# EXPERIMENTAL STUDY, MATHEMATICAL MODELLING FOR SOLUTION POLYMERIZATION OF ACRYLONITRILE

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## Abstract

Free radical solution polymerization of acrylonitrile in dimethyl sulfoxide (DMSO) solvent using 2,2'-azobisisobutyronitrile (AIBN) initiator was carried out to prepare polyacrylonitrile (PAN) solution for spinning acrylic precursor fiber for carbon fiber. The polymerization reaction was conducted in a batch reactor at constant temperature, whereas, initiator concentration was varied to achieve desired molecular weight and polymer conversion. The polymer prepared in these reactions yielded narrow molecular weight distribution (1.71-1.84). A mathematical model for free radical polymerization was derived through method of moments, simulated using MATLAB software and result compared with experiments. The kinetic rate constants for polymerization were taken from literature except chain transfer to solvent, which was estimated through model fitting to experimental results as 0.025 $m^3$/mol.min. The predicted molecular weights and conversion agreed reasonably well with the experimental results.

Keywords: Acrylonitrile solution polymerization, AIBN, DMSO, Carbon fiber, method of moments, Modelling, simulation

## 1. Introduction

Polyacrylonitrile (PAN) fibers are the most preferred precursor to prepare high performance carbon fibers. Despite the superior properties like corrosion resistance, high specific strength etc., the carbon fibers could not substitute the conventional engineering materials yet in general engineering sector due to its high cost. The major cost component in manufacturing of carbon fibers is the precursor cost, which accounts for >50% of overall production cost of carbon fiber [1]. In this context, synthesizing PAN using solution polymerization method is very effective step to reduce cost of carbon fiber. The polymer solution obtained through solution polymerization can be used directly for fiber spinning without the need of polymer isolation and re-dissolution of polymer, as in the case of slurry polymerization process. The elimination of these energy intensive operations from the process, have profound effect in cost reduction. The polymer solution after the removal of unreacted acrylonitrile (AN) and adjustment of PAN concentration can directly be extruded for preparation of acrylic precursor fiber. The solution polymerization is carried out in organic solvent such as Dimethyl formamide (DMF), Dimethyl acetamide (DMAc), Dimethyl sulfoxide (DMSO) etc. using free radical initiator. The rate constant for chain transfer reaction is much lower for DMSO than those of DMF and DMAc solvents, which makes it suitable for achieving higher

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molecular weights at much faster reaction rates [2]. It has been well known that the co-monomers have a significant effect on stabilization process, enhancing the segmental mobility of the polymer chains resulting in better orientation and mechanical properties of the precursor and resulting carbon fibers [3]. A very small amount of 0.5-1.0 mol % of itaconic acid co-monomer hugely improves the resultant carbon fiber properties [4]. In recent years, many researchers have studied the reaction kinetics of acrylonitrile solution polymerization. The temperature dependence on the monomer reactivity ratios of AN and IA and the homo-polymerization kinetics of AN in DMSO was investigated by free radical solution polymerization [5].The dissociation constant ($k_d$) for AIBN in DMSO at 60-80°C reaction temperature has been evaluated experimentally and reported as $4.3375x10^{15}\left(\dfrac{-131.054x10^{-8}}{RT}\right)$ sec$^{-1}$. Where, 'R' is gas constant and 'T' is the dissociation temperature of AIBN. The polymerization propagation reaction rate constants for AN homo-polymerization at 25, 50 and 75 °C in bulk were reported as1910, 3200 and 4600 L mol$^{-1}$ s$^{-1}$ respectively and the overall termination rate constants for homo-polymerization of AN in DMSO at 25, 50 and 78 °C have been reported as 2.9 x $10^8$, 3.0 x $10^8$ and 3.1 x $10^8$ Lmol$^{-1}$s$^{-1}$ respectively [6], [7]. The termination reaction studies [8] of acrylonitrile polymerization in DMF reveals that termination occurs predominantly by coupling [~ 92 %] rather than by disproportion [~ 8 %].

The acrylonitrile solution polymerization reaction kinetics is studied by various researchers. However, a mathematical model for solution polymerization of acrylonitrile to evaluate both molecular weight and conversion in batch mode has not been attempted. In this paper, a mathematical model has been developed for acrylonitrile solution polymerisation at 58.5±1 °C in DMSO solvent using AIBN initiator. The effect on intrinsic viscosity (IV), molecular weights and conversion of PAN with respect to change in initiator concentration have been examined using this model. Also examined experimentally the similar effect and results have been compared.

## 2. Materials And Methods

### A. Materials

Acrylonitrile (AN), Itaconic acid (IA), dimethyl sulfoxide (DMSO) and AIBN were used to prepare the PAN polymer. Tae Kwang Industrial Co Ltd make acrylonitrile was procured from Karnataka Chemicals, India. Itaconic acid was supplied by NR Chemicals Pvt Ltd, Mumbai, India. 2,2'-azobisisobutyronitrile(AIBN) was supplied by Avra synthesis Pvt Ltd, Hyderabad, India. Hubei Xingfa Chemicals Group Co Ltd make dimethyl sulfoxide was purchased from Gem Corporation, India. The procured chemicals were used as received in the polymerisation reaction.

### B. Polymerisation reactor set up

As shown in Fig. 1, a glass kettle with lid connected with condenser and other accessories were used for polymerization. An oil bath was used to control the temperature of reaction mass inside the glass kettle. The oil bath temperature was controlled through dual mode controller employed for heating and cooling. A variable speed control agitator was used to enable uniform mixing of reaction mass throughout the reaction. The temperature control of polymerization was very critical because of reaction exothermicity and progressive viscosity build up during polymerization.
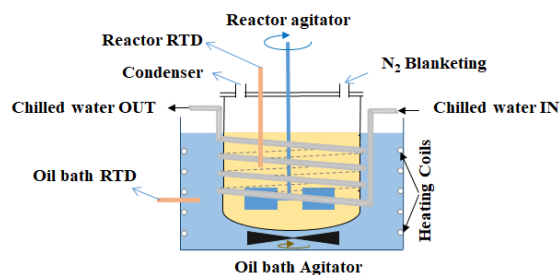
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**Fig. 1** Solution polymerization set up with dual mode temperature control

### C. Solution Polymerisation process

Acrylonitrile (AN) and itaconic acid (IA) monomers were used for preparing polymer using dimethyl sulfoxide (DMSO) as solvent in a glass batch reactor. The required amount of solvent and monomer were taken in a glass kettle. High purity nitrogen gas was purged through the reaction mixture before commencing of reaction. The solution was then heated in a constant temperature oil bath, AIBN initiator was added when the reaction temperature reached 58°C. The reaction was carried out for 300 minutes and the temperature during the progress of the reaction was maintained at 58.5± 1 °C through the heating and cooling modes. The polymerization condition is shown in Table I. The amount of solvent and monomer was kept constant, whereas, initiator concentration was varied from 0.54 % to 0.81 % (w/w). These experiments are denoted as Ex. 1, Ex. 2 and Ex.3. The initiator concentration was minimum in Ex. 1 and increased incrementally in Ex. 2 and Ex.3.

**Table I**: Solution polymerization reaction parameters

| Experiment No. | AIBN %[w/w] | Monomer %[w/w] | Reaction temperature [°C] |
|---|---|---|---|
| Ex.1 | 0.54 | 27 | 58.5± 1 |
| Ex.2 | 0.68 | 27 | 58.5± 1 |
| Ex.3 | 0.81 | 27 | 58.5± 1 |

The initiator concentration range was selected based on the desired molecular weight useful for carbon fiber preparation. The reaction mixture slowly becomes viscous with progress of reaction hence the agitator speed was kept high at 300 rpm to keep uniform mixing. A small quantity of polymer solution was withdrawn during the reaction at regular time intervals. The conversion and polymer content in the solution were estimated by precipitating the accurately weighed quantity of sample in distilled water. The polymer obtained was washed several times with freshwater and dried to constant weight in a hot air oven.The polymer prepared was characterized for intrinsic viscosity, molecular weights, molecular weight distribution (MWD) and Fourier transform infrared spectrum (FTIR) analysis.

### D. Characterisation of polymer

*Ubbelhode viscometer*

A 0.1% w/v of PAN in dimethylformamide was prepared to determine the inherent viscosity of polymer solution. Time of flow of the solvent and the polymer solution through the

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capillary of Ubbelhode viscometer was measured. The inherent viscosity is calculated from the following equation

$\eta_{0.1} = \frac{\ln(t_2 - t_1)}{c}$ Where $\eta_{0.1}$ is inherent viscosity, $t_2$ is time of flow for solution through the capillary, $t_1$ is time of flow for solvent through the capillary and c is polymer concentration in solution. The intrinsic viscosity $[\eta$ is calculated by the following equation

$$[\eta] = \left[ \frac{\left[ \frac{\eta_{sp}}{c} \right] - \eta_{0.1}}{c * 0.5} \right]^{0.5}$$

Where,

$\eta_{sp}$ is specific viscosity $\left\{ \left( \frac{t_2}{t_1} \right) - 1 \right\}$ and c is polymer concentration. The relationship between intrinsic viscosity of polymer and the weight average molecular weight of polymer is defined [9] as given below.

$$[\eta] = 2.78 * 10^{-4} [M_w]^{0.76} \dots. (1)$$

The Eq. (1) is used to calculate intrinsic viscosity of polymer predicted by the model and correlated with experimental results.

*Gel permeation Chromatography (GPC)*

Molecular weights of the polymer were determined using gel permeation chromatography, model GBC LC 1445 using Refractive Index (RI) detector. Dimethylformamide with 0.05 M lithium bromide was used as mobile phase at a flow rate of 1ml/min. Polymer Laboratories (PL) gel mixed B column was used. Universal calibration curve method using polyethylene oxide standards were used to determine the molecular weights of the PAN.

*Fourier transform infrared spectroscopy (FTIR)*

Polymer spectra were collected in the wavelength range of 4000-400 cm^{-1} with Perkin Elmer Frontier FTIR spectrometer equipped with Diamond ATR crystal accessory. Each spectrum was recorded at a resolution of 8 cm^{-1} utilizing 32 scans per sample. The frequency scale is accurate to 0.02 cm^{-1}. Individual polymer samples were placed onto the ATR crystal and the anvil was hand-tightened to apply pressure. Spectra of the polymer were collected using the data acquisition software of Frontier FTIR spectrometer.

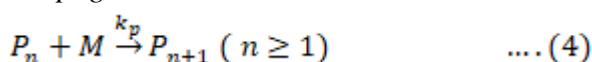### 3. Reaction Kinetics And Mathematical Model Development:

#### A. Reaction kinetics of batch solution polymerization of acrylonitrile

The overall kinetics of free radical solution polymerization involves four competing reactions- initiation, propagation, chain transfer and termination.
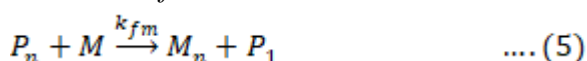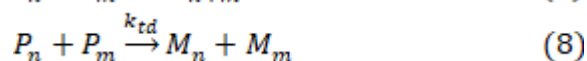
*Initiation*

$$I \xrightarrow{k_d} 2R \qquad \qquad \dots. (2)$$

$$R + M \xrightarrow{k_i} P_1 \qquad \qquad \dots. (3)$$

*Propagation*

$$P_n + M \xrightarrow{k_p} P_{n+1} \ (n \geq 1) \qquad \dots. (4)$$

*Chain transfer to monomer and solvent*

$$P_n + M \xrightarrow{k_{fm}} M_n + P_1 \qquad \dots. (5)$$

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$$P_n + S \xrightarrow{k_{fs}} M_n + P_1 \qquad \qquad \dots (6)$$

*Termination*

$$P_n + P_m \xrightarrow{k_{tc}} M_{n+m} \qquad \qquad (7)$$

$$P_n + P_m \xrightarrow{k_{td}} M_n + M_m \qquad \qquad (8)$$

In above equation, $I$ is initiator, $R$ is free radical, $P_n$ is the live polymer chain with $n$ numbers of repeating units of monomer, $M_n$ is the dead polymer chain with $n$ number of repeating units of monomer. Monomer and solvent are denoted by $M$ and $S$ respectively. $k_d$, $k_i$, $k_p$, $k_{fm}$, $k_{fs}$, $k_{tc}$, and $k_{td}$ are the rate constants for dissociation of initiator, initiation, propagation, chain transfer to the monomer, chain transfer to the solvent, termination by coupling and termination by disproportion reaction respectively.

Using the above rate equations, a mathematical model is derived for free radical acrylonitrile solution polymerization with following assumption.

 a. All radicals propagate with the same velocity constant ($k_p$), undergo termination with the same velocity constant ($k_t$), and transfer with the same velocity constant ($k_{tr}$).
 b. Addition and propagation steps proceed

with the same velocity constant ($k_i \sim k_p$).

 c. Since co-monomer content is < 1 mol %

only, it could be considered as homo-polymerization reactions
    for model simplification.

 d. Change in reaction volume during

polymerization is constant.

### B. Derivation of equations governing the process of batch polymerization

From Eq. (2) to Eq. (8), the following differential equations are derived for rate of initiation, propagation, rate of chain transfer, rate of termination for solution polymerization in batch mode.

*Rate of initiation*

$$-\frac{d[I]}{dt} = k_d[I] \qquad \qquad \dots (9)$$

$$\frac{d[R]}{dt} = 2fk_d[I] - k_i RM \qquad \qquad \dots (10)$$

*Rate of propagation*

$$\frac{-d[M]}{dt} = k_i MR + k_p[M] \sum_{n=1}^{\infty} [P_n] \qquad \dots (11)$$

*Rate of chain transfer to monomer*

$$\frac{-d[M]}{dt} = k_{fm}[M] \sum_{n=1}^{\infty} [P_n] \qquad \qquad \dots (12)$$

*Rate of chain transfer to solvent*

$$\frac{-d[S]}{dt} = k_{fs}[S] \sum_{n=1}^{\infty} [P_n] \qquad \qquad \dots (13)$$

*Rate of termination reaction by Coupling and disproportion*

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$$\frac{-d[P_n]}{dt} = (k_{tc} + k_{td})[P_n] \sum_{m=2}^{\infty} [P_m] \quad \dots (14)$$

Method of moments has been used by many authors for modelling and simulation in polymerization [10]-[12]. This tool is being used for modelling the polymerization process to estimate molecular weights and molecular weight distribution (MWD). In the polymerization kinetics the live and dead polymeric chain are defined as below,

$$\lambda_k = \sum_{n=1}^{\infty} n^k [M_n]$$

And

$$\mu_k = \sum_{n=1}^{\infty} n^k [P_n] \qquad \dots (15)$$

$\lambda_k$ and $\mu_k$ are defined as live and dead chain polymer moments respectively. Where, $k = 0,1,2$ are called $0^{th}$, $1^{st}$, $2^{nd}$ moments and so on. The $0^{th}$ moment $\lambda_0 = \sum_{n=1}^{\infty}[P_n]$ represents total concentration of live radicals and $\mu_0 = \sum_{n=1}^{\infty}[M_n]$ represents total concentration of dead polymer. The number average and weight average molecular weight are defined as follows,

$$MW_{No.avg.} = M_0 \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \qquad \dots (16) \text{ and}$$

$$MW_{Wt.avg.} = M_0 \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \qquad \dots (17)$$

Where, $M_0$ is the molecular weight of monomer.

As the concentration of live chain radicals is much smaller compared to dead chain, it can be ignored for molecular weight estimation. So Eq. (16) reduces to

$$MW_{No.avg.} \approx M_0 \frac{\mu_1}{\mu_0}$$

And Eq. (17) reduces to

$$MW_{Wt.avg.} \approx M_0 \frac{\mu_2}{\mu_1} \qquad \dots (18)$$

The live and dead chain moments equations for the batch reactor polymerization are derived in Appendix. The following derived differential equations for $0^{th}$, $1^{st}$ and $2^{nd}$ dead moments are given in Appendix as Eq. (m), Eq. (r) and Eq. (v) respectively.

$$\frac{d[\mu_0]}{dt} = (1 - \alpha)K_p[M]P + \frac{1}{2}k_{tc}P^2(1 - 2\alpha) \quad \dots (19)$$

$$\frac{d[\mu_1]}{dt} = \frac{P}{(1 - \alpha)}\left[k_{tc}P + \left((1 - \alpha)(2 - \alpha)K_p[M] - K_{tc}P\alpha(2 - \alpha)\right)\right] \quad \dots (20)$$

$$\frac{d[\mu_2]}{dt} = \frac{P}{(1 - \alpha)^2}[\{k_p[M](4 - 7\alpha + 4\alpha^2 - \alpha^3)\}$$
$$+ k_{tc}P\{2 - 3\alpha + 3\alpha^2 - \alpha^3\}] \qquad \dots (21)$$

The rate of total monomer consumption from Eq. (11)

$$\frac{d[M]}{dt} = -\left[k_i MR + k_p[M] \sum_{n=1}^{\infty} [P_n] + k_{fm}[M] \sum_{n=1}^{\infty} [P_n]\right] \quad \dots (22)$$

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The term $k_i MR$ in above Eq. (22) can be neglected as monomer consumed by this initiation reaction is much lower than monomer consumed by propagation and transfer to the solvent. So the above Eq. (22) is reduced to

$$\frac{d[M]}{dt} = -(k_p + k_{fm})[M]\lambda_0 \qquad \dots (23)$$

On substituting $\lambda_0$ from Appendix Eq. (e) in above Eq. (23)

$$\frac{d[M]}{dt} = -(k_p + k_{fm})[M]\sqrt{\frac{2fk_d[I]}{(k_{td} + k_{tc})}} \qquad \dots (24)$$

Fractional conversion (X) for the reaction is defined as ratio of monomer concentration to the initial monomer concentration in reaction

$$\frac{d[X]}{dt} = \frac{-(k_p + k_{fm})[M]\sqrt{\frac{2fk_d[I]}{(k_{td} + k_{tc})}}}{[M]_0} \qquad \dots (25)$$

Where, $[M]_0$ is the initial monomer concentration.

### C. Model Parameters:

The rate constants for the solution polymerization with AIBN and DMSO system are taken from literature as shown in Table II. The effect of initiator efficiency on polymerization is reported [13], [14] that it declines rapidly after certain stage of polymerization and continues in this manner till the end of reaction. Also, a free volume theory based empirical model was proposed to account the decrease in the efficiency of initiator with initial efficiency of 0.5 at the start of reaction. For the model simplification, the overall initiator efficiency is considered constant throughout the reaction and estimated through experimental data as 0.3.

**Table II**: Rate constants for polymerization at 58.5 °C temperature

| Rate constants | Values | Unit | Reference |
|---|---|---|---|
| $k_d$ | 0.00058 | l/min | [5] |
| $k_p$ | 218.36 | $m^3$/mol.min | [6], [7] |
| $k_{fm}$ | 0.0044 | $m^3$/mol.min | [15] |
| $k_{td}$ | 1454571 | $m^3$/mol.min | [6]- [8] |
| $k_{tc}$ | 16727571 | $m^3$/mol.min | [6]-[8] |
| $k_{fs}$ | 0.025 | $m^3$/mol.min | † |
| $f$ | 0.3 | - | ‡ |

† ‡ *estimated through simulated data fitting to experiments*

The rate constant for chain transfer to monomer ($k_{fm}$) is studied by Bernas, and Danon , as cited in [15]  and it is reported there the ratio of rate constant for chain transfer (to monomer) to the rate constant for propagation as 2 x 10^-5. The ratio of rate constant for chain transfer to solvent to propagation rate constant reported in literature is as low as 1.1 x 10^-5 at 50 °C [15]. This ratio is also reported by Ulbricht as cited in [15] as high as 7.9 x 10-5 at 50 °C. The rate constants reported in literature for initiator dissociation ($k_d$), propagation ($k_p$) and termination ($k_t$) by different researchers are nearly similar. Whereas, several values for rate constant for chain transfer to solvent is reported in literatures. In the present work, the rate constant for chain transfer to solvent is evaluated by experimental intrinsic viscosity and

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conversion data curve fitting with the simulated mathematical model with the rate constant parameters as mentioned in Table II. The best fit to the rate constant for chain transfer to solvent was observed as 0.025 $m^3$/mol. min at 58.5 °C.

## 4. Results And Discussion:

The Intrinsic viscosity and the molecular weight distribution of the polymer obtained in solution polymerization experiments were as shown in Table III. The intrinsic viscosities of the polymer formed in these experiments were found to reduce with increase in AIBN concentration.

**Table III**: Solution polymerization results

| Experiment No. | AIBN %[w/w] | Intrinsic Viscosity [dL/g] | MWD |
|---|---|---|---|
| Ex.1 | 0.54 | 2.38 | 1.71 |
| Ex.2 | 0.68 | 2.03 | 1.84 |
| Ex.3 | 0.81 | 1.86 | 1.82 |

The GPC signal response was normalized with respect to its peak values and the logarithmic molecular weight was plotted against it. GPC analysis of polymer sample from these experiments shown in Fig. 2 and the results in Table III confirmed narrow molecular weight distribution (1.71-1.84) for the polymer prepared in present work.
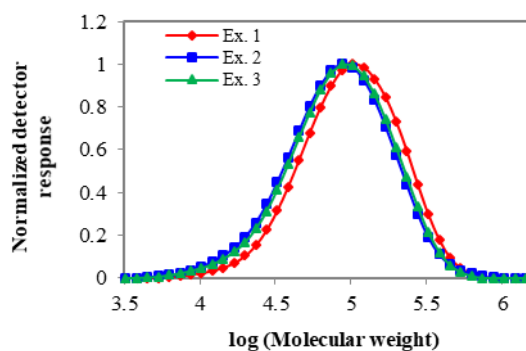


**Fig. 2** Normalized detector response of GPC vs Logarithmic molecular weight of polymers

Considering the model parameters as shown in Table II for all three reaction conditions (Ex. 1, Ex.2 and Ex.3), the differential equations [Eq. (9)], Eq. (13)] Eq. (19), Eq. (20), Eq. (21) and Eq. (25)] were solved using MATLAB software.
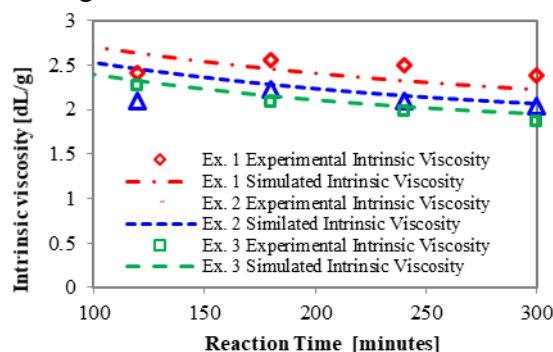


**Fig. 3** Experimented and simulated intrinsic viscosities (IV) of polymer with reaction progression

The intrinsic viscosities for experimental and simulated results are compared in Fig. 3. As it indicates, the intrinsic viscosities of polymer obtained are decreasing with the progress of polymerization. Intrinsic viscosity of polymer is directly proportional to its molecular

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weights. It also shows that increase in initiator concentration in polymer recipe leads to lower molecular weight polymer.
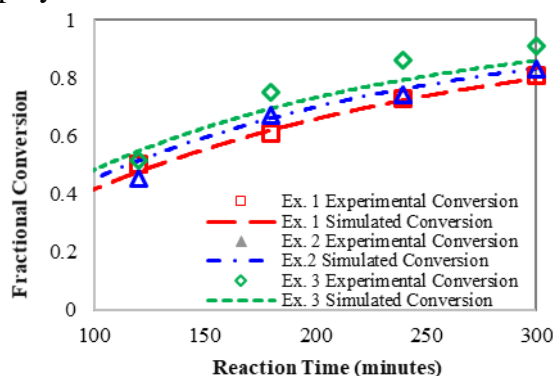


**Fig. 4** Experimented and simulated fractional conversion of polymer with reaction progression

In a free radical polymerisation reaction, higher initiator concentration present leads to more probability of free radicals and more possible number of growing/ propagating chains. The higher numbers of propagating chains reduce the chances of longer chain formation which lower the overall molecular weight of the polymer. The predicted data from mathematical model simulation and the experimental value for intrinsic viscosity of polymer are in agreement within experimental error as in Fig. 3.
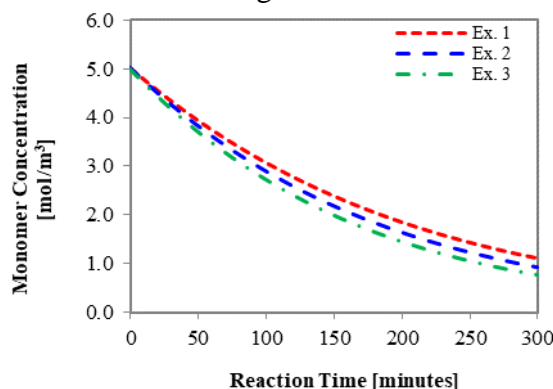


**Fig. 5 (a)** Simulated monomer concentration with reaction progression

Also, fractional conversion for the polymerization reactions predicted by the model and experimental values are shown in Fig. 4. The fractional conversion is increasing along with the progress of reaction. The agreement between the set of data is reasonably good. As the conversion is directly proportional to the square root of initiator content (Eq. (25)), the Ex. 3 polymer has given maximum conversion.
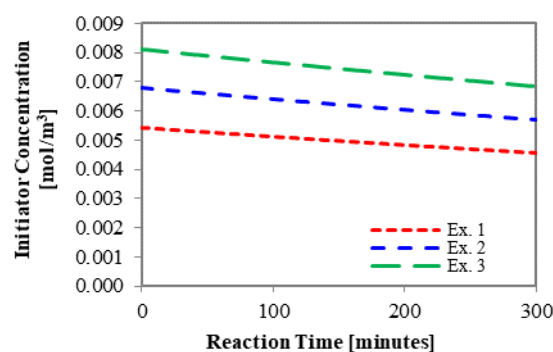


**Fig. 5 (b)** Simulated initiator concentration with reaction progression

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The simulated data further plotted as shown in Fig. 5 (a) and Fig. 5(b) for monomer and initiator concentration changes along with progress of reaction respectively. As Fig. 5(a) shows, the reduction in monomer concentration in Ex.3 is slightly faster as compared to Ex.1 and Ex. 2. The higher initiator content in Ex.3 promotes more active sites for chain initiation which leads to more consumption of monomer. The Fig. 5 (b) is the reduction in concentration of initiator with respect to reaction time. The plot for Ex. 3 reflects faster depletion of initiator concentration as compared to Ex. 1 and Ex. 2 indicating more consumption and also validates the monomer consumption as shown in Fig. 5(a). As the only variant in polymer reaction is initiator concentration, Fig. 5 (a) and Fig. 5 (b) also indicate the probability of difference in polymer molecular weights formed in these reactions.
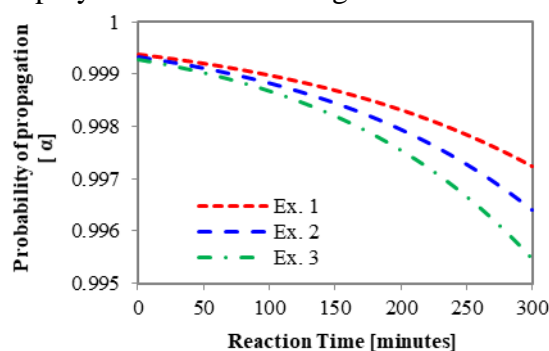


**Fig. 6** Simulated probability of propagation in polymerization with reaction progression

This could be better explained with probability of propagation ($\alpha$).The probability of propagation ($\alpha$) is defined in Appendix Eq. (*h*).The Fig. 6 displays the simulated data for probability of propagation during polymerization. This figure shows that higher concentration of initiator in Ex. (3) reflects more drop in probability of propagation which leads to the formation of lower molecular weight polymer.
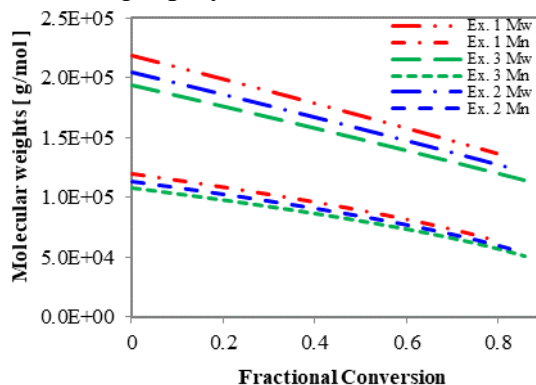


**Fig. 7** Simulated Molecular weight of polymers with respect to the fractional conversion

The Fig. 7 indicates the model simulated weight average molecular weight ($M_w$) and number averages molecular weight ($M_n$) with respect to the fractional conversion during polymerization. The molecular weight drop with fractional conversion also reflects decline of propagation rate towards the end of reaction.
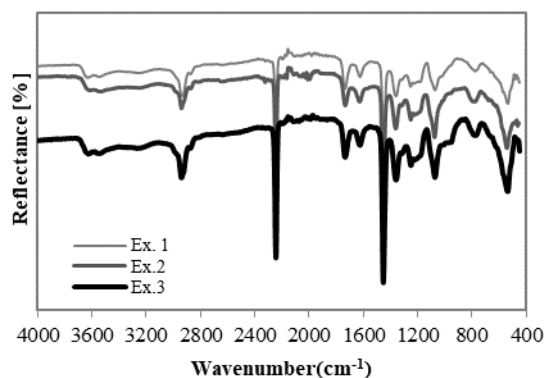
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**Fig. 8** FTIR spectra of polymer samples

The polymer samples were analysed by FTIR as shown in Fig. 8 for functional group, The broad band in the range $3100\sim2700\text{cm}^{-1}$ with its maximum at $2940\text{cm}^{-1}$ is assigned to the C—H stretching in CH, $CH_2$, $CH_3$ (including symmetrical and unsymmetrical stretching); the position of the -C≡N absorption at $2240\text{cm}^{-1}$ which is the strong absorption band in the polymers, indicates the presence of uninterrupted long sequences AN unit in polymers. The strong band in the range of $1750\sim1700\text{cm}^{-1}$ is due to the carbonyl (C=O) stretching band of itaconic acid co-monomer, the bands in the regions $1460\sim1440\text{cm}^{-1}$, $1370\sim1350\text{cm}^{-1}$ and $1270\sim1220\text{cm}^{-1}$ are assigned to the C—H vibrations of different modes. PAN prepared in these experiments gave similar FTIR spectrum.

## 5. Conclusions

Acrylonitrile solution polymerization in dimethyl sulfoxide solvent with varying 2,2'-azobisisobutyronitrile (AIBN) initiator content was conducted isothermally under batch mode operation. The molecular weight of the polymer (or intrinsic viscosity) had reduced with increase in initiator concentration. The mathematical model for batch solution polymerization with certain assumptions correlated well with experimental data. The agreement between the simulated and the experimental data lend credibility to the estimated rate constant for chain transfer to solvent was 0.025 $\text{m}^3$/mol. min at 58.5 °C. The narrow molecular weight distribution (1.71-1.84) of the polymer synthesised is suitable to produce a better precursor fiber for carbon fiber.

## 6. Acknowledgement:

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## APPENDIX

### *A. The live chain balance equation:*

The live chain balance for the batch reactor polymerization as defined in section III.B [Eq. (9) to Eq. (14)] can be written as

$$\frac{d[P_n]}{dt} = k_p M P_{n-1} - k_P[M][P_n] - (k_{fm}M + k_{fs}S)[P_n] - k_{td}[P_n]\sum_{m=2}^{\infty}[P_m]$$

$$- k_{tc}[P_n]\sum_{m=2}^{\infty}[P_m] \quad \ldots(a)$$

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The total live radical concentration is defined as $\lambda_0 = \sum_{n=1}^{\infty}[P_n]$, is noted as $P$

$0^{th}$ Live moment is defined as

$$\frac{d[\lambda_0]}{dt} = \frac{d[P_1]}{dt} + \frac{d[P_2]}{dt} + \frac{d[P_3]}{dt} + \cdots \quad ..(b)$$

$$\frac{d[P_1]}{dt} = k_i[M][R] - k_p[M][P_1] - (k_{fm}M + k_{fs}S)(P - [P_1]) - (k_{td} + k_{tc})[P_1]\sum_{m=2}^{\infty}[P_m]$$

$$\frac{d[P_2]}{dt} = k_p[M][P_1] - k_p[M][P_2] - (k_{fm}M + k_{fs}S)([P_2]) - (k_{td} + k_{tc})[P_2]\sum_{m=2}^{\infty}[P_m]$$

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Applying quasi steady state assumption (QSSA) which assumes the effective rate of change in radical chain formation is close to zero. Adding all the terms in Eq. (*b*) and can be written as

$$0 = \frac{d[\lambda_0]}{dt} = k_i[M][R] - (k_{td} + k_{tc})[P]\sum_{m=2}^{\infty}[P_m] \quad ...(c)$$

Also QSSA for section III.B Eq. (10)

$$0 = \frac{d[R]}{dt} = 2fk_d[I] - k_i[R][M] \quad ...(d)$$

Combining Eq. (*c*) and Eq. (*d*) and eliminating [R] from it,

$$\lambda_0 = \sqrt{\frac{2fk_d[I]}{(k_{td} + k_{tc})}} \quad ...(e)$$

By applying QSSA, the live chain moment Eq. (a) reduces as below

$$0 = \frac{d[P_n]}{dt} = k_pM[P_{n-1}] - k_p[M][P_n] + (k_{fm}M + k_{fs}S)[P_n] - k_{td}[P_n]\sum_{m=2}^{\infty}[P_m]$$

$$- k_{tc}[P_n]\sum_{m=2}^{\infty}[P_m] \quad ...(f)$$

On rearrangement,

$$\left[\frac{k_pM}{[k_p[M] + (k_{fm}M + k_{fs}S) + (k_{td} + k_{tc})P]}\right][P_{n-1}] = [P_n] \quad ..\ ...(g)$$

On defining a probability α of propagation reaction in polymerization as

$$\alpha = \left[\frac{k_pM}{[(k_p[M] + (k_{fm}[M] + k_{fs}[S]) + (k_{td} + k_{tc})[P])]}\right]$$
$$\qquad \qquad ...\ ...\ .....(h)$$

So, we can write Eq. (g) as

$$\alpha[P_{n-1}] = [P_n]$$
$$[P_2] = \alpha[P_1]$$
$$[P_3] = \alpha[P_2] = \alpha^2[P_1]$$

·········

$$[P_n] = \alpha^{n-1}P(1 - \alpha) \quad .....(i)$$

### B. The dead chain balance equations

The dead polymer chain balance for batch reactor polymerization as defines in section III.B

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[Eq. (9) to Eq. (14)] can be written as

$$\frac{d[M_n]}{dt} = \left(k_{fm}[M] + k_{fs}[S]\right)[P_n] + k_{td}P_n \sum_{n=1}^{\infty}[P_n] + \frac{1}{2}k_{tc}\sum_{n=1}^{\infty}\sum_{m=1}^{n-1}[P_m][P_{n-m}] \qquad \text{..... } (j)$$

The $0^{th}$ dead chain moment equation can be defined as:

$$\frac{d[\mu_0]}{dt} = \frac{d}{dt}\sum_{n=1}^{\infty}[M_n]$$

Or

$$\frac{d[\mu_0]}{dt} = \frac{d[M_1]}{dt} + \frac{d[M_2]}{dt} + \frac{d[M_3]}{dt} \qquad \text{..... } (k)$$

$$\frac{d[M_1]}{dt} = (k_{fm}[M] + k_{fs}[S])P_2 + k_{td}P_2P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_1][P_{2-1}]$$

$$\frac{d[M_2]}{dt} = (k_{fm}[M] + k_{fs}[S])P_3 + k_{td}P_3P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_2][P_{3-1}]$$

…

Adding all terms for R.H.S of Eq.(k)

$$\frac{d[\mu_0]}{dt} = (k_{fm}[M] + k_{fs}[S])(P_2 + P_3 + P_4 + \cdots \ldots\ldots) + k_{td}P(P_2 + P_3 + P_4 + \cdots \ldots)$$
$$+ \frac{1}{2}k_{tc}P^2$$

$$\frac{d[\mu_0]}{dt} = (k_{fm}[M] + k_{fs}[S] + k_{td}P)(P - P_1) + \frac{1}{2}k_{tc}P^2 \qquad \text{..... } (l)$$

On inserting the Eq.($h$) & Eq.($i$), the Eq.($l$) reduces to

$$\frac{d[\mu_0]}{dt} = (1 - \alpha)K_p[M]P + \frac{1}{2}k_{tc}P^2(1 - 2\alpha) \quad \text{.... } (m)$$

The $1^{st}$ dead moment equation can be defined as:

$$\frac{d[\mu_1]}{dt} = \frac{d}{dt}\sum_{n=1}^{\infty}[n.M_n]$$

$$\frac{d[\mu_1]}{dt} = \frac{d}{dt}\sum_{n=1}^{\infty}n[M_1] + n[M_2] + n[M_3] + \cdots$$

$$\frac{d[\mu_1]}{dt} = \sum_{n=1}^{\infty}n.\left[\frac{dM_1}{dt}\right] + n.\left[\frac{dM_2}{dt}\right] + n.\left[\frac{dM_3}{dt}\right] + \quad \text{..... } (n)$$

$$\frac{d[\mu_1]}{dt} = \sum_{n=2}^{\infty}\left[n\left((k_{fm}[M] + k_{fs}[S])P_2 - k_{td}P_2P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_1][P_{2-1}]\right)\right]$$
$$+ \sum_{n=2}^{\infty}n\left((k_{fm}[M] + k_{fs}[S])P_3 - k_{td}P_3P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_2][P_{3-1}]\right)$$
$$+ \quad \text{...} (o)$$

With the Eq.($h$) and Eq.($i$), above Eq. ($o$) is simplified as,

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$$\frac{d[\mu_1]}{dt} = (k_{fm}[M] + k_{fs}[S])P(1-\alpha)\sum_{n=2}^{\infty} n.\alpha^{n-1} + k_{td}P^2(1-\alpha)\sum_{n=2}^{\infty} n.\alpha^{n-1}$$

$$+ \frac{1}{2}k_{tc}P^2(1-\alpha)^2\sum_{n=2}^{\infty} n(n-1).\alpha^{n-2} \quad ..... (p)$$

With the help of arithmetic-geometric series expansion, the addition of the above equation is solved as

$$\sum_{n=2}^{\infty} n.\alpha^{n-1} = \frac{(2\alpha - \alpha^2)}{(1-\alpha)^2}$$

And

$$\sum_{n=2}^{\infty} n(n-1).\alpha^{n-2} = \frac{2}{(1-\alpha)^3}$$

On substituting the above in the Eq. ($p$), it reduces to

$$\frac{d[\mu_1]}{dt} = \frac{1}{(1-\alpha)}[k_{tc}P^2 + (k_{fm}[M] + k_{fs}[S] + Pk_{td})P(2\alpha - \alpha^2)] \,...(q)$$

On inserting the Eq.($h$) and Eq.($i$) in the Eq. ($q$) it reduces to

$$\frac{d[\mu_1]}{dt} = \frac{P}{(1-\alpha)}[k_{tc}P + ((1-\alpha)(2-\alpha)K_p[M] - K_{tc}P\alpha(2-\alpha))] \quad....(r)$$

The 2$^{nd}$ dead chain moment is defined as

$$\frac{d[\mu_2]}{dt} = \frac{d}{dt}\sum_{n=1}^{\infty} [n^2.M_n]$$

$$\frac{d[\mu_2]}{dt} = n^2\frac{d[M_1]}{dt} + n^2\frac{d[M_2]}{dt} + n^2\frac{d[M_3]}{dt} \,......$$

$$\frac{d[\mu_2]}{dt} = \sum_{n=2}^{\infty}\left[n^2\left((k_{fm}[M] + k_{fs}[S])P_2 - k_{td}P_2P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_1][P_{2-1}]\right)\right]$$

$$+ \sum_{n=2}^{\infty} n^2\left((k_{fm}[M] + k_{fs}[S])P_3 - k_{td}P_3P + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1}[P_2][P_{3-1}]\right)$$

$$+ \quad ......(s)$$

On inserting Eq.($h$) and Eq.($i$), the above Eq. ($s$) reduces to

$$\frac{d[\mu_2]}{dt} = (k_{fm}[M] + k_{fs}[S])P(1-\alpha)\sum_{n=2}^{\infty} n^2.\alpha^{n-1} + k_{td}P^2(1-\alpha)\sum_{n=2}^{\infty} n^2.\alpha^{n-1}$$

$$+ \frac{1}{2}k_{tc}P^2(1-\alpha)^2\sum_{n=2}^{\infty} n^2(n-1).\alpha^{n-2} \quad .....(t)$$

The arithmetic-geometric series summation is simplified as

$$\sum_{n=2}^{\infty} n^2.\alpha^{n-1} = \frac{(4\alpha - 3\alpha^2 + \alpha^3)}{(1-\alpha)^3}$$

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$$\sum_{n=2}^{\infty} n^2 (n-1).\alpha^{n-2} = \frac{2\alpha + 4}{(1-\alpha)^4}$$

On substitution above in Eq. ($t$), the 2$^{nd}$ dead chain moment become as

$$\frac{d[\mu_2]}{dt} = \frac{P}{(1-\alpha)^2} \left[ (k_{fm}[M] + k_{fs}[S]) + k_{td}P) (4\alpha - 3\alpha^2 + \alpha^3) + k_{tc}P(\alpha + 2) \right] \quad ..... (u)$$

Or with insertion of Eq.($h$) and Eq.($i$), the Eq.($u$) reduces to

$$\frac{d[\mu_2]}{dt} = \frac{P}{(1-\alpha)^2} \left[ \{k_p[M](4 - 7\alpha + 4\alpha^2 - \alpha^3)\} + k_{tc}P\{2 - 3\alpha + 3\alpha^2 - \alpha^3\} \right] \quad ...(v)$$

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