrylamide conversion (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 length of polymer chain. More and more monomers were away from the cyclodextrin cavity, which decreases the R_p. On increasing the acrylamide concentration (0.4 – 0.9 mol) in the mixture, R_p was found to be decrease. Now the availability of acrylamide at β-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 0.00315 to 0.00784 (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. This will show more and more molecules of acrylamide away from β-CD cavity which decreases the chain length and thereby the rate was decreased.

Comparison of R_p at different oxidant concentration.**Table 1. Variation of oxidant without β -CD**

$$[\text{Ce(IV)}] = 0.0209 \text{ mol. dm}^{-3}$$

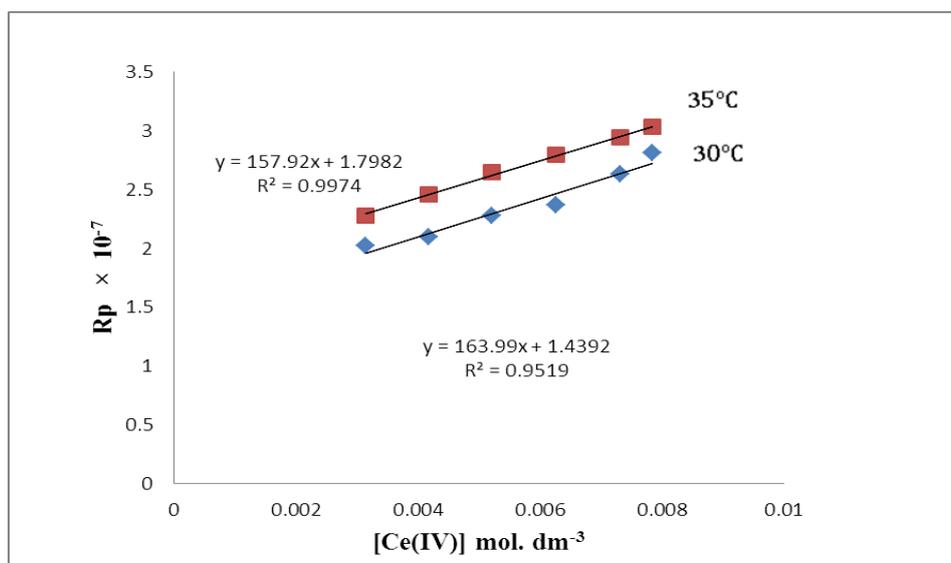
$$\mu = 1.1 \text{ mol. dm}^{-3}$$

$$[\text{LA}] = 0.2 \text{ mol. dm}^{-3}$$

$$\text{Temperature} = 30^\circ\text{C} \ \& \ 35^\circ\text{C}$$

$$[\text{M}] = 0.02 \text{ mol. dm}^{-3}$$

| [Ce(IV)] mol. dm ⁻³ | R _p × 10 ⁻⁷ | |
|-----------------------------------|-----------------------------------|--------|
| | 30°C | 35°C |
| 0.00315 | 2.0215 | 2.2788 |
| 0.00418 | 2.0951 | 2.4626 |
| 0.00522 | 2.2788 | 2.6464 |
| 0.00627 | 2.3707 | 2.7934 |
| 0.00731 | 2.628 | 2.9405 |
| 0.00784 | 2.8118 | 3.0324 |

**Variation of oxidant without β -CD.****Table 2. Variation of oxidant with β -CD.**

$$[\text{Ce(IV)}] = 0.0209 \text{ mol. dm}^{-3}$$

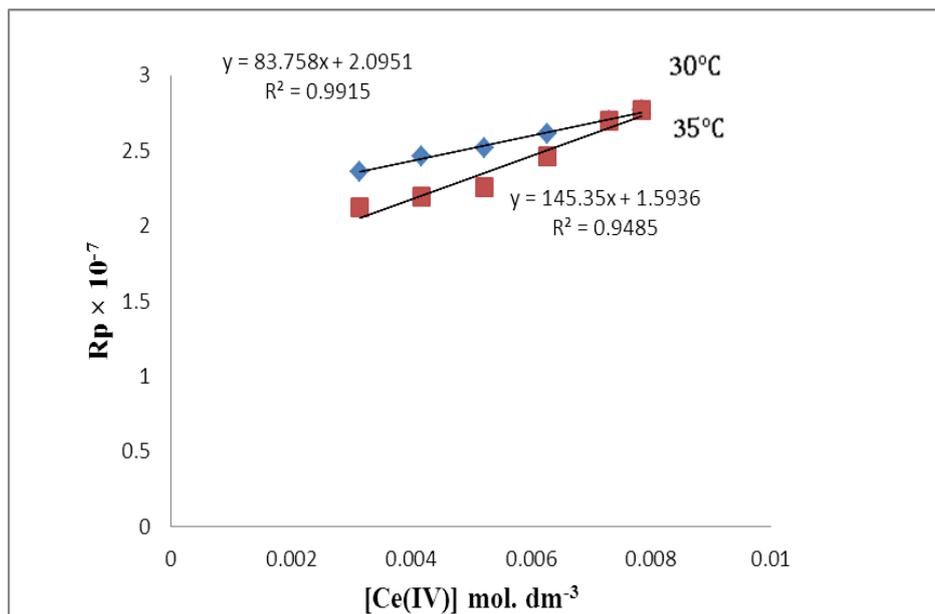
$$\mu = 1.1 \text{ mol. dm}^{-3}$$

$$[\text{LA}] = 0.2 \text{ mol. dm}^{-3}$$

$$\text{Temperature} = 30^\circ\text{C} \ \& \ 35^\circ\text{C}$$

$$[\text{M}] = 0.02 \text{ mol. dm}^{-3}$$

| [Ce(IV)] mol. dm ⁻³ | R _p × 10 ⁻⁷ | |
|-----------------------------------|-----------------------------------|--------|
| | 30°C | 35°C |
| 0.00315 | 2.3599 | 2.1223 |
| 0.00418 | 2.4616 | 2.1902 |
| 0.00522 | 2.5128 | 2.2581 |
| 0.00627 | 2.6147 | 2.4616 |
| 0.00731 | 2.6996 | 2.6996 |
| 0.00784 | 2.7675 | 2.7675 |



Variation of oxidant with β -CD

Variation of monomer

In the variation of monomer concentration from 0.4 to 0.9M, 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 it was observed in table – 2. This is also due to β -CD cavity which separates the monomer and oxidant.

Table 2: Comparison of R_p at different monomer concentration.

Table 3. Variation of Monomer with β -CD

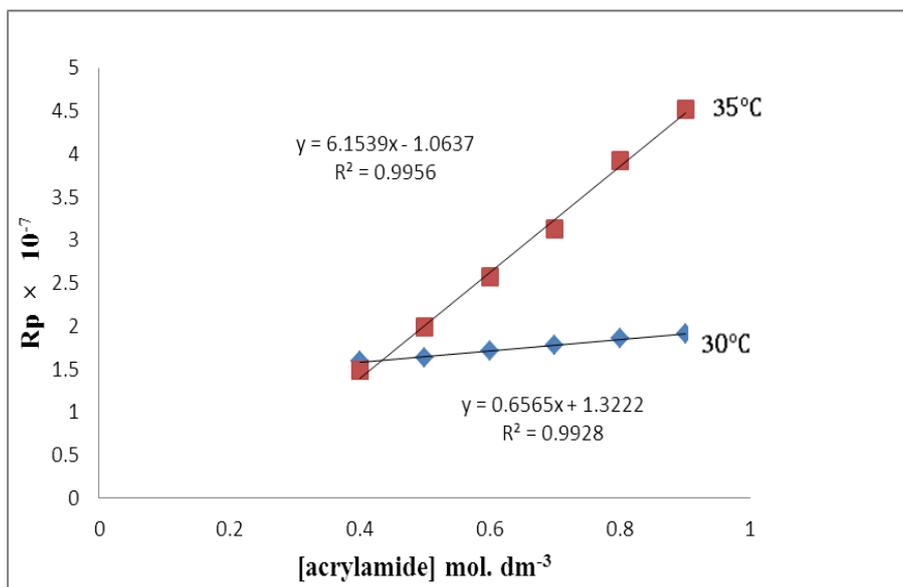
$$[\text{LA}] = 0.2 \text{ mol. dm}^{-3}$$

$$[\text{H}_2\text{SO}_4] = 5 \text{ mol. dm}^{-3}$$

$$\mu = 1.1 \text{ mol. dm}^{-3}$$

$$\text{Temperature} = 30^\circ\text{C} \ \& \ 35^\circ\text{C}$$

| [acrylamide] mol. dm ⁻³ | $R_p \times 10^{-7}$ | |
|---------------------------------------|----------------------|--------|
| | 30°C | 35°C |
| 0.4 | 1.5988 | 1.4825 |
| 0.5 | 1.6356 | 1.9909 |
| 0.6 | 1.7091 | 2.5729 |
| 0.7 | 1.7826 | 3.1304 |
| 0.8 | 1.8562 | 3.9206 |
| 0.9 | 1.9113 | 4.5209 |



Variation of Monomer with β -CD

Table 4: Variation of Monomer without β -CD.

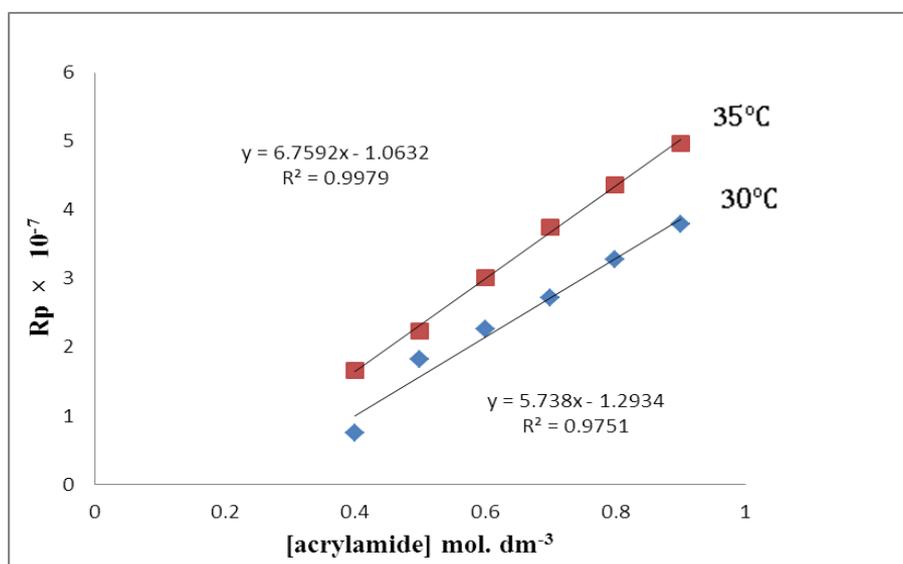
[LA] = 0.2 mol. dm⁻³

μ = 1.1 mol. dm⁻³

[H₂SO₄] = 5 mol. dm⁻³

Temperature = 30°C & 35°C

| [acrylamide] mol. dm ⁻³ | Rp × 10 ⁻⁷ | |
|---------------------------------------|-----------------------|--------|
| | 30°C | 35°C |
| 0.4 | 0.7436 | 1.6639 |
| 0.5 | 1.8252 | 2.2335 |
| 0.6 | 2.2581 | 3.0052 |
| 0.7 | 2.7137 | 3.7438 |
| 0.8 | 3.2825 | 4.3692 |
| 0.9 | 3.7947 | 4.9662 |



Variation of Monomer without β -CD

Variation of reductant

On increasing the lactic acid concentration (0.02 – 0.06 mol) in the mixture, R_p was found to be decrease. As β -CD cavity holds smaller percentage of reductant lactic acid in small entity and more and more molecules are outside the cavity it decreases the rate of polymerization and thereby decrease in the length of polymer chain.

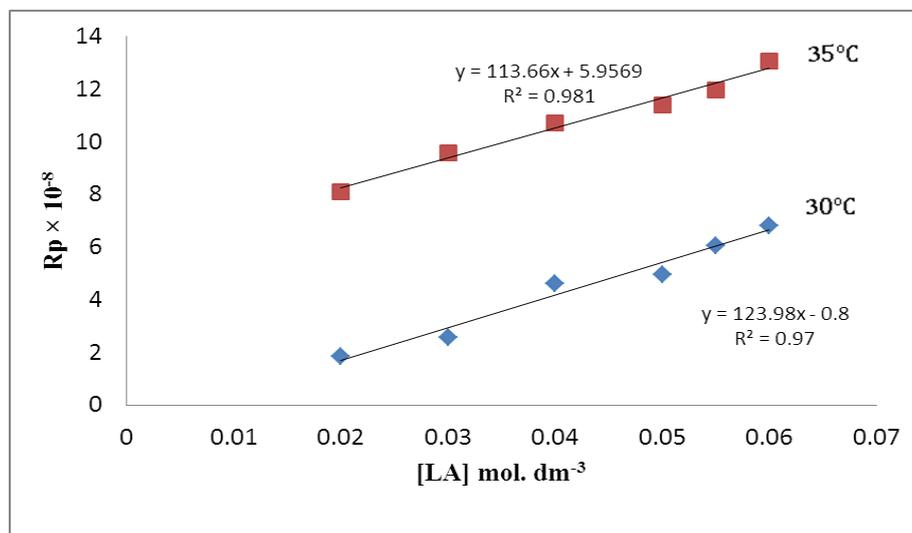
Comparison of R_p at different reductant concentration.

Table 5. Variation of Reductant without β -CD

$[Ce(IV)] = 0.0209 \text{ mol. dm}^{-3}$
 $[H_2SO_4] = 5 \text{ mol. dm}^{-3}$

$\mu = 1.1 \text{ mol. dm}^{-3}$
 Temperature = 30°C & 35°C

| [LA] mol. dm ⁻³ | $R_p \times 10^{-8}$ | |
|-------------------------------|----------------------|--------|
| | 30°C | 35°C |
| 0.02 | 1.8378 | 8.0863 |
| 0.03 | 2.5565 | 9.5565 |
| 0.04 | 4.5944 | 10.695 |
| 0.05 | 4.962 | 11.394 |
| 0.055 | 6.0647 | 11.945 |
| 0.06 | 6.7998 | 13.048 |



Variation of Reductant without β -CD

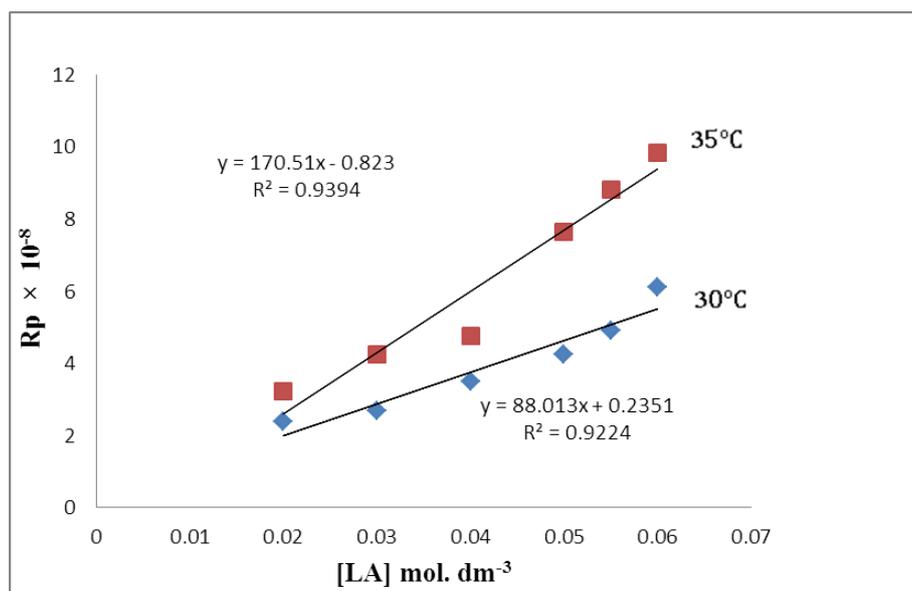
Table 5. Variation of Reductant with β -CD

$[Ce(IV)] = 0.0209 \text{ mol. dm}^{-3}$
 $[H_2SO_4] = 5 \text{ mol. dm}^{-3}$

$\mu = 1.1 \text{ mol. dm}^{-3}$
 Temperature = 30°C & 35°C

| [LA] mol. dm ⁻³ | $R_p \times 10^{-8}$ | |
|-------------------------------|----------------------|--------|
| | 30°C | 35°C |
| 0.02 | 2.3771 | 3.2258 |
| 0.03 | 2.6853 | 4.2446 |
| 0.04 | 3.5111 | 4.7539 |

| | | |
|-------|--------|--------|
| 0.05 | 4.2445 | 7.6405 |
| 0.055 | 4.9236 | 8.8289 |
| 0.06 | 6.1123 | 9.8477 |



Variation of Reductant with β -CD

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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