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Photo Polymerization Of Methyl Methacrylate In Homogeneous Aqueous Medium By Host-Guest Complexation With Β-Cyclodextrin

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Abstract:

Photo polymeruization of Methyl Methacrylate (MMA) by host-guest complexation with β-cyclodextrin was investigated in homogeneous aqueous medium. Vinyl monomers like MMA, Styrene etc. become water soluble due to complexation with β-CD and can easily be polymerized in aqueous solution in the presence of free radical initiator. Polymerization was also carried out with uncomplexed monomer and in presence of organic solvent. A systematic study of the kinetics of photosensitized polymerization of MMA with dye (acriflavin) , reducing agent(ascorbic acid) under buffered condition (Na_2HPO_4 – citric acid) in presence of β-CD in aqueous solution has been made against the different variables like concentration of monomer, dye, ascorbic acid, time and temperature. Presence of β-CD showed obviously effects on the polymerization, so as to increase the rate of polymerization and percentage conversion of monomer, increase of molecular weight of polymer. The mechanism of polymerization and kinetic scheme proposed was examined in the light of the experimental results. Thermal degradation pattern of the polymer sample was studied by thermo gravimetric analysis.

Keywords – ***Acryflavin, ascorbic acid, citrate-phosphate buffer, cyclodextrin, host-guest complexes***

1 Introduction

Photo initiated free radical polymerization is a well accepted technology, which finds industrial application in coating on various materials , adhesives , printing inks and photo resists[1-5] . Environmental issues involving conventional organic solvents are one of the major concerns in such applications. Photo polymerization in aqueous solution is a highly effective approach to use water instead of the organic solvents. Pioneering work by Ritter demonstrated that hydrophobic vinyl monomers become water soluble due to the complexation of β-cyclodextrin(CD) and can easily be polymerized in aqueous solution [6-9].

Cyclodextrins are natural products, obtained from starch by action of cyclodextrin glucosyl transferase (CGTase), an enzyme produced by several organisms. These are cyclic oligosaccharides consisting of 6(α), 7(β), 8(γ) units of (α-1, 4) linked glucopyranose units those present in a truncated cone formed with a hydrophobic central cavity and a hydrophilic outer surface. 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. Due to above mentioned enclose hydrophobic molecules to form host-guest compounds Hydrophobic monomers become water soluble on treatment with aqueous solutions of cyclodextrins without any chemical modification 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 [10-14]. This is because there are no covalent bonds formed in the host-guest interaction of cyclodextrin and the water insoluble monomers. Therefore, CDs are being used to obtain complexes with various monomers in aqueous environments and those complexed monomers are being successfully polymerized via free radical initiation in water. In nearly all cases of polymerization of vinyl monomers, the polymerizations in the presence of CD usually are in high monomer conversion and high rate of polymerization. Synthetic dyes play an important role in polymerization, photo oxidation – reduction and photolysis reactions [15-17]. Initiation of polymerization in the presence of light with dyes and reducing agent systems has also been studied by typical behavior of CDs, polymerization of various monomers can be done. Cyclodextrins are able to.

various workers [18-20].

2 EXPERIMENTAL

Methyl methacrylate 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, acryflavin 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 acryflavin 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.

3 RESULTS AND DISCUSSION

In the present investigation a systematic study of the kinetics of vinyl polymerization sensitized by dye (acriflavine)-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 monomer (reaction 1-3 in table-1) and ascorbic acid (reaction 7-9 in table-1, 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.

3.1 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 , after which a decreasing trend was observed at a fixed monomer concentration of 0.4694M/L as in fig. 1.

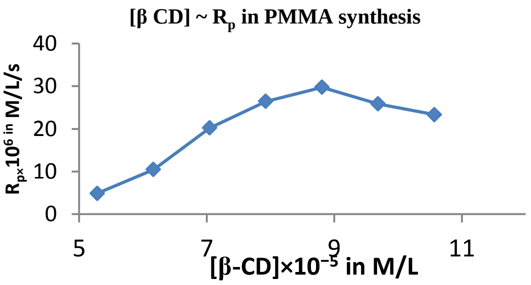

Fig-1

3.2 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 0.7041 M/L of Methyl methacrylate and beyond that it decreases, irrespective of the absence(series-1) and presence of β-CD (series-2) as in figure -2

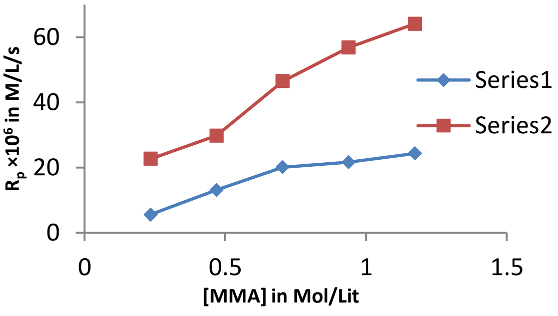

Fig-2

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A plot of rate of polymerization versus [Methyl methacrylate] is found to be linear (fig-3), which satisfies the mechanism and indicate that the termination was the mutual type according to eq^n -1.

$$R_P = \frac{k_p}{{k_t}^{½}} \left\{ \frac{k_i\, k_r\, k_{\in}\, K[AA]\, I}{k_6\, k_7} \right\}^{½} [M]^{3/2} \quad \ldots(1)$$

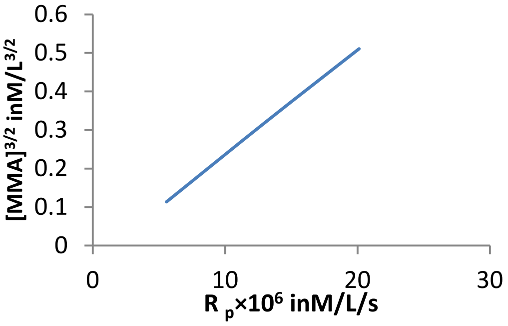

Fig-3

3.3 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-5).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. This trend is same where reaction occurs in absence of β-CD (series-1) or in presence of β-CD (series-2).

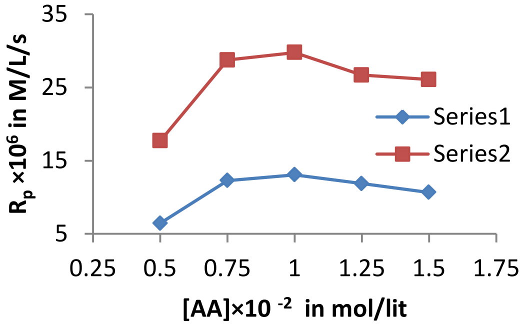

Fig-4

When graph was plotted between of rate of polymerization versus [Ascorbic acid] ^{½} it was found to be linear (fig-5). It satisfies the mechanism and indicates that the termination was the mutual type according to the equation -1.

3.5 Influence of time- Time – conversion curves at a fixed concentration of monomer, initiator are shown in fig-8. It was found that, the percentage conversion of

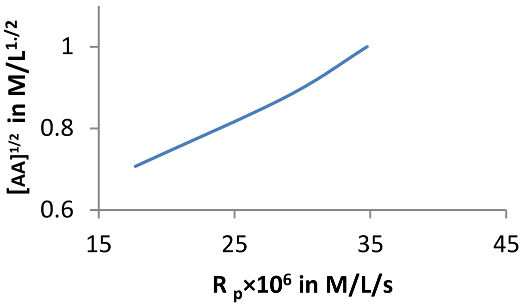

Fig-5

3.4 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.6). Taking three different temperatures within the range between 35^{o}c and 45^{o}c, the overall energy of activation was computed from the corresponding Arrhenius plot (fig.7) and found to be 1.85 K.cal/mol.

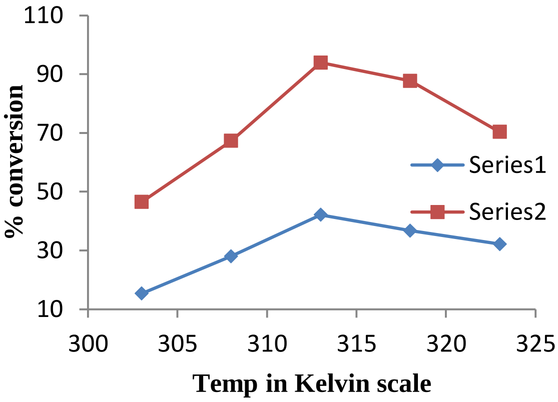

Fig-6

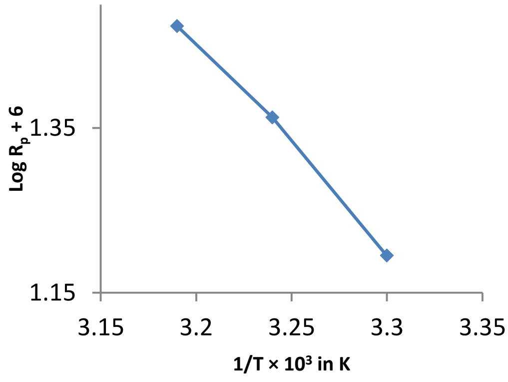

Fig-7

3.6 Influence of Dye- The rate of polymerization at different concentrations of dye (acryflavin) was studied. Polymerization rate is highest at dye monomer into polymer increased up to 4 hours, after which a decreasing trend was observed. This trend is same for uncomplexed polymerization (series-1) and complexed polymerization (series-2).

concentration of 2 × 10^{-6} M/L. Series -1 represents polymerization in absence of β-cyclodextrin and series -2 represents polymerization in presence of β-cyclodextrin .

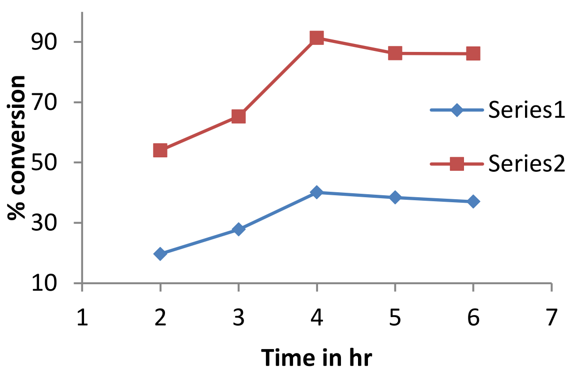

Fig-8

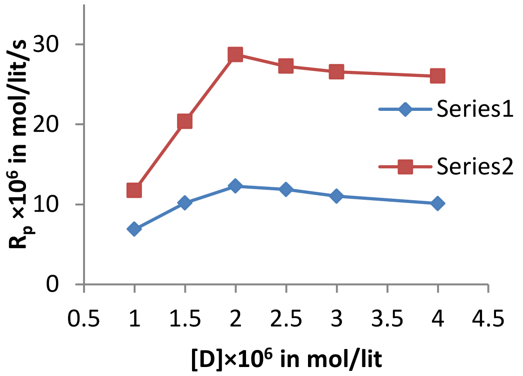

Figure-9

Table-1 Overview of the reaction parameters and results of the polymerization of MMA (4 hours at 40^0C).

Reaction	Conc. of β-CD in M/L	Conc. of Monomer in M/L	[Ascorbic acid] × 10^{-2} in M/L	Percentage conversion	R_p × 10^6M/L/S
1	0	0.4694	2	40.1063	13.0745
2	0	0.7041	2	41.1206	20.1078
3	0	0.9388	2	33.1862	21.6372
4	7.9295	0.4694	1	81.1063	26.4404
5	8.8105	0.4694	1	91.3085	29.7663
6	9.6916	0.4694	1	79.3404	25.8647
7	8.8105	0.4694	0.75	88.1170	28.7259
8	8.8105	0.4694	1	91.3085	29.7663
9	8.8105	0.4694	1.25	81.8404	26.6797

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.

Graphs are drawn in figure-10 in which [η] = 1.57 and 1.63 for two samples of PMMA synthesized in absence of β-CD . Molecular weight of these two polymer samples are 14.88×10^5 and 15.69×10^5 respectively. [η] = 1.82 and 2.03for synthesis of two samples of PMMA when prepared in presence of β-CD . Molecular weight of these two polymer samples are 18.37×10^5 and 21.48×10^5 respecyively.

Conclusion

From above experimental findings 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 β-CD/ photoinitiator complex . Molecular weight of polymers are also more in presence of β-cyclodextrin those have higher fibre drawability and strength. Using β-cyclodextrin can also lead to surfectant free polymerization.The polymer particles, with narrow polydispercity, prepared with β-CD , but without using surfectants and organic solvent , can be used directly as taken from the reaction vessel without further purification steps. As CDs are solids , these are easily handled than volatile organic solvents from industrial standpoint.

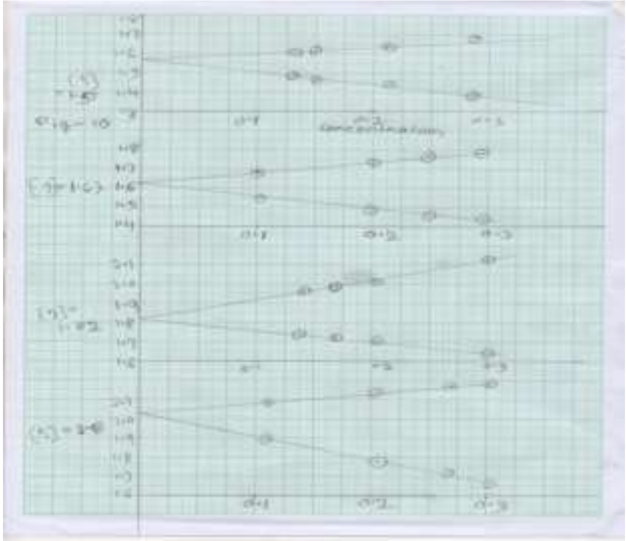

Figure-10

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 . During past few decades, each successful photo polymerization application stimulated research which in turn led to additional applications and improved processes such as radiation curing, surface coating, photo resists and holography those have wide applications in printing industry and medicines. We expect that this trend will continue for near future. It is incontrovertible that the numerous novel initiators, methodology, and applications based on photo polymerization of vinyl monomers await new discovery and exploration.

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