Data Article

Real time control data for styrene acrylonitrile copolymerization system in a batch reactor for the optimization of molecular weight

Sharanya Suraboyina, Saipushpita Vudata, Anand Polumati*

Process Engineering & Technology Transfer, CSIR- Indian Institute of Chemical Technology, Hyderabad, 500 007, India

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ABSTRACT

This work describes an approach towards experimental implementation of real time control studies conducted on a batch polymerization reactor. The information is related to the controlling of molecular weight for styrene acrylonitrile copolymerization system in a batch reactor generated under a varied range of temperatures, reactant concentrations and retention times. The operating conditions of 6 hrs and temperature of 343 K for yielding a molecular weight in the range of 39,900–40,000 gmol\(^{-1}\) is established using simulation studies. A real time control facility consisting of a batch reactor, data acquisition software “LabVIEW” and a PC for monitoring and control is used to implement these operating conditions. The resulting product is analyzed by gel permeation chromatography (GPC). The data generated can be used by researchers, academicians and industry for generating control strategies, automation and scale up of polymerization reactors.

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* Corresponding author.
E-mail address: anandp@csiriict.in (A. Polumati).

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1. Data

The dataset in this article describes the experimental studies for styrene acrylonitrile copolymerization in a batch reactor with varying temperatures. Real time temperature monitoring using DAQ with desired setpoint is shown in Fig. 1. Experimental conditions with varying temperatures shown in Table 1. GPC analysis results were shown in Table 2. Table 3 describes data acquired during the course of the reaction using DAQ system. Results of GPC calibration at bench scale experiment for optimum molecular weight is shown in Fig. 2. Fig. 3 shows the comparison of temperatures of reactor and jacket. Fig. 4 shows the heat duty and control action during the reaction. Fig. 5. GPC analysis report for the polymer in pilot scale experimentation.

2. Process and model description

In this work, styrene acrylonitrile copolymer is chosen where it is also modeled prior to experimentation [2,3]. The feed is a mixture of monomers \(M_1, M_2\), solvent and initiator \(I\). The mathematical model of the process is given as follows:
\[ \frac{dM_1}{dt} = u \left( M_{1f} - M_1 \right) / V - \left[ (k_{p11} + k_{f11}) P + (k_{p21} + k_{f21}) Q \right] M_1 \] (1)

\[ \frac{dM_2}{dt} = u \left( M_{2f} - M_2 \right) / V - \left[ (k_{p22} + k_{f22}) Q + (k_{p12} + k_{f12}) P \right] M_2 \] (2)

\[ \frac{dt}{dt} = u \left( I_f - I \right) / V - k_d I \] (3)

\[ \frac{dV}{dt} = u \] (4)

Table 1
Experimental condition with varying temperatures.

| Exp | Temp (K) | Styrene (g) | Acrylonitrile (g) | AIBN (g) | Xylene (g) | Polymer formed (g) | Mol. weight |
|-----|----------|-------------|-------------------|----------|------------|-------------------|-------------|
| 1   | 323      | 90.9        | 81.0              | 0.1      | 86.1       | 0.2989            | 64,200      |
| 2   | 333      | 90.9        | 81.0              | 0.1      | 86.1       | 3.5138            | 45,300      |
| 3   | 343      | 90.9        | 81.0              | 0.1      | 86.1       | 11.576            | 39,900      |

Table 2
GPC analysis.

| S.no | Elution volume (ml) | Retention time (min) | Mn   | Mw   | MP   | Mz   | Mz+1  | Mz/Mw |
|------|---------------------|----------------------|------|------|------|------|-------|-------|
| 1    | 16.70               | 16.72                | 50,880| 64,140| 73,800| 73,720| 81,030| 1.15  |
| 2    | 17.10               | 17.10                | 31,550| 45,270| 58,440| 55,510| 63,570| 1.22  |
| 3    | 17.07               | 17.07                | 24,100| 39,990| 59,520| 52,650| 61,980| 1.32  |

Fig. 1. Display of temperature of the reactor and set point during the reaction.
The moment equations for dead polymers are given by three moments:

\[
\frac{d\lambda_0^d}{dt} = (k_{tc11}/2 + k_{td11})P^2 + (k_{tc22}/2 + k_{td22})Q^2 + (k_{tc12} + 2k_{td12})PQ
\]

\[
+ (k_{f11}M_1 + k_{f12}M_2)P + (k_{f22}M_2 + k_{fj21}M_1)Q - \left(\lambda_0^d/V\right)u
\]

\[\text{(5)}\]

\[
\frac{d\lambda_1^d}{dt} = \left(k_{tc11}P + k_{td11}P + k_{tc12}Q + k_{td12}Q + k_{f11}M_1 + k_{f12}M_2\right)P_1
\]

\[
+ \left(k_{tc22}Q + k_{td22}Q + k_{tc12}P + k_{td12}P + k_{f22}M_2 + k_{fj21}M_1\right)Q_1 - \left(\lambda_1^d/V\right)u
\]

\[\text{(6)}\]

\[
\frac{d\lambda_2^d}{dt} = \left(k_{tc11}P + k_{td11}P + k_{tc12}Q + k_{td12}Q + k_{f11}M_1 + k_{f12}M_2\right)P_2
\]

\[
+ \left(k_{tc22}Q + k_{td22}Q + k_{tc12}P + k_{td12}P + k_{f22}M_2 + k_{fj21}M_1\right)Q_2 + k_{tc11}P_1^2
\]

\[
+ k_{tc22}Q_1^2 + 2k_{tc12}P_1Q_1 - \lambda_2^d/V
\]

\[\text{(7)}\]

The rate constants, \(k_d\), \(k_{ij}\), \(k_{pij}\), \(k_{tcij}\) and \(k_{tdij}\) are Arrhenius functions of temperature, the pre-exponential factors and activation energies of which are reported \[4\].

3. Experimental design, materials, and methods

Experiments were conducted for styrene acrylonitrile polymerization process in a batch reactor with the conditions mentioned in Table 1. Styrene and acrylonitrile of technical grade were used as the reactants. The solvent used is xylene and initiator is AIBN. The experiment was carried out for a constant set point of 343 K (70 °C). The total experiment was carried out for six hours. The product is just cooled to de-activate the polymerization and then precipitated the product into methanol to isolate the polymer. The sample at the end of reaction is given to GPC analysis for molecular weight determination. The monomer used in this study was obtained with 99% purity from Sigma Aldrich.

| Time (min) | Reactor Temperature(K) | Jacket inlet temperature(K) | Jacket outlet temperature(K) | Average temperature (K) | set point (K) | Control output | Duty cycle | Coolant Flow |
|------------|------------------------|-----------------------------|-----------------------------|------------------------|--------------|----------------|------------|--------------|
| 30         | 343.2373               | 278.7965                    | 329.610                     | 304.2036               | 343          | –4.1605        | 0.0000     | 0.0056       |
| 60         | 339.6759               | 280.4680                    | 319.048                     | 299.7580               | 343          | 12.2869        | 12.2869    | 0.0050       |
| 90         | 344.7579               | 282.1240                    | 321.5317                    | 301.8279               | 343          | 2.6171         | 2.6171     | 0.0050       |
| 120        | 341.8712               | 283.6707                    | 320.4821                    | 302.0764               | 343          | 9.0822         | 9.0822     | 0.0050       |
| 150        | 344.0171               | 285.1796                    | 321.4157                    | 303.2976               | 343          | 4.6150         | 4.6150     | 0.0050       |
| 180        | 342.5700               | 286.5934                    | 320.9544                    | 303.7739               | 343          | 7.4371         | 7.4371     | 0.0050       |
| 210        | 341.9505               | 282.6208                    | 321.1993                    | 301.9100               | 343          | 10.3653        | 10.3653    | 0.0050       |
| 240        | 345.1563               | 284.2869                    | 327.4002                    | 305.8435               | 343          | –1.4093        | 0.0000     | 0.0052       |
| 270        | 341.3274               | 285.8014                    | 319.9136                    | 302.8575               | 343          | 13.8799        | 13.8799    | 0.0050       |
| 300        | 345.5229               | 274.4257                    | 331.2528                    | 302.8392               | 343          | –3.9297        | 0.0000     | 0.0055       |
| 330        | 337.3121               | 274.2209                    | 318.6480                    | 296.4344               | 343          | 12.7421        | 12.7421    | 0.0050       |
| 360        | 346.4253               | 275.5112                    | 327.2502                    | 301.38078              | 343          | –3.1347        | 0.0000     | 0.0054       |
feedstock was maintained under a temperature of 4 °C in a cold room. The solvent used was xylene purchased from Aldrich with a purity of 99%, and was used without any further purification. Initially, the mixture of styrene and acrylonitrile was heated up to the desired initial temperature of 70 °C.

4. Data aquisition software

The data was monitored using a data aquisition software “LabVIEW” which is a commercial software package installed in the personnel computer to acquire, monitor, handle, analyze and log the data. All the control logic and the program for data logging is written using functions in the block diagram. All the controls and indicators are displayed in the front panel where we can also have online monitoring of the process in the form of charts at runtime. In the block diagram the process parameters are...
read using the input DAQ Assistant function. These values are logged into text files using the write to measurement file function. The process variable is given to the PI control function and the obtained controller output is fed back to the O/P modules using the output DAQ Assistant function. The required process values are given to a chart to have an online trend while running the process which can be seen on the front panel.

5. **Bench scale experiments**

Free radical polymerization experiments were carried out in 250 ml glass reactor to establish and optimize the process conditions. The experiment is conducted with varying temperatures (323, 333 and 343K) is listed in Table 1. The molecular weight is analyzed through GPC analysis and a molecular weight of approximate value of 39,900—40,000 is observed. GPC analysis as tabulated in Table 2, indicate the conformity of results with the simulated results Anand et al, 2013, 2014 [2,3].
Real time temperature monitoring using DAQ with desired set point is shown in Fig. 1. Results of GPC calibration at bench scale experiment for optimum molecular weight is shown in Fig. 2. Fig. 3 shows the comparison of temperatures of reactor and jacket. Fig. 4. Shows the heat duty and control action during the reaction. Fig. 5. GPC analysis report for the polymer in pilot scale experimentation.

6. Gel permeation chromatography (GPC)

The polymer synthesized at the end of the reaction time is subjected to GPC analysis for determination of molecular weight. The sample is first dissolved in solvent (THF-tetrahydrofuran) and is injected into a continually flowing stream of tetrahydrofuran (THF) without disturbing the continuous mobile phase flow at a flow rate of 0.05 ml/min. The mobile phase flows through millions of highly porous, rigid particles tightly packed together in a column. The column separates sample components from one another with rapid analyses. Detector used is refractive index to monitor molecular weight distribution which is directly proportional to concentration. In this procedure the molecular weight of the sample is determined based on the standards obtained by plotting the retention time against the log of molecular weight. The operating conditions for these methods are established as flow rate of 0.05 ml/min, detectors were refractive index, the temperature is 24 °C and the column porosities are 10000 Å. The molecular weight of SAN copolymer obtained through this method is 30,000.

7. Pilot scale experiments

The operating conditions of reaction time for 6 hrs and temperature of 343 K yield a molecular weight of 39,900 g mol⁻¹ which is nearer to the desired molecular weight of 40,000 g mol⁻¹ is selected as the best operating conditions. The experiment with optimal operating conditions is repeated in a 2 L batch reactor having a PC for online monitoring with data acquisition software. The experimental setup consists of a stainless-steel reactor (Parr) of 2 L capacity with an external jacket with an electric coil for heating, and also with an internal cooling coil. A total volume of 1200 ml of mixture (70% of styrene and 30% of acrylonitrile) was used to carry out the experiments. The experiments were carried out by monitoring and controlling the reactor temperature using the manipulated heater with the aid PID controller algorithms accordingly. The optimum operating conditions that are used in pilot scale experiments were temperature: 343K, styrene: 160ml, acrylonitrile:160ml, xylene:800ml and azobisobutyronitrile: 1.6 g.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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