

# Study of rate of polymerization of acrylonitrile in Ce(IV) – lactic acid redox system with cyclic oligosaccharide.

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**Abstract:** The polymerization rate was measured under various conditions at different concentration of monomer [acrylonitrile], initiator [Ce(IV)], reductant [LA], and sulphuric acid [H<sup>+</sup>]. The results in the presence and in the absence of oligosaccharides ( $\beta$ -cyclodextrin) were compared. This study was done at a temperature 35°C and the time duration was 30 min. Temperature variation study was also carried out from 30°C to 70°C. Temperature variation run was used to study the rate of polymerization  $R_p$  and thermodynamic parameters. Due to its ability to form host-guest complexes with organic components and due to the presence of cavity in  $\beta$ -cyclodextrin the rate of polymerization increases. The presence of  $\beta$ -cyclodextrin enhances the rate of polymerization in this redox system.

**Key words:** acrylonitrile, oligosaccharides, redox system, host-guest complex, cavity.

## I. INTRODUCTION

Polymers play a vital role in our day today life such as in food, clothing, shelter, transportation, communication and in modern technologies. Biological polymers such as muscles, sinews, genes and chromosomes constitute our body and it forms foundation of life. Compound with one or more polymeric structural units is known as monomer. The monomer molecules are bonded together to form a macro molecule, polymer and the process is known as polymerization. The macro molecules with same monomers are known as homopolymers and with different types of monomers are known as co-polymer or mixed polymer.

Metal ions such as Cr<sup>3+</sup>, V<sup>5+</sup>, Ce<sup>4+</sup>, Co<sup>3+</sup>, Mn<sup>3+</sup>, 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<sub>4</sub> - ceric salt redox system 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]. CigdemYagci, Ufuk Yildiz [10] reported decrease in rate of polymerization of methyl meth acrylate(MMA) on increasing the concentration of Ce(IV) and MMA. In redox systems, oxidant initially forms a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization. Many redox pairs with organic and inorganic components as polymerization initiator have been used successively.

Commonly used oxidants include peroxides; persulphates, permanganates, etc. are 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. For the oxidation of many organic compounds, Ce(IV) ion has been used in the form of ceric ammonium nitrate, ceric ammonium sulfate, ceric sulfate and ceric perchlorate.

Cyclodextrins are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. Torus-shaped cyclic oligosaccharide  $\beta$ -cyclodextrin contains six to twelve glucose units. Cyclodextrins are well-known host-guest molecules that find extensive use in complexation due to its well defined cavities and small size [11]. The structure of CD gives rise to the remarkable ability to form inclusion complexes with inorganic [12-14], organic [15-18] and ionic compounds [12,13], and also with polymers [19-23]. In the present investigation the polymerization of acrylic acid initiated by Ce(IV) - lactic acid redox system in the presence and in the absence of  $\beta$ -CD were carried out. Ce(IV) was chosen as the oxidizing agent because it has been found to be an active oxidant in vinyl polymerization. This study was carried out in the presence of  $\beta$ -CD and in the absence of  $\beta$ -CD at 35°C temperature for 30 min. time duration and the results were compared. The rates of polymerization in the presence and in the absence of  $\beta$ -CD at various concentrations of monomer, oxidant, reductant, sulphuric acid, etc. were compared.

## II. EXPERIMENTAL METHODOLOGY

The monomer acrylonitrile(AN), reductant lactic acid were distilled under reduced pressure and  $\beta$ -CD was used as such. Sulphuric acid which was used as acid medium and sodium bisulphite was used to maintain ionic strength were of analar grade and used as such. The pyrex glass tubes were used as reaction tubes for the experiments. Nitrogen gas was used to deaerate the experimental system and it 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 H<sub>2</sub>SO<sub>4</sub> were added. The contents of the flask were tightly stoppered and kept in dark for about 30 minutes with intermittent shaking to allow the liberated bromine to add on to the double bonds in the monomer. To the mixture, KI was then added and the iodine liberated by the excess bromine was titrated against std. NaHSO<sub>4</sub> 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 [-d(Ce)] 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<sub>p</sub> was calculated by using the following formula.

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

### III. RESULT AND DISCUSSION

A) Variation of Monomer Conc.

Table:1 Effect of Monomer (Acrylonitrile) Conc. on Polymerization Rate in Presence of  $\beta$ -CD

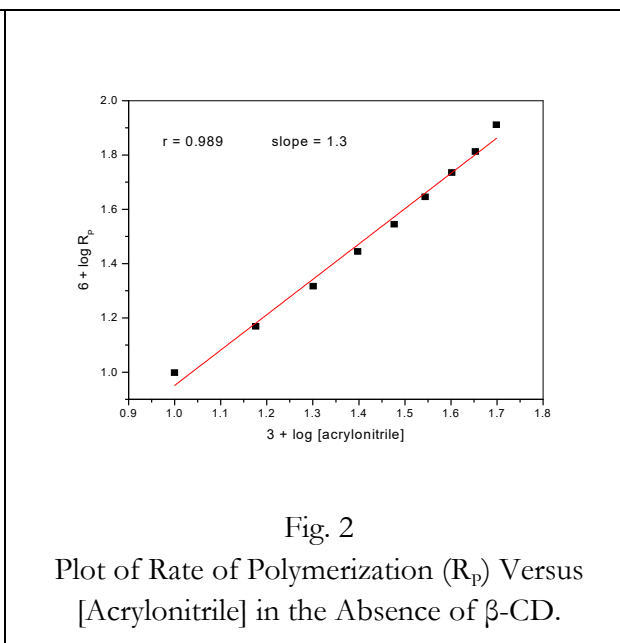
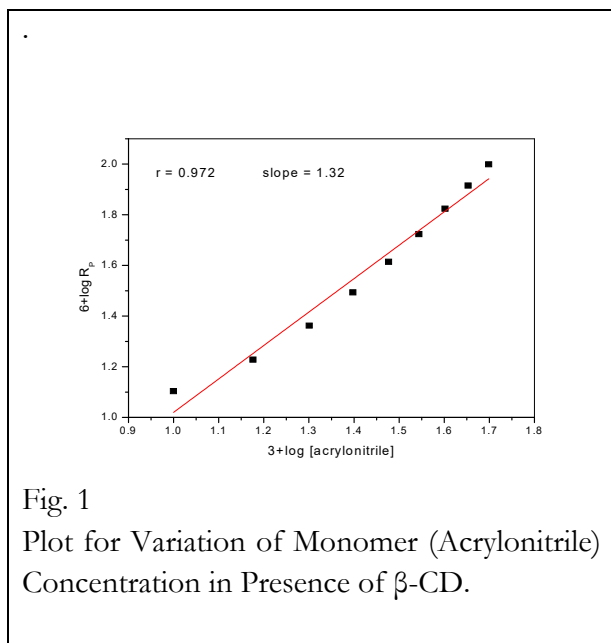
$[Ce(IV)] = 0.02 \text{ mol.dm}^{-3}$        $[LA] = 0.2 \text{ mol.dm}^{-3}$        $[H^+] = 5 \text{ mol.dm}^{-3}$   
 $[\beta\text{-CD}] = 0.02 \text{ mol.dm}^{-3}$       Temp. = 35°C      Time = 30 min.

[AN] mol.dm <sup>-3</sup>	3+log[AN]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
0.01	1	0.0242	12.695	1.1036	0.726
0.015	1.1761	0.0322	16.883	1.2274	0.966
0.02	1.301	0.0440	23.035	1.3623	1.32
0.025	1.3979	0.0595	31.149	1.4934	1.785
0.03	1.4771	0.0785	41.096	1.6138	2.355
0.035	1.5441	0.1010	52.875	1.7232	3.03
0.04	1.6021	0.1272	66.617	1.8235	3.816
0.045	1.6532	0.1570	82.192	1.9148	4.71
0.05	1.6989	0.1907	99.861	1.9993	5.721

Table:2 Effect of Monomer (Acrylonitrile) Conc. on Polymerization Rate in Absence of  $\beta$ -CD

$[Ce(IV)] = 0.02 \text{ mol.dm}^{-3}$        $[LA] = 0.2 \text{ mol.dm}^{-3}$        $[H^+] = 5 \text{ mol.dm}^{-3}$   
 Temp. = 35°C      Time = 30 min.

[AN]mol.dm <sup>-3</sup>	3+log[AN]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
0.01	1	0.0190	9.9517	0.9979	0.57
0.015	1.1761	0.0281	14.7333	1.1683	0.843
0.02	1.301	0.0396	20.7300	1.3166	1.188
0.025	1.3979	0.0531	27.8227	1.4444	1.593
0.03	1.4771	0.0669	35.0671	1.5449	2.007
0.035	1.5441	0.0843	44.1672	1.6457	2.529
0.04	1.6021	0.1038	54.3501	1.7352	3.114
0.045	1.6532	0.1240	64.9381	1.8125	3.72
0.05	1.6989	0.1556	81.4704	1.911	4.668



The rate of polymerization was studied by varying the concentration of monomer[AN] from 0.01 to 0.05M by keeping the concentration of [Ce(IV)], [LA], [H<sup>+</sup>] and [β-CD] as constant and their concentrations are 0.02 mol.dm<sup>-3</sup>, 0.2 mol.dm<sup>-3</sup>, 5.0 mol.dm<sup>-3</sup>, 0.2 mol.dm<sup>-3</sup> respectively. This study was carried out at a temperature 35°C for 30 min. time duration. In the presence of β-CD, the rate of polymerization (R<sub>p</sub>) was increased from 12.695 × 10<sup>6</sup> mol.dm<sup>-3</sup>.sec<sup>-1</sup> to 99.861 × 10<sup>6</sup> mol.dm<sup>-3</sup>.sec<sup>-1</sup> (Table 1) and in the absence of β-CD (R<sub>p</sub>) was increased from 9.9517 × 10<sup>6</sup> mol.dm<sup>-3</sup>.sec<sup>-1</sup> to 81.4704 × 10<sup>6</sup> mol.dm<sup>-3</sup>.sec<sup>-1</sup> (Table 2). The logarithmic plot of R<sub>p</sub> versus [acrylonitrile] the order of reaction ≈ 0.972 in the presence of β-CD (Fig. 1) and it is ≈ 0.989 in the absence of β-CD (Fig. 2) i.e., approximately equal to 1 with respect to monomer concentration may be described to a dependence of the initiation rate on monomer concentration[24]. In the presence of β-CD, R<sub>p</sub> and the percentage conversion of monomer into polymer was increased with the concentration of monomer (acrylonitrile) but in the absence of β-CD, the percentage of conversion of monomer was decreased.

B) Variation of Initiator

Table:3 Effect of Initiator Conc. on Polymerization Rate in Presence of β-CD

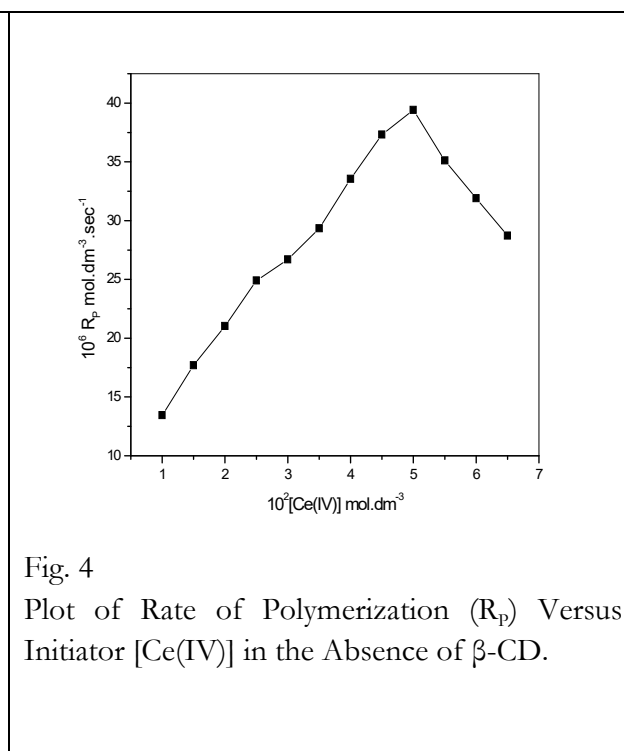
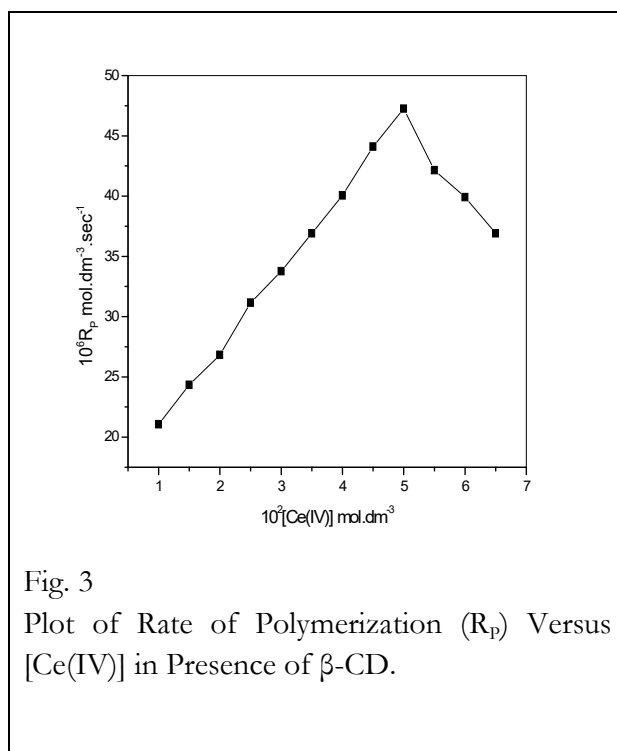
[AN] = 0.02 mol.dm<sup>-3</sup>                      [LA] = 0.2 mol.dm<sup>-3</sup>                      [H<sup>+</sup>] = 5 mol.dm<sup>-3</sup>  
 [β-CD] = 0.02 mol.dm<sup>-3</sup>                      Temp. = 35°C                      Time = 30 min.

10 <sup>2</sup> [Ce(IV)] mol.dm <sup>-3</sup>	3+log[Ce(IV)]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
1	1	0.0394	21.072	1.314	1.182
1.5	1.1761	0.0465	24.344	1.386	1.395
2	1.301	0.0524	26.830	1.439	1.572
2.5	1.3979	0.0595	31.149	1.493	1.785
3	1.4771	0.0645	33.766	1.528	1.935
3.5	1.5441	0.0705	36.908	1.567	2.115
4	1.6021	0.0765	40.049	1.603	2.295
4.5	1.6532	0.0842	44.106	1.644	2.526
5	1.6989	0.0881	47.247	1.664	2.643
5.5	1.7404	0.0805	42.143	1.625	2.415
6	1.7782	0.0762	39.918	1.601	2.286
6.5	1.8129	0.0705	36.908	1.567	2.115

Table:4 Effect of Initiator Conc. on Polymerization Rate in Absence of β-CD

[LA] = 0.2 mol.dm<sup>-3</sup>                      [AN] = 0.02 mol.dm<sup>-3</sup>                      [H<sup>+</sup>] = 5 mol.dm<sup>-3</sup>  
 Temp. = 35°C                      Time = 30 min.

10 <sup>2</sup> [Ce(IV)] mol.dm <sup>-3</sup>	3+log[Ce(IV)]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
1	1	0.0256	13.4400	1.1284	0.768
1.5	1.1761	0.0337	17.6893	1.2477	1.011
2	1.301	0.0417	21.0280	1.3227	1.251
2.5	1.3979	0.0475	24.8968	1.3961	1.425
3	1.4771	0.0510	26.6999	1.4265	1.53
3.5	1.5441	0.0560	29.3465	1.4675	1.68
4	1.6021	0.0641	33.5422	1.5255	1.923
4.5	1.6532	0.0712	37.3216	1.5719	2.136
5	1.6989	0.0752	39.4062	1.5955	2.256
5.5	1.7404	0.0670	35.1123	1.5454	2.01
6	1.7782	0.0609	31.8965	1.5037	1.827
6.5	1.8129	0.0548	28.7213	1.4582	1.644



The rate of polymerization was examined by varying the initiator concentration from  $1 \times 10^{-2}$  to  $6.5 \times 10^{-2}$  M by keeping concentration of monomer ( $[\text{AN}] = 0.02 \text{ mol.dm}^{-3}$ ), reductant ( $[\text{LA}] = 0.2 \text{ mol.dm}^{-3}$ ), acid ( $[\text{H}^+] = 5 \text{ mol.dm}^{-3}$ ) and cyclodextrin ( $[\beta\text{-CD}] = 0.02 \text{ mol.dm}^{-3}$ ) as constant at a temperature of  $35^\circ\text{C}$  both in the presence and in the absence of  $\beta$ -CD at constant temperature  $35^\circ\text{C}$  for 30 min. time duration. The rate of polymerization was greater in the presence of  $\beta$ -CD (Table 3) and which is lower in the absence of  $\beta$ -CD (Table 4). Initially, the rate of polymerization increases upto  $5 \times 10^{-2}$  concentration of  $\text{Ce(IV)}$  and it decreases as the concentration of  $\text{Ce(IV)}$  increases. This was shown by the plot of  $R_p$  versus  $[\text{Ce(IV)}]$  (Fig.3) and (Fig.4). This indicates that at high concentration, the oxidation and termination process increases. Same behavior has also been reported by Fernandez and Guzman et al[24].

### C) Variation of Reductant

The rate of polymerization was found out by varying the amount of reductant  $[\text{LA}]$  from 0.1M to 0.5 M by keeping the concentration of monomer ( $[\text{acrylonitrile}] = 0.02 \text{ M}$ ), initiator ( $[\text{Ce(IV)}] = 0.02 \text{ M}$ ), acid ( $[\text{H}^+] = 5 \text{ M}$ ) and cyclodextrin ( $[\beta\text{-CD}] = 0.02 \text{ M}$ ) as constant at constant temperature  $35^\circ\text{C}$  for 30 min. duration. The rate of polymerization increases with the increase in concentration of reductant. The rate of polymerization was increased from  $23.3184 \times 10^6 \text{ mol.dm}^{-3} \cdot \text{sec}^{-1}$  to  $52.3336 \times 10^6 \text{ mol.dm}^{-3} \cdot \text{sec}^{-1}$  in the presence of  $\beta$ -CD (Table 5) and which is lower i.e.,  $18.6895 \times 10^6 \text{ mol.dm}^{-3} \cdot \text{sec}^{-1}$  to  $43.274 \times 10^6 \text{ mol.dm}^{-3} \cdot \text{sec}^{-1}$  in the absence of  $\beta$ -CD (Table 6). This suggests that the presence of  $\beta$ -CD enhances the polymerization rate. The logarithmic plot of  $R_p$  versus  $[\text{LA}]$  shows that the order of reaction was nearly half (0.5) in the presence of  $\beta$ -CD (Fig.5) and (0.52) in the absence of  $\beta$ -CD (Fig.6). This indicates that the reaction may be initiated by primary radical with termination by the reaction of two growing polymer radicals.

Table:5 Effect of Reductant Conc. on Polymerization Rate in Presence of  $\beta$ -CD

$[Ce(IV)] = 0.02 \text{ mol.dm}^{-3}$        $[acrylic \text{ acid}] = 0.02 \text{ mol.dm}^{-3}$        $[H^+] = 5 \text{ mol.dm}^{-3}$   
 $[\beta\text{-CD}] = 0.02 \text{ mol.dm}^{-3}$       Temp. =  $35^\circ\text{C}$       Time = 30 min.

[LA] mol.dm <sup>-3</sup>	2+log[LA]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
0.1	1	0.0445	23.3184	1.3677	1.335
0.15	1.1761	0.0530	27.7642	1.4434	1.59
0.2	1.301	0.0598	31.3396	1.4960	1.794
0.25	1.3979	0.0684	35.8421	1.5543	2.052
0.3	1.4771	0.0727	38.0850	1.5807	2.181
0.35	1.5441	0.0805	42.1699	1.6250	2.415
0.4	1.6021	0.0848	44.4213	1.6475	2.544
0.45	1.6532	0.0927	48.5680	1.6863	2.781
0.5	1.6989	0.0999	52.3336	1.7187	2.997

Table:6 Effect of Reductant Conc. on Polymerization rate in the Absence of  $\beta$ -CD

$[Ce(IV)] = 0.02 \text{ mol.dm}^{-3}$        $[AN] = 0.02 \text{ mol.dm}^{-3}$        $[H^+] = 5 \text{ mol.dm}^{-3}$   
 Temp. =  $35^\circ\text{C}$       Time = 30 min.

[LA] mol.dm <sup>-3</sup>	2+log[LA]	Weight of polymer	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
0.1	1	0.0357	18.6895	1.2715	1.071
0.15	1.1761	0.0420	21.996	1.3423	1.26
0.2	1.301	0.0481	25.2183	1.4017	1.443
0.25	1.3979	0.0551	28.8751	1.4605	1.653
0.3	1.4771	0.0581	30.4225	1.4831	1.743
0.35	1.5441	0.0655	34.339	1.5357	1.965
0.4	1.6021	0.0720	37.7251	1.5766	2.16
0.45	1.6532	0.0758	39.6833	1.5986	2.274
0.5	1.6989	0.0826	43.274	1.6362	2.478

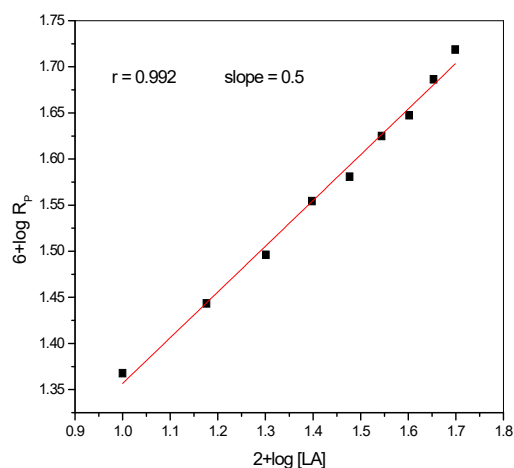


Fig. 5  
 Plot for Variation of Reductant [LA] Concentration in Presence of  $\beta$ -CD.

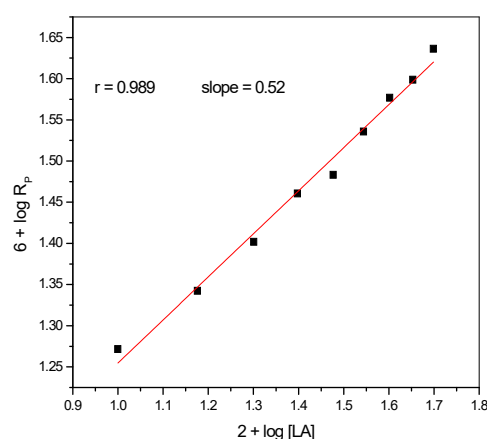


Fig. 6  
 Plot for Variation of Reductant [LA] Concentration in the Absence of  $\beta$ -CD

**D) Variation of Acid**

Table:7 Effect of Acid Conc. on Polymerization Rate in Presence of β-CD

[Ce(IV)] = 0.02 mol.dm<sup>-3</sup>      [LA] = 0.2 mol.dm<sup>-3</sup>      [AN] = 0.02 mol.dm<sup>-3</sup>  
 [β-CD] = 0.02 mol.dm<sup>-3</sup>      Temp. = 35°C      Time = 30 min.

[Acid] mol.dm <sup>-3</sup>	log[Acid]	Weight of polymer(g)	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
4.0	0.6021	0.0595	31.149	1.493	1.785
4.5	0.6532	0.0667	34.945	1.543	2.001
5.0	0.6989	0.0877	45.939	1.662	2.631
5.5	0.7404	0.1060	55.493	1.744	3.18
6.0	0.7782	0.1257	65.832	1.818	3.771
6.5	0.8129	0.1135	59.419	1.774	3.405
7.0	0.8451	0.0957	50.127	1.700	2.871
7.5	0.8751	0.0800	41.881	1.622	2.4
8.0	0.9031	0.0675	35.337	1.548	2.025

Table:8 Effect of Acid Conc. on Polymerization Rate in the Absence of β-CD

[Ce(IV)] = 0.02 mol.dm<sup>-3</sup>      [LA] = 0.2 mol.dm<sup>-3</sup>      [AN] = 0.02 mol.dm<sup>-3</sup>  
 Temp. = 35°C      Time = 30 min.

[Acid] mol.dm <sup>-3</sup>	log[Acid]	Weight of polymer(g)	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	% conversion
4.0	0.6021	0.0556	29.1462	1.4645	1.668
4.5	0.6532	0.0609	31.8965	1.5037	1.827
5.0	0.6989	0.0779	40.7998	1.6106	2.337
5.5	0.7404	0.0957	50.1123	1.6999	2.871
6.0	0.7782	0.1076	56.346	1.7508	3.228
6.5	0.8129	0.0967	50.6423	1.7045	2.901
7.0	0.8451	0.0798	41.8212	1.6213	2.394
7.5	0.8751	0.0673	35.264	1.5473	2.019
8.0	0.9031	0.0624	32.6725	1.5141	1.872

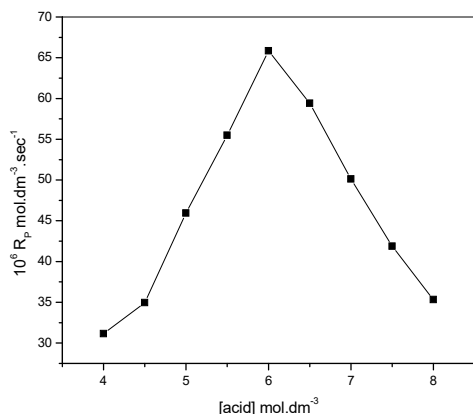


Fig. 7  
 Plot of Rate of Polymerization (R<sub>p</sub>) Versus [H<sup>+</sup>] in Presence of β-CD.

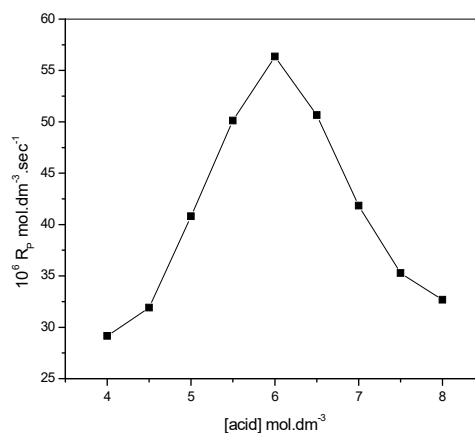


Fig. 8  
 Plot of Rate of Polymerization (R<sub>p</sub>) Versus [H<sup>+</sup>] in Absence of β-CD

The rate of polymerization ( $R_p$ ) was measured with different concentrations of sulphuric acid at constant temperature 35°C for 30 min. time duration with the above mentioned concentrations of other substances. The sulphuric acid concentration was changed from 4.0 to 8.0 mol.dm<sup>-3</sup>. It shows that, the rate of polymerization was increased from 4.0 to 6.0 M and it was decreased from 6.0 to 8.0 M both in the presence and in the absence of  $\beta$ -CD (Table 7) and (Table 8). Initially, at lower concentration the rate is increased and at higher concentration the rate is decreased. At lower concentration the reducing agent lactic acid may be deprotonated which prevents complexation, and it makes polymerization easy hence the  $R_p$  increases. But at higher concentration the complexation may be high and hence the  $R_p$  decreases. The same effect was reported for polymerization of acrylonitrile by by Fernandez and Guzman et al [24].

**E) Variation of Temperature**

Table:9 Effect of Reaction Temperature on Polymerization Rate in Presence of  $\beta$ -CD

[Ce(IV)] = 0.02 mol.dm<sup>-3</sup>                      [LA] = 0.2 mol.dm<sup>-3</sup>                      [AN] = 0.02 mol.dm<sup>-3</sup>  
 [β-CD] = 0.02 mol.dm<sup>-3</sup>                      [H<sup>+</sup>] = 5 mol.dm<sup>-3</sup>                      Time = 30 min.

Temperature K	Weight of polymer(g)	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	10 <sup>3</sup> /T K <sup>-1</sup>	8+log (R <sub>p</sub> /T)
303	0.0455	23.819	1.377	3.30	0.8954
308	0.0535	28.007	1.447	3.25	0.9587
313	0.0595	31.149	1.493	3.19	0.9979
318	0.0652	34.159	1.534	3.14	1.0310
323	0.0732	38.348	1.583	3.09	1.0745
328	0.0780	40.834	1.611	3.05	1.0951
333	0.0855	44.761	1.651	3.00	1.1284
338	0.0797	41.750	1.621	2.95	1.0917
343	0.0770	40.311	1.605	2.92	1.0701

Table:10 Effect of Reaction Temperature on Polymerization Rate in the Absence of  $\beta$ -CD

[Ce(IV)] = 0.02 mol.dm<sup>-3</sup>                      [LA] = 0.2 mol.dm<sup>-3</sup>                      [AN] = 0.02 mol.dm<sup>-3</sup>  
 Time = 30 min.                      [H<sup>+</sup>] = 5 mol.dm<sup>-3</sup>

Temperature K	Weight of polymer(g)	10 <sup>6</sup> R <sub>p</sub> mol.dm <sup>-3</sup> .sec <sup>-1</sup>	6+log R <sub>p</sub>	10 <sup>3</sup> /T K <sup>-1</sup>	8+log (R <sub>p</sub> /T)
303	0.0427	22.3666	1.3496	3.30	0.8681
308	0.0484	25.3863	1.4046	3.25	0.9160
313	0.0547	28.6483	1.4571	3.19	0.9615
318	0.0626	32.8202	1.5161	3.14	1.0137
323	0.0668	34.9967	1.5440	3.09	1.0348
328	0.0751	39.3332	1.5947	3.05	1.0788
333	0.0792	41.501	1.6180	3.00	1.0956
338	0.0732	38.3283	1.5835	2.95	1.0546
343	0.0694	36.342	1.5604	2.92	1.0251



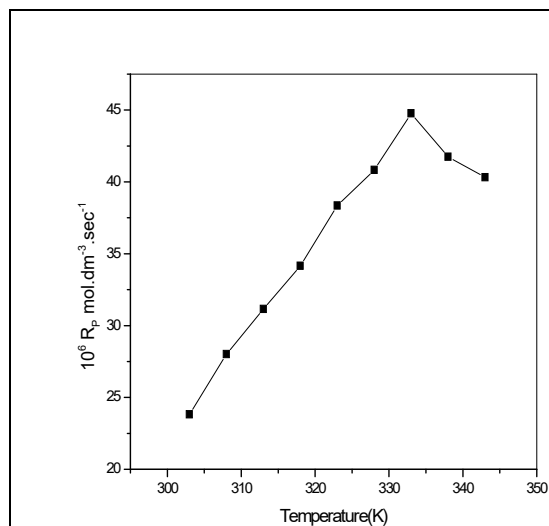


Fig. 9

Plot of Rate of Polymerization ( $R_p$ ) Versus Temperature in Presence of  $\beta$ -CD.

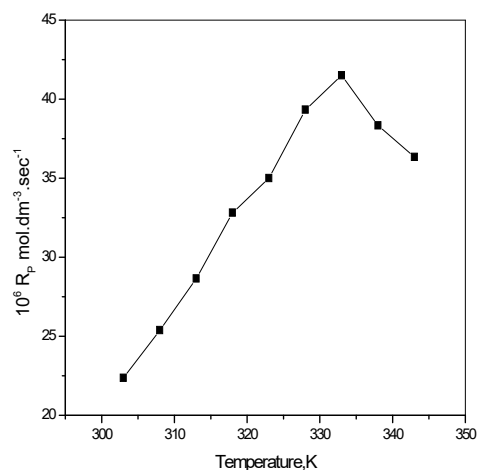


Fig. 10

Plot of Rate of Polymerization ( $R_p$ ) Versus Temperature in the Absence of  $\beta$ -CD

The rate of polymerization was measured by varying the temperature of the reaction from 303 to 348 K by keeping the concentration of monomer ( $[\text{acrylonitrile}] = 0.02 \text{ mol.dm}^{-3}$ ), substrate ( $[\text{LA}] = 0.2 \text{ mol.dm}^{-3}$ ), initiator ( $[\text{Ce(IV)}] = 0.02 \text{ mol.dm}^{-3}$ ), acid ( $[\text{H}^+] = 5 \text{ mol.dm}^{-3}$ ) and cyclodextrin ( $[\beta\text{-CD}] = 0.02 \text{ mol.dm}^{-3}$ ) as constant for 30 min. time duration (Table 9 &10). The increase in temperature increases the mobility of ions but at higher temperature the  $\beta$ -CD lost its structure. So there was restriction in the movement of ion which was found by the lowering in  $R_p$  value. But in the absence of  $\beta$ -CD there is regular increase in  $R_p$ . On comparing the rate of polymerization, in the absence of  $\beta$ -CD  $R_p$  decreases.

## IV. CONCLUSION

In all the runs,  $R_p$  is higher in presence of  $\beta$ -CD but which is lower in the absence of  $\beta$ -CD.  $R_p$  increases in the presence of  $\beta$ -CD because it is a host-guest molecule. Cyclodextrin is a separate entity which holds the monomer, oxidant and substrate in its cavity and therefore they are very close in solution state. The monomers are nearer to one another and enhance the polymerization rate.

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