

# Hybrid modeling approach for terpolymerization reactions in CSTR

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**Abstract:** In order to produce terpolymer of desired quality a model capable of simulating terpolymerization is required. Terpolymerization involves complex reactions, full-scale modeling using the first principle model is not practical to simulate reaction because there are many parameters to be estimated. In this study, a hybrid model that integrates the first-principles model and the DNN model is proposed. The proposed hybrid model reduces the parameters that need to be estimated using a cumulative composition model, through the steady-state assumption. Afterward, DNN model in a hybrid model estimates the conversion using measurement data from process sensors, and the terpolymer composition according to conversion is calculated. In the process, by estimating model parameters with error in variables model, hybrid model specific to the system is constructed. Validation of the hybrid model is performed using measurement data of 600 days and the result shows a good agreement with the actual data. The proposed hybrid model has high fidelity, scalability and robustness to other terpolymerization process.

*Keywords:* Terpolymerization, Hybrid model, Deep neural network(DNN), First-principle model, Process modeling and identification

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## 1. INTRODUCTION

A polymer using one or two monomers often fails to achieve desired physical and chemical properties. For this reason so-called terpolymerization, a polymerization that includes an additional third component as a reactive monomer, has been suggested to obtain the desired properties (Brar and Hekmatyar (1999)). Meanwhile, operating conditions including the reaction temperature and pressure along with the initial feed ratio of the monomers play a key role in the composition of terpolymer and product properties. In the polymer manufacturing process, CSTR (continuous stirred-tank reactor) is widely used for continuous operation. Several experimental studies showed the effect of variables such as feeding ratio and initiator concentration on terpolymerization in CSTR (Moslemi et al. (2018), Lee et al. (2001)). In order to produce a polymer of desired quality, it is important to know the reaction mechanism and internal composition, which is currently being measured through samples. Therefore, many studies have attempted to model terpolymerization through first principles (Alfrey and Goldfinger (1946), Dubé et al. (1997), Keramopoulos and Kiparissides (2003), Luciani and Choi (2021)).

A first-principle model of multi-component chain-growth polymerization has been presented by Dubé et al. (1997). Terpolymerization involving three reactive monomers has numerous reaction mechanisms and kinetic equations including the thermal and chemical initiation, reinitiation, propagation, chain transfer, and termination reaction. Each reaction has kinetic parameters, which need to be

estimated by experimental data. However, since estimating all the parameters is very difficult, full-scale modeling of the system is not a practical option. Instead, Kazemi (2010) suggested a new cumulative model for the reaction with a few parameters to be estimated through several assumptions. The model predicts the composition of the terpolymer with respect to the reaction conversion using the parameters. In this sense, in order to apply the model to the CSTR process, estimation of the conversion has to be conducted in advance.

DNNs (Deep neural networks) can generalize and predict highly nonlinear behaviors such as chemical reactions. Gbadago et al. (2021) estimate the yield and conversion of butadiene polymerization process using DNN. In this study, we integrate the first-principle model and DNN as a digital twin to simulate terpolymerization in CSTR. Specifically, the DNN model estimates the conversion from the process measurement data and the first-principle model calculates the product composition using the estimated conversion. Since the integrated model is based on both the first-principle model and the data, The constructed model is robust, simple, and physically interpretable. Simulation of acrylonitrile (AN)-styrene (St)-methyl methacrylate (MMA) terpolymization using the hybrid model is conducted as a case study. Due to its high ionic conductivity and acceptable mechanical stability, this terpolymer is widely used in the industry of batteries as a polymer matrix of the electrolytes (Kim and Sun (1998))

## 2. SIMULATION SETUP

### 2.1 First-principle model

The AG (Alfrey-Goldfinger) model suggested by Alfrey and Goldfinger (1946) is based on the terminal model and steady state approximation. The model reduces the model parameters for the terpolymerization system using reactivity ratios as reduced parameters and the resulting instantaneous composition equations are

$$\frac{\partial f_1}{\partial f_2} = \frac{F_1}{F_2} = \frac{f_1(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}})(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}})}{f_2(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{13}r_{23}})(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}})} \quad (1)$$

$$\frac{\partial f_1}{\partial f_3} = \frac{F_1}{F_3} = \frac{f_1(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}})(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}})}{f_3(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}})(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}})} \quad (2)$$

$$\frac{\partial f_2}{\partial f_3} = \frac{F_2}{F_3} = \frac{f_2(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{13}r_{23}})(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}})}{f_3(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}})(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}})} \quad (3)$$

where  $f_1, f_2$  and  $f_3$  are the mole fraction of unreacted monomer 1, 2 and 3, respectively,  $F$  is the instantaneous terpolymer composition and  $r_{ij}$  is the reactivity ratio between monomers  $i$  and  $j$ .

Kazemi (2010) showed the performances of the instantaneous model and cumulative model are similar at a low conversion level (less than 5-10%), but the instantaneous model shows performance degradation at a high conversion level because it ignores the initial feed change. Besides, the instantaneous model also requires instantaneous terpolymer composition which is practically not possible to measure using sensors. Meanwhile the cumulative model using DNI (direct numerical integration) approach developed by Kazemi et al. (2011) does not require the instantaneous data. Instead, the cumulative terpolymer composition and mole fraction of unreacted monomer are used. The composition and mole fraction are expressed as a function of conversion using the Skeist equation;

$$\frac{\partial f_i}{\partial X_n} = \frac{f_i - F_i}{1 - X_n} \quad (4)$$

$$\bar{F}_i = \frac{f_{i,0} - f_i(1 - X_n)}{X_n} \quad (5)$$

, where the overall molar conversion  $X_n$  is expressed as

$$X_n = X_w \frac{M_{w1}f_{1,0} + M_{w2}f_{2,0} + M_{w3}f_{3,0}}{M_{w1}\bar{F}_1 + M_{w2}\bar{F}_2 + M_{w3}\bar{F}_3} \quad (6)$$

where  $X_w$  is the weight conversion,  $f_{i,0}$  is the initial composition of monomer  $i$ ,  $\bar{F}_i$  is the cumulative terpolymer composition of monomer  $i$ , and  $M_{wi}$  is the molecular weight of monomer  $i$ .

### 2.2 EIV model reactivity ratio estimation

Terpolymerization reactions are highly sensitive to the changes in the model parameters. However, most of the

previous terpolymer studies generally adopt the kinetic parameters from binary polymerization reactions. Scott and Penlidis (2018) showed that parameter estimation specific to the system is essential in that the ternary reactivity ratio is significantly different from the binary reactivity ratio.

As one of the methods for parameter estimation, EIV (error in variables) model takes into account the non-linearity of the system and the measurement error which are the general characteristics of the terpolymerization process Reilly and Patino-Leal (1981). The error in measurement and the optimization problem of the EIV model are represented in (7) - (9).

$$x_i = \tilde{x}_i + \epsilon_i \quad (7)$$

$$\min_{\tilde{x}_i, \theta} \sum_i \frac{(\tilde{x}_i - x_i)^2}{\sigma^2} = \min_{\tilde{x}_i, \theta} \phi \quad (8)$$

$$\text{subject to } g(x_i, \theta) = 0 \quad (9)$$

where  $\phi$  is the objective function,  $g$  is the cumulative model function,  $\theta$  is the parameter vector,  $x_i$  is the measurements,  $\tilde{x}_i$  is the true value and  $\epsilon_i$  is the measurement noise which is assumed to be independent of  $\tilde{x}_i$ .

Parameter estimation scheme for nonlinear model based on nested-iterative EIV model is suggested by Kazemi et al. (2013). The nested-iterative EIV algorithm has two iteration loops, inner loop and outer loop. The true values are found through inner loop using measurement values and the covariance matrix as shown in (10).

$$V = \begin{bmatrix} \sigma_{x_1}^2 & \sigma_{x_1x_2}^2 & \cdots & \sigma_{x_1x_j}^2 \\ \sigma_{x_2x_1}^2 & \sigma_{x_2}^2 & \cdots & \sigma_{x_2x_j}^2 \\ \vdots & \vdots & \cdots & \vdots \\ \sigma_{x_jx_1}^2 & \sigma_{x_jx_2}^2 & \cdots & \sigma_{x_j}^2 \end{bmatrix} \quad (10)$$

The covariance matrix represents the variance of each measurement and the covariance between measurements. We transform (8) into (11) using the covariance matrix

$$\min_{\tilde{x}_i, \theta} \sum_i r_i (\bar{x}_i - \tilde{x}_i)' V^{-1} (\bar{x}_i - \tilde{x}_i) = \min_{\tilde{x}_i, \theta} \phi \quad (11)$$

where  $r_i$  is the number of repeated measurements for the same sample.

Through Taylor expansion in  $\tilde{x}_i$  near  $x_i$ , equation (9) can be linearized as

$$g(\tilde{x}_i, \theta) + B_i(x_i - \tilde{x}_i) = 0 \quad (12)$$

$$B_i = \left[ \frac{\partial g(\tilde{x}_i, \theta)}{\partial g(\tilde{x}_i)_t} \right]_{\tilde{x}_i = \tilde{x}^k} \quad (13)$$

where  $B_i$  is the vector of partial derivatives of function respect to variables.

Iterative calculation is performed for predicting  $\tilde{x}_i$ . The  $\tilde{x}_i$  is set as the  $x_i$  at the initial time step, and the  $\tilde{x}_i$

of the next time step obtain towards to minimize the  $\phi$ . Estimation of  $\tilde{x}_i$  at  $k + 1$  step is expressed as

$$\tilde{x}_i^{(k+1)} = \bar{x}_i - VB'_i(B_iVB'_i)^{-1}[g(\tilde{x}_i^{(k)}, \theta) + B_i(\bar{x}_i - \tilde{x}_i^{(k)})] \quad (14)$$

where  $k$  denotes the iteration step.

In the outer loop, the parameters are estimated using the estimate of  $\tilde{x}$  from the inner loop. Vector of partial derivatives of the objective function with respect to the parameters  $q$  and expected information matrix  $G$  are shown in equations (16) and (17). Parameters at next step is estimated using equation (15) by minimizing the  $\phi$ .

$$\theta^{(u+1)} = \theta^{(u)} - G^{-1}q \quad (15)$$

$$q = \left[ \frac{d\phi}{d\theta_m} \right] = \sum_i r_i Z'_i (B_i V B'_i)^{-1} B_i (\bar{x}_i - \tilde{x}_i) \quad (16)$$

$$G = \left[ \frac{d^2\phi}{d\theta_i d\theta_j} \right] = \sum_i r_i Z'_i (B_i V B'_i)^{-1} B_i Z_i \quad (17)$$

$$Z_i = \left[ \frac{\partial g(\tilde{x}_i, \theta)}{\partial \theta_t} \right] \quad (18)$$

All inner and outer loops iterate until the parameter values are converged with a specified stopping criterion.

### 2.3 Deep neural network model for estimating conversion

In order to calculate the cumulative composition of terpolymer in the first-principle model, weight conversion is required. However, unlike the batch reactor, CSTR reactor is difficult to determine the conversion at a specific inlet composition because the residence time appears as a distribution. However, if there is sufficient data on temperature and inlet composition at CSTR, a conversion prediction model considering residence time distribution can be created through the data driving technique. To overcome the shortcomings of the first-principle model, a new approach for predicting conversion using the DNN model is proposed in this study.

DNN is comprised of the interconnection of nodes called artificial neurons. Each artificial neuron consists of a set of adjustable weights, that is, numerical parameters that can be adjusted by a learning algorithm (Bengio et al. (2013)). In this study, a fully-connected seven-layer DNN model with five hidden layers which used the ReLU(rectified linear unit) activation function was used to estimate the conversion. Supervised learning using the mean squared error loss function was performed with molecular conversion data corresponding to the measurement data. In order to reduce the possibility of overfitting, taking 60% of the data set model training, 20% of the data set for validation, and using the remaining 20% for test. Early stopping was also applied to prevent overfitting. Overfitting degrades the performance and generalizability of the DNN model. Instead of using all the measurement variables, few variables having high correlation with the conversion through Spearman's rank correlation was used for learning. Spearman's rank correlation coefficient represents the nonlinear correlation of two variables (Spearman (1961)).

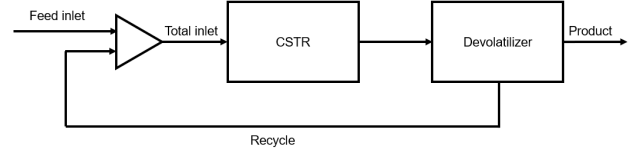


Fig. 1. Schematic flow diagram of AN-St-MMA terpolymerization process

### 2.4 AN-St-MMA terpolymerization simulation using hybrid model

In the process of terpolymerization, as shown in Fig. 1, the monomers are recycled after passing through CSTR and devolatilizer. The flow rate of each monomer at the feed inlet stream and recycle stream along with the temperature and pressure of CSTR at various locations are measured in real-time through the sensors. In this study, we suggest a hybrid model for estimating the concentration of each monomer in the recycle stream. The overall procedure of the simulation scheme is shown in Fig. 2.

- Initial concentration of each monomer in the recycle stream is obtained experimentally.
- Next, molecular conversion is estimated from the pre-trained DNN model using measurement data from the sensors.
- The flow rate and concentration of the total inlet stream are calculated using the concentrations in the recycle stream and the flow rate of the inlet stream.
- Afterward, cumulative product composition is calculated through the first-principle model.
- The next step concentration in the recycle stream is calculated through the mass balance.
- The process simulation is conducted sequentially by estimating the molecular conversion of the cumulative product composition until the end of simulation.

## 3. RESULT AND DISCUSSION

### 3.1 Reactivity ratio estimation

Estimation of reactivity ratio was conducted as in Section 2.2 using EIV model. Cumulative composition of terpolymer and reactivity ratio were set as measurement variable and the parameter. The binary reactivity ratios were used as the initial value from Steinfatt and Schmidt-Naake (2001) and the actual data was provided by LG Chem. Table 1 shows the initial values of binary reactivity ratio and ternary estimation result using EIV model. The estimated ternary reactivity ratio shows a difference of up to 27% compared with the initial values. This shows that the estimation of reactivity ratio specific to the terpolymerization system is essential.

Table 1. Reactivity ratio estimation result (monomer 1: AN, monomer 2: St, monomer 3: MMA)

|         | $r_{12}$ | $r_{13}$ | $r_{21}$ | $r_{23}$ | $r_{31}$ | $r_{32}$ |
|---------|----------|----------|----------|----------|----------|----------|
| binary  | 0.02     | 0.07     | 0.65     | 0.42     | 0.98     | 0.61     |
| ternary | 0.0259   | 0.0825   | 0.897    | 0.500    | 1.254    | 0.565    |

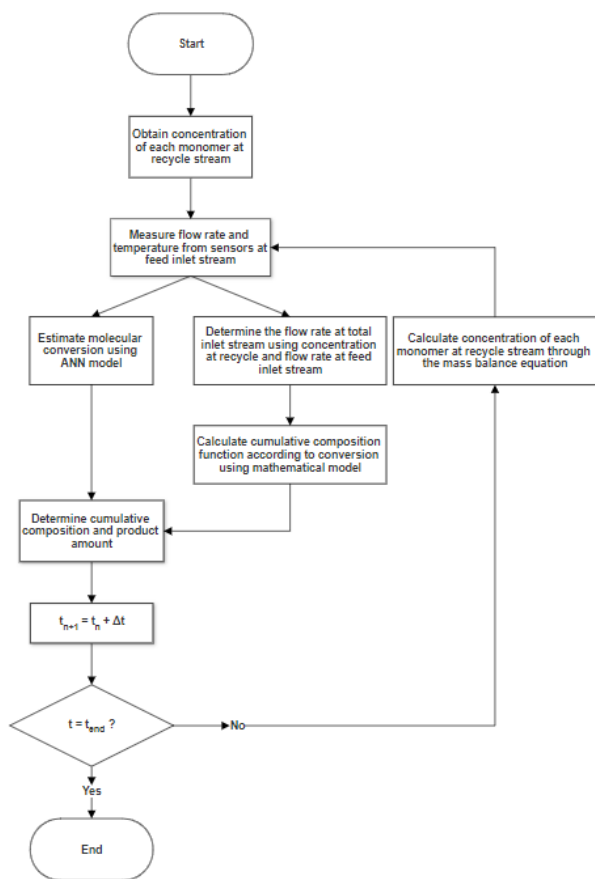


Fig. 2. Flowsheet representation of terpolymerization simulation using hybrid model

### 3.2 Validation of the DNN model

DNN model was used to predict the conversion from the process measurement data as in Section 2.3. The measurement data set from the sensor consists of a total of 46 variables: the temperature and pressure according to the position of each reactor, the flow rate of each monomer in the inlet stream, and the recovery amount of recycle stream. In order to reduce the number of input variables for the convenience of training the model, Spearman's rank correlation coefficient for the conversion was used. Through the results of Spearman's rank correlation coefficient, 28 variables having an absolute value of 0.20 or more of the correlation coefficient with the conversion were selected as the input variables. Prediction of the conversion using the trained DNN model in the test set are shown in Fig. 3, and the MAPE (mean absolute percentage error) was 0.4056%.

### 3.3 Cumulative composition of terpolymer prediction

Based on the estimated reactivity ratio and predicted conversion, the cumulative composition of terpolymer can be calculated from the first-principle model. Cumulative composition of terpolymer was scaled to the range of 0–1. The estimation results of each monomer are shown in Fig. 4. The MAPEs of AN, St, and MMA are 1.217%, 1.403%, and 0.2832%, respectively, implying that the error of the composition estimates are insignificant and the process

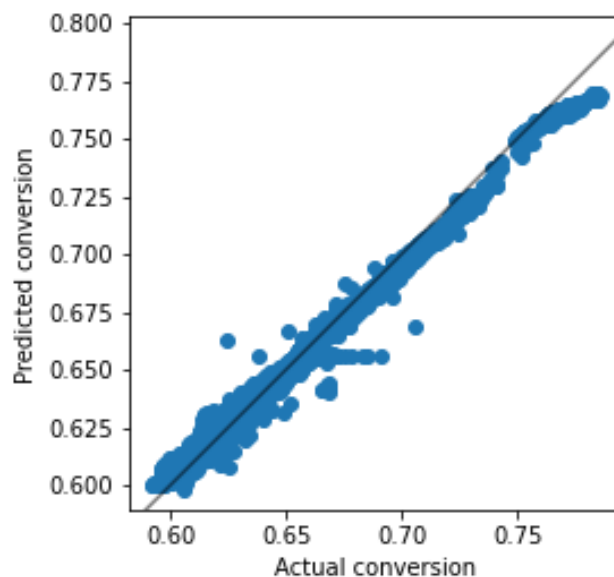


Fig. 3. Prediction of molecular conversion

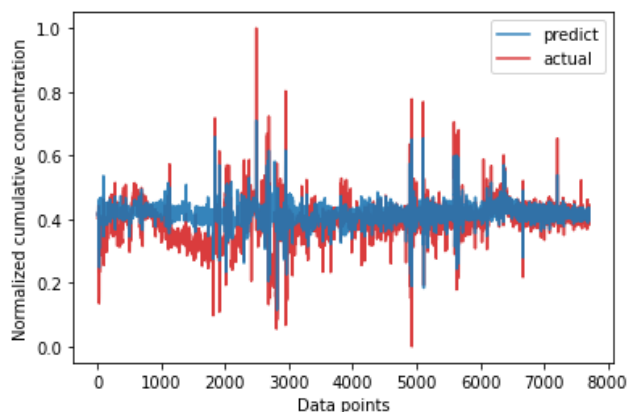
simulation using hybrid model shows a high fidelity. Although the absolute error values of each composition are almost the same, the MAPE of MMA having a large absolute value compared to the other components is smaller than that of AN and St. Meanwhile, a bias in the prediction results also exist. It could be inferred that unmeasured variables such as flow rates of solvents and contaminants affect the overall model.

### 3.4 AN-St-MMA terpolymerization simulation

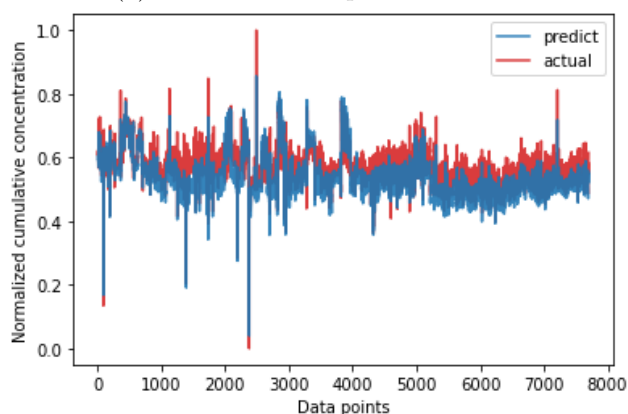
The terpolymerization simulation was performed using 600 days of measurement data and initial concentration of each monomer at the recycle stream. As mentioned above, 28 variables were selected as the measurement data. The concentration of each monomer at recycle stream was predicted every 2 hours for 600 days. For the validation of simulation result, the predicted concentration was compared with the actual data every 4 hours. All the concentration was scaled to the range of 0–1. Fig. 5 shows the simulated and actual concentrations of each monomer at recycle stream. The MAPE of the simulation result was less than 3% for each monomer and that the simulation shows a good agreement with the actual data. The MAPEs of AN, St, and MMA are 2.933%, 2.606% and 0.423 %, respectively. As with the result of cumulative composition prediction, MAPE of MMA with a large absolute value showed a small error compared to that of AN and St and bias existed due to the variables that were not taken into account.

## 4. CONCLUSION

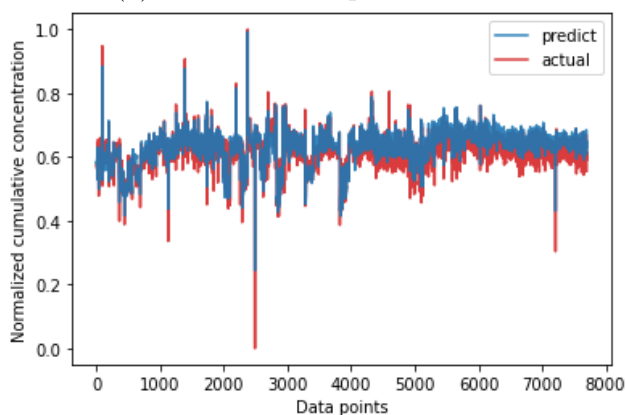
This study proposed a hybrid model for simulating terpolymerization in CSTR. For hybrid model, we developed the DNN model for estimating conversion using measurement from sensor, and integrated the cumulative model with the DNN model for the prediction of cumulative composition using measurement data only. When training the DNN model, 28 variables having high correlations with



(a) Cumulative composition of AN



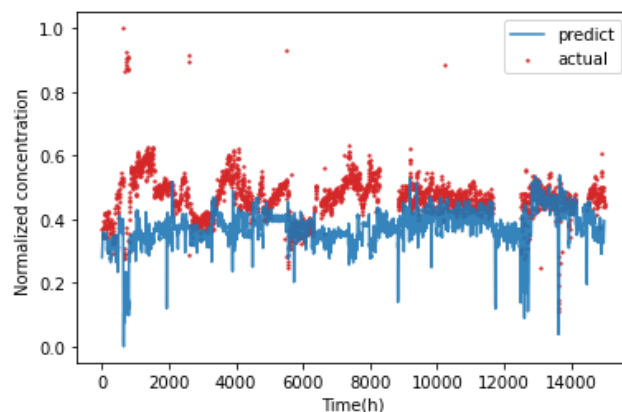
(b) Cumulative composition of St



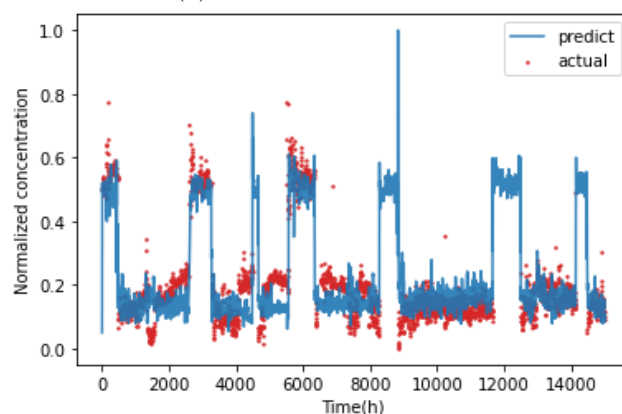
(c) Cumulative composition of MMA

Fig. 4. Cumulative composition of terpolymer

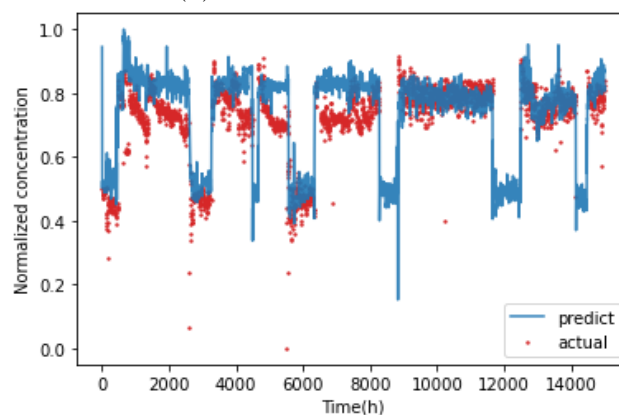
the conversion were selected as the input variables through Spearman's rank correlation coefficient, and the conversion prediction result was acceptable when compared with the actual data. For terpolymerization simulation, model parameters, reactivity ratios of AN-St-MMA terpolymerization, were estimated by EIV model. Validation of the hybrid model was conducted using actual data of 600 days and the result showed a good agreement with the actual data. Instead of experimentally measuring the concentration, we proposed a high-fidelity and reliable hybrid model for predicting the concentration using measurement data from sensors. The model is expected to be extended to other terpolymerization process and the resulting concen-



(a) Concentration of AN



(b) Concentration of St



(c) Concentration of MMA

Fig. 5. Concentration of monomer at recycle stream

tration prediction in real time through the model can be used for the process optimization and control.

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