Comparison study of rate of polymerisation of acrylic acid in the presence and in the absence of β- cyclodextrin in Ce(IV) – lactic acid redox system

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Abstract: **The rate of polymerization was studied under various conditions, by varying the concentration of monomer [acrylic acid], oxidant [Ce(IV)], reductant [LA], and sulphuric acid [H^+] in the presence and in the absence of β-cyclodextrin and the results were compared. The study was carried out at a temperature 35ºC for 30 min. duration of time. Temperature variation study was also carried out from 30ºC to 70ºC. As the temperature increases rate of polymerization R_P increases. Due to the presence of cavity in β-cyclodextrin the rate of polymerization increases. The cavity in β-cyclodextrin enhances the complexation of oxidant, reductant and monomer, etc. in this redox system.**

***KEYWORDS*: acrylic acid, redox system, β-cyclodextrin, cavity.**

INTRODUCTION

Chemical compound with one or more polymerizable structural units is identified as monomer. The monomer molecules are bonded together to form a macro size molecule (polymer) and this process is known as polymerization. The macromolecules consisting of same 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]. 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. Ce(IV) ion has been used for the oxidation of many organic compounds, 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. 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 β-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 both in the presence and in the absence of β-CD at 35ºC temperature for 30 min. 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, sulphuric acid, etc. were compared.

EXPERIMENTAL METHODOLOGY

The monomer acrylic acid 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 H_2SO_4 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. 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. 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 = wt.of polymer/ mol.wt.of monomer X 1000/vol.taken X 1/time in sec.

RESULT AND DISCUSSION

Variation of monomer

Table:1 Effect of monomer (acrylic acid) conc. on polymerization rate in presence of β-CD

Variation of monomer (acrylic acid) conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

[β-CD] = 0.2 mol.dm^{-3} Temp. = 35ºC Time = 30 min.

[Acrylic acid] mol.dm^{-3}	3+log[Acrylic acid]	Weight of polymer(g)	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	% conversion
0.01	1.0000	0.0208	8.0260	0.9045	0.624
0.015	1.1761	0.0327	12.6299	1.1014	0.981
0.02	1.3010	0.0490	18.9147	1.2768	1.47
0.025	1.3979	0.0700	27.0001	1.4313	2.1
0.03	1.4771	0.0959	36.9897	1.5680	2.877
0.035	1.5441	0.1259	48.5634	1.6863	3.777
0.04	1.6021	0.1544	59.5525	1.7749	4.632
0.045	1.6532	0.1887	72.7779	1.8620	5.661
0.05	1.6989	0.2318	89.3922	1.9513	6.954

Table:2 Effect of monomer (acrylic acid) conc. on polymerization rate in absence of β-CD

Variation of monomer conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

Temp. = 35ºC Time = 30 min.

[acrylic acid] mol.dm^{-3}	3+log[acrylic acid]	Weight of polymer	10^6 R_P mol.dm-^{3}.sec^{-1}	6+log R_p	% conversion
0.01	1.0000	0.0361	13.9347	1.1441	1.083
0.015	1.1761	0.0544	21.0038	1.3222	1.632
0.02	1.3010	0.0776	29.9290	1.4760	2.328
0.025	1.3979	0.0908	35.0192	1.5443	2.724
0.03	1.4771	0.1141	43.9946	1.6433	3.423
0.035	1.5441	0.1404	54.1432	1.7335	4.212
0.04	1.6021	0.1678	64.6841	1.8107	5.034
0.045	1.6532	0.1841	70.9788	1.8511	5.523
0.05	1.6989	0.2353	87.7168	1.9576	6.059

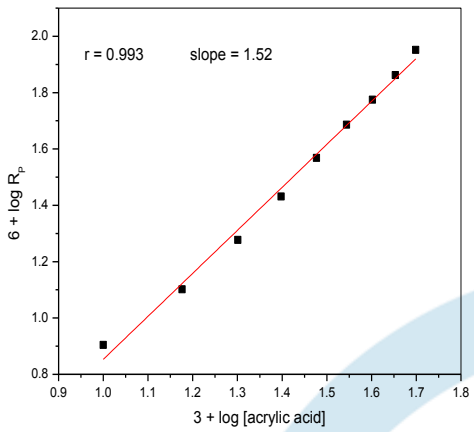

Figure : 1
Plot for variation of monomer (acrylic acid) concentration in presence of β-CD

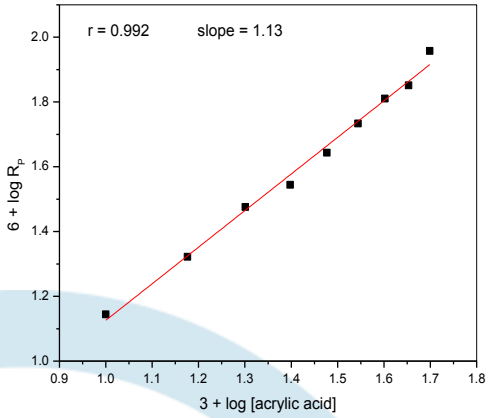

Figure : 2
Plot for variation of monomer (acrylic acid) concentration in the absence of β-CD

The rate of polymerization was studied by varying the concentration of monomer from 0.01 to 0.05M by keeping the concentration of [Ce(IV)], [LA], [H+] and [β-CD] as constant at a temperature 35ºC for 30 min. duration of time. In the presence of β-CD rate of polymerization (R_P) was increased from 8.0260 × 10^6 mol.dm^{-3}.sec^{-1} to 89.3922 × 10^6 mol.dm^{-3}.sec^{-1} (Table 1) and in the absence of β-CD (R_P) was increased from 13.9347 × 10^6 mol.dm^{-3}.sec^{-1} to 87.7168× 10^6 mol.dm^{-3}.sec^{-1} (Table 2). The logarithmic plot of R_P versus [acrylic acid] the order of reaction ≈ 0.993 in the presence of β-CD (Figure 1) and it is ≈ 0.992 in the absence of β-CD (Figure 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.[97] In the presence of β-CD, R_P and the percentage conversion of monomer into polymer was increased with the concentration of monomer (arylic acid) but in the absence of β-CD, the percentage of conversion of monomer was decreased.

Variation of initiator

Table:3 Effect of initiator conc. on polymerization rate in presence of β-CD

Variation of initiator conc.

[acrylic acid] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

[β-CD] = 0.2 mol.dm^{-3} Temp. = 35ºC Time = 30 min.

10^2[Ce(IV)] mol.dm^{-3}	3+log[Ce(IV)]	Weight of polymer	10^6 R_P mol.dm-^{3}.sec^{-1}	6+log R_P	% conversion
1	1.0000	0.0365	14.0929	1.1490	1.095
1.5	1.1761	0.0473	18.2463	1.2611	1.419
2	1.3010	0.0565	21.7972	1.3384	1.695
2.5	1.3979	0.0654	25.2133	1.4016	1.962
3	1.4771	0.0735	28.3466	1.4525	2.205
3.5	1.5441	0.0811	31.2653	1.4950	2.433
4	1.6021	0.0895	34.5120	1.5379	2.685
4.5	1.6532	0.1004	38.7123	1.5878	3.012
5	1.6989	0.1096	42.2642	1.6259	3.288
5.5	1.7404	0.0959	37.0051	1.5682	2.877
6	1.7782	0.0876	33.8041	1.5289	2.628
6.5	1.8129	0.0825	31.8197	1.5026	2.475

Table:4 Effect of initiator conc. on polymerization rate in absence of β-CD

Variation of initiator conc.

[LA] = 0.2 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

Temp. = 35ºC Time = 30 min.

10^2[Ce(IV)] mol.dm^{-3}	3+log[Ce(IV)]	Weight of polymer	10^6 R_P mol.dm-^{3}.sec^{-1}	6+log R_P	% conversion
1	1.0000	0.0340	13.1099	1.1176	1.02
1.5	1.1761	0.0427	16.4778	1.2169	1.281
2	1.3010	0.0491	18.9443	1.2774	1.473
2.5	1.3979	0.0569	21.9587	1.3416	1.707
3	1.4771	0.0639	24.6703	1.3921	1.917
3.5	1.5441	0.0706	27.2505	1.4353	2.118
4	1.6021	0.0784	30.2494	1.4807	2.352
4.5	1.6532	0.0860	33.1894	1.5210	2.58
5	1.6989	0.0988	38.0994	1.5575	2.964
5.5	1.7404	0.0873	33.6734	1.5272	2.619
6	1.7782	0.0788	30.4005	1.4828	2.364
6.5	1.8129	0.0726	27.9917	1.4470	2.178

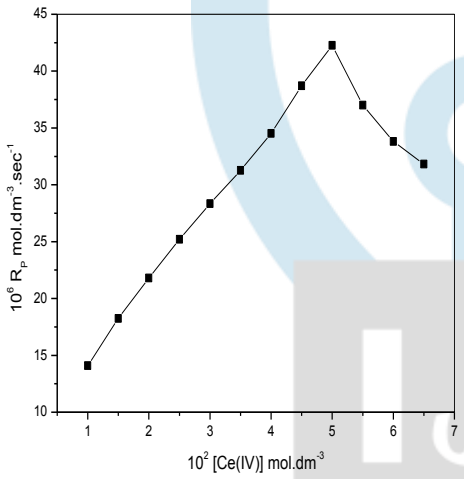

Figure : 3
Plot of rate of polymerization (R_P) versus [Ce(IV)] in presence of β-CD.

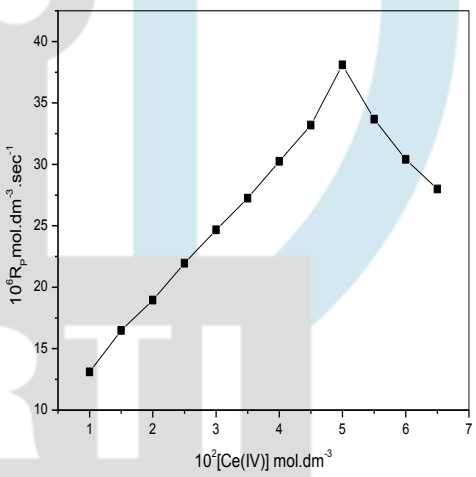

Figure : 4
Plot of rate of polymerization (R_P) versus initiator [Ce(IV)] in the absence of β-CD.

The rate of polymerization was measured by varying the initiator concentration from 1×10^{-2} to 6.5×10^{-2}M both in the presence and in the absence of β-CD at constant temperature 35ºC for 30 min. time duration. The rate of polymerization was greater in the presence of β-CD (Table 3) and which is lower in the absence of β-CD (Table 4). The rate of polymerization was increased from 1×10^{-2} to 5×10^{-2}M and after that R_P decreases. This is shown by the plot of R_P versus [Ce(IV)] (Figure 3) and (Figure 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].

Variation of reductant

The rate of polymerization was foundout with different concentrations of reductant [LA] from 0.1M to 0.5 M by keeping the concentration of monomer ([acrylic acid] = 0.02 M), initiator ([Ce(IV)] = 0.02 M), acid ([H^+] = 5 M) and cyclodextrin ([β-CD] = 0.02 M) as constant at constant temperature 35ºC for 30 min. duration. The rate of polymerization increases with the increase in concentration of reductant but R_P was greater in the presence of β-CD (Table 5) and which is lower in the absence of β-CD (Table

6). This suggests that the presence of β-CD enhances the polymerization rate. The logarithmic plot of R_P versus [LA] shows that the order of reaction was nearly half (0.602) in the presence of β-CD (Figure 5) and (0.592) in the absence of β-CD (Figure 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 β-CD

Variation of reductant conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

[β-CD] = 0.2 mol.dm^{-3} Temp. = 35ºC Time = 30 min.

[LA] mol.dm^{-3}	2+log[LA]	Weight of polymer	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	% conversion
0.1	1	0.0459	17.7128	1.2482	1.377
0.15	1.1761	0.0563	21.7326	1.3371	1.689
0.2	1.301	0.0648	25.0112	1.3981	1.944
0.25	1.3979	0.0777	29.9861	1.4769	2.331
0.3	1.4771	0.0841	32.4564	1.5113	2.523
0.35	1.5441	0.0950	36.6238	1.5637	2.85
0.4	1.6021	0.1008	38.8697	1.5896	3.024
0.45	1.6532	0.1113	42.9327	1.6327	3.339
0.5	1.6989	0.1209	46.6193	1.6685	3.627

Table:6 Effect of reductant conc. on polymerization rate in the absence of β-CD

Variation of reductant conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3} [H^+] = 5 mol.dm^{-3}

Temp. = 35ºC Time = 30 min.

[LA] mol.dm^{-3}	2+log[LA]	Weight of polymer	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	% conversion
0.1	1.0000	0.0424	16.3492	1.2134	1.272
0.15	1.1761	0.0509	19.6345	1.2930	1.527
0.2	1.3010	0.0616	23.7638	1.3759	1.848
0.25	1.3979	0.0700	26.9889	1.4311	2.1
0.3	1.4771	0.0772	29.7629	1.4736	2.316
0.35	1.5441	0.0844	32.5471	1.5125	2.532
0.4	1.6021	0.0911	35.1212	1.5455	2.733
0.45	1.6532	0.1022	39.4309	1.5958	3.066
0.5	1.6989	0.1103	42.5535	1.6289	3.309

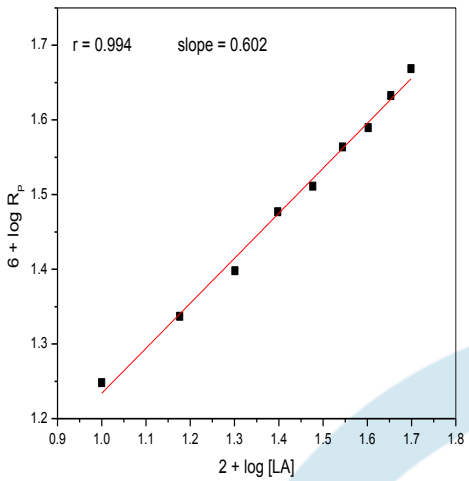

Figure : 5
Plot for variation of reductant [LA] concentration in presence of β-CD.

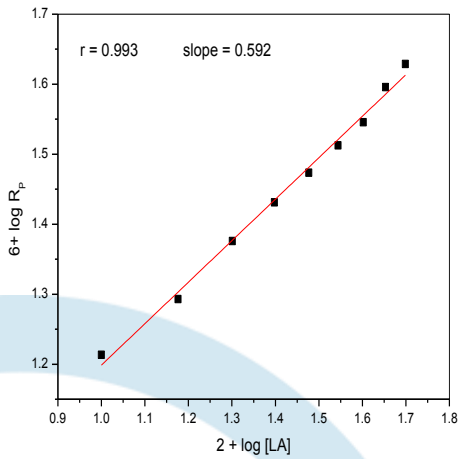

Figure : 6
Plot for variation of reductant [LA] concentration in the absence of β-CD

Variation of acid

Table:7 Effect of acid conc. on polymerization rate in presence of β-CD

Variation of sulphuric acid conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3}

[β-CD] = 0.2 mol.dm^{-3} Temp. = 35°C Time = 30 min.

[Acid] mol.dm^{-3}	log[Acid]	Weight of polymer(g)	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	% conversion
4.0	0.6021	0.0596	23.0020	1.3617	1.788
4.5	0.6532	0.0752	29.0214	1.4627	2.256
5.0	0.6989	0.1029	39.6831	1.5986	3.087
5.5	0.7404	0.1274	49.1329	1.6913	3.822
6.0	0.7782	0.1518	58.5329	1.7674	4.554
6.5	0.8129	0.1382	53.2846	1.7266	4.146
7.0	0.8451	0.1144	44.1085	1.6445	3.432
7.5	0.8751	0.0927	35.7500	1.5532	2.781
8.0	0.9031	0.0786	30.3114	1.4816	2.358

Table:8 Effect of acid conc. on polymerization rate in the absence of β-CD

Variation of sulphuric acid conc.

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3}

Temp. = 35ºC Time = 30 min.

[Acid] mol.dm^{-3}	log[Acid]	Weight of polymer(g)	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	% conversion
4.0	0.6021	0.0556	21.4458	1.3313	1.668
4.5	0.6532	0.0690	26.6237	1.4252	2.07
5.0	0.6989	0.0842	32.4653	1.5114	2.526
5.5	0.7404	0.1170	45.1372	1.6545	3.51
6.0	0.7782	0.1452	55.9723	1.7479	4.356
6.5	0.8129	0.1340	51.6578	1.7131	4.02
7.0	0.8451	0.1147	44.2313	1.6457	3.441
7.5	0.8751	0.0879	33.9045	1.5302	2.637
8.0	0.9031	0.0685	26.4263	1.4220	2.055

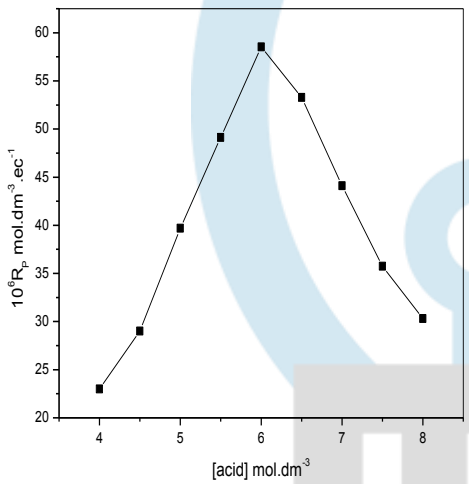

Figure : 7
Plot of rate of polymerization (R_P) versus [H^+] in presence of β-CD.

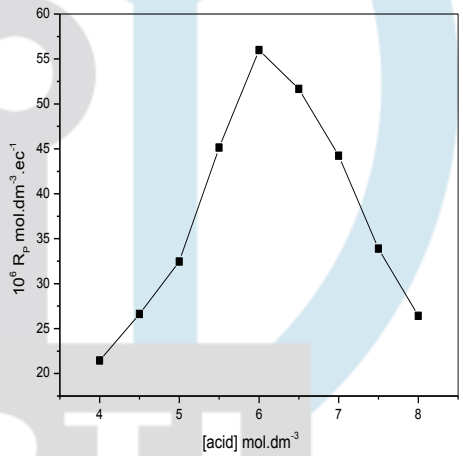

Figure : 8
Plot of rate of polymerization (R_P) versus [H+] in absence of β-CD

The rate of polymerization (R_P) was measured with different concentrations of sulphuric acid at constant temperature 35ºC for 30 min. time duration. The sulphuric acid concentration was changed from 4.0 to 8.0 mol.dm^{-3} (Table 46). It shows that, the rate of polymerization was increased from 4.0 to 6.0 mol.dm^{-3} and it was decreased from 6.0 to 8.0 mol.dm^{-3} both in the presence and in the absence of β-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 [24].

Variation of temperature

Table:9 Effect of reaction temperature on polymerization rate in presence of β-CD

Variation of reaction temperature

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3}

[β-CD] = 0.2 mol.dm^{-3} [H^+] = 5 mol.dm^{-3} Time = 30 min.

Temperature K	Weight of polymer(g)	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	10^3/T K^{-1}	8+log (R_P/T)
303	0.0506	19.5261	1.2906	3.30	0.8091
308	0.0596	22.9987	1.3617	3.25	0.8731
313	0.0684	26.4026	1.4216	3.19	0.9261
318	0.0765	29.5265	1.4702	3.14	0.9677
323	0.0907	34.9981	1.5440	3.09	1.0348
328	0.0985	37.9878	1.5796	3.05	1.0637
333	0.1074	41.4273	1.6172	3.00	1.0948
338	0.1000	38.5626	1.5861	2.95	1.0572
343	0.0933	35.9904	1.5561	2.92	1.0208
348	0.0879	33.8899	1.5300	2.87	0.9884

Table:10 Effect of reaction temperature on polymerization rate in the absence of β-CD

Variation of reaction temperature

[Ce(IV)] = 0.02 mol.dm^{-3} [LA] = 0.2 mol.dm^{-3} [acrylic acid] = 0.02 mol.dm^{-3}

Time = 30 min. [H^+] = 5 mol.dm^{-3}

Temperature K	Weight of polymer(g)	10^6 R_P mol.dm^{-3}.sec^{-1}	6+log R_P	10^3/T K^{-1}	8+log (R_P/T)
303	0.0446	17.1949	1.2354	3.30	0.7539
308	0.0498	19.2087	1.2835	3.25	0.7949
313	0.0573	22.0953	1.3443	3.19	0.8487
318	0.0650	25.0899	1.3995	3.14	0.8970
323	0.0711	27.4283	1.4382	3.09	0.9289
328	0.0771	29.7508	1.4735	3.05	0.9576
333	0.0858	33.1054	1.5199	3.00	0.9974
338	0.0745	28.7408	1.4585	2.95	0.9295
343	0.0702	27.0769	1.4326	2.92	0.8973
348	0.0678	26.1456	1.4174	2.87	0.8758

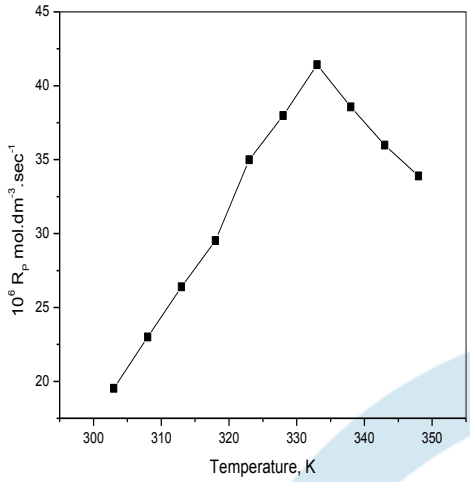

Figure : 9
Plot of rate of polymerization (R_P) versus temperature in presence of β-CD.

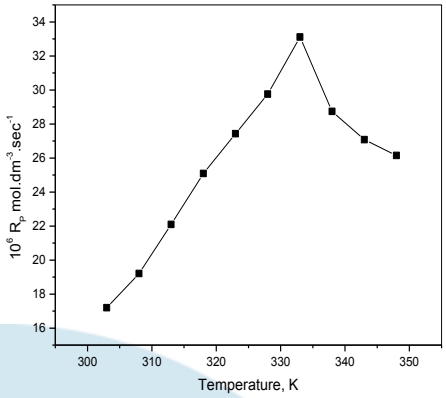

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Figure : 10
Plot of rate of polymerization (R_P) versus temperature in the absence of β-CD

The rate of polymerization was measured by varying the temperature of the reaction from 303 to 348 K by keeping the concentration of monomer ([acrylic acid] = 0.02 mol.dm^{-3}), substrate ([LA] = 0.2 mol.dm^{-3}), initiator ([Ce(IV)] = 0.02 mol.dm^{-3}), acid ([H^+] = 5 mol.dm^{-3}) and cyclodextrin ([β-CD] = 0.02 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 β-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 β-CD there is regular increase in R_P. On comparing the rate of polymerization, in the absence of β-CD R_P decreases.

CONCLUSION

In all the runs, R_P is higher in presence of β-CD but which is lower in the absence of β-CD. R_P increases in the presence of β-CD because it is a host-guest molecule. So it holds the monomer, oxidant and reductant in its cavity and enhances the polymerization rate.

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