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Predicting Molecular Weight at Certain Temperature Isothermally using Neural Network

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Abstract: In this study, molecular weight control studies and the development of advance control were carried out. In-line measurement device such as Gel Permeation Chromatography (GPC) has become available, however, it is very expensive and the results always posses substantial time-delayed measurements from analytical laboratory measuring devices. A method of predicting molecular weight performance during polymerization process was proposed using neural network system. A neural network model was developed to predict leading moments of molecular weight using backpropagation algorithm of neural networks system for Methyl methacrylate (MMA) polymerization. Plant input and output were simulated from the first principle model for MMA polymerization and then been utilized to train multilayer neural network system. Process inputs such as reaction temperature, monomer conversion and initiator concentration were the main variables affecting properties of molecular weight averages. A neural network model was generated from the training process after it successfully learned the relationship between process inputs and product outputs. This neural network model was applied when predicting molecular weight of Polymethyl methacrylate (PMMA) which is useful in implementation of the on-line control of polymerization process.

Key words: Backpropagation algorithm, batch polymerization, MMA polymerization, modeling, molecular weight control, neural network

INTRODUCTION

Polymerization is well known as a very complex reaction process as it exhibits multiple steady states with a complex nonlinear behaviour and the reaction is extremely exothermic. Polymer end properties are very important as they affect the quality of the desired final form and shape (Achilias and Kiparissides, 1992). This end properties (mechanical properties) and characteristics of polymer end product have a very strong correlation with molecular weight properties. Many researchers have studied the importance of controlling polymer molecular weight properties to get the desired quality of polymer product (Ponnuswamy *et al*., 1987; Takamatsu *et al*., 1988; Bersted and Anderson, 1990; Soroush and Kravaris, 1992; Crowley and Choi, 1997). Therefore, it is essential to control molecular weight properties on-line to achieve better quality of polymer product.

Studies on molecular weight control have been done as well as developing advanced process control by researchers. Yet it is still not fully been applied in polymer reaction control industries due to limitation of efficient measuring devices and expensive operating cost such as in-line Gel Permeation Chromatography (GPC). Furthermore, GPC results always possess substantial time-delayed measurement from analytical laboratory measuring device. Advance process control design and fabrication needed to be sophisticated for manufacturing practice by emphasizing on the maximization of monomer conversion, minimization of reaction rate and operation cost but not to disregard the importance of safety feature throughout the polymerization process.

Leading moments of molecular weight which are the number average molecular weight (M_n) and weight average molecular weight (M_w) are the key variables of polymer product quality control. These variables cannot be measured directly and accurately during polymerization process. Another way of determining these variables is by using mathematical equations. Many methods of modeling and control of polymerization systems have been developed by a number of authors and has been well elucidated in a study by Kiparissides (1996).

In this study, modeling neural network system using simulation data has been studied. A neural network system was developed using backpropagation algorithm to predict the leading moments of molecular weight. Simulation model of Chiu *et al*. (1983) had been utilized as actual plant data input and output to train the neural network model. Multilayer neural network system was used in training process.

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MMA BATCH POLYMERIZATION

MMA polymerization has become a research choice over the past decade. This polymer is often polymerized by free-radical, chain addition mechanism which normally involves three common fundamental steps: initiation, propagation and termination. Polymerization process is initiated by chemical compound which is called the initiator. The common used initiator for producing free-radical for MMA polymerization process are the 2, 2'-Azobisisobutyronitrile (AIBN) and Benzoyl peroxide (BPO). Initiation process begins with the creation of an 'active' centre such as a free-radical or carbonium ion. It continues to propagate by addition of more monomer to the growing chain end. Finally, the addition of monomer molecule to the growing chain end is deactivated by chain termination which can occur in two ways: termination by combination and termination by disproportionation. In polymerization process, these three steps are fundamental. However, polymerization occasionally involves side reaction which happens when a radical abstracts a hydrogen atom from a neighbour molecule. This reaction is called chain transfer reaction. It is a chain-breaking reaction which decreases the size of the propagating polymer chain. In this study, chain transfer reaction is ignored for convenience. Kinetic reactions by Chiu *et al.* (1983) have discussed the importance of a fundamental understanding of the various factors governing the reaction kinetics of polymerization including gel effect region. This model was developed by examining the gel effect and glass effect also considering the effect on the termination and propagation rate. The model consists of reaction mechanism of straightforward initiation, propagation and termination with negligent of chain-transfer. The developed model has described the polymerization process over the entire course of reaction using first principle, model make it the choice of this simulation work. MMA polymerization has been conducted isothermally at different temperatures at 50, 70 and 90°C.

Figure 1a-c show initiator, conversion and molecular weight average profile of MMA polymerization at 50°C, respectively. Figure 2a-c are the results for initiator, conversion and molecular weight average of MMA polymerization at 70°C, respectively. Figure 3a-c are the results for initiator, conversion and molecular weight average of MMA polymerization at 90°C, respectively.

Figure 1a, 2a and 3a show the initiator profiles for MMA polymerization at different isothermal temperatures which are 50, 70 and 90°C, respectively with initiator loading $I_0 = 0.0258$ mol L^{-1} and $I_0 = 0.01584$ mol L^{-1}. By definition, the initiator concentration is number of mol

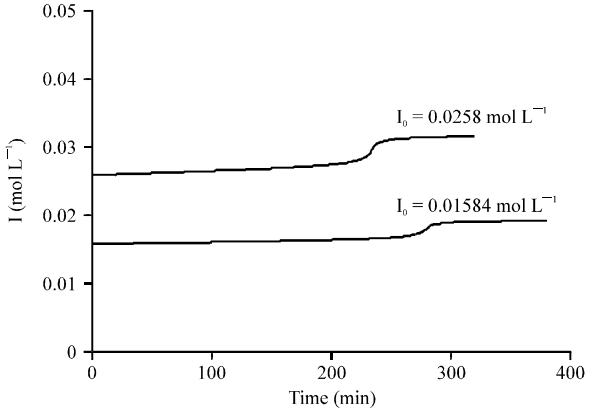

Fig. 1a: Initiator (I) concentration vs. time of MMA polymerization at 50°C for $I_0 = 0.0258$ and 0.01584 mol L^{-1}

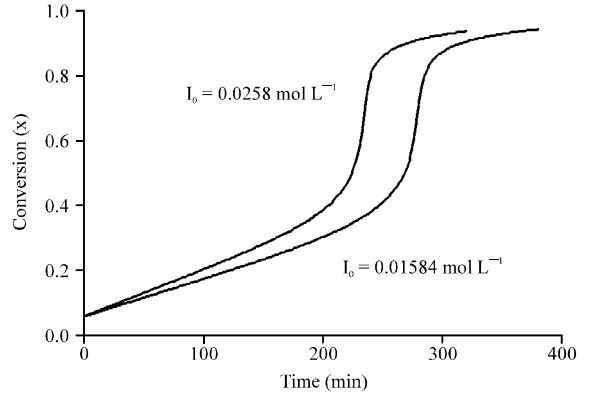

Fig. 1b: Conversion vs. time of MMA polymerization at 50°C for $I_0 = 0.0258$ and 0.01584 mol L^{-1}

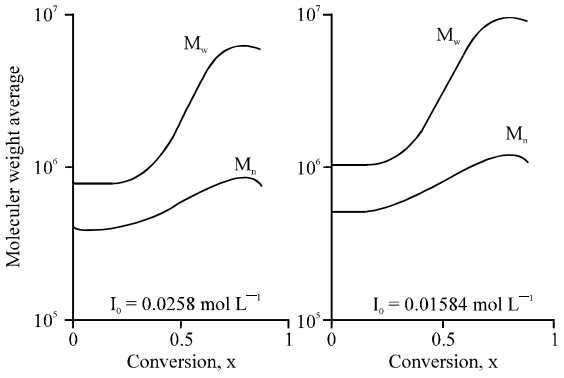

Fig. 1c: Molecular weight average vs. conversion of MMA polymerization at 50°C for $I_0 = 0.0258$ and 0.01584 mol L^{-1}

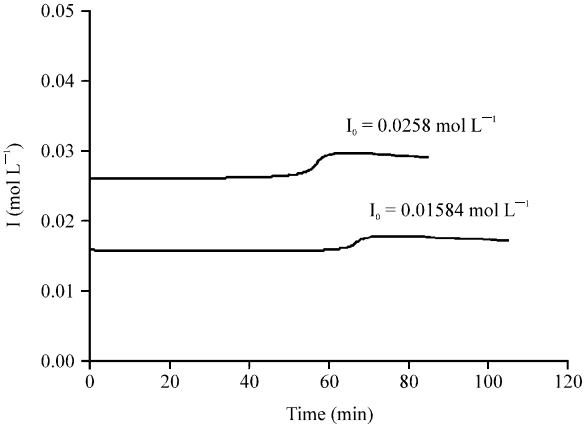

Fig. 2a: Initiator (I) concentration vs. time of MMA polymerization at 70°C for I_0 = 0.0258 and 0.01584 mol L^{-1}

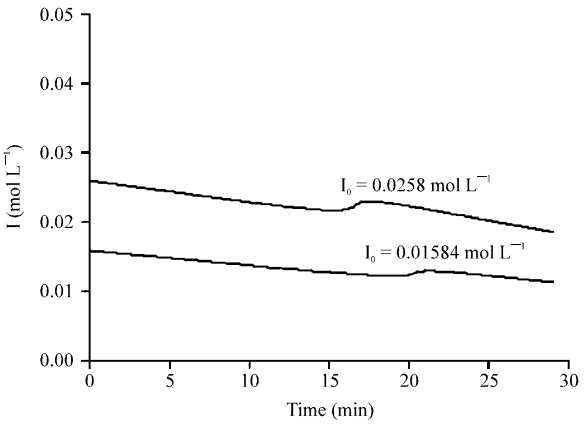

Fig. 3a: Initiator (I) concentration vs. time of MMA polymerization at 90°C for I_0 = 0.0258 and 0.01584 mol L^{-1}

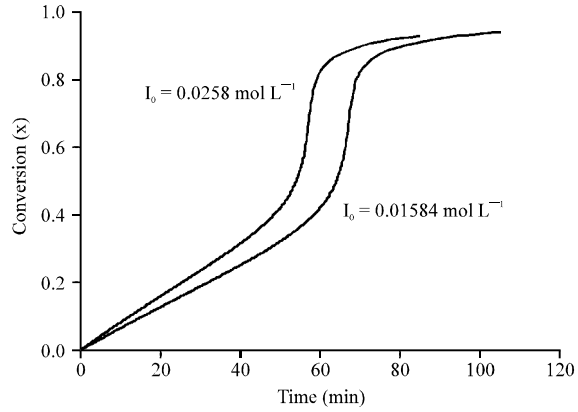

Fig. 2b: Conversion vs. time of MMA polymerization at 70°C for I_0 = 0.0258 and 0.01584 mol L^{-1}

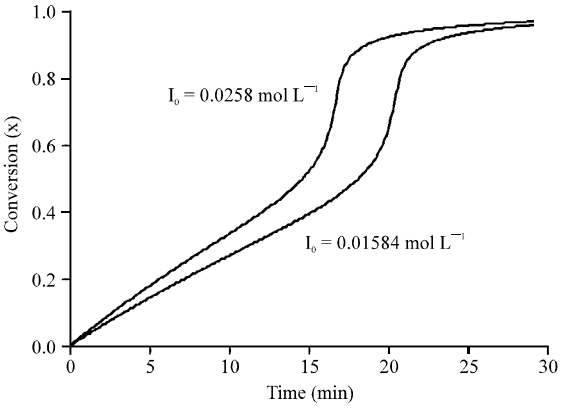

Fig. 3b: Conversion vs. time of MMA polymerization at 90°C for I_0 = 0.0258 and I_0=0.01584 mol L^{-1}

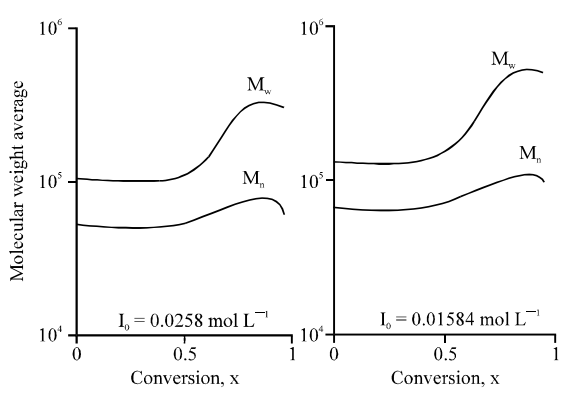

Fig. 2c: Molecular weight average vs. conversion of MMA polymerization at 70°C for I_0 = 0.0258 and 0.01584 mol L^{-1}. M_w: Molecular weight average, M_n: Numbers of molecular weight average

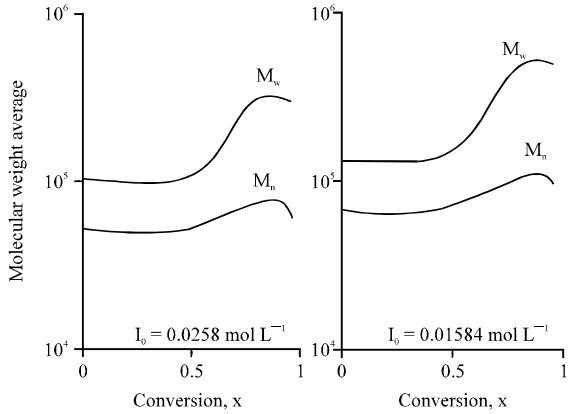

Fig. 3c: Molecular weight average vs. conversion of MMA polymerization at 90°C for I_0 = 0.0258 and 0.01584 mol L^{-1}. M_w: Molecular weight average, M_n: Numbers of molecular weight average

over reactant volume (mol vol.$^{-1}$). In this case, reactant volume decreases over polymerization time correspondingly by volume expansion factor equation, $\epsilon = (\rho_m - \rho_p)/\rho_p$ where, ρ_m is monomer density and ρ_p and is polymer density. This incident had caused the volume expansion factor (ϵ) decreases during the polymerization reaction which also means decrease in reactant volume. Since, the concentration is inversely proportional to volume, decrease in volume had increased the value of concentration. This is the reason why initiator profiles were slightly escalating over the polymerization process time which is not due to addition of more initiator amount, except because of the declining in reactant volume itself. This was supported by sudden increased in monomer conversion as shown in the conversion profiles at 50, 70 and 90°C in Fig. 1b, 2b and 3b, respectively.

Fig. 1b, 2b and 3b show conversion profiles. From the figures, the conversion profile for MMA polymerization started to increase gradually. After a certain time, the conversion increased drastically for several minutes before it started to slowly stabilize and constant for the remaining operating time. Most of the MMA has been hugely used up to produce PMMA causing the drastic increase of conversion profiles. The initiator profiles Fig. 1a, 2a and 3a, become slightly increased at the same point of time as the conversion was drastically increased. The conversion started to become constant slowly as the gel effect occurs. This is a common phenomenon as MMA bulk polymerization entails very high gel effect condition.

Fig. 1c, 2c and 3c show the number average molecular weight (M_n) and weight average molecular weight (M_w) profiles for PMMA over conversion at isothermal temperature which are 50, 70 and 90°C, respectively with initial initiator loading $I_0 = 0.0258$ and 0.01584 mol L^{-1}. These simulation results were used as actual plant inputs and outputs in training the NN model.

Initiator effect: Initial initiator loading concentrations, I_0 used in this work were 0.0258 and 0.01584 mol L^{-1}. From the conversion profiles, it is obvious that initiator concentration has a significant influence to the process. As we can see from Fig. 1b, 2b and 3b, conversion of MMA was quicker when using higher initial initiator loading concentration which is $I_0 = 0.0258$ mol L^{-1}. The condition applies for polymerization at all different isothermal operating temperatures.

Temperature effect: Same goes to the polymerization operating temperature. MMA polymerization simulation has been conducted at temperature 50, 70 and 90°C. At higher operating temperature, monomer conversion seems to drastically increase faster in a similar way which the initial initiator loading concentration influenced monomer conversion. MMA started to speed up converting to PMMA as early after 15 min of operating time at 90°C (Fig. 3b) followed by 55 min at 70°C (Fig. 2b) and 180 min at 50°C (Fig. 1b). The faster the MMA is converted to PMMA, the shorter batch time needed to produce output polymer product. Thus, it complies with polymerization goal which are time reduction and cost effectiveness. The initial initiator loading concentration $I_0 = 0.0258$ mol L^{-1} and the operating temperature 90°C has been chosen as the optimum condition to be used later in neural network training.

NEURAL NETWORK SYSTEM

Neural network has become increasingly popular for modeling, optimization and control application of polymerization processes recently (Zhang *et al*., 1998; Krothapally *et al*., 1999; Zhang, 1999; Nascimento *et al*., 2000; Kuroda and Kim, 2002; Tian *et al*., 2002; Fernandes *et al*., 2004; Roy *et al*., 2006). Neural network is recognized for its function of information-processing capabilities to learn and generalize data in order to solve complex problems. It is also available in MATLAB with all-encompassing function which enable user to build and simulate neural network model. Size of neural network was determined by the number of neurons in a system. A neural network system basically consists of three layers; input layer, hidden layers and output layer. In this study, a two-layer network is used which contains 3 inputs in the input layer, 10 number of neurons in a hidden layer and 2 outputs in the output layer. The input and output data were generated by simulation using MATLAB software programming based on first-principle model. Initiator concentration, monomer conversion and operating temperature will be the input and M_n and M_w as output. A multilayer network is used to approximate virtually the function of interest consists of hyperbolic tangent sigmoid in the first-layer and a linear transfer function in the output layer.

A neural network model was developed in a written MATLAB programme. Neural network training usually involve a large number of data and parameters and in this study; a total of 1455 data were used. These data were split into three subsets of data and were assigned for training, validation and testing set to improve generalization while training the network model offline using backpropagation algorithm. This algorithm used mean square error (MSE) as the performance index. It is also the most extensively adopted algorithm for the learning phase in current times makes it a convenient choice of this study. Running the simulation created a network which contains values for network parameters

(network weights and biases) which were stored as net. These network weights and biases were adjusted by the algorithm to minimize the mean square error. The net was used to generate new output prediction.

SIMULATION RESULTS

A neural network programme has been developed by using MATLAB software. Input and output data at operating temperature 90°C were loaded to the written neural network system to learn and apprehend the relationship between input and the target output. After the training, the network had stored all the network parameters based on information supplied. This information (network parameters) was used to simulate new output. To verify the NN prediction model, the output results were compared with the molecular weight data that have been used to train the network as in Fig. 4. From Fig. 4, it was confirmed that neural network can predict the output accurately. NN output followed the exact same pattern as the molecular weight trained data.

To demonstrate the robustness of the NN prediction model, noise has been introduced to the simulation data. Noise has been introduced to each input and the existing NN model was used to simulate output response using this new data (noise data). This procedure was intended to imitate real plant data. Figure 5-7 show the initiator, monomer conversion and temperature profile with noise, respectively. The NN output prediction is shown in Fig. 8. As can be seen from Fig. 8, NN prediction is acceptable regardless of small range turbulence introduces on the input data. The NN model can still predict very well for M_w and M_n.

Initiator and temperature effect: The effect of different initiator loading and operating temperature has also been

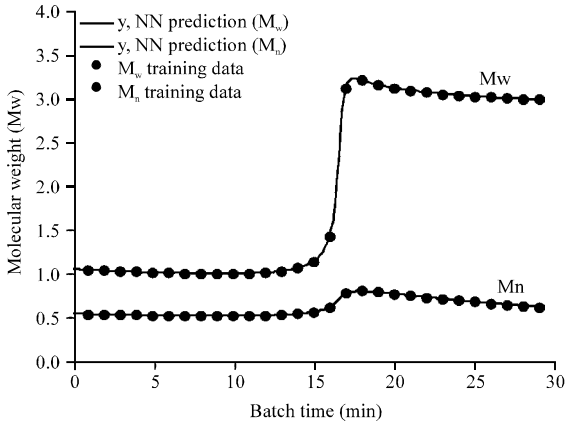

Fig. 4: Molecular weight data and NN output prediction at 90°C for $I_0 = 0.0258$ mol L^{-1}

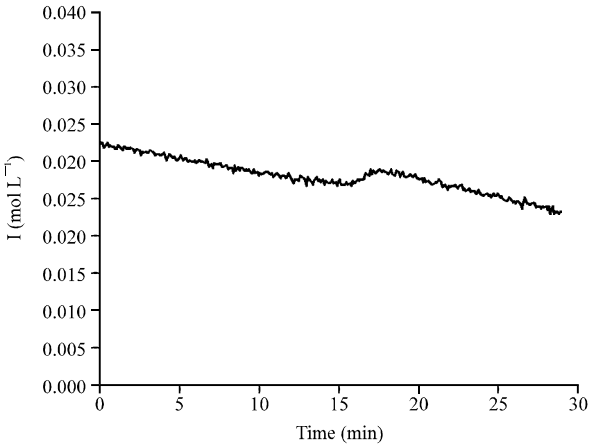

Fig. 5: Initiator (I) concentration vs. time with noise introduction at 90°C for $I_0 = 0.0258$ mol L^{-1}

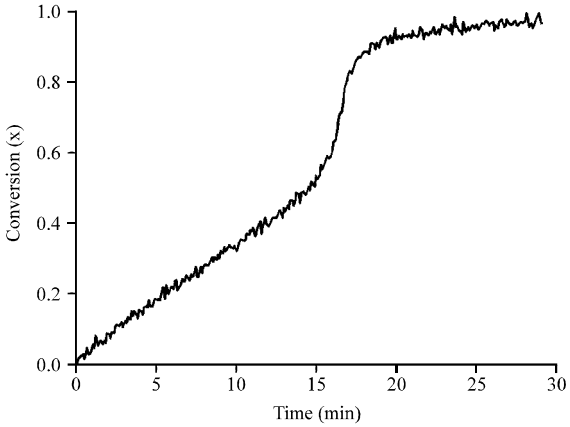

Fig. 6: Conversion vs. time with noise introduction at 90°C for $I_0 = 0.0258$ mol L^{-1}

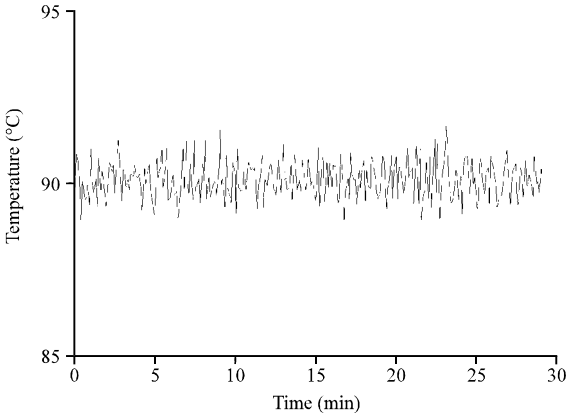

Fig. 7: Temperature profile vs. time with noise introduction at the temperature of 90°C for $I_0 = 0.0258$ mol L^{-1}

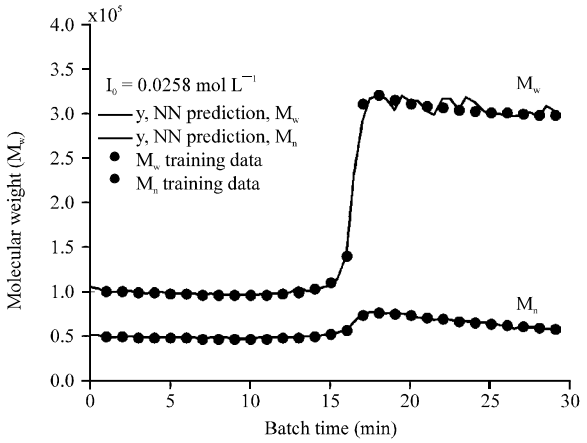

Fig. 8: Comparison of molecular weight trained data and NN prediction using noise data

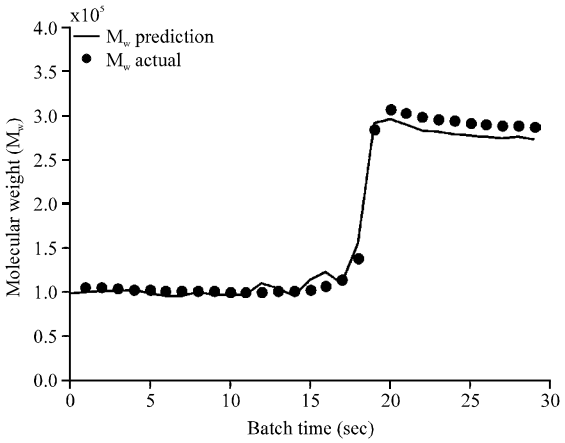

Fig. 9: NN prediction of weight average molecular weight at 89°C, I_0 = 0.0258 mol L^{-1}

Table 1: Different polymerization condition used to test the trained NN model

Different temperature				Different initiator			
		RMSE				RMSE	
T (°C)	I_0 (mol L^{-1})	M_w	M_n	I_0 (mol L^{-1})	T (°C)	M_w	M_n
87	0.0258	0.1112	0.0731	0.0250	90	0.1159	0.0921
88	0.0258	0.0848	0.0515	0.0253	90	0.0784	0.0616
89	0.0258	0.0555	0.0321	0.0255	90	0.0506	0.0386
91	0.0258	0.0530	0.0296	0.0261	90	0.0533	0.0417
92	0.0258	0.1036	0.0478	0.0263	90	0.0855	0.0663
93	0.0258	0.1988	0.0636	0.0266	90	0.1293	0.1032

studied using the existing NN model. Table 1 shows the conditions used to test the trained network. Different operating temperature with same initiator loading and different initiator loading at 90°C as tabulated in Table 1 have been used to test the NN model which was trained at temperature 90°C and I_0 = 0.0258 mol L^{-1}. Temperature different were taken in a range of ±3°C while initiator loading range were ±3%.

Figure 9-14 show the results for NN prediction of the weight average molecular weight (M_w) using different operating temperature with same initiator loading. As can be seen from the graphs, the minimum temperature difference from the original operating temperature (±1°C) at 89 and 91°C as in Fig. 9 and 12 which show the least error of the NN prediction followed by the temperature 88 and 92°C (with ±2°C difference) in Fig. 10 and 13. NN prediction for the operating temperature difference ±3°C at 87 and 93°C presented in Fig. 11 and 14 which showed that NN prediction is the most inaccurate which is supported by the value of the root means-square error (RMSE) of each NN prediction is shown in Table 1.

Figure 15-20 which show the results for NN prediction of the number average molecular weight (M_n) using different operating temperature with same initiator

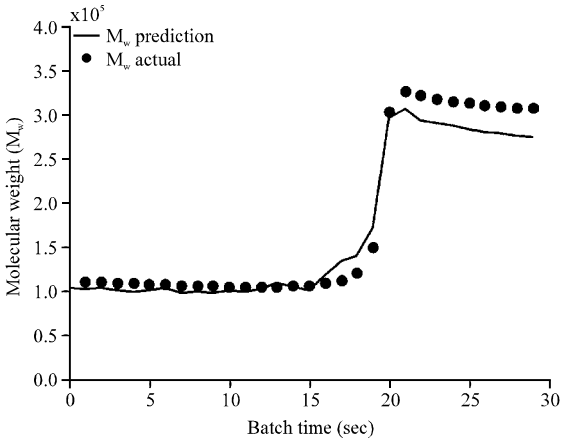

Fig. 10: NN prediction of weight average molecular weight at 88°C, I_0 = 0.0258 mol L^{-1}

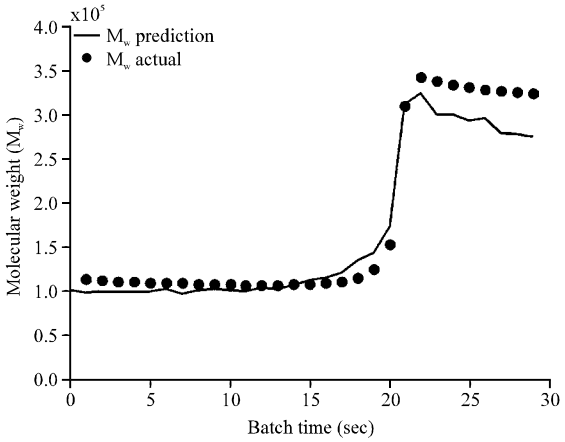

Fig. 11: NN prediction of weight average molecular weight at 87°C, I_0 = 0.0258 mol L^{-1}

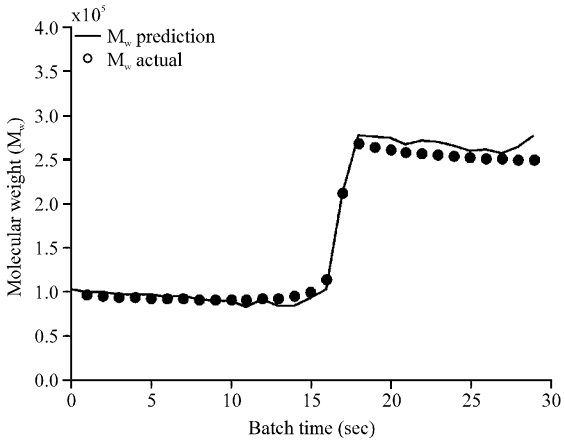

Fig. 12: NN prediction of weight average molecular weight at 91°C, I_0 = 0.0258 mol L^{-1}

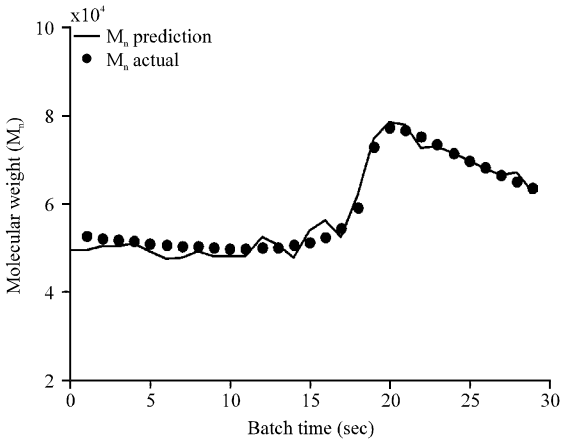

Fig. 15: NN prediction of number average molecular weight at 89°C, I_0 = 0.0258 mol L^{-1}

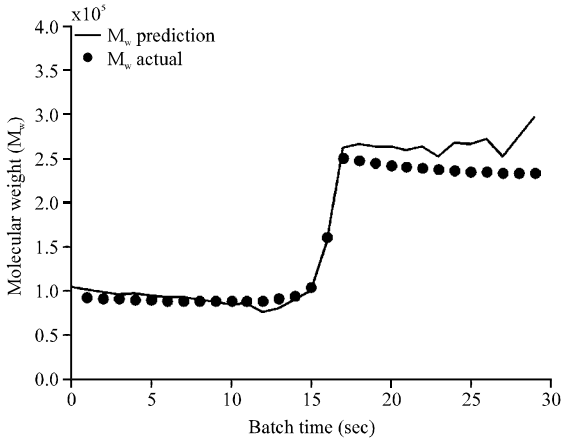

Fig. 13: NN prediction of weight average molecular weight at 92°C, I_0 = 0.0258 mol L^{-1}

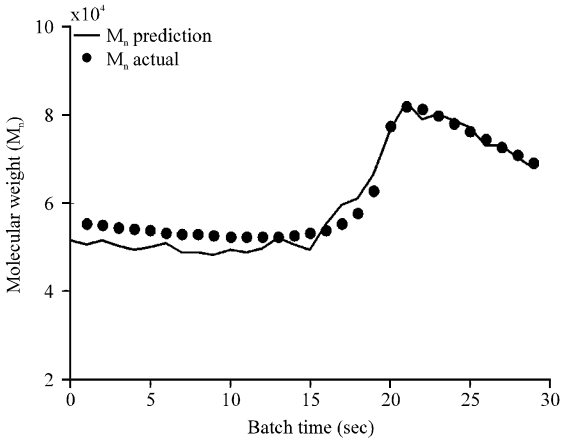

Fig. 16: NN prediction of number average molecular weight at 88°C, I_0 = 0.0258 mol L^{-1}

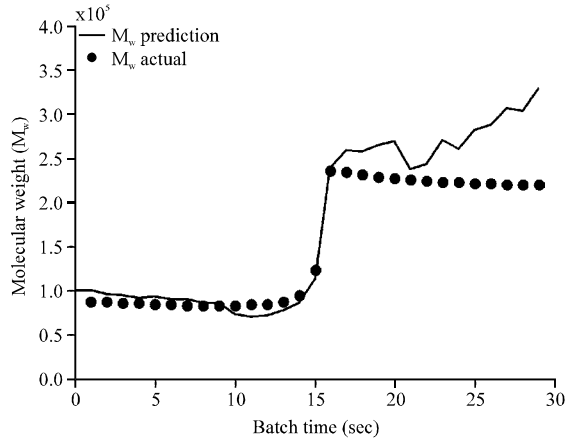

Fig. 14: NN prediction of weight average molecular weight at 93°C, I_0 = 0.0258 mol L^{-1}

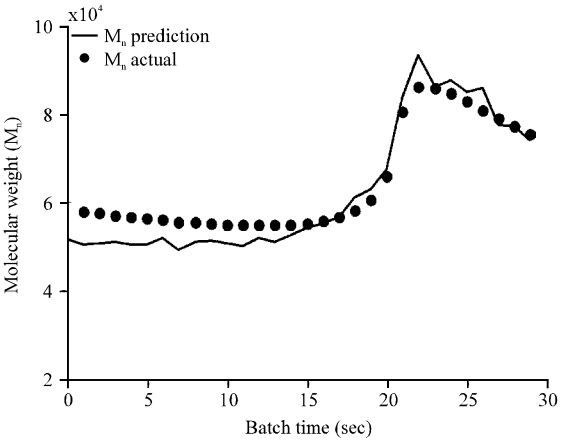

Fig. 17: NN prediction of number average molecular weight at 87°C, I_0 = 0.0258 mol L^{-1}

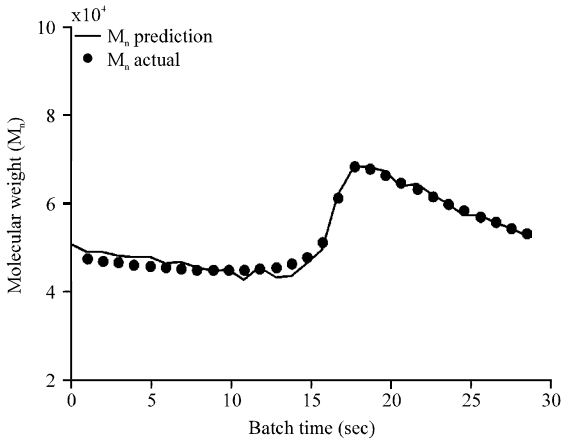

Fig. 18: NN prediction of number average molecular weight at 91°C, I_0 = 0.0258 mol L^{-1}

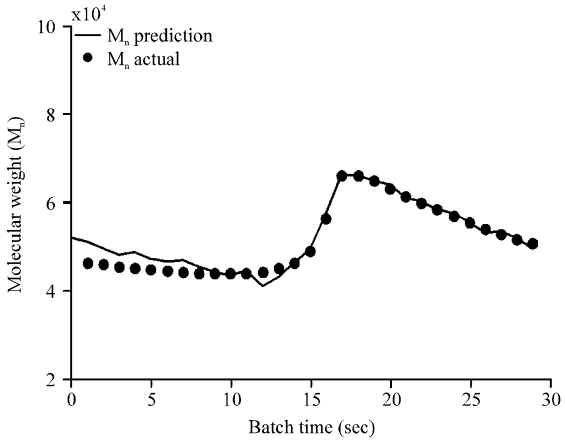

Fig. 19: NN prediction of number average molecular weight at 92°C, I_0 = 0.0258 mol L^{-1}

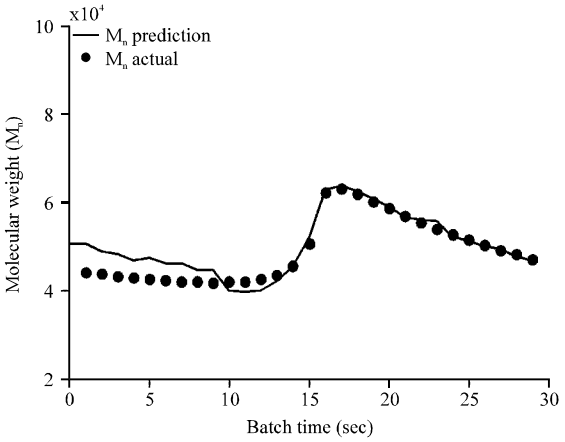

Fig. 20: NN prediction of number average molecular weight at 93°C, I_0 = 0.0258 mol L^{-1}

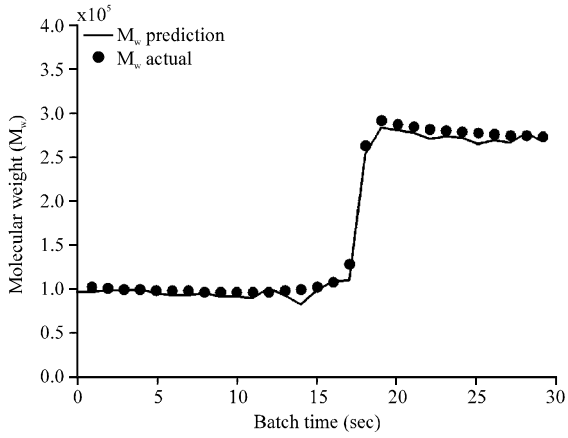

Fig. 21: NN prediction of weight average molecular weight at I_0 = 0.0255 mol L^{-1}, T = 90°C

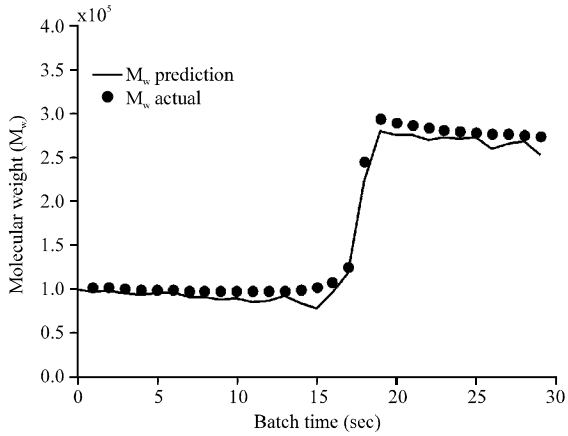

Fig. 22: NN prediction of weight average molecular weight at I_0 = 0.0253 mol L^{-1}, T = 90°C

loading. The trend of NN prediction for M_n seems to follow the trend of NN prediction for M_w. However, the overall NN predictions for M_n from ±1°C to the maximum difference ±3°C were not as vague as the prediction for M_w based on the plotting trend and the RMSE value. It was observed that temperature is affecting more on to the M_w than M_n.

Figure 21-32 show the results when using different initiator loading at 90°C, respectively to test the NN model (trained at temperature 90°C and I_0 = 0.0258 mol L^{-1}). Figure 21-26 show the results for the NN prediction of weight average molecular weight, M_w while Fig. 27-32 represent results for the NN prediction of number average molecular weight, M_n. RMSE value for NN prediction is higher at ±3% difference in initiator loading and lowest at ±1% of difference in initiator loading. These trends are same with the temperature effect on molecular weight prediction.

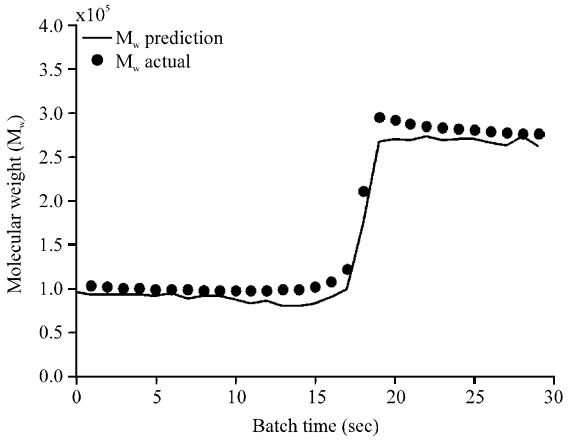

Fig. 23: NN prediction of molecular weight average at $I_0 = 0.0250$ mol L^{-1}, T = 90°C

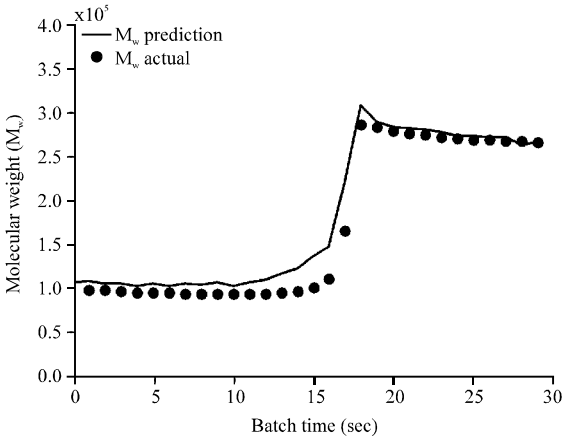

Fig. 26: NN prediction of molecular weight average at $I_0 = 0.0266$ mol L^{-1}, T = 90°C

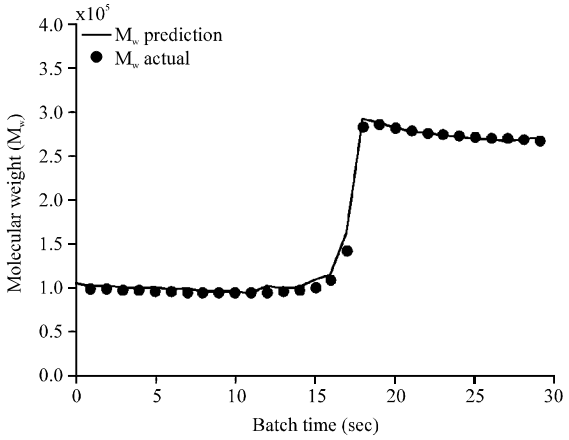

Fig. 24: NN prediction of molecular weight average at $I_0 = 0.0255$ mol L^{-1}, T = 90°C

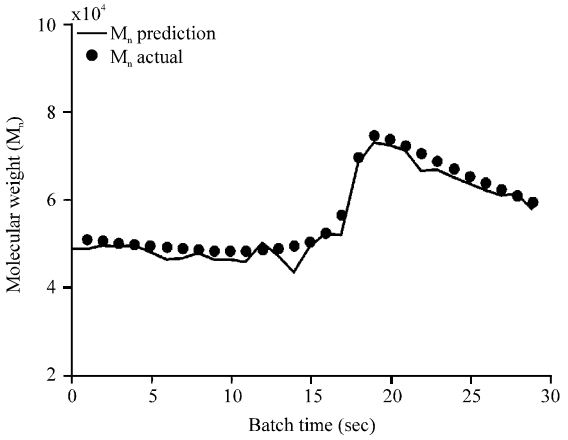

Fig. 27: NN prediction of number average molecular weight at $I_0 = 0.0255$ mol L^{-1}, T = 90°C

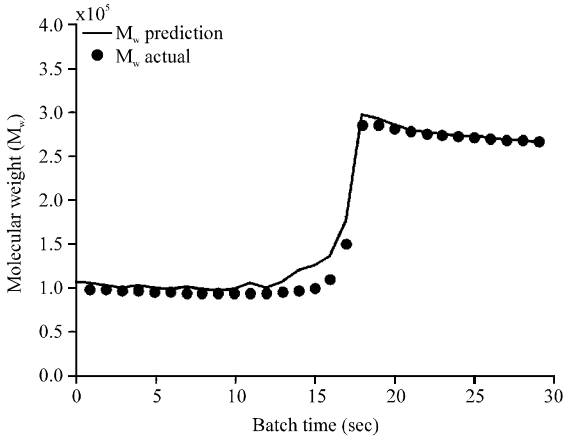

Fig. 25: NN prediction of molecular weight average at $I_0 = 0.0263$ mol L^{-1}, T = 90°C

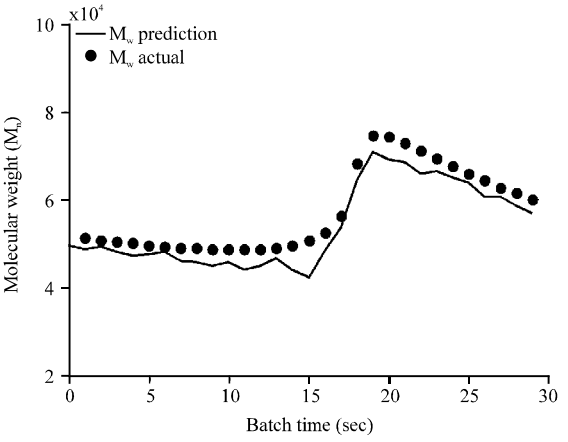

Fig. 28: NN prediction of number average molecular weight at $I_0 = 0.0253$ mol L^{-1}, T = 90°C

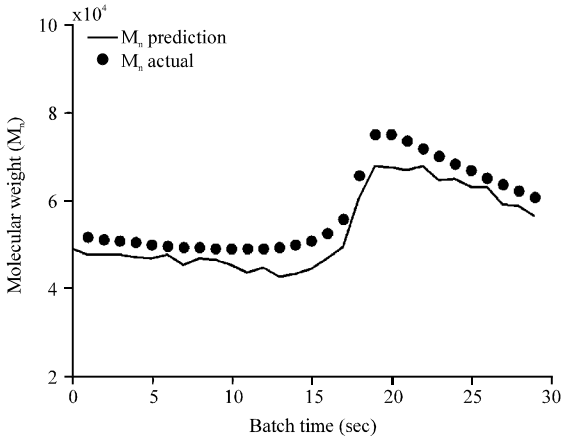

Fig. 29: NN prediction of number average molecular weight at I_0 = 0.0250 mol L^{-1}, T = 90°C

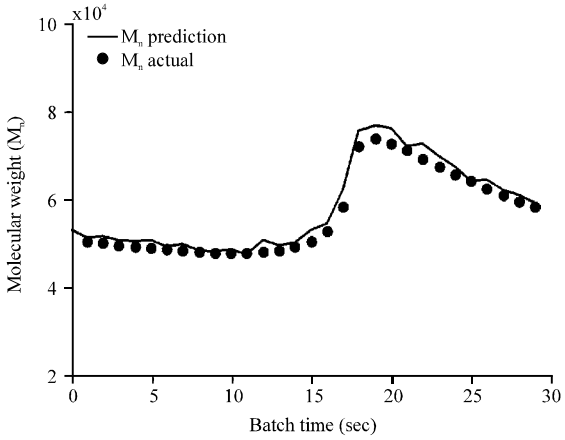

Fig. 30: NN prediction of number average molecular weight at I_0 = 0.0261 mol L^{-1}, T = 90°C

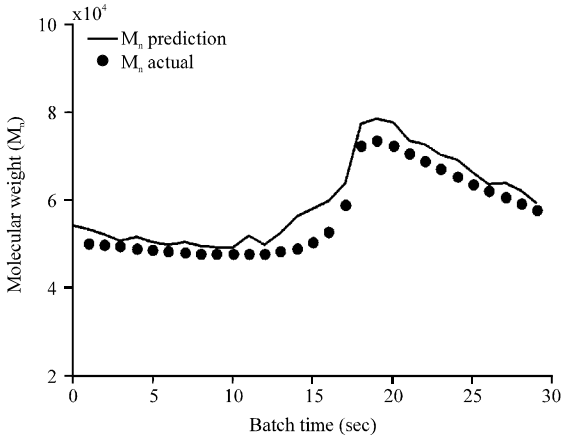

Fig. 31: NN prediction of number average molecular weight at I_0 = 0.0263 mol L^{-1}, T = 90°C

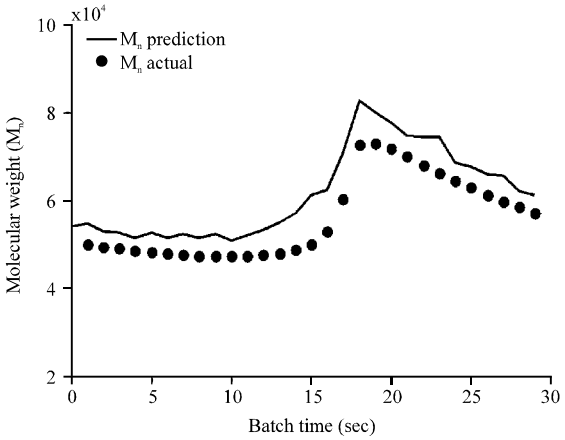

Fig. 32: NN prediction of number average molecular weight at I_0 = 0.0266 mol L^{-1}, T = 90°C

From the observation, it was confirmed that neural network prediction can only be modelled around the operating condition which data is gathered. Hence, we can conclude that the previously trained NN model could not be used to predict other operating condition. The network parameters are modelled exclusively only to predict the trained operating condition at 90°C and initial initiator loading I_0 = 0.0258 mol L^{-1}. To predict molecular weight using parameters other than the data that have been used in training neural network is unfeasible. Therefore, in order to be able to predict molecular weight using parameters other than the data that used in training neural network, it is suggested that the network are trained again using the data at its desired operating condition.

CONCLUSION

In this study, written NN programme from MATLAB is developed. It shows that this NN model is convincingly able to predict future performance accurately and it can be used for further application. Feedforward neural network system using past or history data can also be used to give more data to train the network in order to improve neural network model generalization. This study did offer another approach in simplifying polymerization reactor modeling process using neural network system.

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REFERENCES

Achilias, D.S. and C. Kiparissides, 1992. Development of a general mathematical framework for modeling diffusion-controlled free-radical polymerization reactions. Macromolecules, 25: 3739-3750.

Bersted, B.H. and T.G. Anderson, 1990. Influence of molecular weight and molecular weight distribution on the tensile properties of amorphous polymers. J. Appl. Polym. Sci., 39: 499-514.

Chiu, W.Y., G.M. Carrat and D.S. Soong, 1983. A computer model for the gel effect in free-radical polymerization. Macromolecules, 16: 348-357.

Crowley, T.J. and K.Y. Choi, 1997. Discrete optimal control of molecular weight distribution in a batch free radical polymerization process. Indus. Eng. Chem. Res., 36: 3676-3684.

Fernandes, F.A.N., L.M.F. Lona and A. Penlidis, 2004. Inverse modeling applications in emulsion polymerization of vinyl acetate. Chem. Eng. Sci., 59: 3159-3167.

Kiparissides, C., 1996. Polymerization reactor modeling: A review of recent development and future direction. Chem. Eng. Sci., 51: 1637-1659.

Krothapally, M., B. Bennett, W. Finney and S. Palanki, 1999. Experimental implementation of an on-line optimization scheme to batch PMMA synthesis. ISA Trans., 38: 185-198.

Kuroda, C. and J. Kim, 2002. Neural network modeling of temperature behavior in an exothermic polymerization process. Neurocomputing, 43: 77-89.

Nascimento, C.A.O., R. Giudici and R. Guardani, 2000. Neural network based approach for optimization of industrial chemical processes. Comput. Chem. Eng., 24: 2303-2314.

Ponnuswamy, S.R., S.L. Shah and C.A. Kiparissides, 1987. Computer optimal control of batch polymerization reactors. Indus. Eng. Chem. Res., 26: 2229-2236.

Roy, N.K., W.D. Potter and D.P. Landau, 2006. Polymer property prediction and optimization using neural networks. IEEE Trans. Neural Networks, 17: 1001-1014.

Soroush, M. and C. Kravaris, 1992. Nonlinear control of a batch polymerization reactor: An experimental study. AIChE J., 38: 1429-1448.

Takamatsu, T., S. Shioya and Y. Okada, 1988. Molecular weight distribution control in a batch polymerization reactor. Indus. Eng. Chem. Res., 27: 93-99.

Tian, Y., J. Zhang and J. Morris, 2002. Optimal control of a batch emulsion copolymerisation reactor based on recurrent neural network models. Chemi. Eng. Proc., 41: 531-538.

Zhang, J., 1999. Inferential estimation of polymer quality using bootstrap aggregated neural networks. Neural Networks, 12: 927-938.

Zhang, J., A.J. Morris, E.B. Martin and C. Kiparissides, 1998. Prediction of polymer quality in batch polymerisation reactors using robust neural networks. Chemi. Eng. J., 69: 135-143.