BATCH SUSPENSION POLYMERIZATION OF POLY ACRYLONITRILE: STUDY OF DIFFERENT INITIATORS

[1] **Y S Patel**, [2] **P K Patel**
[1]Lecturer , [2]Lecturer
[1]Chemical Engineering Department,
[1]Government Polytechnic Gandhinagar
[1]Gandhinagar, India

Abstract: This Experimental work provides information about synthesis of high molecular weight Poly Acrylonitrile polymers by batch suspension polymerization carried out at 55^0C in the pH range 2.5–3.0. Effect of different mixed initiators i.e. ammonium persulphate (APS), potassium persulphate, (KPS) and 2,2, Azo bis isobutyronitrile (AIBN) along with co initiators i.e. sodium meta bi sulphite(MBS) on final conversion, intrinsic viscosity ,molecular weight were studied. Final polymer was characterized by IR and DSC. The best quality of product was obtained using mixed initiator APS+MBS system (APS conc. =0.00583 mol/lit & MBS conc. =0.00292 mol/lit).The maximum molecular weight of PAN was obtained $1.12*10^5$ and optimum conversion was 73%. IR spectrum indicates a true homopolymer was formed and from DSC analysis, the glass transition temperature of final PAN polymer was **300^0C** which is higher as compared to copolymer.

Index Terms: **Batch suspension polymerization, poly acrylonitrile, initiator.**

I. INTRODUCTION

Suspension Polymerization is a heterogeneous process in which the monomer or mixture of monomers are suspended as the continuous phase of droplets (0.001-1Cm diameter)by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. Final polymer is obtained in form of fine spherical particles suspended in a continuous medium so this polymerization also known as Pearl Polymerization, Bead Polymerization or granular polymerization.[1]This is the most important industrial method for the preparation of a wide variety of industrial polymers like, Poly Styrene, PVC, Styrene Acrylonitrile, Polymers and co polymers of various acrylates etc. It has following advantages compared with other polymerization processes (viz. Bulk, Solution and Emulsion) .[2]

- ➢ Easy heat removal and temperature control.
- ➢ Low dispersion viscosity
- ➢ Low levels of impurities in the polymerization products
- ➢ Low separation cost
- ➢ Final product as spherical beads

U. S. satpathy et al studied the influence of reaction pressure on the rate of polymerization and intrinsic viscosity in acrylonitrile, (AN), Methyl acrylate (MA) and itaconic acid (IA) ternary suspension polymerization system using free radical forming potassium persulphate and sodium metabisulphite water soluble redox initiator pair. They found the conversion decrease while the IV increase with an increase in reaction pressure from normal to 6 bar.[3] Experimental work was carried out by D.C.Gupta et al to observe the effect of different co monomers such as Vinyl acetate, Methyl sulfonate, and Sodium salt on the thermal degradation of PAN by using DSC. The initial decomposition temperatures for all copolymers are less than that for PAN.[4] Konar et al studied the kinetics of aqueous batch polymerization of ACN initiated by the Permanganate-Oxalic acid redox pair at 32ºC they found the steady state rate varies approximately linearly at high monomer concentration. At low monomer concentration the steady state rate is not attained.[5]

Acrylonitrile is an active monomer capable of forming high molecular weight products with unique properties by addition polymerization. On the other hand, Ultra high molecular weight (MW) PAN is a potential candidate for making high tenacity fiber which can be used ultimately for making carbon fiber via carbonization process. As such homo PAN is a useful material for commodity application. MW and MWD have an important effect on the mechanical properties of the PAN. High MW PAN is suitable for producing specialty polymer which used in carbon fiber manufacturing. High MW polymer favour better orientation due to high degree stretch ability of polymer chain which lead to produce high tenacity fiber.[5]

In this work number of experiments were carried out to understand the kinetic features of suspension polymerization of ACN with use of different initiators and mixed initiating systems. Key process variables namely, initiator concn., temperature, iron dose etc. were optimized to achieve high molecular weight PAN.[6]

Materials and Methods: Total fifty experiments were carried out to prepare Poly Acrylonitrile polymer by batch suspension polymerization using monomer acrylonitrile (128 gm AR grade) and water (450 gm) as a basic ingredients, small quantity of $FeCl_2$ is added as an activator. Three different initiator systems were studied i.e. ammonium persulphate (APS), potassium persulphate, (KPS) and 2,2, Azo bis isobutyronitrile(AIBN) along with co initiators i.e. sodium meta bi sulphite(MBS). Polymerization was carried out in two liter, four -necked glass reactor placed in constant temperature bath at 55^0C and in the pH was maintained 2.5–3.0, using 10% dilute H_2SO_4. The agitator speed was maintained at 250 rpm as measured by STROBOSCOPE. Nitrogen was purged to maintain inert atmosphere and under this inert environment batch polymerization reaction was carried out for one hour. After completion of reaction time the instantaneous conversion was measured and tabulated.[6]

Characterization of final Polymer: Final PAN Polymer was characterized by following analysis.

Instantaneous Conversion: After completion of reaction for 1 hr the reaction mass was cooled up to 30 ^{0}C and PAN polymer was precipitated with D.M. water, filtered using whatmann filter paper and then dried at 50-55 ^{0}C in vacuum oven. Instantaneous conversion was calculated by weighing the final dried polymer.[6]

Intrinsic Viscosity : Solution of final polymer (0.2- 0.1wt%) was prepared using Dimethyl formamide as a solvent at 30^{0}C and intrinsic viscosity was determined using Ubbelohde suspended level viscometer at constant temperature of 30^{0}C. From Intrinsic Viscosity, viscosity average molecular weight (Mv) was determined by using Mark-Houwkin's equation: $[\eta] = k\,(Mv)^{a}$
Where,$[\eta]$ is intrinsic viscosity; k and a are constants for a given polymer/solvent/temperature system($k=3.335* 10^{-4}$, $a=0.75$).[7]

Final polymer Composition by IR Spectroscopy: The IR spectra of the selected polymer samples were recorder on PERKIN ELNER / 600 FTIR SPECTRO PHOTOMETER as shown in Fig.1.

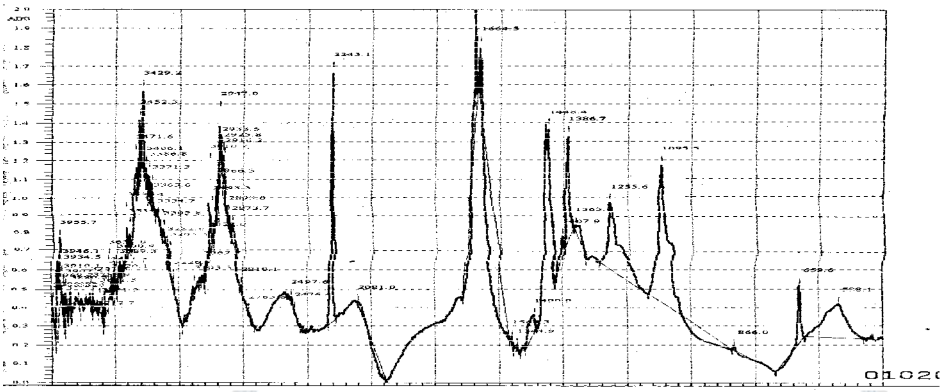

Fig. 1 IR Spectra for final PAN Polymer

IR spectra is free from absorption at 1720 cm^{-1} which clearly indicate the absence of ester carbonyl group from acrylate monomer..Absence of characteristic absorption at 1120 cm^{-1} ruled out the presence of acrylate. [6]

Glass Transition Temperature: The glass transition temperature of final polymer was obtained
Using PERKIN-ELMER 7 SERIES Thermal Analysis System.[6] The observed peak temperature is **300^{0}C** which is higher as compared to copolymer.[6]

RESULTS AND DISCUSSION:

[I] Mixed redox initiating system (APS+MBS):

(1) **Effect of APS concentration:** Four different concentration of APS i.e. 0.0029, 0.0058, 0.097, 0.14 mol/lit were studied by keeping all other parameters as per standard recipe. The conversion increases with increasing the concentration of APS as shown in fig 2. At low concentration of APS less number of free radicals are formed hence conversion is less while maximum conversion is obtained at optimum concentration0.097 mol/lit.

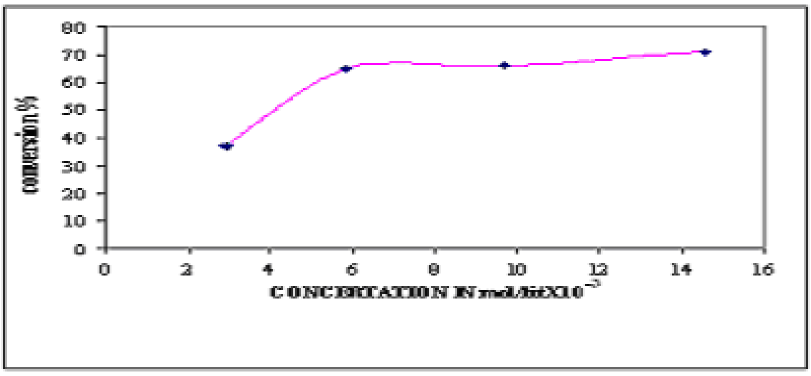

Fig. 2 Effect of APS concentration On % Conversion

Both intrinsic viscosity and molecular weight decrease with increasing APS concentration.1.07*105 is the h highest molecular weight of PAN which was obtained at low APS concentration 0.0029 mol/lit but the percentage conversion is only 37.1%. By optimizing APS concentration with respect to molecular weight and % conversion the optimum value is 0.00583 mol/lit with 64.84% conversion.[6]

(2) **Effect of MBS concentration:** Four different concentration of MBS i.e. 0.0035, 0.00876, 0.029, 0.046 mol/lit were studied by keeping all other parameters as per standard recipe. The conversion sharply increases with increasing the concentration of MBS as shown in fig 3.the optimum value of MBS concentration is 0.029 mol/lit obtain high molecular weight of 1.12*10^{5} with 73% conversion.[6]

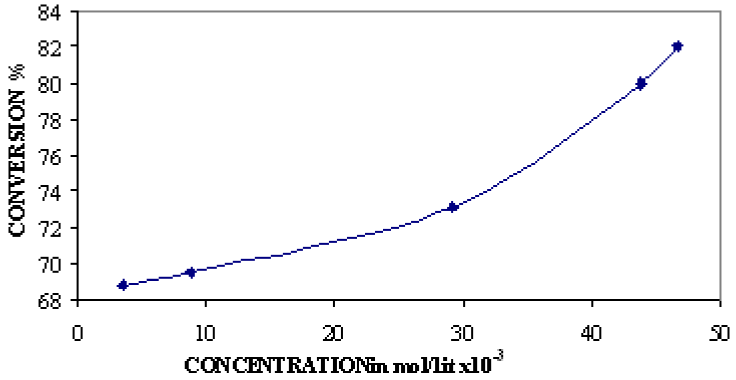

Fig. 3 Effect of MBS concentration On % Conversion

[II] Effect of oil soluble initiator (AIBN):

(1) **APS+AIBN system:** In this combination, AIBN is varied from 0.00677 to 0.00745 mol/lit and APS (0.0097 mol/lit) is fixed. With increase of AIBN, IV of polymer has decreased and conversion has increased but enhancement in conversion is not very significant i.e.61% only. This is due lower initiation rate of the mixed initiation system but MW of polymer is quite high. This is a good recipe for achieving high MW in the range of 36 to 21 lacs.

(2) **APS+MBS+AIBN system:** In a mixed initiation system, five different AIBN concentrations were varied keeping fixed concentration of APS and MBS in blend. All other variables were kept constant for polymerization of PAN. Increasing concentration of AIBN followed a usual trend i.e. with increase of AIBN concentration Molecular weight of polymer decreases from $1.34*10^5$to $0.72*10^5$ and conversion increases from 57.45% to 72.26% as shown in fig.4.[6]

In mixed initiation system, Desorption of radicals from particles increases the radical concentration in the aqueous system and decrease the termination event in the polymer particles and there bye influence on MW and MWD of polymer in mixed initiation system.[6]

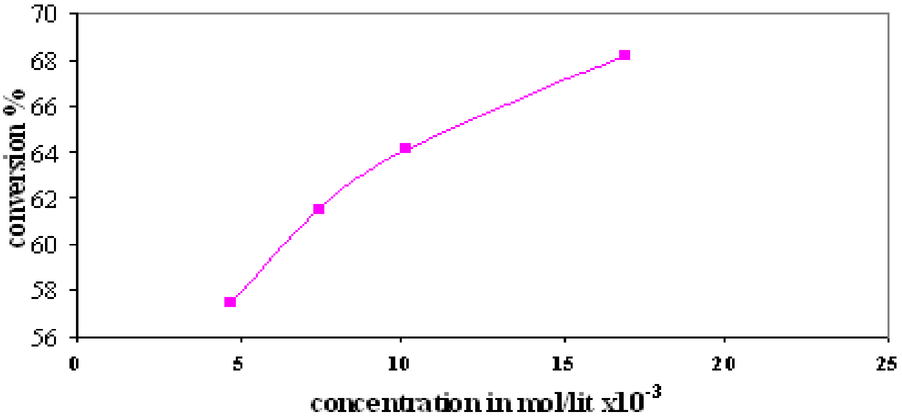

Fig. 4 Effect of AIBN conc. On % Conversion

[III] Effect of water soluble Thermal initiator (KPS): Two different concentration of KPS i.e. 4.11 and 8.22 mol/lit was studied for the fixed concentration of AIBN(0.006775mol/lit) molecular weight of polymer decrease with increase KPS concentration due to formation of more free radicals. At 4.11 mol/lit concentration highest molecular weight $6.14*10^5$ is obtained which is higher than APS+AIBN system but the conversion was very low only 51%.[6]

IV SUMMARY

SR. NO	INITIATION SYSTEM	%CONVERSION	MOLECULAR WEIGHT
1.	APS+MBS(BY VARYING APS CONCENTRATION)	64.84%	$0.93736*10^5$
2.	APS+MBS(BY VARYING MBS CONCENTRATION)	73%	$1.12*10^5$
3.	APS+AIBN(BY VARYING AIBN CONCENTRATION)	61%	$4.01288*10^5$
4.	APS+MBS+AIBN(BY VARYING AIBN CONCENTRATION)	68.2	$0.81451*10^5$
5.	KPS+AIBN(BY VARYING KPS CONCENTRATION)	51	$6.14*10^5$

From the present study on laboratory synthesis of High Molecular Weight Poly Acrylonitrile by one hr Batch Suspension Polymerization at 550C, the best quality of product was obtained for by separate mode of addition of initiator with 128/450 acrylonitrile/water weight ratio and APS+MBS mixed initiator system (APS conc.=0.00583 & MBS conc.=0.00292 mol/lit).The maximum molecular weight of PAN was obtained 1.12*105 and optimum conversion was 73%.These polymers had good solubility with organic polar solvent like Dimethylformamide (DMF), Dimethylsulphoxide (DMSO) etc. which indicate polymer has high degree purity with free from molecular defects.

REFERENCES

1. Elliot Farber, Suspension Polymerization, Encyclopedia of Polymer Science and Technology, Herman, F.Mark, Norman G. G.Ayloaro, Norbert. M.Bikales, 13,552-557, (1970).
2. Fred.W.Billmayer,Jr., Textbook Of Polymer Science,3rded, John Wiley & Sons,Inc., New York,1984.
3. U.S.Sathpathy, P.V.C.Rao, R.C.Jain; High Pressure Synthesis and Charactrization of Acrylonitrile Based Copolymers In Aqueous Free Radical Polymerization Usying NMR spectroscopy"; Inter.J.Polymeric Mater; 18, 105, (1992).
4. D.C.Gupta, J.P.Agrval and R.C.Sharma; Effect of Co Monomer on Thermal Degradation of Polyacrylonitrile. J.Appl.Polym. Sci.; 38,265, (1989).
5. R.S.Konar and S.S.Palit; Permanganate-Oxalic Acid as Redox Initiator of Acrylonitrile Polymerization In Aqueous Media"; J.Polym.Sci.General Papers; Part-1, **2**, 1731, (1964).
6. Yamini Patel, Synthesis and Charactrization of Polyacrylonitrile by free radical suspension polymerization , M.E.Thesis, D.D.I.T,Deemed University, Nadiad, 2005-2006
7. R.L.Cleland and Walter H. Stockmayer; an Intrinsic Viscosity-Molecular Weight Relation For Polyacrlonitrile; J.Polym. Sci.; 17,473, (1955).
8. Odian George, Principles of Polymerization, 2nd edn , John Wiley and Sons, New York, 1970.