DYE-SENSITIZED PHOTOPOLYMERIZATION OF STYRENE BY HOST-GUEST COMPLEXATION WITH B-CYCLODEXTRIN:

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ABSTRACT

The use of photo polymerization is continuously growing in industry as reflected by the large number of applications in not only conventional areas such as coatings, inks and adhesives but also high-tech domains, optoelectronics, laser imaging, stereo lithography and nanotechnology. In this perspective photo polymerization of styrene is realized by host-guest complexation with β-Cyclodextrin(CD) in homogeneous aqueous medium in presence of initiator, dye (erythrosine) , reducing agent(ascorbic acid) under buffered condition (Na_2HPO_4 – citric acid), leading to formation of water insoluble poly styrene. The effects of change of monomer, dye, ascorbic acid concentration, time and temperature on rate of polymerization are studied. The drawback of environmental issues for using conventional organic solvent for polymerization is overcome. The polymerization is also carried out with uncomplexed monomer with organic solvent (ethanol) medium. The rate of polymerization is measured gravimetrically and molecular mass by viscosity method. Presence of β-Cyclodextrin shows effects on the polymerization, so as to increase of rate of polymerization and percentage conversion of monomer, increase of molecular weight of polymer. The mechanism of polymerization and kinetic scheme proposed are examined in the light of the experimental results. Thermal degradation pattern of the polymer sample is studied by thermo gravimetric analysis.

Keywords – Erythrosine, host-guest complexes, photo polymerization, citrate-phosphate buffer, cyclodextrin, styrene.

1.INTRODUCTION

In recent years, photo initiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. For more than 30 years, photo polymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics [1-5].

Environmental issues involving conventional organic solvents are one of the major concerns in such applications. Photo polymerization of vinyl monomers by inclusion complexation with cyclodextrin (CD) in homogeneous aqueous solution is a highly effective approach to use water instead of the organic solvents. Rimmer and coworkers report that monomer, n-butyl methacrylate, can be polymerized with high percentage conversion in aqueous medium in absence of any type of surfectant[6]. Ritter and coworkers are the second group involved in cyclodextrin mediation of aqueous polymerization of monomers like phenyl and cyclohexyl methacrylates with a water soluble free radical initiator [7]. This 'green rout' for polymerization has been extensively studied by Ritter and his research group [8-15]. Among the different compounds that can act as host molecules (i.e.calixarenes, rotaxane and crown ethers to name a few) CDs are preferred for a number of different reasons like relatively nonreactive nature, stable in alkaline solution, fairly good resistance to UV and IR light, thermally stable up to 270℃ and acid hydrolysis only results in nontoxic glucose products[16].

Cyclodextrins are oligosaccharides, consisting of 6(α), 7(β), 8(γ) units of α-(1,4)-linked D- glucopyranose units with torus-shaped structure[17], which have a hydrophobic inner cavity with definite diameter, recognize specific organic molecules(guests) by their sizes and accept them into the cavity to form the corresponding inclusion complexes in a aqueous solution. Because of this unique property, commonly referred to as inclusion complex formation, cyclodextrins have been used to design polymeric materials. . Hydrophobic vinyl monomers, such as Styrene and Methyl Methacrylate become 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. 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 [18-19]. Also CD mediation gives high yield of polymers with narrower particle size distributions and narrower molecular weight polydispersity [8]. Polymer particles can be used directly without further purification steps. Synthetic dyes play an important role in polymerization, photo oxidation –

reduction and photolysis reactions [20-21]. 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 [25-26]. The present investigation is focused on the photo polymerization of styrene initiated by dye (erythrosine), reducing agent (ascorbic acid) under buffered condition (Na₂HPO₄ – citric acid) in presence of host, β-Cyclodextrin, in aqueous medium and in absence of β-CD in ethanol solvent medium. In nearly all cases, yields and molecular weights of polymers are higher in aqueous medium than those obtained from organic solvents. The surfactant free polymerization technique in aqueous medium is a new alternative method to emulsion polymerization, which has been established as industrial process for decades.

2. EXPERIMENTAL
2.1 Materials

The inhibitor was removed from styrene (purchased from LOBA CHEME Pvt. LTD) by washing with 5% aqueous solution of NaOH and washed with water to remove alkali, dried over anhydrous $CaCl_2$ and distilled under reduced pressure. Dye, erythrosine, and host, 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) and used throughout. Nitrogen gas was supplied by Indian Oxygen Ltd.

2.2 Preparation of polymer

The polymerization was carried out in pyrex 100 ml 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 connected through a constant voltage transformer. The reaction vessel was kept in a thermostat at required temperature. β-cyclodextrin was dissolved in deionised water. The resulting solution was flushed with nitrogen for 15 minutes .Then desired dose of styrene was added and the resulting dispersion was stirred to give homogeneous host-guest solution. Different concentrations of buffer solution, ascorbic acid solution and erythrosine dye solution were added to above host-guest solution under nitrogen atmosphere. After required time 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.
The rate of polymerization (R_p) and percentage (%) conversion were calculated as follows.

$$R_p = \frac{1000 \times w}{v \times t \times M_w \times 60 \times 60} \text{ mol/l/s}$$

Where w = wt of polymer formed v = total volume taken t = time in second, M_w = molecular weight of monomer.

$$\text{Conversion \%} = \frac{\text{mass of polymer}}{\text{mass of monomer}} \times 100$$

Molecular weight of polymer sample is determined by Mark – Houwink equation $[\eta] = K M^a$.
Where $[\eta]$ is the intrinsic viscosity, 'K' and 'a' are constants, 'M' is the molecular mass of polymer.

3. RESULTS AND DISCUSSION

In the present investigation kinetics of vinyl polymerization is studied sensitized by dye (erythrosine)-reducing agent (ascorbic acid) and in presence of citrate – phosphate buffer. Influence of each parameter is studied in absence and in presence of host,β-CD. Preliminary experiments revealed that a reducing agent, such as, ascorbic acid is necessary for polymerization, that the erythrosine alone cannot initiate. Polymerization also does not occur in the absence of buffer. It is 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 is necessary for initiation of the polymerization and the dye – ascorbic acid –buffer is a more efficient initiator system. Kinetic study has been made by varying concentration of monomer, dye, ascorbic acid in presence and in absence of host, β-CD, along with the influence of time and temperature.

3.1 Influence of β-cyclodextrin concentration -

Concentration of β-cyclodextrin has a significant effect on the percentage conversion and rate of polymerization. The percentage conversion increases up to 8.8105×10^{-3} M/L of β-CD concentration , after which a decreasing trend was observed at a fixed monomer concentration of 0.4694 M/L as in figure- 1.
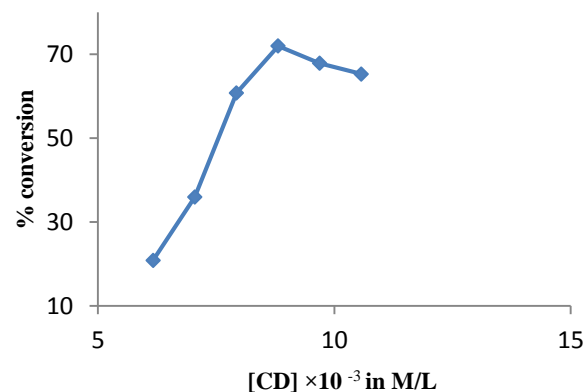

Figure-1 [β-CD] ~ % conversion

3.2 Influence of time-

Effect of time is studied in reaction 1-4 in table-1. In 4 hour yield is more. As expected, there is 3-4 fold increase of rate of polymerization in presence of β-CD (figure-1). Series -1 points are the reactions done in absence of β-CD, series-2 points are the reactions done in presence of β-CD.
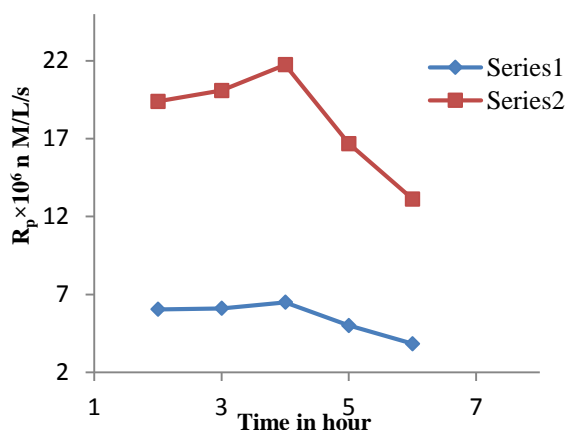

Figure-2 Time ~ Rate of polymerization
 Series-1   (polymerizations in absence of β-CD)
 Series-2   (polymerizations in presence of β-CD)

3.3 Influence of Styrene concentration-

During the study of percentage conversion at various concentrations of monomer, it is observed that, the percentage conversion of polymerization increases up to 0.8699 M/L of styrene concentration, beyond which it decreases as in figure -3.
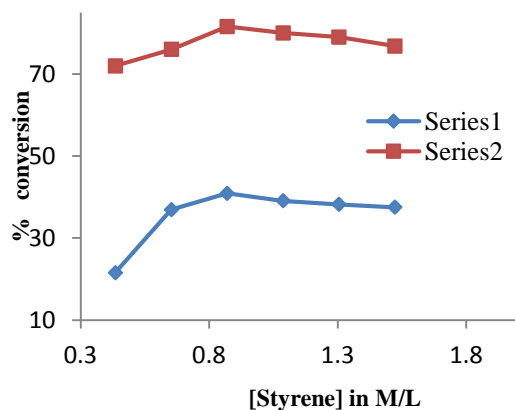

Figure-3 [Styrene] ~ % conversion.
Series-1   (polymerizations in absence of β-CD)
 Series-2   (polymerizations in presence of β-CD)

3.4 Influence of initiator –

Erythrosine dye is taken as photo initiator. The rate of polymerization at various concentrations of erythrosine is studied. It increased up to 2.5×10^{-6} M/L and then shows a decreasing trend (figure-4).
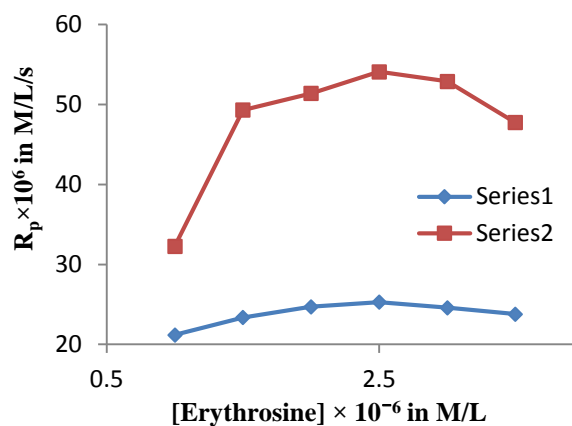

Figure-4 [Erythrosine] ~ Rate of polymerization.
 Series-1   (polymerizations in absence of β-CD)
 Series-2   (polymerizations in presence of β-CD)

3.5 Influence of ascorbic acid concentration-

Influence of ascorbic acid concentration on percentage conversion is studied keeping other parameters constant. It is observed that at lower concentration that is below 0.5×10^{-2} M/L of ascorbic acid concentration, polymerization does not occur (fig-5).However, with increase of ascorbic acid concentration up to 1.25×10^{-2} M/L, percentage conversion increases and thereafter shows a decreasing trend. This trend is same whether reactions occur in absence of β-CD (series-1) or in presence of β-CD (series-2).
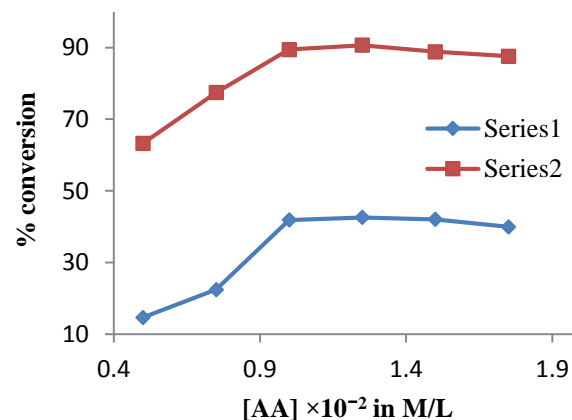

Figure-5 [Ascorbic acid] ~ percentage conversion.
 Series-1   (polymerizations in absence of β-CD)
 Series-2   (polymerizations in presence of β-CD)

3.6 Influence of temperature-

At various temperatures, rate of polymerization is studied keeping concentration of other additives constant. R_p increases up to 313K temperature, after this it decreases (fig.6). Within temperatures the range of 35°c to 45°c, the overall energy of activation is calculated from the corresponding Arrhenius plot (fig.7) and found to be 3.74 K.cal/mol.
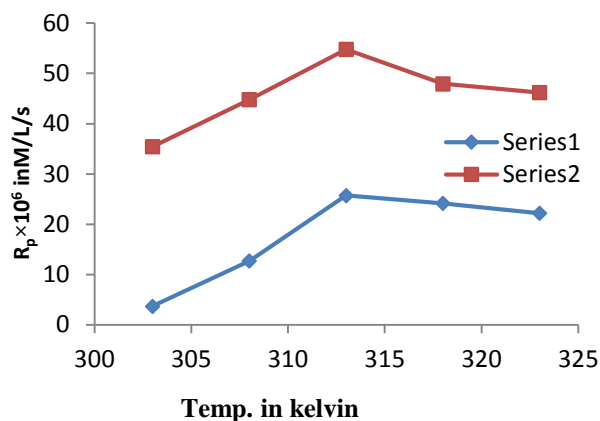
Fig.6 Temperature ~ rate of polymerization.
Series-1   (polymerizations in absence of β-CD)
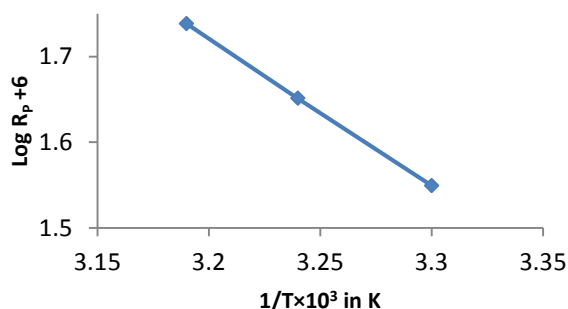 Series-2   (polymerizations in presence of β-CD)

Fig-7 Arrhenious plot for calculation of Activation Energy
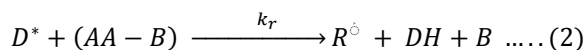
MECHANISM

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 in the dark, to produce free radicals 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.
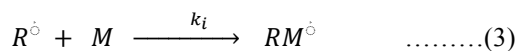
$$D \xrightarrow[k_\epsilon I]{h\gamma} {}^3[D]^* \qquad \ldots\ldots\ldots\ldots(1)$$

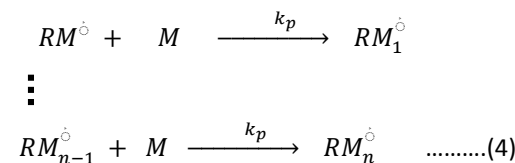Here, D = Dye, $^3[D]^*$ is triplet state of the dye.

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.
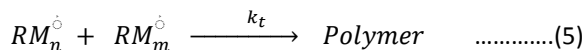
$$D^* + (AA-B) \xrightarrow{k_r} R^{\dot{\circ}} + DH + B \ldots.(2)$$

iii. Initiation of polymerization.

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

iv. Propagation.

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

$$\vdots$$

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

v. Termination.

a)Mutual termination

$$RM_n^{\dot{\circ}} + RM_m^{\dot{\circ}} \xrightarrow{k_t} Polymer \qquad \ldots\ldots\ldots.(5)$$

b)Termination by primary radical, $R^{\cdot}$:

$$RM_n^{\dot{\circ}} + R^{\dot{\circ}} \xrightarrow{k_{t_1}} Polymer \qquad \ldots\ldots.(6)$$
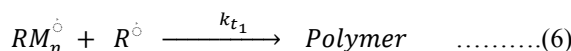
c)Termination by dye (D) itself:

$$RM_n^{\dot{\circ}} + D \xrightarrow{k_{t_2}} Polymer \qquad \ldots\ldots..(7)$$
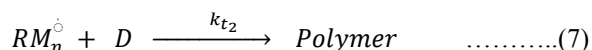
d) Deactivation of $R^{\dot{\circ}}$ to give stable products

$$R^{\dot{\circ}} \xrightarrow{k_6} S \qquad \ldots\ldots\ldots(8)$$

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

$$D^* \xrightarrow{k_7} D \qquad \ldots\ldots\ldots.(9)$$

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 can be derived.   Considering mutual termination,

$$\frac{d\left[R^{\dot{\circ}}\right]}{dt} = 0 \quad \text{and} \quad \frac{d\left[RM_n^{\dot{\circ}}\right]}{dt} = 0 \quad \ldots\ldots..(10)$$

Where, $R^{\dot{\circ}}$ is the primary radical and $RM_n^{\dot{\circ}}$ denotes the radical chain.

Assuming the termination by mutual combination of the growing chain radicals.

$$\frac{d\left[R^{\dot{\circ}}\right]}{dt} = k_r[D^*][AA-B] - k_i[R^{\dot{\circ}}][M] - k_6[R^{\dot{\circ}}]$$
$$= 0 \qquad \ldots\ldots..(11)$$

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

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

$$[R^{\dot{\circ}}] = \frac{k_r[D^*][AA-B]}{k_i[M] + k_6} \qquad \ldots\ldots\ldots(12)$$

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

$$= 0 \qquad \ldots\ldots\ldots(13)$$

$$or \quad [D^*] = \frac{k_\in I}{(k_r [AA - B] + k_7)} \quad \dots\dots (14)$$

Substituting equation (14) in equation (12),

$$[R^\circ]$$
$$= \frac{k_r k_\in I [AA - B]}{(k_r [AA - B] + k_7)(k_i [M] + k_6)} \quad \dots\dots (15)$$

$$\frac{d\left(RM_n^\circ\right)}{dt} = k_i[R^\circ][M] - k_t\left[RM_n^\circ\right]^2 = 0 \quad \dots\dots (16)$$

Or

$$\left[RM_n^\circ\right] = \left\{\frac{k_i [R^\circ] [M]}{k_t}\right\}^{\frac{1}{2}} \quad \dots\dots. (17)$$

Substituting equation (15) in equation (17),

$$\left[RM_n^\circ\right] = \left\{\frac{k_i k_r k_\in I[AA - B][M]}{k_t (k_r[AA - B] + k_7) (k_i [M] + k_6)}\right\}^{\frac{1}{2}}$$
$$\dots\dots\dots(18)$$

$$R_P = -\frac{d [M]}{dt} = k_P\left[RM_n^\circ\right] [M] \quad \dots\dots\dots. (19)$$

$$R_P =$$

$$\frac{k_p}{k_t^{\frac{1}{2}}} \left\{\frac{k_i k_r k_\in I[AA - B]}{(k_r[AA - B] + k_7) (k_i [M] + k_6)}\right\}^{\frac{1}{2}} [M]^{3/2}$$
$$\dots\dots\dots\dots(20)$$

Assuming that, (a) only a fraction of radicals produced are utilized for 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. $k_r [AA - B] \ll k_7$, we have,

$$R_P = \frac{k_p}{k_t^{\frac{1}{2}}} \left\{\frac{k_i k_r k_\in I[AA - B]}{k_6 k_7}\right\}^{\frac{1}{2}} [M]^{\frac{3}{2}} \quad \dots\dots (21)$$

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
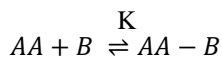
$$AA + B \overset{K}{\rightleftharpoons} AA - B$$

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

Substituting this K [AA] for [AA − B] in eqⁿ(21)

$$R_P = \frac{k_p}{k_t^{\frac{1}{2}}} \left\{\frac{k_i k_r k_\in K[AA] I}{k_6 k_7}\right\}^{\frac{1}{2}} [M]^{3/2} \quad \dots. (22)$$

Hence, equation (22) represents the kinetics of rate of polymerization, when mutual termination is considered. It signify that graph of $[monomer]^{3/2} \sim$ Rate of polymerization must be a straight line. This is verified from figure-8.
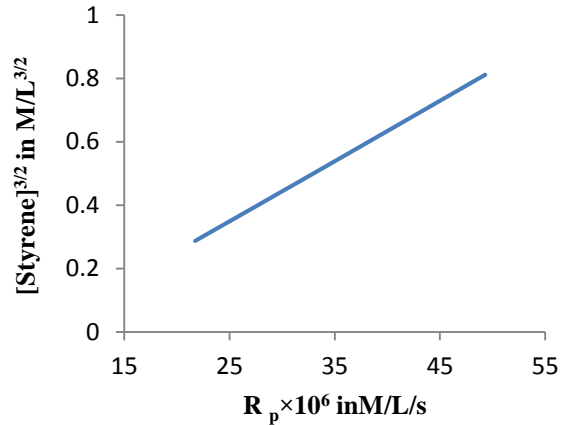

Figure-8 $[Styrene]^{3/2}$ versus rate of polymerization

Also from above kinetic equation, graph of [ascorbic acid]$^{1/2} \sim$ rate of polymerization should be a straight line, which is verified from figure-9.
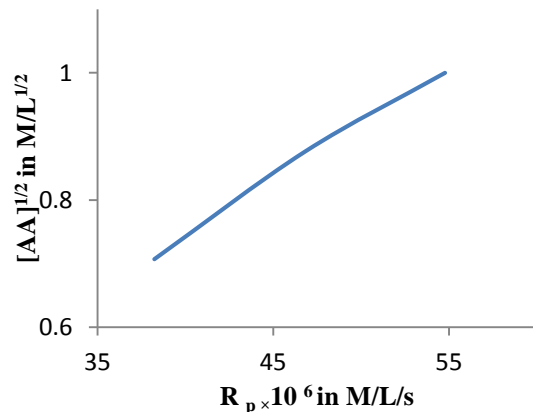

Figure-9 $[AA]^{1/2}$ versus rate of polymerization

CONCLUSION

In this work, we aim to improve the yield of polymers and also the characteristics of polymers through the formation of inclusion compounds formed by monomer with cyclodextrin in aqueous medium. It replaces our conventional organic solvent for polymerization process. From the above experimental findings, it is evidenced that the percentage of conversion of monomers into polymer and rate of polymerization are more than two fold when compared the polymerization of complexed styrene with uncomplexed styrene. This may be due to increase in monomer reactivity. Cyclodextrin might aid transport of the monomer to the loci of polymerization, which correspondingly increases the monomer concentration at the locus of polymerization and thus increases monomer conversion. Decrease in change of free energy would be thermodynamically responsible for improving the monomer conversion. The viscosity and molecular weight of polymers synthesized from complexed styrene is found to be higher in comparison to uncomplexed styrene.

It is expected, chains will have extended conformations with ordered and unentangled chains. The reorganisation of polymer chains in the bulk phase would improve the physical properties of polymers, such as glass transition temperature, crystallinity, thermal stability, melting point.

Aqueous solution of β-cyclodextrin is also capable of isolating the pollutants present in the monomer and other additives. Hence, the use of β-cyclodextrin opens green way for polymer synthesis. The other observation includes the requirement of reducing agent and buffer (pH = 6) for the polymerization of styrene sensitized by dyes, like erythrosine.

Virtually, so far, the explanations are rather qualitative, quantitative aspects still need more investigations. Some additional information regarding temperature, time waits to be considered. Complexation of a liquid crystalline monomer for the purpose of polymerization in a non-solvent is a novel investigation. This work can be extended for selective polymerization of multifunctional monomers in cyclodextrin mediation by shielding one or more reactive sites within the cyclodextrin cavity. The photopolymerization world today is requiring high demands on performance of the related products in a period where sustainability , cost , environmental safty and health aspects are high on the priority of both industry and society . It is uncontroversial that this method of polymerization will provide several avenues of novel applications in future.

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