

Phase transfer catalyzed free radical polymerization of acrylonitrile – A kinetic study

Yoganand K.S^{1*}, Indumathi S², Umapathy M.J²

¹Assistant Professor, Dept. of Chemistry, SRM University, Ramapuram, Chennai-600 089.

²Assistant Professor, Dept. of Chemistry, College of Engineering, Guindy, Anna University, Chennai-600025.

*Corresponding author: E-Mail: yoganand.ks@gmail.com

ABSTRACT

The kinetics of free radical polymerization of acrylonitrile (AN) with water-soluble initiator (potassium peroxydisulfate) and phase transfer catalyst 1, 4-Bis (dimethyldecyl) ethylenediammonium bromide has been studied. The polymerization reactions were carried out under inert and unstirred conditions at a constant temperature of $60 \pm 1^\circ\text{C}$ in cyclohexane/ water diphase media. The effects of [monomer], [initiator] and [PTC] and reaction temperature on the polymerization rate were investigated. The steady state rate of polymerization of acrylonitrile (AN) monomer was ascertained by carrying out the experiments at different intervals of time. Generally an increase in the rate of polymerization (R_p) was obtained and then attained a constant value. The rate of polymerization (R_p) increased with an increase in the concentration of AN, Peroxo Disulfide (PDS), PTC and temperature. Based on the results obtained, a mechanism as been proposed for the polymerization reaction and the polymer Poly acrylonitrile (PAN) formed was characterized using FT-IR and XRD techniques and their thermal stability was studied by using thermal analysis. Activation energies for the polymerization of acrylonitrile monomer were calculated from the log R_p VS $1/T$ in the temperature range 50°C to 65°C .

KEY WORDS: Free radical-polymerization, PTC, PAN, PDS.

1. INTRODUCTION

A PTC in chemistry is a catalyst which facilitates the migration of a reactant in a heterogeneous system from one phase into another phase where reaction takes place. Ionic reactants are often soluble in aqueous phase but insoluble in an organic phase unless the PTC is present. Phase transfer catalysts for anion reactants are often quaternary ammonium salt. The corresponding catalyst for cations is often crown ether. A PTC works by encapsulating the ion. The PTC ion system has a hydrophilic interior containing the ion and a hydrophobic exterior. PTC have been active area of research in polymer chemistry due to high reaction rate under mild experimental conditions, high molecular weight, increased product specificity, Control over all reaction rates and yield, provide commercial methods of manufacturing some polymers. In a polymerization reaction, where the water soluble initiator located in an aqueous phase, PTC have a capability to carry the initiator from the aqueous phase which is highly active species for penetrating the interface into other phase(monomer phase) where the polymerization reaction to take place. It has been reported by the literature that polyacrylonitrile prepared by using quaternary ammonium salt, peroxodixulphate system possesses very high molecular weight. The result substantiated the efficiency of phase transfer catalyst polymerization compared with conventional free radical polymerization.

2. MATERIALS AND METHODS

2.1. Reagents: The distilled water obtained from Still was again distilled over alkaline KMnO_4 and used for the preparation reagent solution as well as further reaction medium. The monomer acrylonitrile were purchased (SRL, Mumbai) and used as such. 1, 4-Bis (dimethyldecyl)ethylenediammonium bromide was synthesized in the laboratory. Potassium peroxydisulphate (SRL, Mumbai), H_2SO_4 (Merck, Mumbai), HCl (SRL, Mumbai), Cyclohexanone (SRL, Mumbai) and methanol (SRL, Mumbai) were purchased and used as such.

2.2. Polymerization technique: Polymerization was carried out in inert atmosphere under unstirred condition at 60°C . The reaction mixture consists or equal volumes of aqueous and organic phases (10ml each). Aqueous phase contained the phase transfer catalyst (PTC), potassium peroxydisulphate, K_2SO_4 (for maintaining the ionic strength) and HCl (for maintaining the uniform acid strength). Organic phase containing the monomer and solvent and was flushed with purified nitrogen gas before starting the experiment. The polymerization reaction was started under nitrogen atmosphere by adding the initiator of known concentration to the reaction mixture and simultaneously starting the stop watch. The reaction tube was then carefully sealed by rubber gaskets to ensure an inert atmosphere throughout. Polymerization started when PDS was added to the reaction mixture and precipitation of polymer was observed. The reaction was arrested by pouring the reaction mixture into an ice-cold methanol containing trace amount of hydroquinone. The polymer were filtered quantitatively through a G4 sintered glass crucible, washed several times with distilled water followed by anhydrous methanol and finally dried at 40°C in a vacuum oven to constant weight. The rate of polymerization (R_p) was calculated from the gravimetric determination of the polymer formed in a given time of polymerization. The conversion was restricted to 15 percent in all polymerization studies.

$$R_p = \frac{100 W}{V. t. M}$$

R_p was calculated from the weight of polymer obtained by using the formula

Where W=Weight of the polymer in gram, V=Volume of the reaction mixture in ml, t=reaction time in seconds, M=molecular weight of the monomer.

3. RESULTS AND DISCUSSION

3.1. Steady state rate of polymerization: It was ascertained by carrying out the experiments at different time intervals. The steady state rate of polymerization of acrylonitrile was obtained after 40 minutes. A sharp increase in R_p was observed initially which decreased thereafter and then attained a constant value (Table 1). The plot of R_p versus time shows an increase to some extent due to less viscosity of the medium which facilitates greater transfer of peroxydisulphate to organic phase, slightly decreased thereafter due to more viscosity of the medium with increasing time and then remains constant (Figure 1). The polymerization reaction was carried out at $60 \pm 1^\circ\text{C}$ with the reaction time of acrylonitrile monomer.

3.2. The effect of monomer concentration on the rate of polymerization (R_p): It was studied by varying monomer concentration in the range $0.9\text{--}1.9\text{ mol dm}^{-3}$ at the fixed concentration of initiator and catalyst (Table 2). The rate of polymerization increases with increasing monomer concentration. The order of the reaction was obtained from a plot of $\log R_p$ versus $\log [\text{AN}]$ and the value was found to be unity. A plot of R_p versus $[\text{AN}]^{1.0}$ is linear passing through the origin (Figure 2).

3.3. Effect of initiator concentration on the rate of polymerization (R_p): It has been studied in the concentration range of $0.00150\text{ to }0.0250\text{ mol dm}^{-3}$ at fixed concentration of monomer and catalyst (Table 3). The rate of polymerization increased with an increase of initiator concentration and the order is found to be unity from plot of $\log R_p$ versus $\log [\text{initiator}]$. A plot of R_p versus $[\text{initiator}]^{1.0}$ is also linear passing through the origin (Figure 3).

3.4. Effect of PTC concentration on rate of polymerization (R_p): It was studied by varying the PTC concentration from $0.0075\text{ to }0.0125\text{ mol dm}^{-3}$ at fixed concentration of monomer and initiator (Table 4). A plot of $\log R_p$ versus $\log [\text{PTC}]$ is found to increase with increase in concentration of PTC. Order of the reaction is found to be 0.5 (Figure 4).

3.5. Effect of temperature on the rate of polymerization (R_p): It was studied by varying the temperature from $50\text{--}65^\circ\text{C}$ at fixed concentration of monomer, initiator and catalyst, R_p is found to increase with an increase in temperature (Table 5). Activation energies for the polymerization of acrylonitrile using the catalyst have been calculated from the slope of a plot of $\log R_p$ versus $1/T$ (Figure 5).

3.6. Characterization of polyacrylonitrile: The polyacrylonitrile prepared by free radical polymerization coupled with phase transfer catalyst was characterized by FT-IR, thermal and XRD analysis.

3.7. FT-IR Spectral analysis of polyacrylonitrile: In the FT-IR Spectral analysis of polyacrylonitrile peak at 1457.3 cm^{-1} was due to C-H bending and peak at 2245.1 cm^{-1} due to the presence of nitrile ($-\text{C}\equiv\text{N}$), peak at 2940 cm^{-1} , 2873 cm^{-1} indicates the presence of $-\text{CH}_2$ symmetric and asymmetric respectively (Figure 6).

3.8. Thermal analysis of polyacrylonitrile: It was carried out by using TA (DSC Q10 TGA Q600) instrument with the sample weight of 4.26 mg at heating rate of 15°C per minutes in temperature range of $30\text{--}600^\circ\text{C}$. The DSC curve indicates the glass transition temperature of polyacrylonitrile as 193.64°C . In TGA curve PAN showed no weight loss upto 279.78°C onset degradation temperature falls at 289.79°C around 474.63°C the compound undergoes maximum decomposition leaving residue of 52.32% (Figure 8).

3.9. XRD analysis of polyacrylonitrile: The wide range angle X-ray diffraction pattern was recorded on PAN analytical Xpert PRO instrument operated at $\text{Cu K}\alpha$ radiation wavelength 1.54 \AA at 45 mA and Kv . The XRD pattern shows the semi-crystalline nature of polyacrylonitrile. (Figure 7).

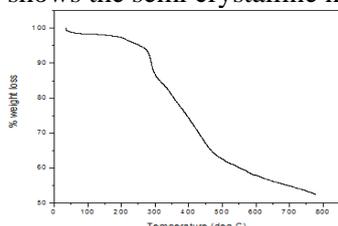


Figure.1.TGA for PAN

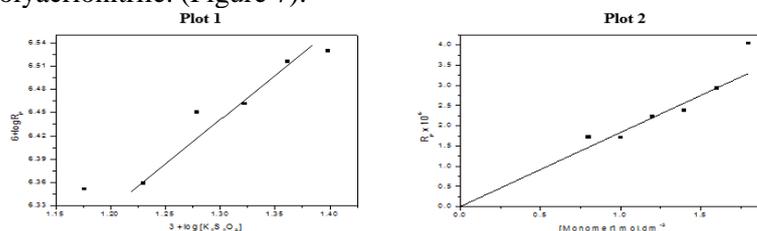


Figure.2.AN-PTC- $\text{K}_2\text{S}_2\text{O}_8$ dependence of R_p on $[\text{Monomer}]$

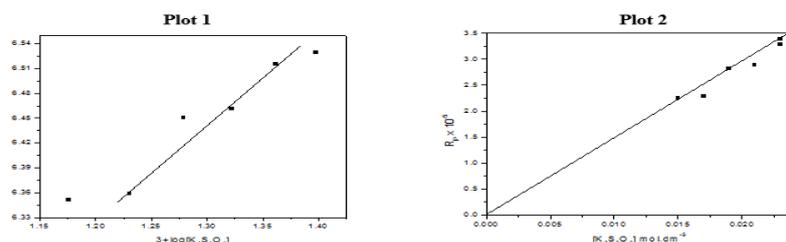


Figure.3. AN-PTC- $\text{K}_2\text{S}_2\text{O}_8$ system Effect of initiator concentration on R_p

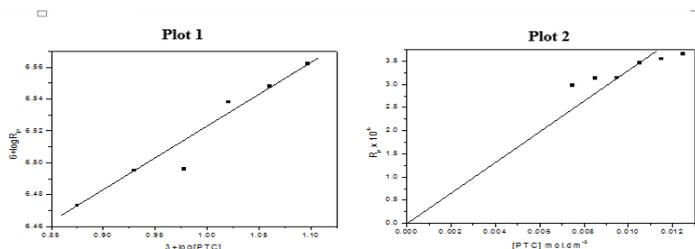


Figure.4.AN-PTC-K₂S₂O₈ dependence of Rp on [PTC]

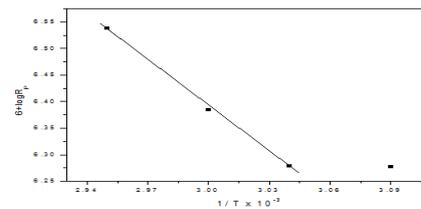


Figure.5.AN-PTC-K₂S₂O₈ System Arrhenius plot

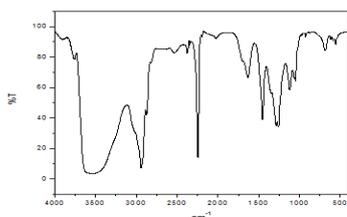


Figure.6.FTIR-IR for PAN

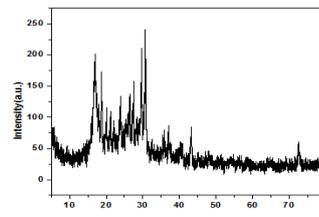


Figure.7.XRD for PAN

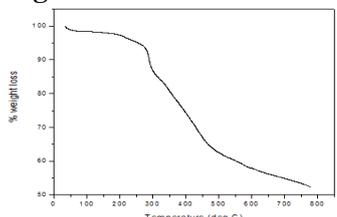


Figure.8.TGA for PAN

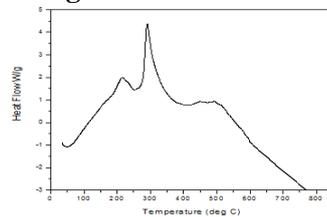


Figure.9.DSC for PAN

Table 1 AN-PTC- K₂S₂O₈ System Steady State Rate of Polymerization

S.No	Time (min)	R _p × 10 ⁻⁵ mol dm ⁻³ s ⁻¹
1	10	9.8630
2	20	5.7010
3	30	4.7116
4	40	3.4905
5	50	2.5537
6	60	3.4700
7	70	3.4000

Table.2.AN-PTC- K₂S₂O₈ System Dependence of Rp on [Monomer]

[AN] mol dm ⁻³	R _p × 10 ⁻⁵ mol dm ⁻³ s ⁻¹	3+log[AN]	6+log[R p]
0.8	1.7240	2.9030	1.2365
1.0	1.7080	3.0000	1.2324
1.2	2.2260	3.0791	1.3475
1.4	2.3790	3.1461	1.3763
1.6	2.9290	3.2041	1.4667
1.8	4.0400	3.2552	1.6063

Table.3.AN-PTC- K₂S₂O₈ System Effect of Initiator Concentration on Rp

[K ₂ S ₂ O ₈] mol.dm ⁻³	RP × 10 ⁻⁵ mol dm ⁻³	3+log[K ₂ S ₂ O ₈]	6+logRP
0.0150	2.2425	1.1760	1.3507
0.0175	2.2851	1.2304	1.3589
0.0190	2.8230	1.2787	1.4507
0.0210	2.8937	1.3222	1.4614
0.0230	23.2785	1.3617	1.5156
0.0250	3.3845	1.3979	1.5294

Table.4.AN-PTC- $K_2S_2O_8$ System Dependence of R_p on [PTC]

[PTC] mol.dm ⁻³	$R_p \times 10^{-5}$ mol dm ⁻³	3+log[PTC]	6+log R_p
0.0075	2.972	0.8750	6.473
0.0085	3.133	0.9299	6.495
0.0095	3.137	0.9777	6.496
0.0105	3.145	1.0211	6.538
0.0115	3.456	1.0606	6.548
0.0125	3.648	1.0969	6.562

Table.5.AN-PTC- $K_2S_2O_8$ system Dependence of R_p on Temperature

Temperature (K)	$R_p \times 10^{-5}$ mol dm ⁻³	1/T $\times 10^{-3}$ (K ⁻¹)	6+log R_p
323	1.8919	3.096	1.2768
328	1.896	3.040	1.2778
333	3.4570	3.003	1.5379
338	2.4230	2.959	1.3343

4. CONCLUSION

The kinetic mechanism of free radical polymerization of acrylonitrile was studied. In the experimental method the chemical employed for the synthesis di-site phase transfer catalyst and other techniques were discussed. The free radical polymerization of acrylonitrile were performed with 1,2 bis (N,N dimethyl N-N decyl) ammonium ethyl dibromide as PTC. The dependence of rate of polymerization on the various experimental conditions such as different concentration of monomer, PTC, initiator and temperature as discussed. The order with respect to monomer catalyst and initiator was found to be 1, 0.5, 1 respectively. Activation energy for the polymerization of AN was calculated from the slope of R_p versus 1/T in the temperature range 55-70° C. This chapter also deals with the characterization of the polymer obtained by various techniques such as FT-IR, XRD and Thermal analysis.

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