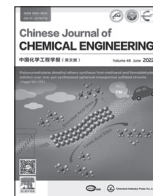




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Full Length Article

Monte Carlo simulation of sequential structure control of AN-MA-IA aqueous copolymerization by different operation modes

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ABSTRACT

The regulation of polyacrylonitrile (PAN) copolymer composition and sequence structure is the precondition for producing high-quality carbon fiber high quality. In this work, the sequential structure control of acrylonitrile (AN), methyl acrylate (MA) and itaconic acid (IA) aqueous copolymerization was investigated by Monte Carlo (MC) simulation. The parameters used in Monte Carlo were optimized via machine learning (ML) and genetic algorithms (GA) using the experimental data from batch copolymerization. The results reveal that it is difficult to control the aqueous copolymerization to obtain PAN copolymer with uniform sequence structure by batch polymerization with one-time feeding. By contrary, it is found that the PAN copolymer with uniform composition and sequence structure can be obtained by adjusting IA feeding quantity in each reactor of a train of five CSTRs. Hopefully, the results obtained in this work can provide valuable information for the understanding and optimization of AN copolymerization process to obtain high-quality PAN copolymer precursor.

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1. Introduction

Sequence structure of polyacrylonitrile (PAN) copolymer precursor greatly affects the performance of PAN-based carbon fiber [1–3]. The comonomer adding into PAN homopolymer, such as methyl acrylate (MA), methyl methacrylate (MMA), itaconic acid (IA) and acrylic acid (AA), could reduce the nitrile-nitrile interactions and change the cyclization reaction mechanism, thereby improve the spinnability [4], solubility [5], hydrophilicity [6], and especially TOS process [7] of PAN. In details, the acidic comonomer with carboxyl group can change the free radical mechanism of cyclization reaction into ion mechanism during TOS process [8], further obtaining a precursor with better properties [9]. Among these acidic comonomers, IA molecular with two carboxyl groups is proved to be the most efficient one to improve cyclization reaction [10]. Researches indicate that the sequence distribution of IA units on the polymer segment plays a crucial role on the cyclization reaction in TOS [2]. Hong *et al.* [11] synthesized a series of AN-IA copolymers with different sequence distributions, and found that copolymer with uniform sequence distribution are more efficient in TOS than that with random sequence distribution. There-

fore, the regulation of uniform distribution of IA on the polymer segment is the key factor to obtain high-quality PAN precursors.

Because of the reaction mechanism, traditional free radical copolymerization (FRP) is difficult to control the composition and sequence structure of the copolymer, which are majorly determined by the intrinsic differences in reactivity ratios between different monomers [12,13]. In order to obtain polymer with controllable sequence structure, different polymerization techniques and operation modes have been adopted [14]. In living polymerization, all polymer chain starts to grow at the same time without chain transfer and termination, so polymers with narrow MWD can be obtained [15]. In controlled radical polymerization (CRP), the active chains are grown in a controlled manner and the polymer segments can be designed to a desired structure [16–18]. Different reactor operation modes include batch reactor, semi-batch reactor, continuous stirred tank reactor (CSTR), tubular reactor and tanks-in-series reactor, *etc.* Luo *et al.* [19] developed a kinetic model of ATRP of methyl methacrylate (MMA) and 2-(trimethylsilyl) ethyl methacrylate (HEMA-TMS) with three operation modes (batch, semi-batch and CSTR), and determined the optimal operating conditions in varying reactors. Schork *et al.* [20] build a chain model and a sequence model to investigate the sequence length distribution for semi-batch polymerization. Zhu *et al.* [21] synthesized styrene/butyl acrylate copolymers with different uniform sequence lengths by a programmed semi-batch

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mini-emulsion copolymerization process. Due to the big gap between the industrial application and the lab work of CRP, the FRP is still the main industrial method for the production of PAN copolymer [22]. Since of the reactivity ratio of IA is far above AN, it is difficult to control the aqueous copolymerization which acts on the sequence structure of PAN [23–27]. To obtain PAN copolymer with uniform sequence structure, the effects of reactor configuration and operation mode are worth studying.

Notably, detailed distribution information on the copolymer segments is difficult to be accurately measured by experiment. Alternatively, simulation is proved to be a powerful and time-saving tool to investigate the composition and sequence distribution of copolymer, which is usually divided into deterministic and statistical methods [28,29]. The method of moments is one of the deterministic ones, which is the solution of a set of mass balance equations derived from the reaction [30,31]. A statistical one, e.g., Monte Carlo (MC) method, is more powerful but requires longer computation time. MC simulation is able to provide details structure information of individual polymer molecule, and the state of all materials at each moment during the entire polymerization process can be obtained [32–34]. In addition, the bivariate molecular weight-copolymer composition (MW-CC) characteristics and the chain sequence length (CSL) characteristics of the growing propagation chains in a copolymerization system can be traced [35]. Reyniers *et al.* [36] applied MC method to the calculation of copolymer composition-chain length distribution (CoC-CLD) in ATRP of MMA and styrene. D'hooge *et al.* [37] presented an innovative design strategy to synthesize sequence-controlled polymers through experiment and MC simulation. McAuley *et al.* [38] proposed a MC model of CSTR by discretizing inflow and outflow separately from reaction steps, and predicted dynamic changes in material concentration, molecular weight and distribution. However, there are few studies of the AN copolymerization using Monte Carlo simulation for the complex mechanism and operation conditions. Chen *et al.* [39] studied the characteristics of the AN copolymer at low conversion with a constant monomer concentration, and the polymer chain length of simulation is fixed. And also, previous MC simulations of polymerization reaction mainly focused on the reaction in a batch reactor, with few reports of CSTR. Therefore, the mechanism of the AN copolymerization is still unclear, especially in a single CSTR or a CSTR train.

In this work, a MC model has been developed for the AN-MA-IA terpolymerization in batch reactor, a single CSTR, and a CSTR train. Machine learning (ML) and genetic algorithms (GA) were used to obtain the unknown parameters used in MC simulation by using experimental data from batch copolymerization. Subsequently, the as-developed MC model was applied to investigate the effects of reactor configuration and operation modes on the chain sequential structure of the resulting copolymer. Critically, the feeding strategy of comonomer IA was optimized to obtain PAN copolymers with uniform sequence structure, especially in a CSTR train model.

2. Material and Methods

2.1. Materials

AN (analytical grade) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China. MA (reagent grade), IA (reagent grade), and AIBA (reagent grade) were purchased from Adamas Chemical Reagent Beijing Co., Ltd., Shanghai, China. AN was purified by alkali washing followed by distillation to remove inhibitor.

2.2. Preparation of AN-MA-IA terpolymer

A typical procedure for preparing AN-MA-IA copolymer was described as follows. The reactor was a 250 ml 4-necked flask that immersed in a temperature-controlled oil bath and connected with a dynamoelectric stirrer, a condenser, a thermometer, a pH meter and a nitrogen inlet. After 30 min of nitrogen purification, calculated amount of AN, MA, IA and deionized water were put into the flask at once. Then the oil bath started to heat up, and AIBA was put into the flask at 70 °C. After a certain polymerization time, the precipitate mixture was isolated by filtration, washed several times by deionized water, and dried under vacuum at 60 °C for 48 h.

2.3. Characterization

Element Analysis (EA). Element analysis (EA) of the AN-MA-IA terpolymer product was conducted using an Elemental Vario EL III. The nitrogen element is supplied from AN, thus the AN composition in the terpolymer was derived by

$$f_{\text{AN}} = N\% \times \frac{53.06}{14} \quad (1)$$

Nuclear Magnetic Resonance (NMR). ^1H NMR spectra was detected using a Bruker AVANCE III 400 MHz spectrometer with dimethyl sulfoxide (DMSO) as solvent. For AN-MA-IA terpolymer, the methyl ($-\text{CH}_3$) proton of MA and methyne (CH) proton of AN and MA is assigned around δ 3.69 and δ 2.90–3.20, respectively. Therefore, the ratio of AN to MA was calculated by the ratio of the two peak areas, and further the MA composition in the terpolymer was obtained by

$$f_{\text{MA}} = f_{\text{AN}} \times \frac{S_{3.69}}{3S_{2.90-3.20} - S_{3.69}} \quad (2)$$

Then IA composition was derived by

$$f_{\text{IA}} = 1 - f_{\text{AN}} - f_{\text{MA}} \quad (3)$$

Gel Permeation Chromatography (GPC). Apparent molecular weights (M_w , M_n) and distribution (M_w/M_n) were obtained by an Agilent Technologies PL-GPC50 equipped with a PLgel 10 μm (50 mm $\times$ 7.5 mm) GUARD column and two PLgel 10 μm (300 mm $\times$ 7.5 mm) MIXED-B columns at 50 °C. *N,N*-dimethylformamide (DMF) containing 10 mmol LiBr served as the eluent. The molecular weights were calibrated with polystyrene (PS) narrow standards and then corrected by PAN broad standards.

2.4. Computation

2.4.1. Monte Carlo algorithm

Monte Carlo simulations of polymerization reaction in this work were based on Gillespie's algorithm [40]. The detailed calculations were described as follows. Supposing that there are N kinds of reactant molecules in a specific volume V , the number of which is X_i ($i = 1, 2, \dots, N$). These reactant molecules undergo M types of chemical reactions R_i ($i = 1, 2, \dots, M$). At time t , the rate of each reaction in the system is

$$R_i = k_{\text{MC}} \cdot X_{i1} \cdot X_{i2} \quad (4)$$

where X_{i1} and X_{i2} are the number of molecules of the two reacting species, respectively.

k_{MC} is the microscopic reaction rate constant, indicating the probability of collision between two molecules. k_{MC} is related to the macroscopic reaction rate constant k_{exp} measured in the experiment, as described in the Eqs. (5)–(7). where N_A is Avogadro constant.

$$k_{MC} = k_{exp} \quad \text{for first order reactions} \quad (5)$$

$$k_{MC} = \frac{k_{exp}}{VN_A} \quad \text{for secondary reactions of different molecules} \quad (6)$$

$$k_{MC} = \frac{2k_{exp}}{VN_A} \quad \text{for secondary reactions of same molecules} \quad (7)$$

At time t , the probability p_i ($i = 1, 2, \dots, M$) of R_i is calculated by the equation

$$p_i = \frac{R_i}{\sum_{i=1}^M R_i} \quad (8)$$

All reaction probabilities are normalized as

$$\sum_{i=1}^M p_i = \sum_{i=1}^M \frac{R_i}{\sum_{i=1}^M R_i} = 1 \quad (9)$$

In all MC simulations, two numbers r_1 and r_2 uniformly distributed between [0, 1] are randomly generated to determine the reaction type occurs at time t and the time interval τ between two reactions, as shown in Eqs. (10) and (11). Note that the number of molecules is updated, new random number is generated in the next reaction, and the cycle stops until the reaction reaches a specific time or the required conversion. In a CSTR model, the additional simulation steps are the inflow and outflow of chemical species and molecule numbers, which are determined by the discretization approach [38]. The number of molecules of each substance is determined by the monomer concentration, monomer ratios and initiator concentration.

$$\sum_{i=1}^{v-1} P_i \leq r_1 \leq \sum_{i=1}^v P_i \quad (10)$$

$$\tau = \frac{1}{\sum_{i=1}^M R_i} \ln \left(\frac{1}{r_2} \right) \quad (11)$$

where v is the selected reaction channel.

AN-MA-IA terpolymerization reaction is a typical free radical polymerization, including chain initiation, propagation, termination, and transfer reaction. The reaction mechanism of AN-MA-IA terpolymerization is described as Eqs. (12)–(28), including 9 propagation reactions. It should be pointed that only radicals terminated by combination and transfer to monomer were considered in current mechanism scheme for simplification.

Chain initiation:



Chain propagation:



Chain termination:



Chain transfer to monomer:



where AIBA is the initiator, I· is the primary free radical, R_i · is propagating radical of various monomers, P_i is the dead polymer, subscript i is the chain length of polymeric species.

2.4.2. Polymerization rate constants

The decomposition constant (k_d) of initiator, the propagation constant (k_p), the reactivity ratios (r), the termination constant (k_t) and the transfer constant of monomer ($C_M = k_p/k_{tr, M}$) used in this work were listed in Table 1. The initiator constant (k_i) was selected in the routine range of free radical polymerization. The homopolymerization constant (k_{p33}) of IA was determined in the range of propagation constant of IA derivatives [41].

As has been shown in the previous work [24], the values of reactivity ratios r_{13} and r_{31} calculated by different methods are different. Herein, the MC simulation using different reactivity ratio values were conducted. As shown in Table 2, the copolymer composition calculated using $r_{13} = 0.505$ and $r_{31} = 1.928$ shows the minimum difference from experimental values (AN: MA: IA = 94.33:2.94:2.72). Therefore, these two parameters were used in the following simulation. In addition, composition data indicates high reactivity of IA in simulations and experiment, which is consistent with previous researches [23,24].

3. Results and Discussion

3.1. Parameters optimization with machine learning and genetic algorithms

For a classical free-radical polymerization process, the viscosity of the system increases as the conversion increases, resulting in hindered rearrangement of polymer segments and difficult termination of radicals [46]. So the chain termination constant k_t decreases as the conversion increases, further causing the inevitable auto-acceleration phenomenon [47]. The propagation constant k_p decreases as the conversion increases to a higher value (>50%) due to the difficult monomer diffusion [48], and the polymerization rate decreases accordingly [49]. However, the propagation constant k_p and the termination constant k_t were both obtained at low conversion in previous researches [43]. The changes of k_p and k_t at high conversion are complicated and difficult to be measured. If k_{p0} and k_{t0} are used to simulate the whole reaction process, the simulation result will be seriously unreasonable. To

Table 1
Kinetic rate constants for MC simulation of AN (1)–MA (2)–IA (3) terpolymerization

Parameter	Value	Source
$k_d/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$9.375 \times 10^{14}\exp(-124,000/RT)$	[42]
$k_i/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	10^9	This study
$k_{p11}/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$3.0 \times 10^7\exp(-17163/RT)$	[43]
$k_{p22}/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	2090	[41]
$k_{p33}/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	70	This study
r_{12}	1.11	[44]
r_{21}	0.84	[44]
r_{23}	0.52	[41]
r_{32}	1.90	[41]
r_{13}	0.505	[24]
r_{31}	1.928	[24]
$k_t/\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$3.0 \times 10^{13}\exp(-22,604/RT)$	[43]
C_M	1.02×10^{-4}	[45]

improve the reliability of the simulation, a classical encounter pair model was employed for the propagation and termination reactions [50]:

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \frac{1}{k_{\text{diff},p}} \quad (29)$$

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \frac{1}{k_{\text{diff},t}} \quad (30)$$

where $k_{\text{diff},p}$ and $k_{\text{diff},t}$ are respectively the diffusion propagation and termination coefficient, and their values are related to the conversion. Further, the formulas can be converted to:

$$\frac{k_p}{k_{p0}} = \frac{1}{1 + \frac{k_{p0}}{k_{\text{diff},p}}} = \text{Pro} \quad (31)$$

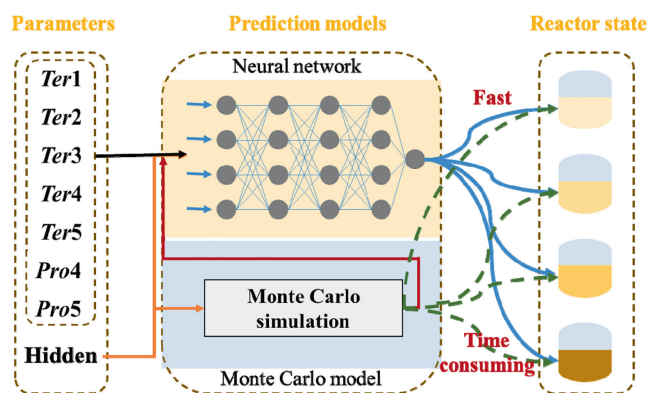
$$\frac{k_t}{k_{t0}} = \frac{1}{1 + \frac{k_{t0}}{k_{\text{diff},t}}} = \text{Ter} \quad (32)$$

where *Pro* and *Ter* are the constants of k_p/k_{p0} and k_t/k_{t0} at different conversion ranges.

In this work, the values of *Pro* and *Ter* were set at different polymerization conversion ranges, as listed in Table 3. After the polymer was precipitated, k_t began to decrease due to the change of the polymerization site, while the k_p decreased after reaching a higher conversion (>50%) [51]. Since MC simulation is time-consuming, it is not plausible to explore all above parameters space to fit the parameters. Therefore, the ML and GA were used

for parameter optimization, which can significantly reduce the computation time.

As shown in Scheme 1, the limited number of MC simulations were performed to generate the simulation data of the conversion and the weight average molecular weight (M_w) for ML. Five levels were chosen for each parameter with $5^7 = 78125$ kinds of combinations. To decrease the number of simulations, orthogonal experiments include 7 factors and 5 levels were designed. After the training on the data prepared by the MC simulation, the ML model can predict the output of the conversion and the M_w over the whole continuous parameters space.



Scheme 1. Schematic diagram of learning MC simulation based on ML.

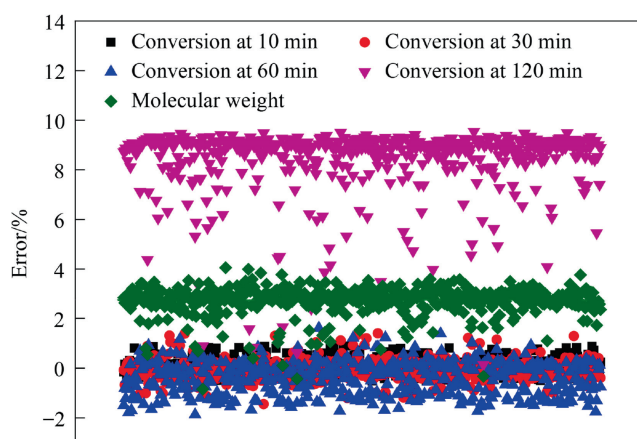


Fig. 1. Relative error of conversion and M_w between the predicted value of ML model and MC simulation.

Table 2
Polymer composition with different monomer reactivity ratios of AN (r_{13}) and IA (r_{31}). Polymerization time = 120 min, M concentration = 15% (mass), I/M = 1% (mass)

Calculating methods	r_{13}	r_{31}	Copolymer composition/% (mass)		
			AN	MA	IA
Q-e schemes	0.505	1.928	94.71	3.02	2.27
Kelen-Tüdös method	0.64	1.37	94.90	3.06	2.04
Fineman-Ross method	0.61	1.47	94.88	3.06	2.07
Experiment	—	—	94.33	2.94	2.72

Table 3
The values of k_p/k_{p0} and k_t/k_{t0} at different polymerization conversion

Conversion/%	0–precipitation	Precipitation–10	10–30	30–50	50–70	>70
k_p/k_{p0}	1	1	1	1	<i>Pro4</i>	<i>Pro5</i>
k_t/k_{t0}	1	<i>Ter1</i>	<i>Ter2</i>	<i>Ter3</i>	<i>Ter4</i>	<i>Ter5</i>

Table 4
Parameters screened and optimized by the GA

Parameter	Ter1	Ter2	Ter3	Ter4	Ter5	Pro4	Pro5
value	0.085	0.02	0.01	0.01	0.01	0.72	0.26

The ML model was built with 7 densely-connected layers. After training for 5000 epochs with a learning rate of 0.001, the neural network predictions with different parameters were compared with the output of MC models, and the results were shown in Fig. 1. The relative error between ML predictions and MC output for conversion is less than 2% when polymerization time is 10–60 min. With the increase of polymerization time, the error of ML for the prediction of conversion increases. The error of ML for prediction of molecular weight is about 3%. Thus, the neural network model is a qualified cheap substitute for first stage parameters optimization of time-consuming MC simulation.

With the established ML model, the output of the time-consuming Monte Carlo simulation, such as the conversion and the M_w , can be predicted by the given parameters of *Ter* and *Pro*. GA is a powerful tool to search for optimum parameters, and multiple GA optimization loops were carried out during the parameter optimization process. After each loop, the top 5% of parameters combination were kept for next stage crossover and mutation, and each parameter increased or decreased for 5%. To improve the reliability of GA, the output in the final searching round was

directly calculated via MC simulation. The parameters screened and optimized by the GA were shown in Table 4.

These parameters were selected for the following MC simulation work. The conversion and M_w of batch polymerization with different monomer (M) concentrations and a constant ratio of initiator to monomer ($I/M = 1\%$ (mass)) were simulated and compared with experimental values, as shown in Fig. 2. The X-abcissa and Y-ordinate represent for the experimental and the simulated values, respectively. The data point is closer to the diagonal line, indicating that the simulated and experimental value are more consistent. The conversion data come from 16 conditions of monomer concentrations of 8% (mass), 15% (mass), 22% (mass) and 29% (mass), with reaction times of 10 min, 30 min, 60 min, and 120 min, while M_w data come from 4 conditions with monomer concentrations of 8% (mass), 15% (mass), 22% (mass) and 29% (mass), with the reaction time of 120 min. The conversion and M_w data are evenly distributed on both sides of the diagonal, and the average relative error of conversion is 4.0%, while that of M_w is 1.6%. Therefore, this MC simulation with specific parameters in this work can well reflect the actual polymerization process.

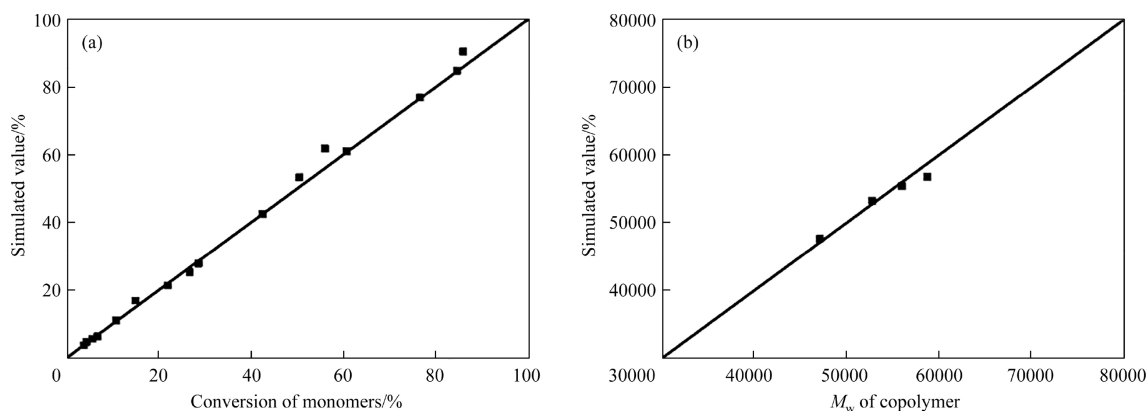


Fig. 2. Comparison of (a) conversion and (b) M_w of simulation and experiment. Simulation conditions: AN: MA: IA = 95:3.2:1.8, M concentration = 8% (mass), 15% (mass), 22% (mass) and 29% (mass), $I/M = 1\%$ (mass).

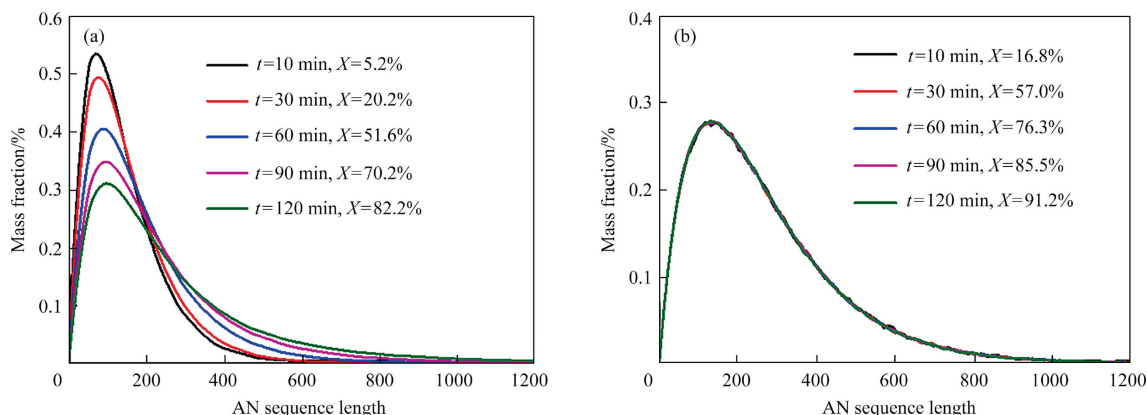


Fig. 3. AN sequence length distribution changes over polymerization time. Simulation conditions: AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), $I/M = 1\%$ (mass).

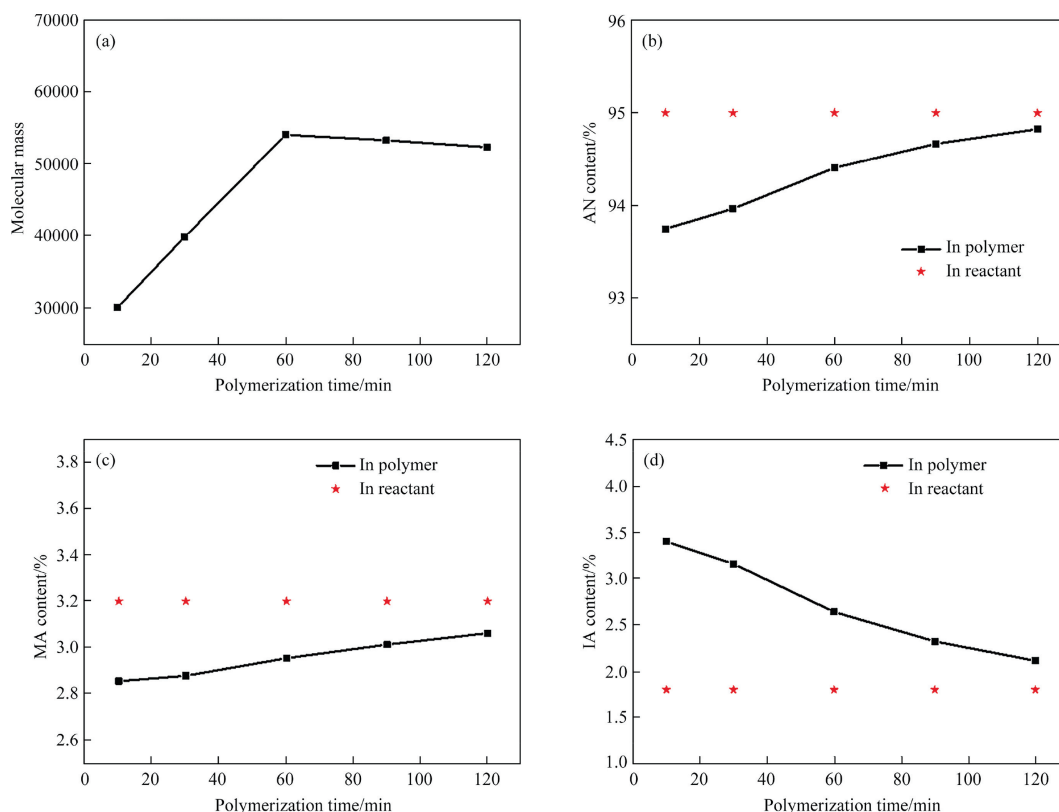


Fig. 4. (a) M_w , (b) AN content, (c) MA content, and (d) IA content changes over polymerization time. Simulation conditions: AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass).

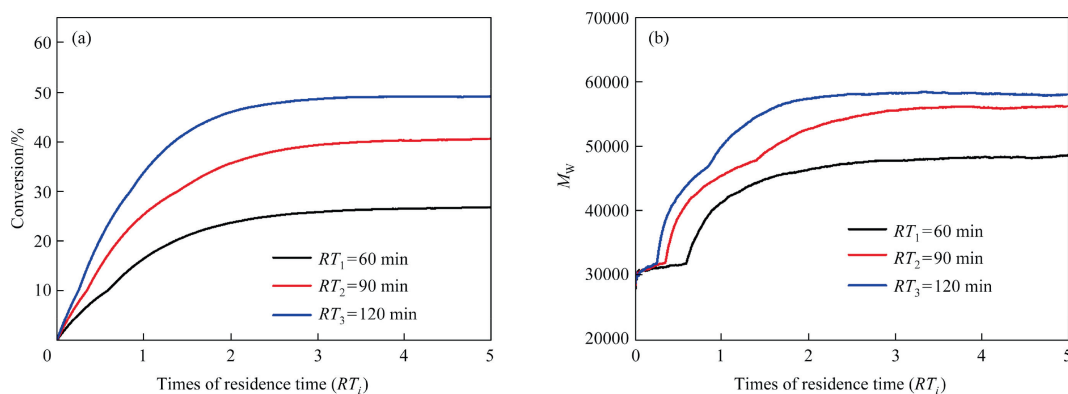


Fig. 5. Change of (a) conversion and (b) M_w in CSTR. Simulation conditions: AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass).

3.2. Simulation of batch polymerization

The AN-MA-IA terpolymerizations in batch reactor with different conversion were simulated using MC method. It should be noted that the reactivity ratio of MA is similar to that of AN ($r_{AN} = 1.11$, $r_{MA} = 0.84$ [44]), implying that it has slight effect on the sequence distribution of polymer product. Moreover, the purpose of this work is to adjust the uniform distribution of IA units in the polymer chain. Therefore, MA was regarded as the same unit as AN in the statistics of sequence length. The results of AN sequence length distribution changes over time were shown in Fig. 3. From Fig. 3(a), the distribution of continuous AN sequence length in the polymer product gradually widens with the increase of conversion, and the weight fraction of longer AN fragment gradually increases. As a comparison, Fig. 3(b) shows the AN sequence

length distribution in the situation without difference in reactivity ratios of AN and IA. The AN sequence length distribution under different polymerization times is consistent, which means that the difference in the reactivity ratios is the cause of the uneven sequence structure.

The changes of the M_w value and the three monomers' composition of the polymer over reaction time were calculated and shown in Fig. 4. From Fig. 4(a), the M_w of the polymer product first goes up with time, which is ascribed to the decreased k_t for the gel effect as the conversion increases. Then the M_w value decreases slightly as time increases. Actually, the monomer diffusion becomes difficult when the conversion is high, leading to a decreased k_p and M_w of polymer. From Fig. 4(b), (c) and (d), it can be seen that the variation of AN content in the polymer over time follows a similar tendency with MA. However, the content

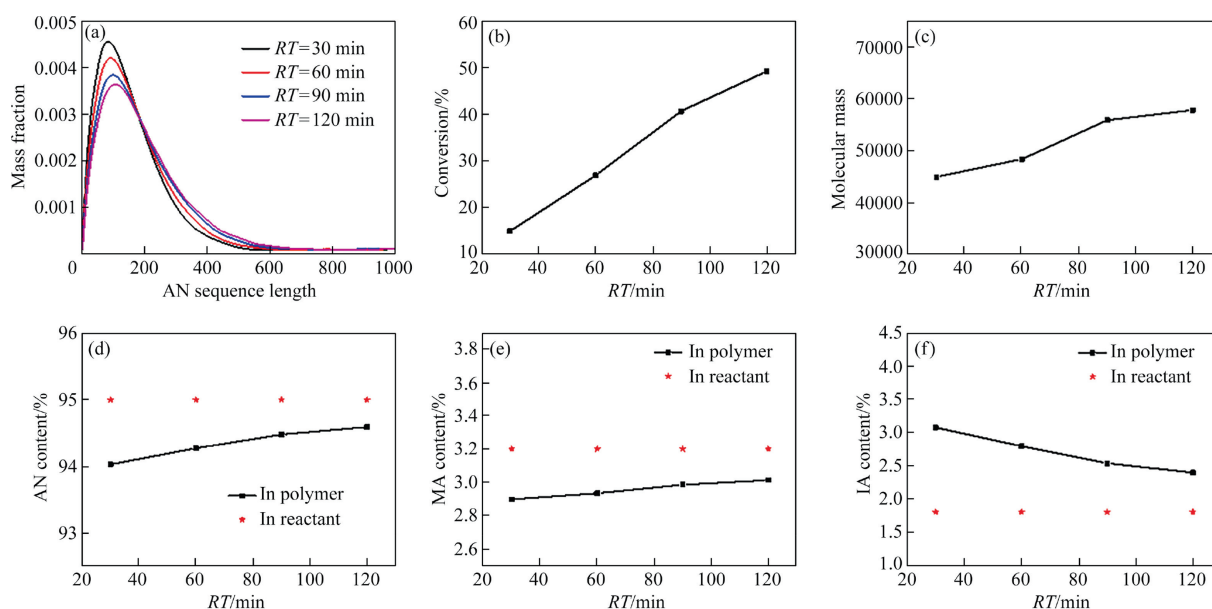


Fig. 6. AN sequence length distribution (a), conversion (b), M_w (c), AN content (d), MA content (e), and IA content (f) at different residence time of CSTR. Simulation conditions: AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass).

Table 5

Simulation results of double kettle series continuous polymerization with different residence time distributions. AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass)

No.		Residence time/min	M_w	Conversion/%	AN content/% (mass)	MA content/% (mass)	IA content/% (mass)
1	#1	30	45,003	14.82	94.02	2.90	3.08
	#2	90	57,230	49.92	94.53	3.00	2.47
2	#1	60	48,450	26.77	94.27	2.93	2.80
	#2	60	55,533	49.91	94.51	2.99	2.50
3	#1	90	55,958	40.55	94.48	2.99	2.54
	#2	30	55,252	50.04	94.53	3.00	2.47
4	#1	120	57,901	49.08	94.59	3.01	2.39

of IA in the polymer at the beginning of the polymerization is much higher than the proportion of IA in the raw material, which is ascribed to the fact that IA is heavily involved in the initial reaction. As the reaction proceeds, the composition of the polymer gradually approaches to the ratio in the raw material. However, the heterogeneous sequence structure of the polymer products is irreversible, which is not conducive to obtaining PAN product of high quality.

To further study the effect of operation conditions on the batch polymerization process, the AN-MA-IA polymerization with different monomer concentrations, initiator concentrations, and IA ratios were calculated, as shown in Figs. S1–S3. It can be concluded that the monomer concentration and the initiator concentration mainly affect the conversion, further influencing the AN sequence length and polymer composition. The conversion and the M_w increase as monomer concentration increases with a fixed I/M value. From Fig. S2, the conversion increases as initiator concentration increases due to the more active centers, whereas the M_w value decreases. The results are similar to Fig. 3 and consistent with the well-accepted mechanism of free radical polymerization. From Fig. S3, the effect of IA ratio on reaction process and product distribution is more obvious than other conditions. For example, the conversion and the M_w decrease sharply as IA amount increases, which is ascribed to the two carboxyl groups and large steric hindrance of IA molecules.

For batch polymerization, the results of MC simulation are consistent with the mechanism of free radical polymerization in actual

polymerization process. The high reactivity of IA than AN and MA causes uneven polymer sequence structure, which is inevitable and unexpected. Therefore, to prepare PAN copolymers with uniform sequence structure, it is necessary to optimize the one-time feeding strategy to regulate the distribution of IA in the polymer. In the following study, the AN-MA-IA terpolymerization in a single CSTR and a CSTR train with multi-feeding method were simulated using MC method.

3.3. Simulation of continuous polymerization in a single CSTR

The AN-MA-IA terpolymerizations in a single CSTR were simulated using MC method. The conversion and the M_w of the product were shown in Fig. 5(a) and (b), respectively. It can be found that the conversion and the M_w value reached a stable state at 5 times the residence time (RT), and the simulation time was applied in the following simulations. The inflection points of the curve in Fig. 5(b) was caused by different k_p and k_t in various conversion ranges.

Special attention was paid to the impact of the residence time on various indicators, as shown in Fig. 6. From Fig. 6(a), the AN sequence length increases as the residence time increases, because the content of AN in the polymer increases as the conversion increases. From Fig. 6(b) and (c), the M_w of the polymer in CSTR is higher than that in batch reactor (Figs. 3(a) and 4(a)) at the same conversion. This phenomenon occurs because the reaction continues at a constant high conversion in CSTR, while the batch polymerization has low molecular weight polymers generated at low

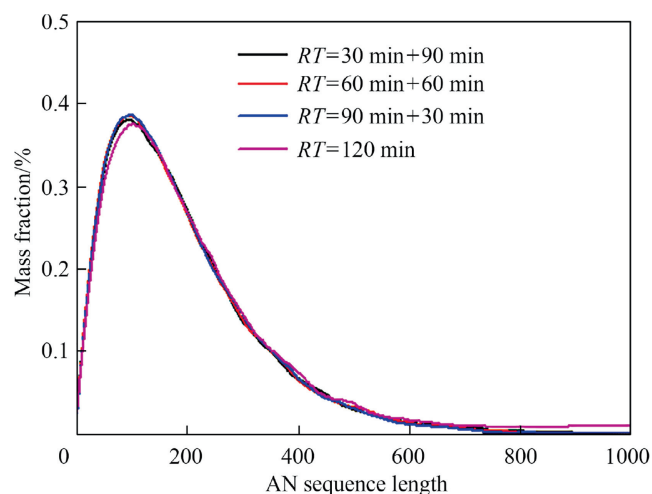


Fig. 7. AN sequence length distribution with different residence time distributions. AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass).

conversion. From Fig. 6(d)–(f), the content of AN and MA in the polymer is always less than the content in raw material, while IA is higher than that in raw material. That is, the one-time feeding method in CSTR still could not play a good role in the regulation of polymer composition and sequence structure. The effects of monomer concentration, initiator concentration, and IA ratio on

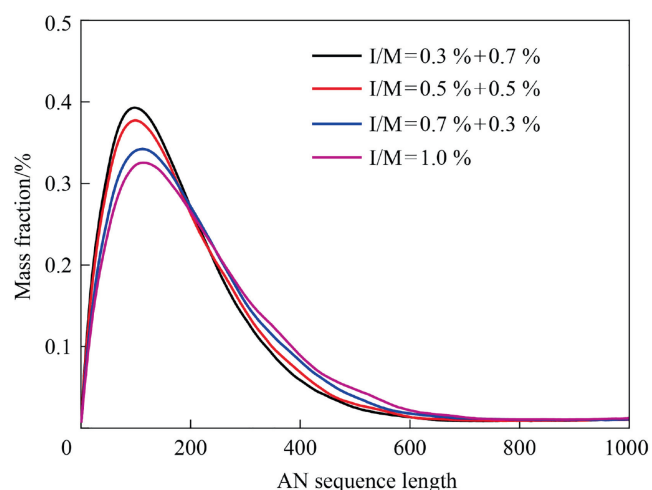


Fig. 8. Simulation value of AN sequence length distribution with different initiator feed distributions. Residence time $RT_1 = RT_2 = 60$ min, AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass).

Table 6

Simulation results of double kettle series continuous polymerization with different initiator feed distributions. Residence time $RT_1 = RT_2 = 60$ min, AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass)

No.		Initiator concentration/% (mass)	M_w	Conversion/%	AN content/% (mass)	MA content/% (mass)	IA content/% (mass)
1	#1	0.3	37,469	4.38	93.75	2.88	3.37
	#2	0.7	51,781	32.39	94.30	2.94	2.77
2	#1	0.5	36,983	9.59	93.92	2.86	3.21
	#2	0.5	53,788	36.21	94.34	2.95	2.71
3	#1	0.7	49,471	18.59	94.10	2.91	2.99
	#2	0.3	57,177	45.01	94.45	2.98	2.58
4	#1	1	48,450	26.77	94.27	2.93	2.80
	#2	0	55,533	49.91	94.51	2.99	2.50

conversion, M_w , copolymer composition, and sequence structure in the CSTR are similar to batch reactor, as shown in Figs. S4–S6.

3.4. Simulation of continuous polymerization in a CSTR train

To figure out the influence of the residence time on a train of two CSTRs in series model, four different residence time allocations were conducted, and the results were shown in Table 5 and Fig. 7. The total residence time of the two reactors in each case is 120 min, and No.4 is the CSTR results with a residence time of 120 min for comparison. From Table 5, the conversion, M_w , and composition of the products in the final reactor are essentially the same in all cases. Simultaneously there is basically no difference in the distribution of AN sequence length in four systems as shown in Fig. 7. The result indicates that the residence time distribution has no effect on the reaction in the case of feeding all the materials in the first reactor at once. Therefore, the residence time of each CSTR is equal in the following calculation.

The results of simulation with four different initiator feed distribution methods were listed in Table 6 and Fig. 8. It can be seen that the more initiator used in the first reactor, the higher conversion of the products in the final reactor. However, the impact on the M_w , composition, and the distribution of the AN sequence length is not obvious. Actually, the initiator participates the reaction once it was added, leading to a fast polymerization and no regulation of polymer segment structure. This is because the earlier the initiator is added, the more it participates in the reaction, allowing the polymerization to occur faster. However, it has no regulatory effect on the polymer segment structure. In the following research on the impact of the batch feed of comonomer IA, the one-time feed scheme of initiator was chosen to get a higher conversion.

The results of simulation with six different IA feed distribution methods were listed in Table 7 and Fig. 9, and the total usage of IA in each case was 1.8% (mass) in No.1–No.5. The conversion is not significantly affected by the IA feed distribution. As the IA usage in the first reactor increases, the IA composition of the copolymer in the second reactor increases, whereas M_w decreases. Actually, the increase of IA usage in the first reactor causes the early participation of IA in the whole reaction, which leads to higher IA composition. Furthermore, high IA composition makes propagation reaction difficult due to the steric hindrance effect of IA, resulting in the decrease of M_w [52].

The IA composition and AN sequence length distribution in the two reactors change with IA feed distribution. In No.5, the IA composition of the copolymer in the first reactor is 1.79% (mass) when the IA feed is 1.25% (mass), which is very close to the designed IA content of 1.8% (mass). However, the IA composition of the copolymer in the second reactor is 2.06% (mass), and AN sequence length distribution is not consistent with that of the first reactor.

Table 7

Simulation results of double kettle series continuous polymerization with different IA feed distributions. Residence time $RT_1 = RT_2 = 60$ min, AN:MA = 95:3.2, M concentration = 22% (mass), I/M = 1.0% (mass)

No.		IA ratio/% (mass)	M_w	Conversion/%	AN content/% (mass)	MA content/% (mass)	IA content/% (mass)
1	#1	0.6	95,313	49.23	96.13	3.07	0.80
	#2	1.2	93,163	57.66	95.61	3.06	1.33
2	#1	0.9	94,648	50.00	95.74	3.06	1.20
	#2	0.9	92,083	59.01	95.33	3.05	1.62
3	#1	1.2	78,607	43.52	95.31	3.02	1.66
	#2	0.6	73,934	55.13	95.01	3.03	1.96
4	#1	1.8	48,450	26.77	94.27	2.93	2.80
	#2	0	55,533	49.91	94.51	2.99	2.50
5	#1	1.25	75,571	40.51	95.21	3.00	1.79
	#2	0.55	70,683	53.46	94.92	3.01	2.06
6	#1	1.25	75,571	40.51	95.21	3.00	1.79
	#2	0.15	69,492	59.49	95.20	3.04	1.77

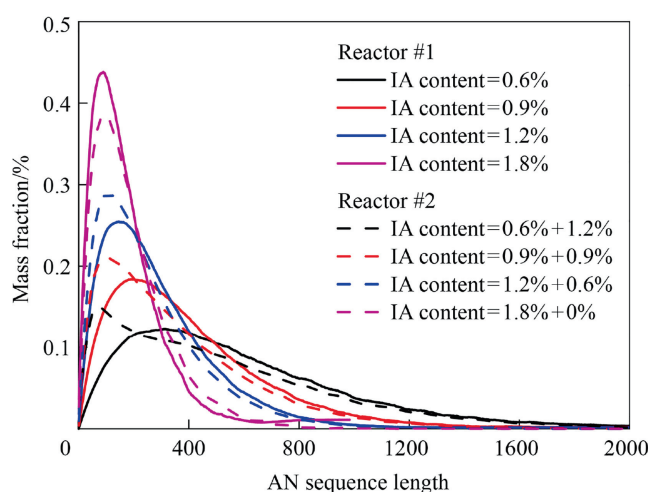


Fig. 9. Simulation value of AN sequence length distribution with different IA feed distributions. Residence time $RT_1 = RT_2 = 60$ min, AN: MA: IA = 95:3.2:1.8, M concentration = 22% (mass), I/M = 1% (mass).

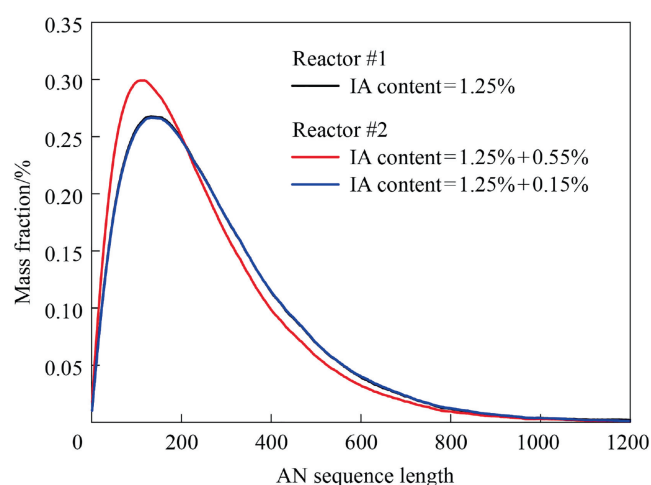


Fig. 10. Simulation value of AN sequence length distribution with different IA feed distributions and dosage. Residence time $RT_1 = RT_2 = 60$ min, AN: MA = 95:3.2, M concentration = 22% (mass), I/M = 1% (mass).

In order to keep the composition and sequence structure of copolymer in the two reactors consistent, the IA feed in the second reactor was set as 0.15% (mass), as shown in No.6. At this time, the IA composition of the copolymer in second reactor is 1.77% (mass), which is very close to the designed IA content of 1.8% (mass). Further, the AN sequence length distribution of No.5 and No.6 were calculated and shown in Fig. 10. It can be seen that the IA feed scheme of 1.25% (mass) + 0.15% (mass) can make the AN sequence length distribution in the two reactors consistent, realizing the regulation of the product segment structure.

To extend the method of regulating polymer sequence structure from two CSTRs to more, a train of three CSTRs and a train of five CSTRs were established and simulated (see Table 8 and Fig. 11). If one-time feeding method was adopted for the CSTR train model, the IA compositions in the copolymer were far above the set value of 1.8% (mass), as shown in No.1 and No.3. The AN sequence length distribution of each reactor was different. For the train of three CSTRs, the IA composition in the products of all the reactor is close to the set value of 1.8% (mass) when the IA feed amount is 1.15% (mass), 0.2% (mass), and 0.1% (mass), as shown in No.2. And the AN sequence length distribution of each reactor was basically coinciding. For the train of five CSTRs, this IA feed amounts of each reactor is set as 1.05% (mass), 0.15% (mass), 0.15% (mass), 0.1% (mass) and 0% (mass), respectively. Compared with the one-time feeding method, adding IA in batches can control the IA composi-

tion in the product and makes the chain structure of product uniform distributed. And also, the overall conversion and M_w of product are increased. So the high performance polyacrylonitrile copolymers which can be used in carbon fiber were obtained.

4. Conclusions

In this work, a kinetic Monte Carlo model has been developed for AN-MA-IA terpolymerization in batch reactor, a single CSTR, and a CSTR train. For the first time, the kinetics parameters were optimized by ML and GA methods. In a batch reaction with a single feed, the IA composition in the product is far above the ratio of monomer feed, and the distribution of polymer sequence structure is uneven in simulation. The uneven sequence distribution of polymer is inevitable and unexpected, which is ascribed to the higher reactivity ratio of IA than AN. PAN copolymers with uniform sequence structure can be obtained in a CSTR train with special feeding strategy of IA. In the train of five CSTRs, IA feed amounts of each reactor is set as 1.05% (mass), 0.15% (mass), 0.15% (mass), 0.1% (mass) and 0% (mass), respectively. In this work, a method of regulating the polymer chain sequence structure is established. Hopefully, this work can provide guidance for the industrial production of high-quality PAN and the design of polymerization process.

Table 8

Simulation results of tanks-in-series model with different IA feed distributions. No.1&2: Residence time $RT_1 = RT_2 = RT_3 = 40$ min. No.3&4: Residence time $RT_1 = RT_2 = RT_3 = RT_4 = RT_5 = 24$ min. AN:MA = 95:3.2, M concentration = 22% (mass), I/M = 1.0% (mass)

No.		IA ratio/% (mass)	M_w	Conversion/%	AN content/% (mass)	MA content/% (mass)	IA content/% (mass)
1	#1	1.8	46,575	18.98	94.12	2.91	2.98
	#2	0	53,281	37.59	94.34	2.95	2.71
	#3	0	54,198	49.98	94.47	2.98	2.55
2	#1	1.15	70,713	28.01	95.23	2.96	1.81
	#2	0.2	71,316	49.93	95.20	3.00	1.80
	#3	0.1	67,902	61.04	95.17	3.03	1.80
3	#1	1.8	32,182	8.67	93.91	2.86	3.23
	#2	0	42,593	19.64	94.06	2.89	3.05
	#3	0	46,059	29.76	94.19	2.91	2.90
	#4	0	51,490	40.19	94.32	2.94	2.74
	#5	0	56,105	49.94	94.44	2.97	2.59
4	#1	1.05	72,092	18.62	95.28	2.94	1.78
	#2	0.15	75,685	36.49	95.25	2.97	1.78
	#3	0.15	74,490	49.97	95.21	3.00	1.79
	#4	0.1	72,148	57.20	95.18	3.01	1.81
	#5	0	70,396	63.87	95.18	3.02	1.80

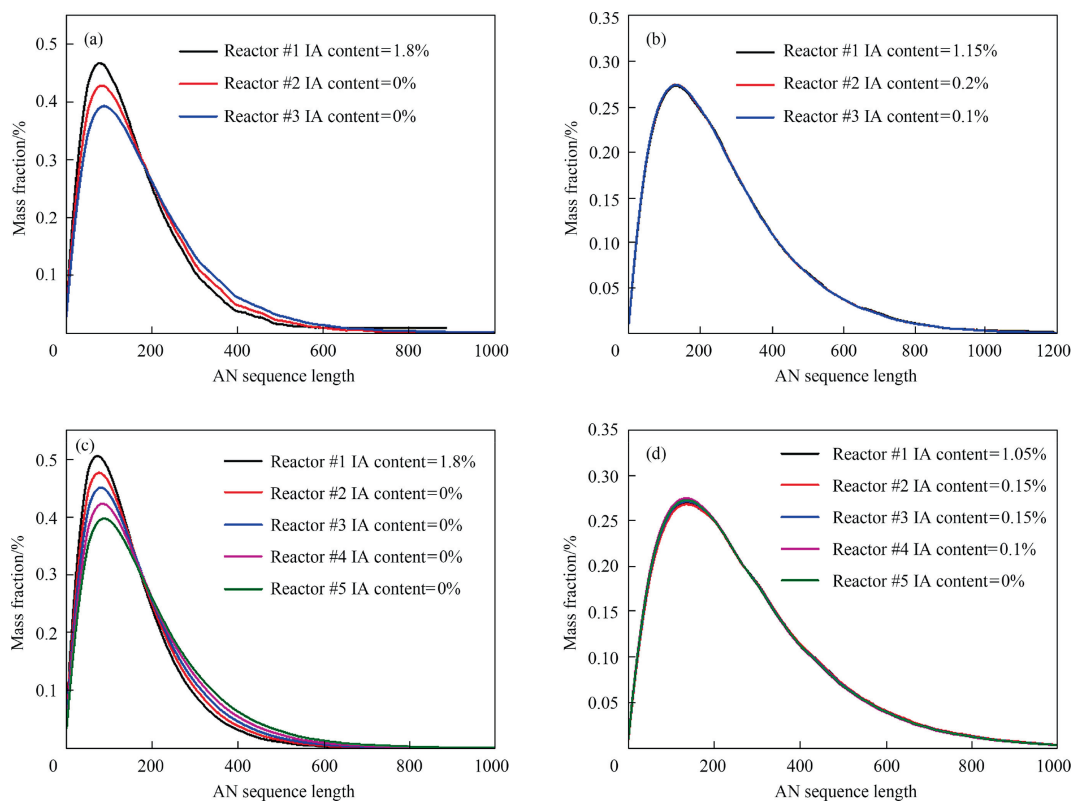


Fig. 11. AN sequence length distribution with different IA feed distributions. No.1&2: Residence time $RT_1 = RT_2 = RT_3 = 40$ min. No.3&4: Residence time $RT_1 = RT_2 = RT_3 = RT_4 = RT_5 = 24$ min. AN:MA = 95:3.2, M concentration = 22% (mass), I/M = 1.0% (mass).

Declaration of Competing 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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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.06.022>.

Nomenclature

C_M	transfer constant of monomer
f_{AN}	AN composition in copolymer, % (mass)
f_{IA}	IA composition in copolymer, % (mass)
f_{MA}	MA composition in copolymer, % (mass)
i	chain length of polymeric species
k_d	decomposition constant
k_{diff}	diffusion coefficient
k_{exp}	macroscopic reaction rate constant
k_i	initiator constant
k_{MC}	microscopic reaction rate constant
k_p	propagation constant
k_t	termination constant
M	number of chemical reactions
M_n	number average molecular weight
M_w	weight average molecular weight
P_i	dead polymer
p	reaction probability
R	chemical reaction
RT	residence time, min
r	reactivity ratios
t	reaction time, min
V	volume of the reaction space
X	molecule number of the reacting specie
v	reaction channel

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