

Monte Carlo Simulation of Molecular Weight Distribution and Copolymer Composition in Transamidation Reaction of Polyamides

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ABSTRACT: Melt mixing of polyamides results in exchange reaction and generation of copolymers. In this work, Monte Carlo method is used to simulate the time evolution of molecular weight distribution (MWD) and copolymer composition during the exchange reaction process between polyamides with AA and BC structure. The influences of initial composition and molecular weight have been investigated. Decrease in the difference between the average molecular weight of two kinds of polyamides results in faster approach of the MWD toward Flory's dis-

tribution and higher probability of producing copolymers. When the ratio between the numbers of initial molecules of two homopolymers is increased, the number of generated copolymers is reduced and the wider MWD is obtained. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: Monte Carlo simulation; transamidation reaction; polyamide; molecular weight distribution; copolymer composition

INTRODUCTION

Blends of polycondensates have received many attentions in the last decades. The interest is not only academic, as polycondensate blends are also very attractive for industrial applications. In a melt mixing process, exchange reaction of polycondensates may occur. As a result of the reaction, portions of the blends can be transformed into multiblock or random copolymers which can effectively improve the properties of the reactive blends.^{1–7}

Molecular weight distribution (MWD) and copolymer composition play important roles in blend properties and manufacturing processes. The theoretical research on MWD of obtained polymer by exchange reaction began as early as 1942. Flory⁸ proved theoretically that molecular weight distribution of polycondensates tend to the Flory's distribution after exchange reaction. Kotliar⁹ and Kudryavtsev^{10–15}

developed the method of probability statistics. They predicted the change of MWD during the exchange reaction process based on certain initial distribution.

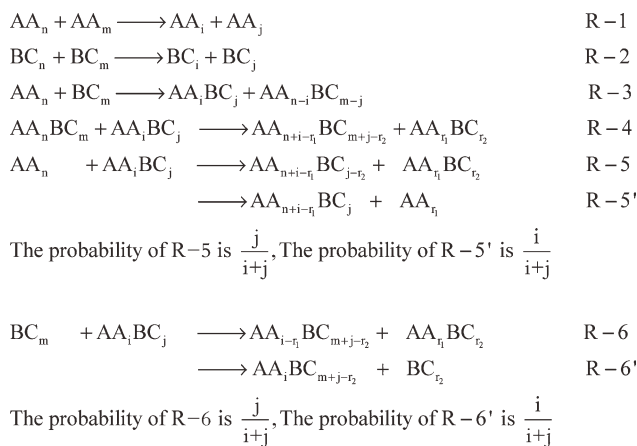
Monte Carlo method can simulate the intermolecular reaction with arbitrary initial distribution and obtain the relationship between MWD and real reaction time by combining macro-kinetics with microscopic molecular reaction.^{14,16–22} Litmanovich et al.¹⁴ developed an algorithm to generate an ensemble of statistical multiblock AB copolymer chains via a polymer-analogous reaction with acceleration. Influences of chain structure, length, and interchain interactions were studied. Kononenko et al.²⁰ simulated the reaction of direct inter-chain exchange in a homogeneous blend of linear polymers by using the Monte Carlo method. Jo et al.²³ analyzed effects of the interchange reaction of poly(ethylene terephthalate) (PET) on its MWD using Monte Carlo simulation method. The results showed that MWD of blends could achieve the Flory's distribution after 0.3 interchange reaction per segment, which means that the average number of interchange reaction involving each molecular chain is 0.3. For the blend of two PET samples with different molecular weight, the simulation results were in agreement with GPC data. Montaudo²⁴ used Monte Carlo approach to predict the exchange reaction in polyesters. The results indicated that the copolymer composition was related to the exchange mechanism. Wang et al.²⁵ simulated the molar fraction variations

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Scheme 1 Possible reactions between polyamide AA and polyamide BC blends.

versus reaction time for melt blending of PA6 and PA69 at 283°C by Monte Carlo technique. Liu et al.²⁶ analyzed influence of amide interchange reaction of polyamide 6 on its MWD by using a kinetic Monte Carlo simulation method. The system had two different types of initial distribution, such as monodisperse and bimodal distribution. The simulation results indicated that MWD was rapidly relaxed to the Flory's distribution.

However, the simulation method predicting the copolymer composition in the exchange reaction process has been reported rarely in the literature. In this paper, Monte Carlo method is used to simulate the exchange reaction between polyamide with AA structure and polyamide with BC structure and predict the time evolution of MWD and composition of the generated copolymers.

THEORY

Reaction equations and probability of different reactions

In the melt blending system, the exchange reaction between polyamide AA and polyamide BC will take place. At the same time, the reactions between obtained copolymers and homopolymers can also occur. All possible reactions are illustrated in Scheme 1, where A represents the repeating units of polyamide AA, B represents the binary acid group, and C represents the diamine group. The subscripts, such as m , n , i , j , r , stand for the number of repeating units (degree of polymerization, DP).

In this work, we assume that the reaction between two stochastic molecules can be described by the same microscopic kinetics constant. Yang et al.²⁷ suggested that the exchange reaction between polyamides 1 and 2 can be described by Eq. (1):

$$\frac{d[M_1]}{dt} = k_{AB}[M_1][M_2][\text{COOH}]^{0.5} + k_{CD}[M_3][M_4][\text{COOH}]^{0.5} \dots \quad (1)$$

Here, carboxyl group plays the role of catalysis.^{25,28,29} $[M_1]$ and $[M_2]$ are concentrations of amides 1 and 2 (mol/kg), and $[\text{COOH}]$ is the concentration of carboxyl in the blending system. k_{AB} is macroscopic reaction rate constant between polyamide 1 and 2.

Hereby, the reaction rate between polyamides AA with n and m repeating unit, i.e. the (R-1) reaction in Scheme 1, can be denoted by Eq. (2):

$$R(1, n, m) = \tilde{\pi}(n-1)NP_{AA_n}(m-1)NP_{AA_m}N_{\text{COOH}}^{0.5} \quad (2)$$

$$\tilde{\pi} = \frac{k}{(\tilde{N}W)^{1.5}} \quad (3)$$

where NP_{AA_n} , NP_{AA_m} , and N_{COOH} stand for the molecular number of AA_n , AA_m , and carboxyl in the blending system, respectively. \tilde{N} is the Avogadro constant and W is the total weight of all components. $\tilde{\pi}$ is the microscopic reaction rate constant. k is macroscopic reaction rate constant.

The sum of reaction rate (R-1) is described by Eq. (4):

$$A_1 = \sum_{m=2}^{\text{MaxAA}} \sum_{n=2}^{\text{MaxAA}} R(n, m), \quad (4)$$

In a similar way, the reaction rates of other four types of reactions can also be calculated:

$$\begin{array}{l}
A_2 = \sum_{m=2}^{\text{MaxBC}} \sum_{n=2}^{\text{MaxBC}} R(n, m) \\
\quad \dots \dots \dots \quad \dots \dots \dots \\
\quad \dots \dots \dots \quad \dots \dots \dots
\end{array} \quad (5)$$

$$A_5 = \sum_{m=2}^{\text{MaxBC}} \sum_{n=2}^{\text{MaxAA}} R(n, m)$$

The following equation is used for describing the probability of a type of reaction occurred:

$$P_i = \frac{A_i}{\sum_{i=1}^6 A_i}$$

The probability of polyamides with various DP being involved in different reaction can be described by following equations:

$$P(1, n, m) = \frac{R(1, n, m)}{A_1}, P_1 = \sum_{m=2}^{\text{MaxAA}} \sum_{n=2}^{\text{MaxAA}} P(1, n, m)$$

$$P(2, n, m) = \frac{R(2, n, m)}{A_2}, P_2 = \sum_{m=2}^{\text{MaxBC}} \sum_{n=2}^{\text{MaxBC}} P(2, n, m)$$

$$P(3, n, m) = \frac{R(3, n, m)}{A_3}, P_3 = \sum_{m=2}^{\text{MaxBC}} \sum_{n=2}^{\text{MaxAA}} P(3, n, m)$$

$$P(4, n, m, i, j) = \frac{R(4, n, m, i, j)}{A_4},$$

$$P_4 = \sum_{m=2}^{\text{MaxBC}} \sum_{n=2}^{\text{MaxAA}} \sum_{i=2}^{\text{MaxBC}} \sum_{j=2}^{\text{MaxAA}} P(4, n, m, i, j) \quad (6)$$

Here, $\sum_i P_i = 1, i = 1, 2, 3, 4, 5, 6$.

The generated copolymers are scarce in the early stages of exchange reaction. Hence, the probability of reaction among obtained copolymers (R-4) is three orders of magnitude smaller than other reactions. Therefore, the exchange reaction among the copolymers is negligible when simulating the initial stage of exchange reaction among polyamides with high polymerization degree.

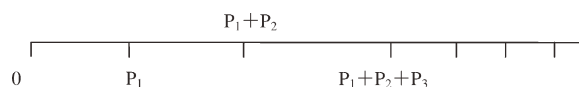
Monte Carlo simulation algorithm

According to the above analysis, the probability of all reactions happening in the blend system can be obtained. Time evolution of the fraction of various components can be obtained using following Monte Carlo simulation process.

1. Give the initial values, including the number of polyamide AA and polyamide BC with different polymerization degree, the number of carboxyl group in polyamide AA and polyamide BC, the total number of molecule, and kinetic constant k .
2. Calculate the intermolecular reaction rate with different polymerization degree: $R(i, n, m), P(i, n, m)$. For instance, the probability matrix $P(1, n, m)$ is calculated for the reaction (R-1):

$$P_{AA} = \begin{bmatrix} P(2, 2) & P(2, 3) & P(2, 4) & \dots & P(2, M_1) \\ & P(3, 3) & P(3, 4) & \dots & P(3, M_1) \\ & & P(4, 4) & \dots & P(4, M_1) \\ & & & \dots & \dots \\ & & & & P(M_1, M_1) \end{bmatrix} \quad (7)$$

3. Determine which reaction occurs according to the generated random numbers as follows:
 - a. Generate a random number, Random 1, within the range of $[0, \sum_{i=1}^6 P_i]$ and determine the type of reaction.



- b. Generate a random number, Random 2, within the range of $[0, 1]$ and determine the DP of polymers involved in the reaction.
 - c. Refer to the type of reaction products and the range of chain length, generate random numbers, Random 3 and 4, to determine the composition of products and the polymerization degree of various repetitive units.
 - d. Calculate the composition of reacting blends.
4. If the required reaction time has not been reached, return to step (2) with the time interval:

$$\tau = \frac{1}{A} \ln \left(\frac{1}{\text{Random } 5} \right) \quad (8)$$

If the required reaction time has been reached, go to step (5).

5. Count the molecule number of homopolymers and copolymers with varies polymerization degree and plot the MWD curves.

Define model parameters

The microscopic reaction rate constant $\tilde{\pi}$ can be obtained from macro-kinetics constant using Eq. (3). However, we only simulate finite molecule number in the actual simulation process. Therefore, the reduction factor c has to be introduced into the equation.²⁴ The $\tilde{\pi}$ used in the simulation process can be calculated by Eq. (10):

$$c = \frac{N_{M_1}^0}{N_{M_1,MC}^0} \quad (9)$$

$$\pi = \tilde{\pi} * c^{1.5} = k * \left(\frac{c}{\bar{N}W} \right)^{1.5} \quad (10)$$

where $N_{M_1}^0$ stands for the initial number of M_1 and $N_{M_1,MC}^0$ is the initial number of M_1 adopted in Monte Carlo simulation.

Several equations for the interchange rate were proposed as shown in eqs. (11)–(15):

$$\text{Rate} = k_2 [\text{CONH}]^2 \quad (11)$$

$$\text{Rate} = k_3 [\text{CONH}]^2 [\text{NH}_2] \quad (12)$$

$$\text{Rate} = k_3' [\text{CONH}]^2 [\text{COOH}] \quad (13)$$

$$\text{Rate} = k_4 [\text{CONH}]^2 [\text{NH}_2] [\text{COOH}] \quad (14)$$

$$\text{Rate} = k_{2,5} [\text{CONH}]^2 [\text{COOH}]^{0.5} \quad (15)$$

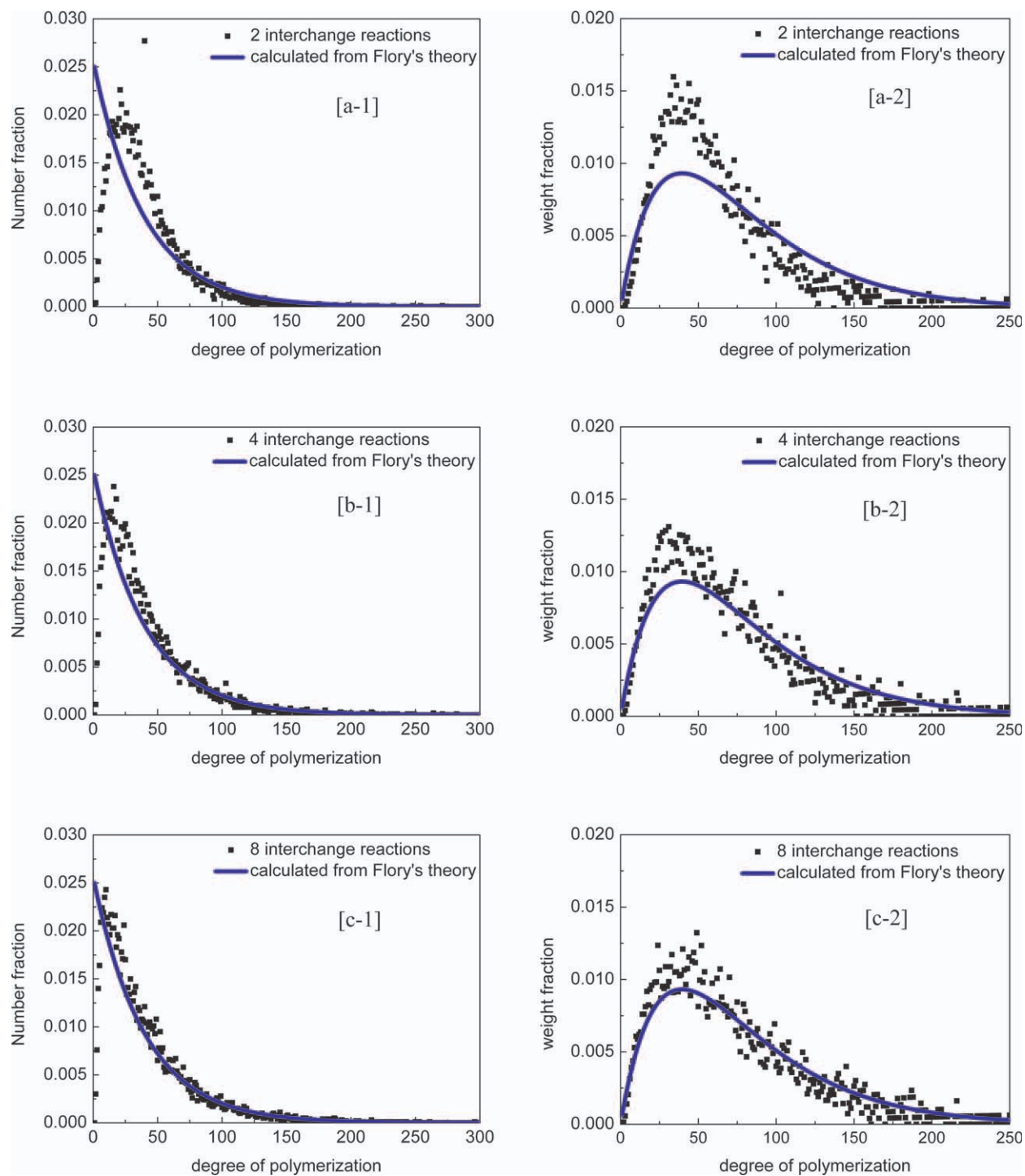


Figure 1 MWD evolution with initial monodisperse distribution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
The Characteristics of Samples Used in MC Simulation

Samples	Polyamide AA		Polyamide BC		Initial distribution
	DP _{AA}	NP _{AA}	DP _{BC}	NP _{BC}	
Run 1	75	10,000	15	10,000	Flory
Run 2	75	14,000	15	6000	Flory
Run 3	75	18,000	15	2000	Flory
Run 4	45	10,000	15	10,000	Flory

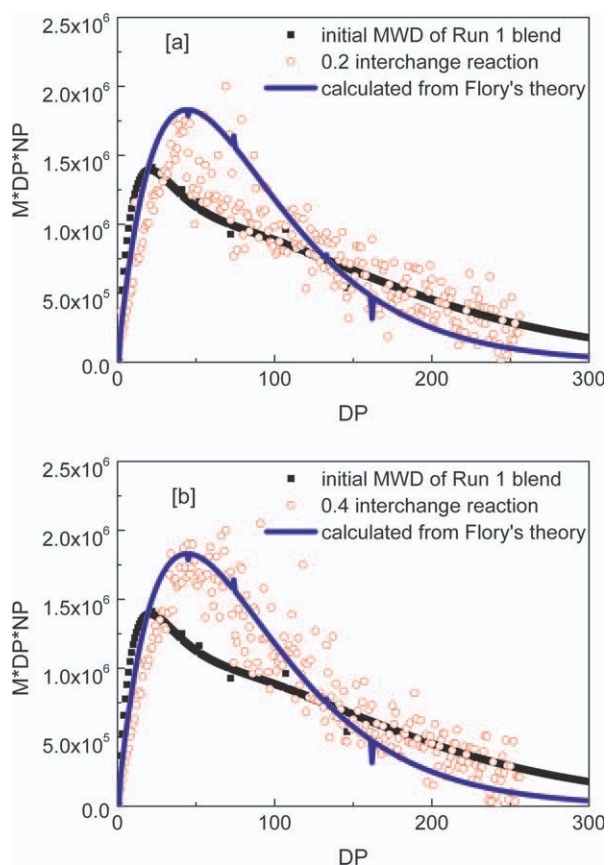


Figure 2 MWD evolution in Run 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Wang et al.²⁵ found that $k_{2.5}$ was more reasonably acceptable to be constant than k_3 , $k_{3'}$, $k_{3''}$, and k_4 by calculating the reaction rate of amide interchange for 50 min at 245°C. They studied the amide interchange between two different polyamides, such as PA6 and PA69, and used the following equation for the interchange rate:

$$\text{Rate} = k[\text{CONH}]^2[\text{COOH}]^{0.5} \quad (16)$$

Assuming an activation energy of 30 kcal/mol, the relationship between k and temperature is

$$\log k = 14.177 - 6660/T \quad (17)$$

Since polyamide AA and polyamide BC are both products of polycondensation, it is reasonable to assume that their initial MWD are in accordance with the Flory's distribution. The molecule number with various DP can be obtained from eqs. (18) and (19):

$$N_x = N * p^{x-1} * (1 - p) \quad (18)$$

$$p \approx 1 - \frac{1}{\bar{\mu}_n} = 1 - \frac{m_A}{\bar{M}_n} \quad (19)$$

Here m_A represents the molecular weight of one repetitive unit and \bar{M}_n represents the number average molecular weight of polymers.

RESULTS AND DISCUSSION

Exchange reaction between the homopolymers

When there is only one kind of homopolymer in the system, the exchange reaction among homopolymers with different polymerization degree will take place (reaction R-1 in Scheme 1). With the development of reaction time, MWD will become the Flory's distribution. Therefore, we can verify our method by simulating this system.

The 10,000 PA molecules with a monodisperse distribution ($DP = 40$) are selected as the initial homopolymer. The simulation results of MWD at different reaction time are described in Figure 1. The monodisperse distribution trends to the Flory's distribution as the reaction time increases. When each molecule goes through eight exchange reactions, the

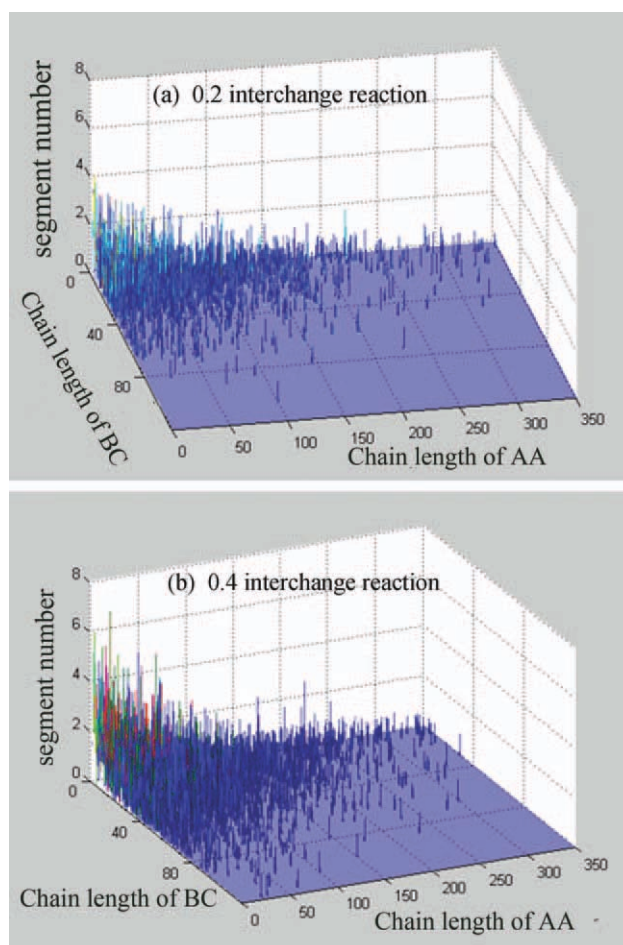


Figure 3 Change of segment number distribution of obtained block copolymers in Run 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

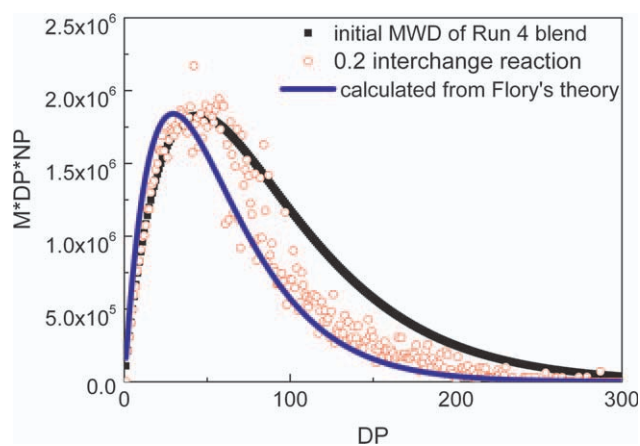


Figure 4 Change of MWD after 0.2 interchange reaction per segment in Run 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight distribution becomes the Flory's distribution.

Exchange reaction of the blends

When simulating exchange reaction of the blends, the number of reaction type and reactants will

increase significantly. The initial conditions are listed in Table I.

In Run 1, the DP ratio between polyamide AA and polyamide BC is 75 : 15 and the ratio of molecule number between polyamide AA and polyamide BC is 1 : 1. The change of MWD at different reaction time is shown in Figure 2. The MWD of blends displays asymmetrical bimodal distribution evidently before reaction. With the development of reaction, the MWD of products trends to equilibrium distribution. When each molecular chain involves in 0.4 times reaction averagely, the MWD of blends is nearly the Flory's distribution.

The quantitative distribution of block copolymers generated at various reaction time is presented in Figure 3. The amount of resulting block copolymers is small at the initial stage of reaction, and the probability of producing short chain block copolymer is high. With the development of reaction, the proportion of short chain block copolymer continues to increase.

Influence of the initial molecular weight of blends

The MWD change of Run 4 with increasing reaction time is described in Figure 4. In Run 4, the ratio

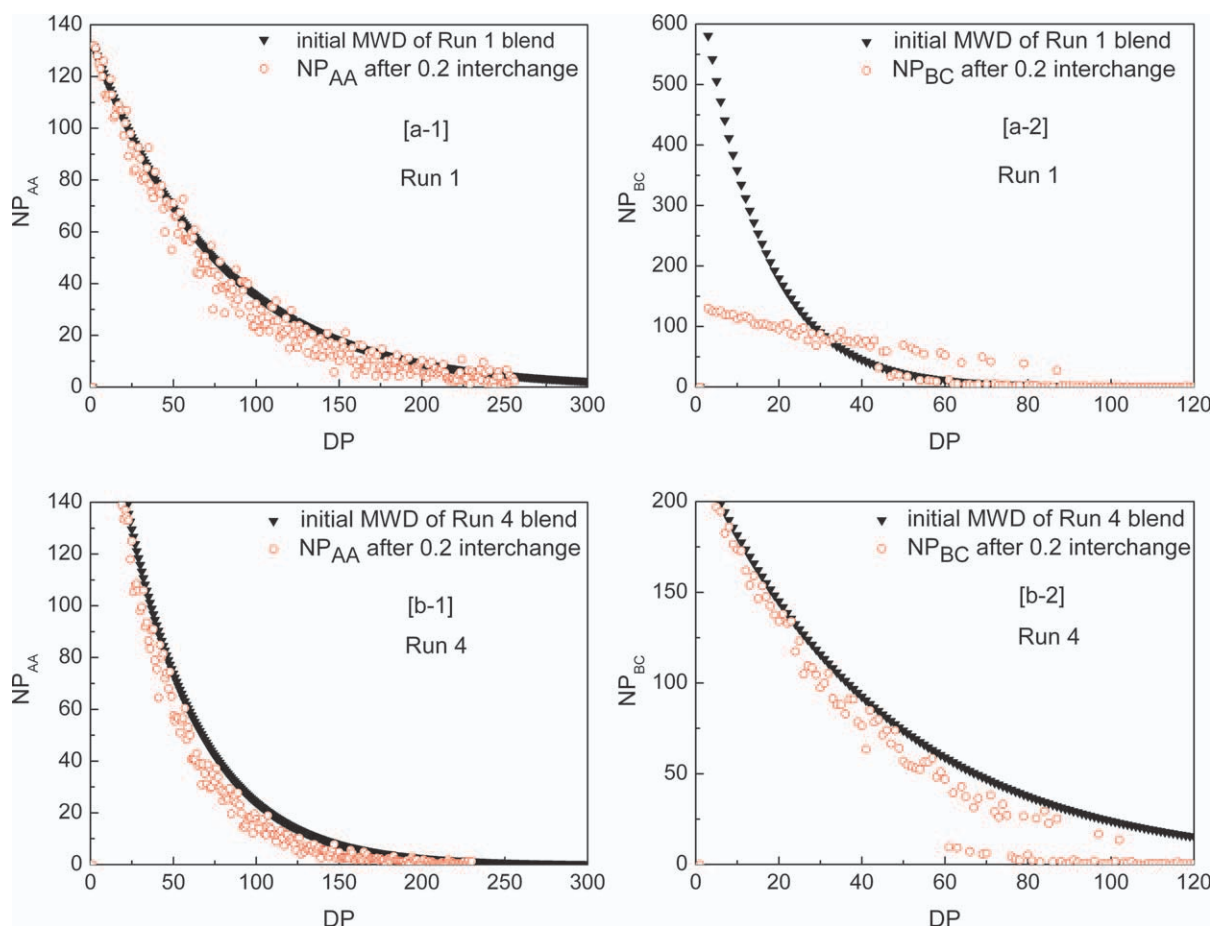


Figure 5 Change of NP distribution in Run 1 and Run 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

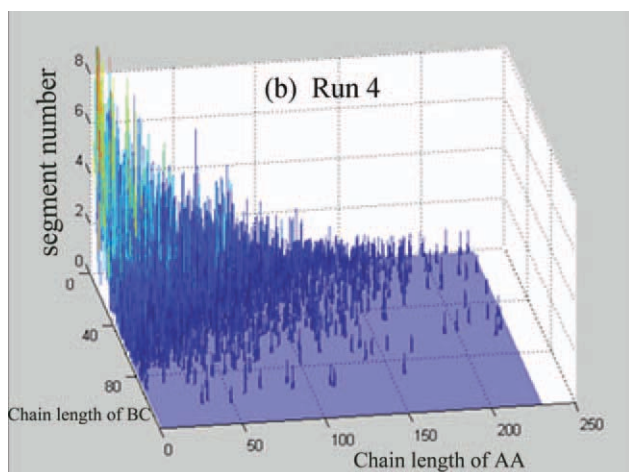


Figure 6 Segment number distribution of obtained block copolymer after 0.2 interchange reaction per segment in Run 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between the DP of AA and BC is 45 : 15. Compared with Run 1, in which the ratio between the DP of AA and BC is 75 : 15, the MWD of products tends to the Flory's distribution faster when difference

between the DP of two reactants is decreased. Jang et al. used the cubic lattice model to study the ester exchange reaction in polyester melt.¹⁶ Their simulation result showed that the copolymerization is accelerated and the MWD of products tends to the Flory's distribution faster as the molecular weight difference becomes smaller. This result is in agreement with our simulation.

The MWD after interchange reaction is narrower than the initial MWD in both Run 1 and 4. When the ratio of initial DP is 75 : 15, the MWD of blends tends to the center and the distribution becomes narrow. When the ratio of initial DP is 45 : 15, the distribution also becomes narrow. However, it is primarily due to the decrease in the proportion of polymers with high molecular weight. The difference is due to various kinds of reactant in the reaction. The contrast between the chain length distribution before and after reaction in Run 1 and Run 4 is presented in Figure 5. The DP of BC involved in the reaction is wholly different in these two runs. When $DP_{AA}:DP_{BC}$ is equal to 75 : 15, AA with higher DP is decreased gradually while for BC with lower DP is decreased and BC with higher DP is increased. However, when $DP_{AA}:DP_{BC}$ is equal to 45 : 15, AA

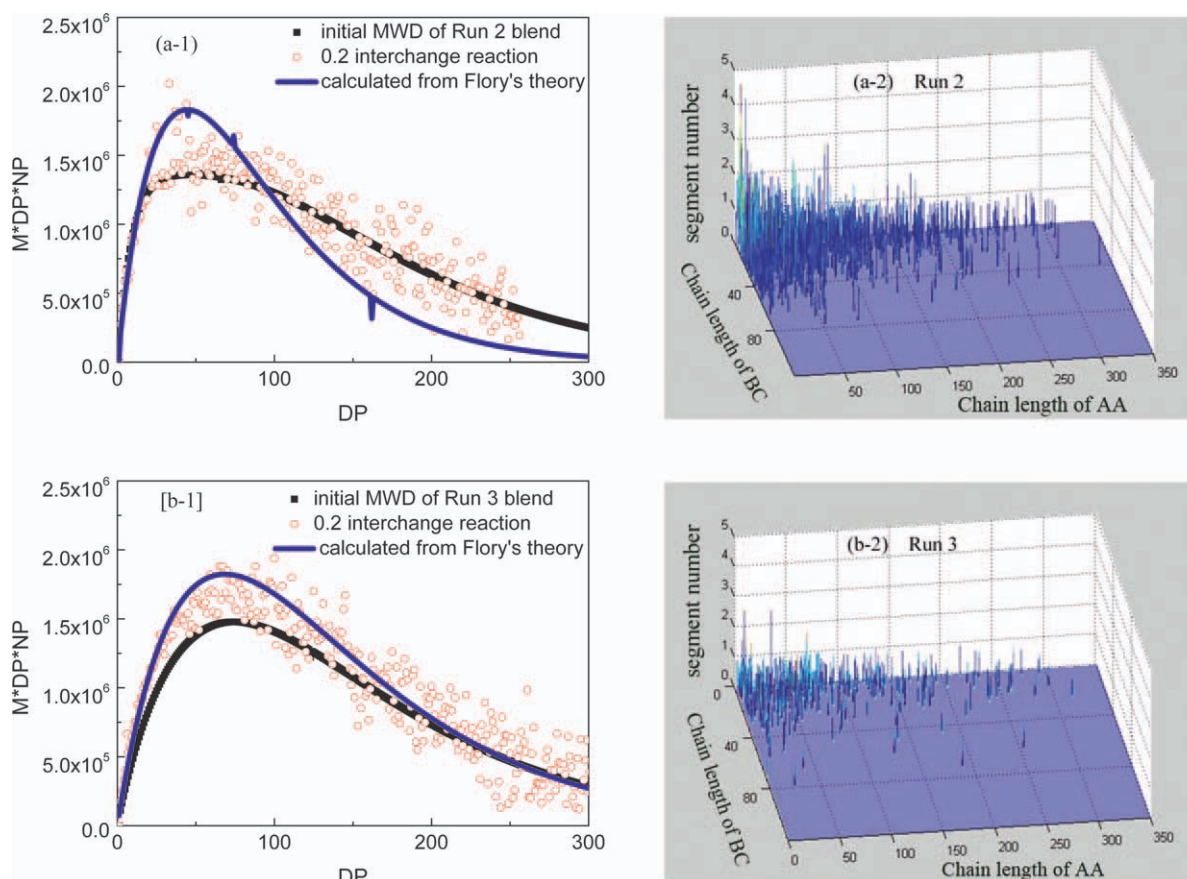


Figure 7 MWD of Run 2 and 3 blends and segment number distribution of obtained copolymers after 0.2 interchange reactions per segment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is decreased more obviously and BC with all DP is also decreased.

The composition of generated copolymers after 0.2 interchange reaction per segment in Run 4 blend is described in Figure 6. When $DP_{AA}:DP_{BC}$ is equal to 45 : 15, the number of generated copolymer chains is much larger than that when $DP_{AA}:DP_{BC}$ is 75 : 15 in Figure 3. The copolymers containing long chain segment BC increase greatly in Run 4.

Influence of the blend composition

The effect of ratio between the number of AA and BC molecules on the time evolution of MWD and copolymer composition is shown in Figure 7. It shows that the MWD can reach the equilibrium distribution faster when the fraction of two components in the blend has more difference. For example, if the ratio of initial molecule numbers is 90/10, the MWD of blends is close to equilibrium distribution after 0.2 exchange reaction. However, it needs 0.4 exchange reaction when the ratio is 50/50. The amount of generated copolymers decreases greatly after the same reaction time when difference between the initial fraction of the two components is increased. The reason is that the probability of producing copolymers drops, which can be seen from Eq. (6). On the other hand, the length distribution of copolymer becomes more uniform when there is large difference between the initial fraction of two components.

The simulation results indicate that the MWD of blends can change significantly if a small amount of polymer BC with low DP is added into polymer AA with high DP. The weight ratio is 11.7 : 1 and 45 : 1 when the mole ratio between AA and BC is 70 : 30 and 90 : 10, respectively. There is a power function relationship between polymer melt viscosity and \overline{M}_w : $\eta = K_V \overline{M}_w^\varepsilon$. The typical value of ε for polymer melt is above one. Therefore, a small amount of polymers with different molecular weight can be used to adjust MWD of polyamides. Accordingly, products with desired rheological behavior can be obtained.³⁰

CONCLUSIONS

Monte Carlo method is used to simulate the exchange reaction of single component polyamide system and two-component polyamide blends. When there is only one kind of polyamide, the simulation results indicate that the given monodispersed molecular weight distribution becomes wider rapidly and trends to the Flory's distribution gradually. When there are two kinds of polyamides in the reaction, the results show that the classes of polyamides involved in the reaction are related to the ratio of DP of the two kinds of polyamides. If difference

between the DP of two kinds of polyamides is reduced, the MWD will trend to equilibrium distribution faster and the probability of producing copolymers is increases. The high DP portion of the polyamides with lower average DP is more involved in the exchange reaction and form more long chain copolymers. Moreover, the influence of the number ratio between two components is also studied by tracking the concentration of copolymers and the composition change of the products in exchange reaction process. When the difference between the number of initial molecule of two homopolymers is increased, the number of generated copolymers is decreased and the MWD of copolymers becomes wider.

NOMENCLATURE

DP	degree of polymerization
$[M_i]$	concentrations of reactants (mol/kg)
$[COOH]$	concentration of carboxyl group (mol/kg)
k	macroscopic rate constant ((mol/kg) ^{-1.5} s)
$\tilde{\pi}$	microscopic rate constant
\tilde{N}	Avogadro constant
NP_i	molecular number of component i
NP_{COOH}	number of carboxyl group
W	total weight of reactants (kg)
τ	time step
A	normalization factor
c	reduction factor
$N_{M_1}^0$	initial number of M_1
$N_{M_1,MC}^0$	initial number of M_1 adopted in Monte Carlo simulation
N_x	number of x
P	reaction possibility
m_A	molecular weight of repetitive unit (kg)
T	reaction temperature (K)
\overline{M}_n	number average molecular weight of polymers

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