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KINETICS OF FREE - RADICAL POLYMERIZATION OF 8 - QUINOLINYL ACRYLATE

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ABSTRACT

The synthesis of water insoluble poly 8-quinolinylacrylate was investigated for free radical polymerization. The kinetics of polymerizatio of 8-quinolinylacrylate initiated by AIBN in DMF at 60-100°C were studied. The rate of polymerization was determined at various concentration of monomer and initiator. The overall activation energy was found to be 15.0 K.J. mol"[1].

Key words: 8-quinolinylacrylate, kinetics and free radical polymerisation.

INTRODUCTION

It is known that 8-hydroxyquinoline and its derivative possess antibacterial, antimycotic and ameobicidal properties, several authors have suggested that their antimicrobial properties are due to their complex forming ability. The chelating ion-exchange properties of 8-HQ and its derivatives have been widely exploited for many application such as in metallurgical operations, separation and estimation of metals, effluent treatment, purification of water and as a catalyst in many organic synthesis. The polymeric 8- HQ derivatives have been synthesized by its condensation with aldehydes and by modification of poly (ethylene glycol) and poly (caprolactone)s. There are few examples of synthesis and polymerization of vinyl monomers containing quinolinyl groups. Data are also lacking for kinetics of polymerization of 8-QA. A number of kinetic studies of the aqueous polymerization of acryl amide have been reported[1-5] but there are few reports on polyacylamides with N-substituted carboxyphenyl residues and little information is available[6-9].

The present article deals with the study of kinetic of solution polymerization of 8-QA in different experimental conditions. The synthesis of 8- quinolinyl acrytlate and some studies on the polymerization and characterization of their polymers have been published[10,1].

EXPERIMENTAL

Materials

All the chemical used during the study were of analytical grade. The solvents and monomers were purified by the conventional method[12]. 2,2'-azobisisobutyronitrite was

recrystalized from methanol and dried in a dessicator.

Monomer synthesis

The monomer 8-quinolinyl acrylate was synthesized from 8-hydroxy quinoline-and acryloyl chloride as described in previous article[10].

Polymerization procedure

A typical polymerization method is described below.

Purified 8-QA(0.1047 mol/L) in DMF (20 ml) and AIBN (1.2195 x 10^3 mol/L) were placed in degassed glass tube and constricted under flame. The polymerization was carried out in a sealed tube by placing in a thermostated oil bath at the required temperature, after polymerization for a given time, the contents of the tube were poured into 100 ml of methanol to precipitate the polymers. The resulting polymer was washed well with methanol and with boiling water and dried in vaccum at room temperature to a constant weight. The values of the weight of polymer was used to compute the rate of polymeriztion (Rp).

RESULTS AND DISCUSSION

Effect of monomer concentration

The kinetics of radial polymerization of monomer (8-QA), the monomer concentration was varied from 0.1047 to 1.3141 mol/ L at fixed concentration of initiaton in DMF. The rate of polymerization was found .to increase linearly with increase of monomer concentration. The plot of Rp versus [M] and $[M]^2$ at different initiator, concentration at 60 and 80°C are found to be linear. The plot of log Rp versus 10g [M] is liner (Figure-1). From the slope of this plot, the order of reaction with respect to monomer for the polymerization of 8-QA in DMF is. found to be around 1.32[13]

Effect of initiator concentration

The effect of initator concentration AIBN from 1.2195 x 10^{-3} mol/L to 3.6585 x 10^3 mol/L at fixed concentration of monomer

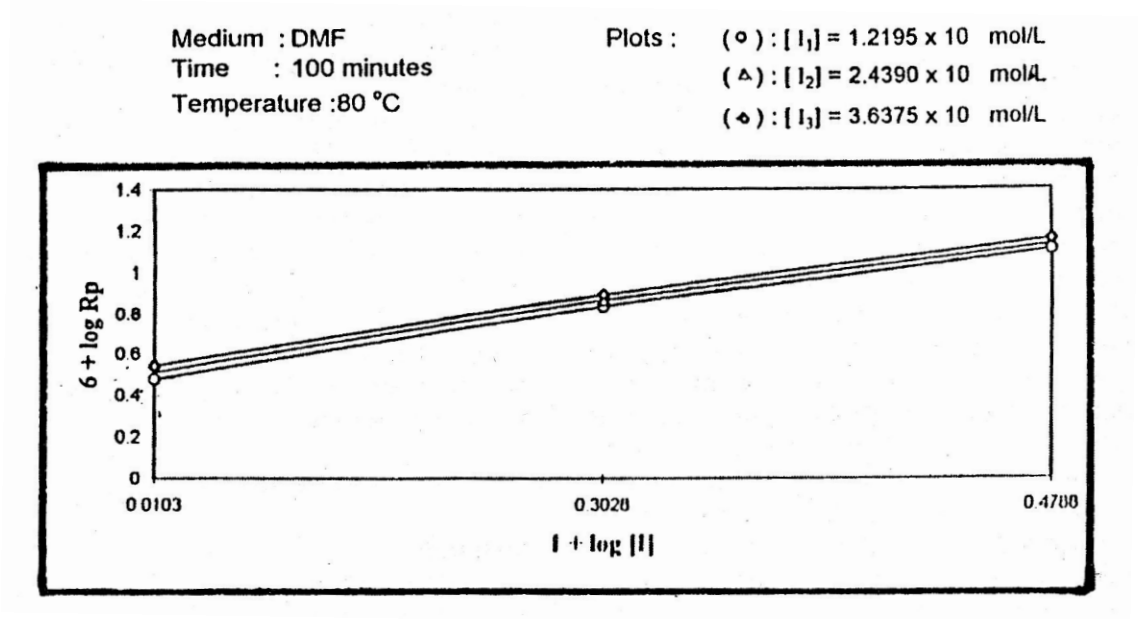

Figure-1: Double Logarithmic plot of rate of Polymerization (Rp) versus Monomer concentration

in DMF. The rate of polymerization was found to increase linerly with the increase of initiator concentration. The plot of Rp versus[I} is linear[14] and its slope constant is around 0.21. Thus the order of reaction with respect to initiator is found to be 0.21 (Figure.2)

Effect of temperature

The polymerization of 8-QA initiated by AIBN was investigated in the temperature range 60-100°C in DMF as reaction medium, keeping the concentration of all other reagents constant. The rate of polymerization was found to increase progressively with rise in temperature. From the Arrhenius plot Rp versus 1/T (Figure- 3), the overall activation energy Ea was computed to be 15.0 K.J./mol.

Relation between concversion and reaction time.

8-quinolinyl acrylate was polymerized in DMF in the temperature range 60,80 and 100°C using AIBN as initiator.Time conversion curves at three different concentration of monomer and initiator respectively are shown in Figure 4 to 6, from which it is concluded that the percentage conversion increases as the monomer and initiators concentration increases. The order of the reaction with respect to initiator concentration for the polymerization of 8-QH has been determined graphically from the double logarithemic plot of rate of polymerization (Rp) versus initiator concentration[13]. The plot is linear and from the slope of-the plot, the order of reaction was found to be around 0.19 (Figure- 7).

CONCLUSION

On the basis of the standard free radical polymerization scheme and the derivation of the kinetic equation suggested in the literature[15], the rate expression is derived.This rate experession satisfactorily explains all the kinetic results obtained, these results of the present study are in agreement with those reported by Suthar et.al[15,16].

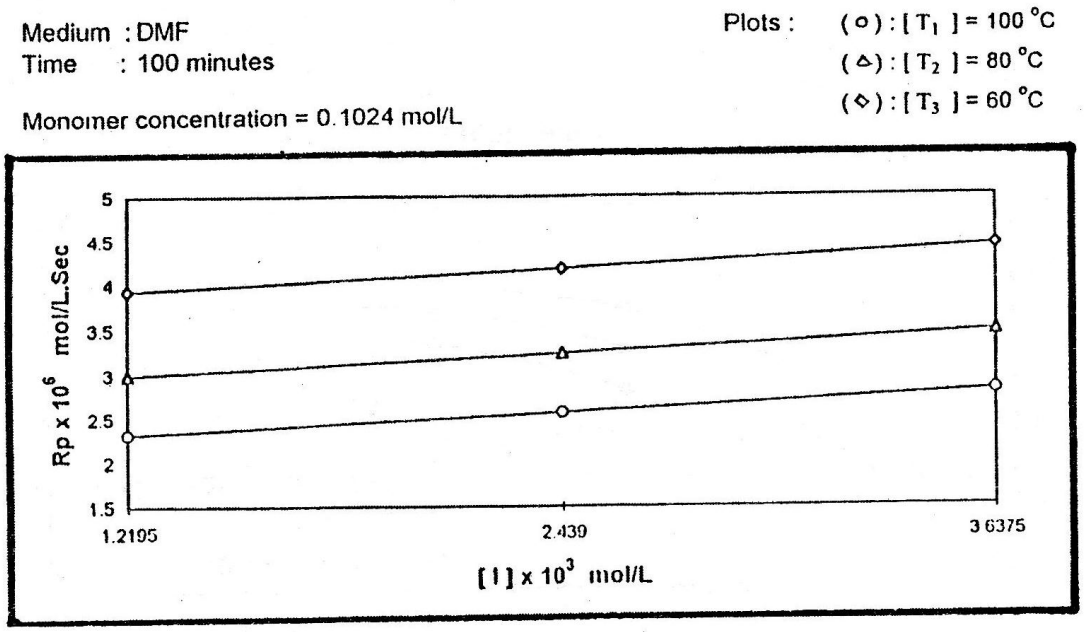

Figure- 2: Effect of initiator concentration on the rate of polymerization

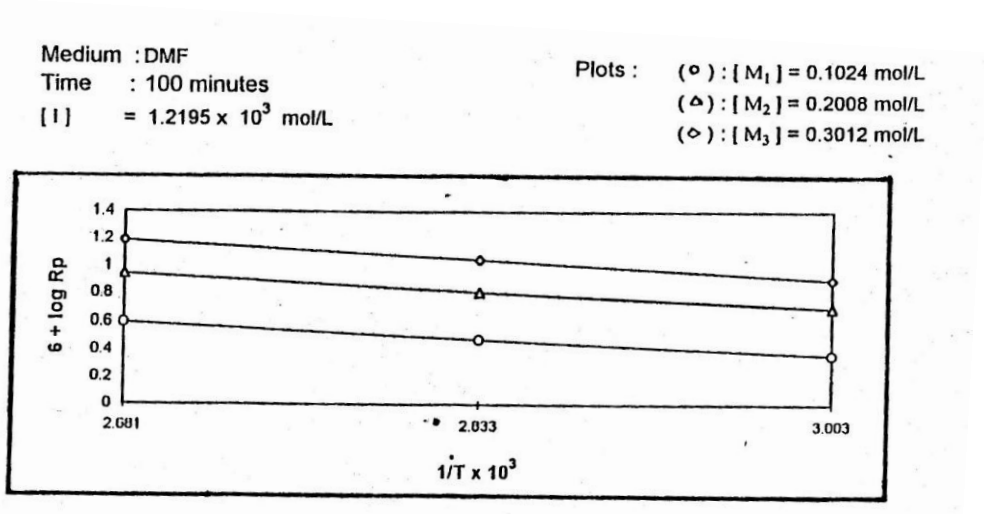

Figure : 3

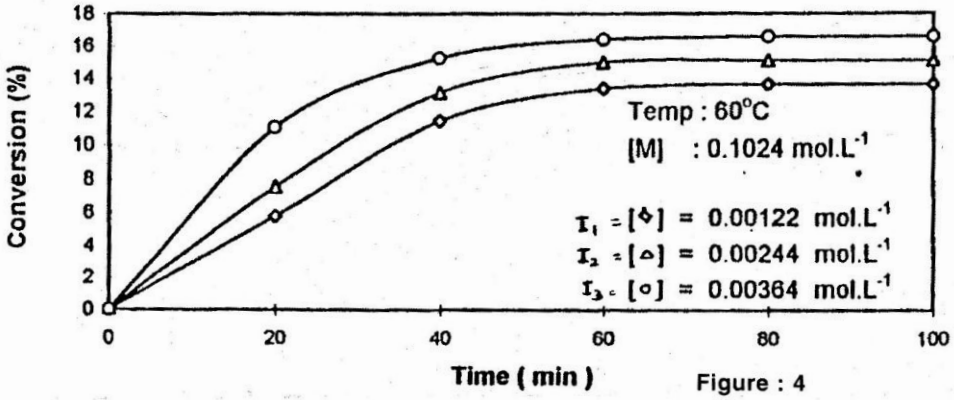

Figure : 4

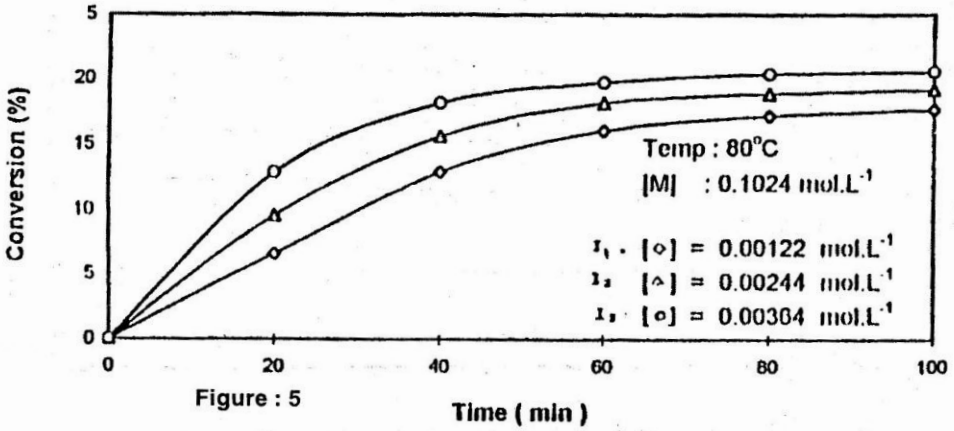

Figure : 5

Figure- 3-5 : Arrhenious plot of log Rp Versus 1/T

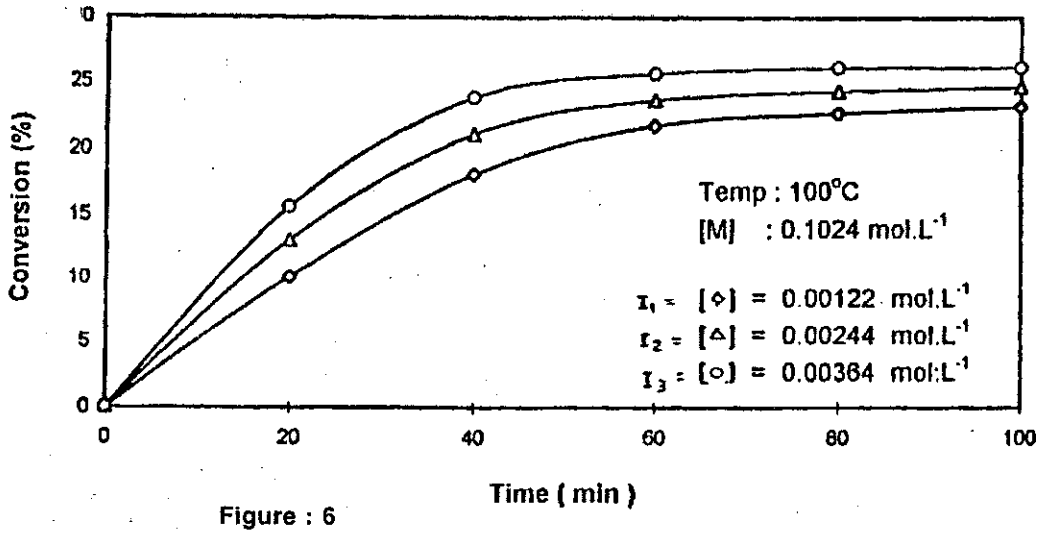

Figure : 6

Plots : (○) 100 °C
(△) 80 °C
(□) 60 °C

Medium : DMF
Time : 100 minutes

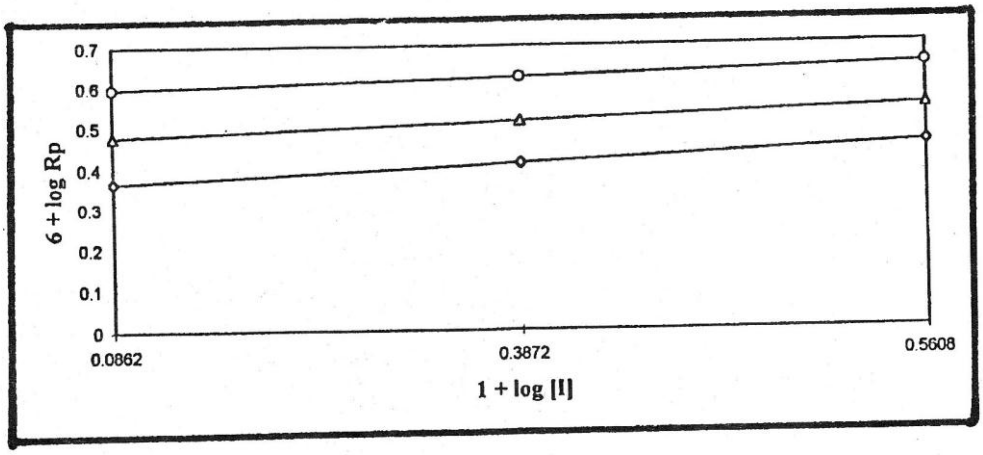

Figure- 7: Double Logarithmic plot of rate of Polymerization (Rp) versus Initiator concentration

REFERENCES

1. Gopalan A., Paulrajan S. and Venkatro K., *Eur. polym. J.,* **20,** 971 (1984)
2. Sukla J.S. and Tiwari R.K., *J. Macromol Sci. Chem.,* A**-18,** 759 (1982)
3. Ng S.G., *Eur Polym. J.,* **18,** 917 (1982)
4. Okieimen E.E., *Ibid.,* **17,** 641 (1981)
5. Deb *R.C.Jbid. ,* **15,** 961 (1979)
6. .Framtisek H. and Jiri W., *Czechoslovakin Patent.,* **158, 428** (1975) cf. C.A., **84** 5860 (1976)
7. Framtisek H. and Jiri W..C.A., **84** 16966 (1976)
8. Yoshikazu K. and Nichiko J., *Japaness kokei,* **151** 526 (1975)
9. Erogozhin E.E. and Sariyeya R.B., *Macromol. chem. rapid commuini.,* 8 171 (1987)
10. Patel P.M. and Patel R.M., *Orient. J. Chem.,* **17(2)** 233 (2001)
11. Patel P.M., Sinha T.J.M. and Patel R.M., *Intern, J. polymerc mater.,* **47,** 139 (2000)
12. Vogel A.I. *Text Book of practical organic chemistry,* London (1978)
13. Mishra G.S. and Bhattacharya S.N. *J. Poly Sci. Poly. Chem. Ed.,* **20,** 131 (1982)
14. Mishra S. and Sahu G., *J Macromol Sci. Chem.,* **A-19(1)** 57 (1983)
15. Suthar B., Desai T. and Patel K., *J. Macromol. Sci. Chem.,* **23,** 319 (1986)
16. Patel B.V., *Ph. D. Thesis,* Sardar Patel University, India (1990)