Photo Polymerization of Host-Guest Complexes of B-Cyclodextrin / Butyl Acrylate in Aqueous Solution, Kinetics And Mechanism

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Abstract: *The Photo polymerization of β-cyclodextrin host–guest complexes of Butyl acrylate sensitized by Fluoroscein sodium in homogeneous aqueous medium has been studied. The polymerization was carried out in presence of citrate – phosphate buffer and ascorbic acid medium, leading to the formation of poly (Butyl acrylate). The effect of change of monomer concentration, dye concentration, time and temperature, on the rate of polymerization was studied. The system was irradiated with UV-light of 365 nm wavelength. The rate of polymerization was measured gravimetrically and molecular mass of polymer by viscometric method. The polymerization was also carried out with uncomplexed monomer and in the presence of organic solvents. The rate of polymerization, the viscosity and the molecular mass of polymer obtained from β-cyclodextrin complexed monomer was found to be higher in comparison to the polymer obtained from uncomplexed monomer. Thermal degradation pattern of the polymer sample was studied by thermo gravimetric analysis. The mechanism of polymerization and kinetic scheme proposed was examined in the light of the experimental results.*

Keywords : *Ascorbic acid, Fluoroscein sodium, citrate-phosphate buffer, cyclodextrin, host-guest complexes.*

I. Introduction

Photo polymerization is applied generally to a variety of processes, which results in the conversion of smaller molecules into larger ones in a photochemical primary step or in a photo activated process [1-4]. Photo induced vinyl addition polymerization results in the formation of high molecular weight polymer material in the imaged area [5]. The unexposed area will consist primarily of unconverted monomeric material. Photo polymerization has been the subject of increasing interest because of their widespread applications in coating, printing ink and adhesives [6-11]. This technology is based on the use of photo initiator systems suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species, which are able to initiate polymerization. The sensitization of vinyl polymerization requires presence of suitable dyes as primary absorber of radiation [12-13]. In photo polymerization, photo reducible and photo oxidizable dye sensitization can be possible. In 1954, Oster [14] reported the first documentation of a dye-sensitized photo redox system.

The demand for environmentally benign processes is growing, as the world becomes increasingly aware of environmental issues involving conventional organic solvents. In an effort to encourage pollution prevention, the research is directed to promote the design of environmentally benign processes that minimize or eliminate the use of toxic substances, such as, organic solvents and reagents. The reaction in aqueous solution is a highly effective approach to use water, instead of organic solvents.

In recent years, cyclodextrins and their derivatives have played a major role in the field of polymer synthesis. Because, cyclodextrin and their derivatives are able to form host-guest complexes between two or more molecules, which are not covalently bonded with each other [15-16]. Cyclodextrin are natural products, which can be obtained from starch. These are cyclic oligoamyloses, consisting of 6(α), 7(β), 8(γ) or 9(δ) units of 1-4 linked glucose. They exhibit a torus shaped structure with a hydrophobic cavity and a hydrophilic outer surface [17].Hence, all those cyclodextrins and their derivatives are used as host molecules, which can trap acrylate monomers into their cavit. Therefore , hydrophobic acrylate monomers, such as methyl methacrylate and butyl acrylate becomes water soluble, when treated with aqueous solution of cyclodextrin and their derivatives, without forming covalent bonds during host-guest interactions and also without making any change in the chemical composition of the guest molecules [18-20]. During polymerization, cyclodextrin slipped off step by step from the growing chain and the polymer precipitated in high yield, while cyclodextrin remained in the aqueous phase. The unthreaded cyclodextrin is soluble in water and thus can be reused to entrap new monomer [21-22]. Synthetic dyes play an important role in polymerization, photo oxidation – reduction and photolysis reactions [23-24]. There have been earlier reports in the literature of vinyl photo polymerization sensitized by dyes. Initiation of polymerization in the presence of light with dyes and reducing agent systems has been studied by various workers.

Fluoroscein sodium is used for photo polymerization if an electron donor or reducing agent for the light-excited dye is present. Here, ascorbic acid, a mild reducing agent is used for electron donor, which does

not of course, reduce the dye in dark [25]. 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. 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 [26-28]. Thus, the present communication includes the result of β-cyclodextrin mediated photo polymerization of Butyl acrylate sensitized by fluoroscein sodium – ascorbic acid system in homogenious aqueous medium.

II. Experimental

Butyl acrylate 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. Fluoroscein sodium 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. .B-cyclodextrin was dissolved in deionised water. The resulting solution was flushed with nitrogen for 15 minutes .Then, the monomer 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 fluoroscein sodium dye were added under nitrogen atmosphere. The buffer solution of citrate-phosphate having PH=6 was prepared previously. 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

The host-guest complexes of β-cyclodextrin and butyl acrylate were photo polymerized in aqueous solution at 40^oc sensitized by fluoroscein sodium –ascorbic acid and in presence of citrate – phosphate buffer having pH=6.0. Preliminary experiments revealed that a reducing agent, such as, ascorbic acid was necessary for polymerization, that the fluoroscein sodium alone could not initiate. Polymerization also does not occur in the absence of buffer. It was also observed that, the polymerization does not occur at lower and higher pH value, but gives good result at Ph = 6.0. Thus, a reducing agent- buffer system was necessary for initiation of the polymerization and the dye – ascorbic acid –buffer was a more efficient initiator system.

3.1 Influence of β-cyclodextrin –

In the present investigation a systematic study of the kinetics of vinyl polymerization sensitized by dye (fluoroscein sodium) - reducing agent (ascorbic acid) systems, has been made to get a clear insight into various aspects. 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 the rate of polymerization and percentage conversion are found to be increased more than two fold when compared the polymerization of complexed Butyl acrylate with uncomplexed Butyl acrylate (table-1). It is observed that percentage conversion of polymerization is highest at β-CD concentration of 8.8105×10^{-5} mol/lit. while other parameters are constant as in fig 1.

 3.2 Influence of time-

A typical set of time ~ Rate of polymerization curve at a fixed concentration of monomer, dye and ascorbic acid is shown in fig 2.The rate of polymerization   increases up to 4 hours, beyond which a decreasing trend was noticed. This trend is similar for complexed and uncomplexed monomer.
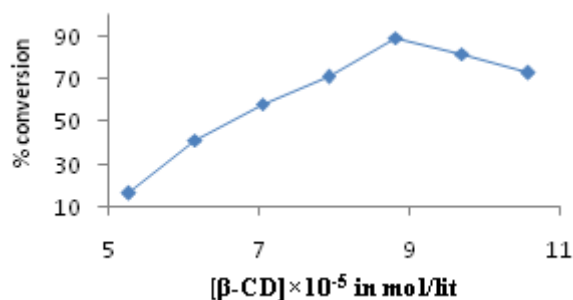
Fig.1 Graphical representation for effect of [β-CD]on percentage conversion
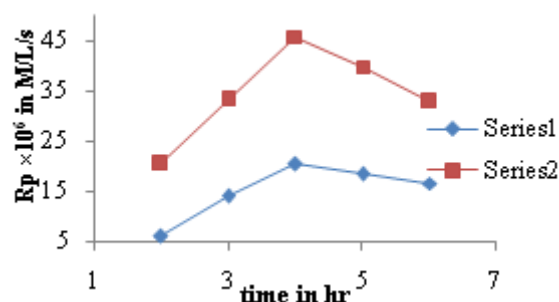

Fig.- 2 Effect of time on rate of polymerization . Series1 (absence of β-CD),Series2 (presence of β-CD).

3.3 Influence of monomer concentration-

During the study of percentage conversion of polymerization in various concentrations of monomer, it was observed that , the rate of polymerization increases up to 0.7021 M/L of Butyl acrylate and beyond that it decreases, irrespective of the presence and absence of β-CD/organic solvent as in fig 3 and table-1. A plot of rate of polymerization versus [Butyl acrylate] is found to be linear (fig 4), which satisfies the mechanism and indicate that the termination was the mutual type.
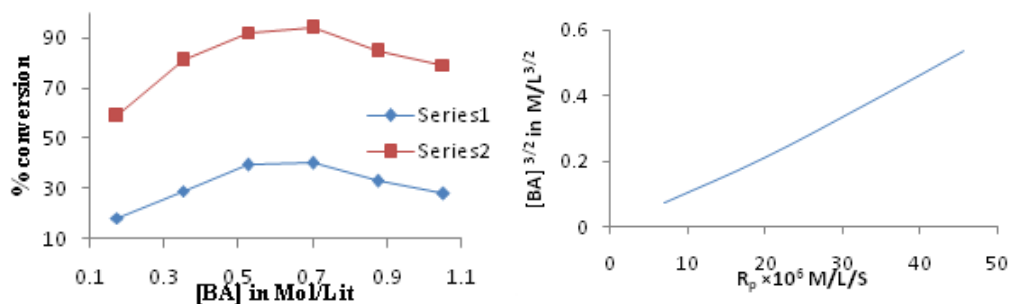

Fig-3 Effect of [BA] on percent conversion.Series-1 (in absence of β - CD) Series-2 (in presence of β-CD).
Fig-4 Plot of $[BA]^{3/2}$ versus rate of polymerization

3.4 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. However, on increase of ascorbic acid concentration up to 1.25×10^{-2} M/L, the rate of polymerization increases and thereafter shows a decreasing trend fig 5. The plot of R_p verses $[AA]^{1/2}$ is linear, which satisfies the mechanism. It is represented in fig 6.
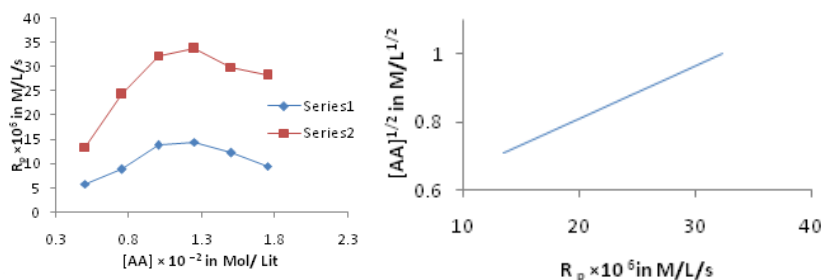
Fig-5 Variation of [AA] on rate of polymerization. Series 1(absence of β-CD), series 2(presence of β-CD)   Fig 6 Plot of [AA]$^{1/2}$ versus rate of polymerization.

3.5 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.7). Taking three different temperatures within the range between 35°c and 45°c , the overall energy of activation was computed from the corresponding Arrhenius plot (fig.8) and found to be 6.46 K.cal/mol.
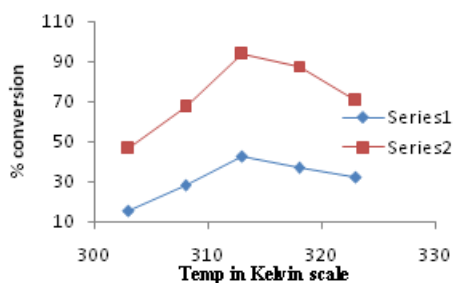

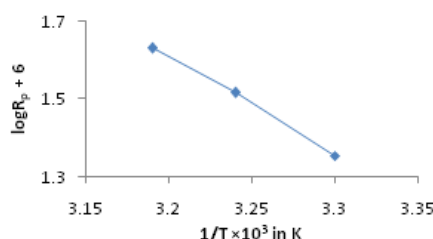**Fig-7** Variation of temp on percent conversion. Series 1(in absence of CD)Series2 (in presence of CD)

Fig -8 Schematic Arrhenious plot for calculation of Activation Energy.

Table-1

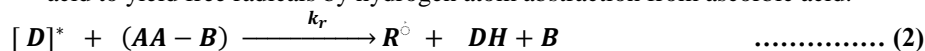| Reaction	Conc. Of β-CD×10^{-5} in Mol/Lit.	Conc. Of Butyl acrylate	Percentage conversion	$R_P×10^6$M/L/s
1	0	0.5266	39.6592	14.5043
2	0	0.7021	40.3111	19.6570
3	0	0.8771	32.9822	20.1040
4	7.9295	0.5266	71.2148	26.0450
5	8.8105	0.5266	89.4518	32.7147
6	9.6916	0.5266	81.7703	29.9054

IV.   Mechanisms

The scheme involves the excitation of the dye in the primary photo chemical act followed by the interaction of the excited dye with the complex, formed between Na_2HPO_4 of the buffer   (Na_2HPO_4 –citric acid) and ascorbic acid , to produce free radicals either rby electron transfer mechanism or by hydrogen atom abstraction from the ascorbic acid.

i. The first step involves the excitation of the dye into triplet state on absorption of incident light of intensity , I .

$$D \xrightarrow[\quad k_\epsilon \quad I \quad]{\quad h\gamma \quad} {}^3[D]^* \qquad \text{............ (1)}$$

Here , D = Dye Fluoroscein sodium . ^{3}[D] * is triplet state of dye.

ii. The excited dye then interacts with the complex (AA-B) formed between Na_2HPO_4 of the buffer and ascorbic acid to yield free radicals by hydrogen atom abstraction from ascorbic acid.

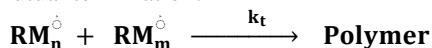$$[D]^* \ + \ (AA - B) \xrightarrow{k_r} R^{\circ} \ + \ DH + B \qquad\qquad …………… (2)$$

iii. Initiation of polymerization.

$$R^{\circ} \ + \ M \xrightarrow{k_i} RM^{\circ} \qquad\qquad …………… (3)$$

iv. Propagation.

$$RM^{\circ} \ + \ M \xrightarrow{k_p} RM_1^{\circ}$$

$$RM_{n-1}^{\circ} \ + \ M \xrightarrow{k_p} RM_n^{\circ} \qquad\qquad …………… (4)$$

v. Termination.

a) Mutual termination:

$$RM_n^{\circ} \ + \ RM_m^{\circ} \xrightarrow{k_t} Polymer$$

b) Termination by primary radical, R$^.$:

$$RM_n^{\circ} \ + \ R^{\circ} \xrightarrow{k_{t_1}} Polymer \qquad\qquad …………… (5)$$

c) Termination by dye (D) itself:

$$RM_n^{\circ} \ + \ D \xrightarrow{k_{t_2}} Polymer \qquad\qquad ……………. (6)$$

d) Deactivation of R$^{\circ}$ to give stable products.

$$R^{\circ} \xrightarrow{k_6} S \qquad\qquad …………… (7)$$

e) The excited dye may lose its extra energy by fluorescence and return to the ground states:

$$D^* \xrightarrow{k_7} D \qquad\qquad …………….. (8)$$
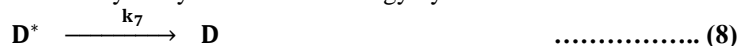
Considering the usual assumption that steady – state principle holds good for radicals or radical chains and that the rate constants for propagations and termination are independent of chain length, the rate expressions for various terminations cited above have been derived.

$$\text{Hence,} \quad \frac{d\left[R^{\circ} \right]}{dt} = 0 \quad \text{and} \quad \frac{d\left[RM_n^{\circ} \right]}{dt} = 0 \qquad\qquad …………… (9)$$

Where, R$^{\circ}$ is the primary radical and RM_n° denotes the radical chain.
Assuming the termination by mutual combination of the growing chain radicals

$$\frac{d\left[R^{\circ} \right]}{dt} = k_r[D^*][AA - B] - k_i[R^{\circ}][M] - k_6[R^{\circ}] = 0$$

$$\therefore \ k_r[D^*][AA - B] = k_i[R^{\circ}][M] + k_6[R^{\circ}]$$

$$= [R^{\circ}](k_i[M] + k_6)$$

$$\text{or,} \qquad [R^{\circ}] = \frac{k_r[D^*][AA - B]}{k_i[M] + k_6} \qquad\qquad …..……..(10)$$

$$\frac{d[D^*]}{dt} = k_{\in} I - k_r[AA - B][D^*] - k_7[D^*] = 0$$

$$\text{or,} \quad [D^*] = \frac{k_{\in} I}{(k_r[AA - B] + k_7)} \qquad\qquad …..……..(11)$$

Substituting equation (11) in equation (10), we get,

$$[R^{\circ}] = \frac{k_r \, k_{\in} \, I [AA - B]}{(k_r[AA - B] + k_7)(k_i[M] + k_6)} \qquad\qquad …..…….. (12)$$

$$\frac{d\left(RM_n^{\circ} \right)}{dt} = k_i[R^{\circ}][M] - k_t\left[RM_n^{\circ} \right]^2 = 0$$

$$\text{or} \quad \left[RM_n^{\circ} \right] = \left\{ \frac{k_i[R^{\circ}][M]}{k_t} \right\}^{1/2} \qquad\qquad ………… (13)$$

Substituting equation (12) in equation (13),

$$\left[RM_n^{\circ}\right] = \left\{\frac{k_i\, k_r\, k_{\in}\, I[AA-B][M]}{k_t\, (k_r[AA-B] + k_7)\, (k_i\,[M] + k_6)}\right\}^{1/2} \qquad \text{…………. (14)}$$

$$R_P = -\frac{d\,[M]}{dt} = k_P\left[RM_n^{\circ}\right][M]$$

On substituting equation (14) in the above equation,

$$R_P = -\frac{d\,[M]}{dt} = k_P\left\{\frac{k_i\, k_r\, k_{\in}\, I[AA-B][M]}{k_t\, (k_r[AA-B] + k_7)\, (k_i\,[M] + k_6)}\right\}^{1/2}[M] \qquad \text{…….……. (15)}$$

Or,

$$R_P = \frac{k_p}{k_t^{1/2}}\left\{\frac{k_i\, k_r\, k_{\in}\, I[AA-B]}{(k_r[AA-B] + k_7)\, (k_i\,[M] + k_6)}\right\}^{1/2}[M]^{3/2} \qquad \text{……….……. (16)}$$

Assuming that, (a) only a fraction of radicals produced are utilized for the polymerization i.e., $k_1\,[M] \ll k_6$ and also, (b) that most of the excited dye molecules are deactivated and only a portion of former are utilized in the reaction, i.e. $k_r\,[AA-B] \ll k_7$, expression for the rate will be:

$$R_P = \frac{k_p}{k_t^{1/2}}\left\{\frac{k_i\, k_r\, k_{\in}\, I[AA-B]}{k_6\, k_7}\right\}^{1/2}[M]^{3/2} \qquad \text{………….. (17)}$$

Since the [buffer] is normally in excess when compared to the [AA] and monomer as it was proved that 1: 1 complex was formed, we may assume the [buffer] as unity and hence from the equation
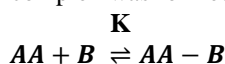
$$AA + B \overset{K}{\rightleftharpoons} AA - B$$

$$K = \frac{[AA - B]}{[AA]\,[B]}, \qquad \text{we have}$$

$$[AA - B] = K\,[AA]$$

Substituting this K [AA] for [AA – B] in equation (17),

$$R_P = \frac{k_p}{k_t^{1/2}}\left\{\frac{k_i\, k_r\, k_{\in}\, K[AA]\, I}{k_6\, k_7}\right\}^{1/2}[M]^{3/2} \qquad \text{…….…….. (18)}$$

Hence, equation (18) represents the kinetics of rate of polymerization, when mutual termination is considered. Here, from the experimental results, fig. 4 and fig. 6, it is concluded that, the termination occurs mutually.

V. Conclusions

The present investigation demonstrates the successful application of β-cyclodextrin in polymer synthesis in aqueous solution via free radical polymerization. Hence, the cyclodextrin mediated polymerization of hydrophobic acrylate monomer, like; butyl acrylate is possible in presence of water soluble initiator without using any organic solvent or surfactants. The percentage conversion of monomers into polymer is much higher in presence of β-cyclodextrin, than even in presence of any organic solvent and found to be very low in absence of β-cyclodextrin. The trend of rate of polymerization also follows the above order. The viscosity and molecular weight of polymers synthesized from complexed Butyl acrylate is found to be higher in comparison to uncomplexed Butyl acrylate. . 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. These polymers can be used directly as taken from the reaction vessel without further purification steps. Hence, the use of β-cyclodextrin opens green way for polymer synthesis. The other observation includes the presence of reducing agents and buffer (pH = 6) is required for the polymerization of Butyl acrylate sensitized by dyes, like sodium fluoroscein . The result of thermogravimetric analysis shows that, polymer sample is stable at 580^0c. Durung past few decades ,each successful photo polymerization process has its applications in different fields like radiation curing, surface coating, photo resists and holography etc. We expect that this trend will continue for near future. It is uncontroversial that numerous novel initiators, methodology and applications based on photo polymerization of vinyl monomers await new discovery and explorations.

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