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PHOTOPOLYMERIZATION OF METHYL METHACRYLATE IN AQUEOUS MEDIA VIA HOST-GUEST COMPLEXATION WITH Β-CYCLODEXTRIN

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***Abstract*—** Polymerization of hydrophobic vinyl monomer, Methyl methacrylate (MMA), was carried out by using dye, Pyronine- Y, as initiator, in homogeneous aqueous medium using β-cyclodextrin as solubilizer,in presence of citrate-phosphate buffer and ascorbic acid medium, leading to formation of poly methyl methacrylate. It is based on the use of at least stoichiometric amount of cyclodextrin , which shows the capacity of forming water soluble inclusion complexes of the monomer. The above process is compared with the polymerization of uncomplexed MMA in organic solvent medium. Comparison of different experimental conditions revealed that percentage conversion, rate of polymerization and molecular weight of polymers obtained by complexed MMA from homogeneous aqueous solution is higher than that of uncomplexed MMA produced from organic solvent. It was also shown that the kinetics of polymerization of complxed MMA is similar to those for classical polymerization in solution where rate of polymerization is proportional to the square root of initiator concentration. It is believed that hydrophobic inner cavity of cyclodextrin molecule is responsible to enclose smaller hydrophobic vinyl monomers to form host – guest complexes without any chemical modification. This inclusion phenomenon leads to significant changes in solution properties and reactivity of the guest molecule.

Keywords— Pyronine Y, ascorbic acid, , photo polymerization, cyclodextrin, host-guest complexes

I. INTRODUCTION

Cyclodextris are a family of cyclic oligosaccharides composed of 6(α), 7 (β), 8 (γ) units of (α-1, 4) linked glucopyranose that present a truncated cone formed with a hydrophobic central cavity and a hydrophilic outer surface [1-3]. These are formed by degradation of starch by amylases. The primary hydroxyl groups in 6 positions are located at the narrow side of the torus, whereas the secondary hydroxyl groups at the wider edges. The central cavity is lined by the skeletal carbons and ether oxygen of the glucose residues, which give it a hydrophobic character [4-5]. Due to above mentioned typical behaviour, cyclodextrins and their derivatives are able to form host-guest complexes with wide range of non-polar solid, liquid and gaseous molecules which can fit dimensionally into its cavity. No covalent bonds are formed or broken during formation of inclusion complexes [6]. The main driving force is the release of entropy rich water molecules from the cavity by hydrophobic guest molecules to attain an apolar - apolar association and decrease of cyclodextrin(CD) ring strain resulting in a more stable lower energy state. In addition to this, cyclodextrins are optically transparent above 300 nm, which make them ideal host molecule for studying photopolymerization of vinyl monomers. As a result of molecular complexation phenomena, CDs are widely used in many industrial products, technologies and analytical methods. The negligible cytotoxic effects of CDs are an important attribute in applications such as rug carrier, food and flavours, cosmetics, packing, textiles, separation processes, environment protection, fermentation and catalysis [7-8].

Our research work is focused on photopolymerization of Methyl methacrylate(MMA) in aqueous medium by complexation with β-cyclodextrin by using pyronine-Y as initiator. This polymerization process is compared with photopolymerization of MMA in absence of β-CD in ethanol solvent medium. In all experimental conditions, it is observed that percentage conversion and rate of polymerization of complexed MMA are higher than that of uncomplexed MMA. Synthetic dyes play an important role in polymerization, photo oxidation – reduction and photolysis reactions [9-10]. Initiation of polymerization in the presence of light with dyes and reducing agent systems has also been studied by various workers [11-14].In the present investigation, dye pyronine-y is taken as photo initiator in presence of ascorbic acid as a mild reducing agent which does not of course, reduce the dye in dark [15-16]. S. Lenka, P. L. Nayak and M. K. Mishra have reported the dye-sensitized photo-polymerization of ethyl acrylate by sodium fluoroscein –ascorbic acid system in aqueous solution, where they have studied the kinetics of the polymerization in the absence of cyclodextrin [17].

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Recently Ritter's research group has reported photo polymerization of N-isopropylacrylamide initiated by the complex of methylated β-CD /2-hydroxy-2-methyl phenylpropan-1-one in aqueous medium [18-20]. We expect this new approach of photo polymerization method will overcome problems associated with the efficiency, environmental safety issues in all photo initiating systems for different mode of activation.

II. EXPERIMENTAL

Methyl methacrylate, purchased from LOBA CHEME Pvt. LTD, was purified by washing with 5% NaOH solution and water; after drying over anhydrous Calcium chloride, it was distilled under reduced pressure and kept under nitrogen until use .Dye, pyronine-y and β-cyclodextrin were used as received from Himedia Laboratories, India. All other chemicals were commercially available products of analytical reagent grade. Water distilled over alkaline permanganate was deionised by passing it through a column of Bio deminrolit resin (Permutit Co. UK). Nitrogen gas was supplied by Indian Oxygen Ltd. .

β -cyclodextrin was dissolved in deionised water. The resulting solution was flushed with nitrogen for 15 minutes .Then, the monomer (MMA) was added and the resulting dispersion was stirred to give homogeneous host-guest solution. Then to the solutions of host-guest complexes of β-cyclodextrin – monomer, required amount of buffer solution, aqueous solution of ascorbic acid and pyronine-y dye were added under nitrogen atmosphere. The polymerization was carried out in pyrex 100ml flask equipped with gas inlet and outlet tubes in a nitrogen atmosphere. The reaction vessel was illuminated by a monochromatic light of 365 nm wavelength by placing a quartz filter in front of a 123 –w, high pressure mercuric lamp (Philip India Ltd.) connected through a constant voltage transformer. The precipitated polymer was filtered, washed repeatedly with water and dried in vacuum at 60^0c for 24 hours. The weight of polymer formed was taken gravimetrically. The rate of polymerization, percentage conversion of monomer and the intrinsic viscosity were calculated. After the collection of precipitated polymer, it was observed that, β-cyclodextrin stays in the solution and can be reused as host- molecule in presence of other guest hydrophobic vinyl monomer. The thermal degradation pattern of the polymer sample was studied using thermo gravimetric analyzer in nitrogen atmosphere.

III. RESULTS AND DISCUSSION

In the present investigation a systematic study of the kinetics of vinyl polymerization sensitized by initiator (Pyronine- Y)-reducing agent (ascorbic acid) systems, has been made to get a clear insight into various aspects. Methyl Methacrylate has been employed as the vinyl monomer. Kinetic study has been made by varying concentration of monomer, dye, ascorbic acid, time and temperature in presence and in absence of β-CD.As expected in presence of β-CD (80 – 90) % of the monomer had been converted (reaction 4-6 in table-1) which is much higher than that in absence of β-CD (reaction 1-3 in table-1). Also at a limiting concentration of initiator (reaction 1-3 in table-2) and ascorbic acid (reaction 4-6 in table-2), rate of polymerization and percentage conversion are high. The main role of β-CD in the polymerization is to aid the transport of monomer to the loci of polymerization. Thus, the acceleration phenomenon of the polymerization resulted from increasing the amount of β-CD in the reaction mixture may be related to the increasing concentration of MMA at the locus of polymerization. Analysis of polymers obtained showed that the kinetics of polymerization in homogeneous aqueous solution is similar to those for classical polymerization in solution where rate of polymerization is proportional to square root of initiator concentration as in figure.

1) Influence of β-cyclodextrin

Concentration of β-cyclodextrin has a significant effect on the percentage conversion and rate of polymerization. The result has been shown in figure-1.The percentage conversion increases up to 8.8105×10^{-2}M/L of β-CD concentration (table-1) , after which a decreasing trend was observed at a fixed monomer concentration of 0.4694 M/L as in fig. 1.

2) Influence of monomer concentration

During the study of percentage conversion of polymerization in various concentrations of monomer, it was observed that, percentage conversion increases up to 0.7041 M/L of Methyl methacrylate conc. and beyond that it decreases (table-1), irrespective of the absence (series-1) and presence of β-CD (series-2) as in figure - 2.Comparision of two polymerization processes revealed that presence of β-CD has profound effect on percentage conversion..

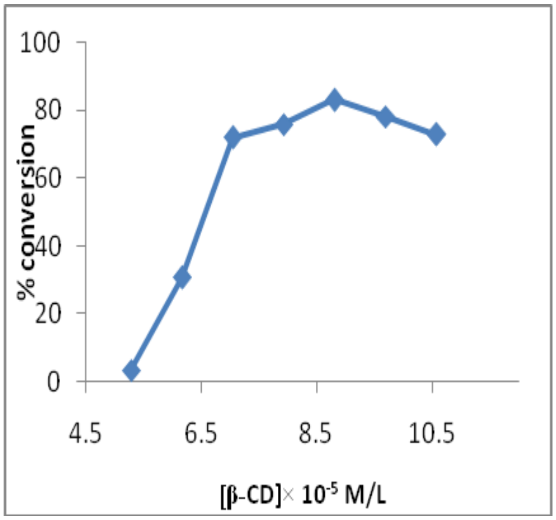

Figure-1 Graphical representation for variation of [β-CD]with percentage conversion

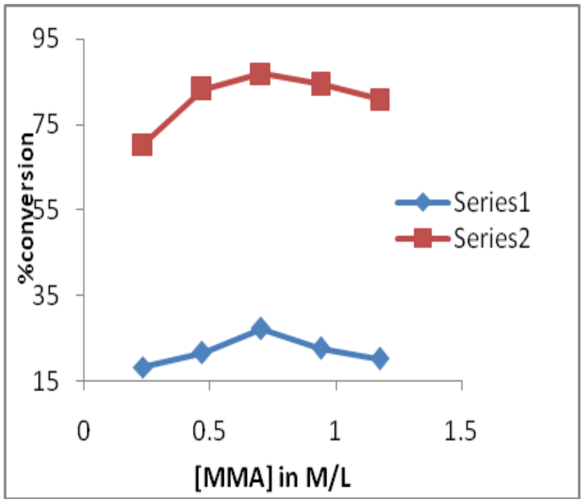

Figure-2 Graphical representation for variation of [MMA] on % conversion. Series 1(in absence of CD), Series2 (in presence of CD)

3) Influence of initiator-

The rate of polymerization at different concentrations of initiator (pyronine-y) was studied. Polymerization rate is highest at initiator concentration of 2 × 10^{-6} M/L as in figure-3 and table-2(reaction7-9). Series -1 represents polymerization in absence of β-CD and series -2 represents polymerization in presence of β-CD. From the graphs we know that polymerization in presence of β-CD gives a higher yield.

4) Influence of ascorbic acid concentration-

Influence of ascorbic acid concentration on the rate of polymerization was studied keeping other parameters constant. It was observed that at lower concentration that is below 0.5×10^{-2} M/L of ascorbic acid concentration, polymerization does not occur (fig-4).However, on increase of ascorbic acid concentration up to 1.0×10^{-2} M/L, the rate of polymerization increases and thereafter shows a decreasing trend(table-2). This trend is same where reaction occurs in absence of β-CD (series-1) or in presence of β-CD (series-2) as in figure-4. Cyclodextrin mediation of polymerization increases rate of polymerization.

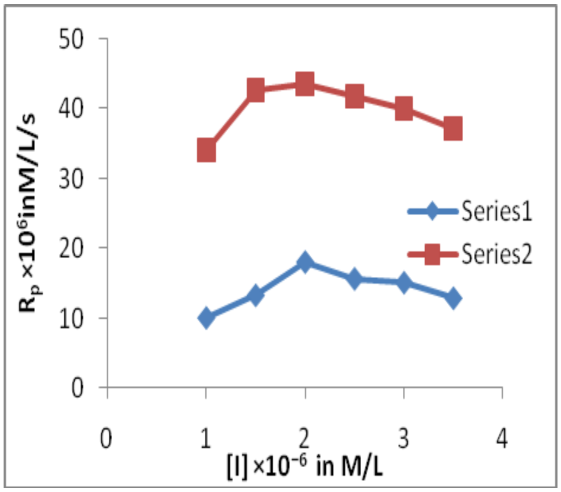

Figure-3 Graphical representation for variation of [pyronine-y] on rate of polymerization. Series1(in absence of β -CD), Series2(in presence of β- CD)

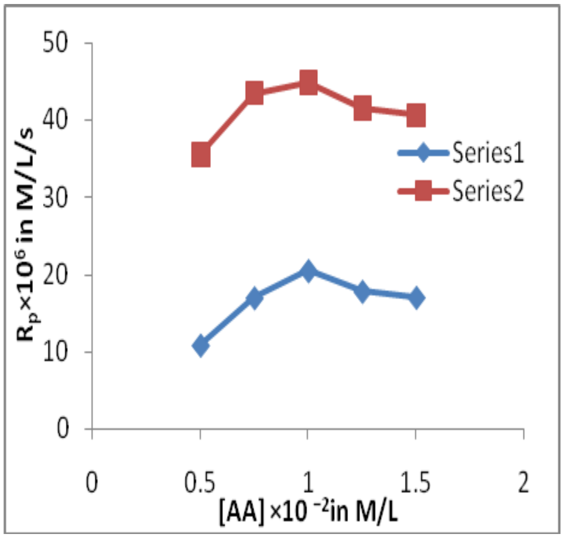

Figure-4 Graphical representation for variation of [Ascorbic acid] on rate of polymerization. Series1(in absence of β- CD), Series2(in presence of β- CD)

5) Influence of temperature-

At various temperatures, percentage conversion was studied keeping other additives constant. It was found to be increased up to 313K, beyond which a decreasing trend was observed (fig.5).

6) Influence of time

Time – conversion curves at a fixed concentration of monomer, initiator are shown in fig-6. It was found that, the percentage conversion of monomer into polymer increased up to 4 hours, after which a decreasing trend was observed. This trend is same for both uncomplexed (series-1) and complexed polymerization (series-2).

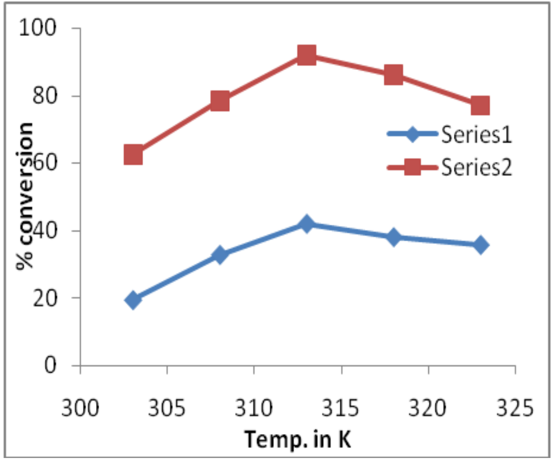

Figure - 5 Graphical representation for variation of temp on percentage conversion. Series-1(in absence of CD), Series-2 (in presence of CD)

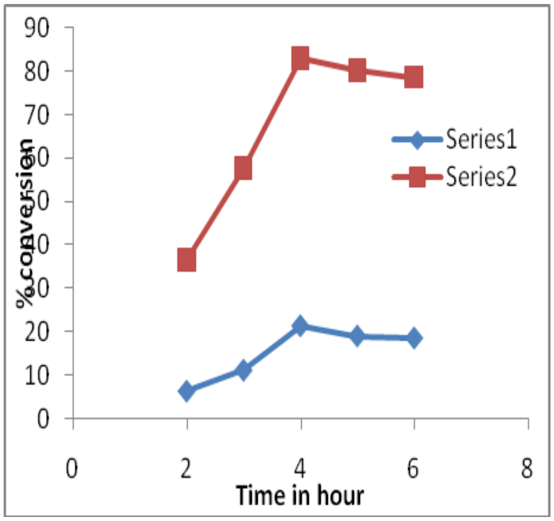

Figure - 6 Graphical representation for variation of time on percentage conversion. Series-1(in absence of CD), Series-2 (in presence of CD)

7) Influence of pH -

The rate of polymerization at different pH was studied. Polymerization rate is highest at pH-6 as in figure-7. Series -1 represents polymerization in absence of β-CD and series -2 represents polymerization in presence of β-CD. From graph it is evident that rate of polymerization is more in presence of cyclodextrin.

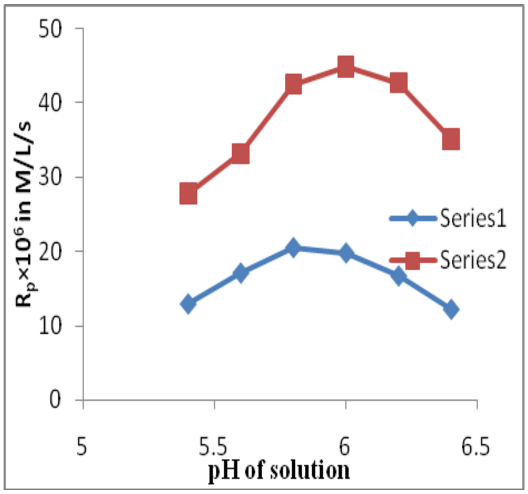

Figure -7 Graphical representation for variation of pH on rate of polymerization. Series1(in absence of CD), Series2 (in presence of CD)

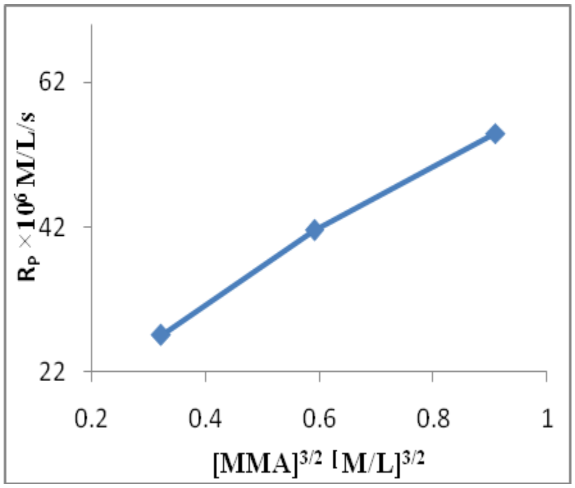

Figure - 8 Plot of $[MMA]^{3/2}$ versus rate of polymerization for polymerization

Table-1 The results of polymerization for variable concentrations of MMA & β-CD (4 hours at 40^0C).

Reaction	Conc. of β-CD×10^{-5} in M/L	Conc. of Monomer in M/L	Solvent	Percentage conversion	$R_p \times 10^6$M/L/S
1	0	0.4694	Ethanol	21.4680	6.9985
2	0	0.7041	Ethanol	27.1914	13.2965
3	0	0.9388	Ethanol	22.6753	14.7843
4	7.9295	0.4694	Water	75.7765	24.7029
5	8.8105	0.4694	Water	83.0638	27.0786
6	9.6916	0.4694	Water	78.2021	25.4937

The conc. of initiator is 1.5× 10^{-6} M/L for reaction 1-3 and 2 × 10^{-6} M/L for reaction 4-6. The conc. of Ascorbic acid is 0.75× 10^{-2} M/L for reaction 1-3 and 1 × 10^{-2} M/L for reaction 4-6.

Table-2 The results of polymerization for variable concentrations of Initiator & Ascorbic acid (4 hours at 40^{0}C).

Reaction	[I] ×10^{-6} M/L	[AA]×10^{-2} M/L	% conversion	R_p× 10^6 M/L/s
7	1.5	0.75	86.9290	42.5080
8	2.0	0.75	88.9007	43.4721
9	2.5	0.75	85.2411	41.6826
10	2	0.75	88.9007	43.4721
11	2	1.0	91.7659	44.8732
12	2	1.25	84.8085	41.4710

The concentration of MMA is 0.7041 M/L and conc. of β-CD is 8.8105×10^{-5} M/L in all above reactions.

IV. GRAPHICAL REPRESENTATION OF KINETICS OF POLYMERIZATION

The rate equation for steady state kinetics of polymerization is represented as below. It signify that graph of [monomer]$^{3/2}$ ~ Rate of polymerization , [AA]$^{1/2}$~ Rate of polymerization and [I] ^{½} ~ Rate of polymerization must be a straight line . This is verified from figure 8,9,10 respectively.

$$R_p = \frac{k_p}{k_t^{½}} \left\{ \frac{k_i\, k_r\, k_E\, K[AA]\, I}{k_6\, k_7} \right\}^{½} [M]^{3/2}$$

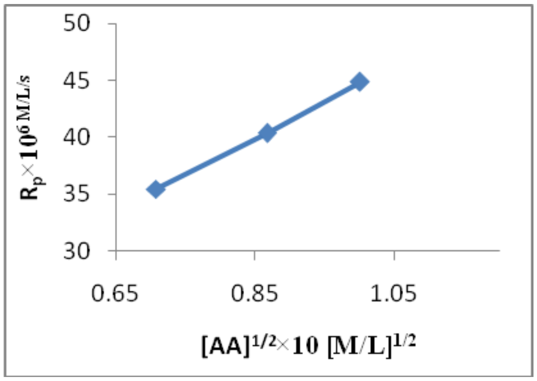

Figure - 9 Plot of [AA]$^{1/2}$ versus rate of polymerization

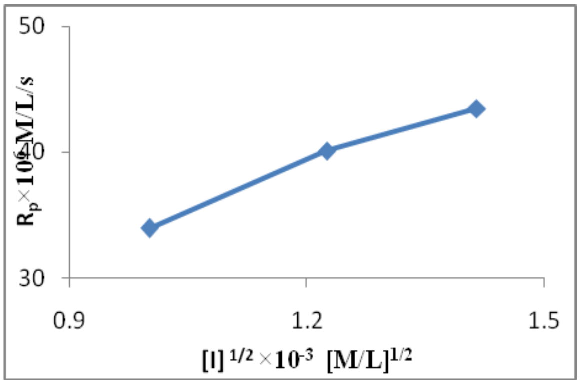

Figure - 10 Plot of [I]$^{1/2}$ versus rate of polymerization

V. DETERMINATION OF MOLECULAR WEIGHT

Molecular weight of polymer is determined by intrinsic viscosity method by double extrapolation plots of reduced viscobity and inherent viscosity against concentration of polymer samples by Mark – Houwink equation [η] = K M^a where [η] is intrinsic viscosity and M is molecular weight of polymer.

From the graphs [η] values are known. [η] = 1.27 and 1.3 for two samples of PMMA synthesized in absence of β-CD . Molecular weight of these two polymer samples are 10.68×10^5 and 10.95×10^5 respectively. [η] = 1.65 and 1.78 for two polymer samples when prepared in presence of β-CD . Molecular weight of these two polymer samples are 15.38 ×10^5 and 17.15×10^5 respecyively. From above experimental finding , we know that molecular weight of polymer synthesized in presence of β-CD in homogeneous aqueous medium is more. The result of thermo gravimetric analysis shows that, polymer sample is stable at 580^{0}c.

VI. CONCLUSION

From above experimental findings it is concluded that β-Cyclodextrin provides a better environment for homogeneous aqueous polymerization , which is a ecofriendly medium that replaces organic solvents for polymerization of water insoluble acrylate monomers . A comparative kinetic study of polymerization reactions initiated with both complexed and uncomplexed photoinitiator revealed a higher polymerization rate and better polymerization yield in the presence of CD/ photoinitiator complex . Aqueous solution of β-cyclodextrin is also capable of isolating the pollutants present in the monomer and other additives. Using CDs can also lead to surfactant free polymerization. Molecular weight of polymers are also more in presence of β-cyclodextrin those have higher fibre drawability and strength. Photopolymerization is an important area of polymer science from both industrial and academic perspectives. Developments in this field are rapidly reflected in the uv curing technology which encompasss a wide range of use in both high volume applications such as coatings, adhesives and printing inks as well as advanced high-technology purposes such as micro-electronics , photo and stereo-lithography and holographic data storage media. We expect this new path way of photopolymerization will find wider applications in near future.Polymerization with defferent CD derivatives can be done with different monomers , initiators.

VII. ACKNOWLEDGEMENT

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