



Monte Carlo Technique to Simulate Amide Interchange Reactions: An Improved Model of PA6/PA66 Blending System

Chaosheng Wang¹, Min Li¹, Huaping Wang*¹, Xiaqin Wang¹,
and Roberto Filippini-Fantoni²

(1) State Key Lab for Modification of Chemical Fibers & Polymer Materials,
College of Material Science and Engineering, Donghua University,
Shanghai 201620, PR China

(2) Mazzaferro Tecnopolimeros Ltd., CEP 09893-000
São Bernardo do Campo (SP), Brazil

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A B S T R A C T

Based on our previous results of a good agreement between Monte Carlo simulation and DSC measurement for amide interchange reactions (AIRs) during PA6/PA66 melt blending processes, an improved Monte Carlo model comprising AIRs, polycondensation, and hydrolysis was established to illustrate the kinetic scheme of randomization for PA6/PA66 blending systems. Validity of the improved Monte Carlo model which transformed the macro-scale rate constant into a micro-scale rate constant in the simulation was testified by experiments. The effect of blending temperature on AIRs and the influence of AIRs on degree of transamidation, randomness, regularity, and number-average block length of various sequences were analyzed in detail with the improved Monte Carlo model describing a kinetic process through a pseudo-random number. One-order exponential decay (Exp-decay 1) technique was employed to correlate melting points of copolyamides measured by differential scanning calorimeter (DSC) with degree of regularity simulated theoretically with the improved Monte Carlo model. First, the model established direct relationship between the mathematical simulation and the experiments then, it was applied to other polyamide blending systems after minor alteration of reaction parameter. It was found that degree of randomness and regularity are independent of blend molar ratio while melting point, molar fractions of amido linkages and number-average block length are blend molar ratio dependent.

Key Words:

amide interchange reactions;
Monte Carlo simulation;
PA6/PA66 blending;
block copolymers;
randomization.

INTRODUCTION

It is important to identify whether the resulting product of an amide interchange reactions (AIRs) is actually a block, a random, or a mixture of homopolyamides in molten state of polyamide blends. AIRs are of great industrial importance since they are essential to manufacturers of polyamides. They are also used to achieve block copolymers via melt blending processes [1-3]. Consequently the

importance of AIRs in the overall technology of polyamides provides sufficient incentive for investigation [4-6]. Although significant progresses have been made in understanding AIRs in general, there is still a lack of information concerning quantitative rates of copolyamide structures in terms of number average block (sequence) length and degree of regularity or randomness [7]. Beste et al.

(*) To whom correspondence to be addressed.
E-mail: wanghp@dhu.edu.cn

reported that when two or more polyamides were heated together, melting points and other physical properties of the mixture continuously approached the properties of the corresponding copolymer [8], in which AIRs occurred by heating, and physical separation of the components was lost. Evidence for copolymer formation has been obtained by measurement of solubility and melting point change for mixtures of polyamide homopolymers heated above polymer melt temperature [9]. Eersels and Walia et al. investigated the variation of thermal properties and crystallization of polyamide blends during the progress of AIRs experimentally [10-12].

Monte Carlo simulation is numerically exact, i.e. the results are free from statistical errors, which are employed to study copolymerization by ester interchange reaction in miscible polyester blends [13,14]. Recently we have published initial results of AIRs during PA6/PA66 melt blending processes with both Monte Carlo simulation and DSC measurement [15]. From our basic Monte Carlo model, what we obtained was a variety of molar fractions of binary bonds vs. AIR time, while from the experiments the evidence was rested on the effect of AIR time on melting points. So far no direct relationship between the mathematical simulation and experiments has been built up. In order to solve this problem, it is essential to create a function that could well incorporate the data of the mathematical model and experimental results.

During melt blending processes of PA6 with other polyamides, very long block copolymers are formed in the initial stages regardless of the specific nature of reactions, and these give way to segmented and eventually random copolymers providing the reactions are continued long enough [12]. Equilibrium yields the same final distribution of the two components in the chain as one would find in a random copolymer prepared by a conventional copolymerization starting with the monomers. The discrepancy between a lower value of polydispersity index Q calculated by our basic model than the theoretical value of 2.0 and reported value of 1.95 is ascribed to the neglect of polycondensation in the basic model, in which AIRs are exclusively considered [16]. Moreover, polycondensation and hydrolysis contribute to randomization as well. Here we established a comprehensive Monte Carlo model comprising AIRs, polycondensation, and

hydrolysis to illustrate the complete kinetic scheme of randomization taking PA6/PA66 blending systems as an example. The validity of the improved Monte Carlo model was tested by comparing the lifetime of block copolymers calculated by an improved Monte Carlo model with that determined by differential scanning calorimeter (DSC) measurement. We also developed some concepts, such as degree of transamidation, randomness, regularity, and number average block length of various sequences in the improved Monte Carlo model on the basis of study carried out by Devaux et al. [17,18]. One-order exponential decay (Exp-decay 1) technique is first employed to obtain a quantitative relationship between simulation and experiments by proposing an exponential relationship between the melting points of the PA6/PA66 blends measured by DSC and degree of regularity computed by the improved Monte Carlo model. Furthermore, AIRs in the PA6/PA66 blends are investigated with an improved experimental method, dissolving the homopolymer mixture in selected solvent and mixing PA6/PA66 at a molecular level by co-precipitation, instead of traditional mechanical blending. Influence of blend molar ratio on AIRs was analyzed systematically. Although it was regarded that copolymerization by ester interchange reactions were independent of blend ratio [12], we found the degree of randomness and regularity are really independent of the blend ratio while variation of melting point, molar fractions of amido linkages, and number average block length are more sophisticated and blend ratio dependent.

Improved Monte Carlo Model

The realization of the Monte Carlo simulation through the pseudo-random number generated by computer is essential for reliability. Only a few research works [19-22] have been done to relate the random number with the kinetic process, however, all these models reveal the computing time but not the reaction time. Their simulation results cannot be compared with the experiment directly. In our proposed model, all probabilities are normalized at first which means the sum of the probabilities of various reactions equals one, and the random number is used to determine the type of the reaction, another random number is generated to determine the interval of each reaction. In order to

simplify the simulation, the equal activity assumption of Flory is put forward into this model. Assuming A as the repeating unit of PA6, $-\text{CO}(\text{CH}_2)_5\text{NH}-$, BC as the repeating unit of PA66, $-\text{NH}(\text{CH}_2)_6\text{NH}-\text{CO}(\text{CH}_2)_4\text{CO}-$, the carboxyl groups located at the chain ends of PA6 are designated as A-COOH, and those at the chain ends of PA66 are C-COOH. Similarly, amine end groups of PA6 are A-NH₂, and those of PA66 are B-NH₂. Therefore, 4 types of possible polycondensation between the reactive end groups and 4 types of possible hydrolysis, which are reverse reactions of polycondensation, are involved in the melt blending systems of PA6 and PA66. Besides, 10 types of AIRs may be present between four kinds of amido linkages [15], i.e. AA, AB, AC, and BC. A general formula of $-(\text{AA})_x-(\text{AB})_y-(\text{AC})_z-(\text{BC})_w-$ represents the resultants according to Devaux et al. [17], in which x, y, z, and w are the average lengths of various sequences. The reaction scheme for the PA6/PA66 melt blending is summarized in Table 1.

The reaction rate constants and equilibrium constant of PA6 polycondensation adopted in this research are [23]:

$$k_2 = k_2^0 + k_2^c[\text{COOH}]$$

$$= 1.8942 \times 10^{10} \exp\left(-\frac{2.3271 \times 10^4}{RT}\right) + 1.2114 \times 10^{10} \exp\left(-\frac{2.0670 \times 10^4}{RT}\right) \cdot [\text{COOH}] \quad (1)$$

$$K_2 = \exp\left(\frac{9.4374 \times 10^{-1}}{R} + \frac{5.9458 \times 10^3}{RT}\right) \quad (2)$$

$$k_2' = k_2 / K_2 \quad (3)$$

$k_{2,5}$ is selected as the AIR rate constant as described in our previous study [15]. The relationship between $k_{2,5}$ and temperature T is [8]:

$$\log k_{2,5} = 14.177 - 6660/T \quad (4)$$

Since Monte Carlo strategy investigates reaction behaviours of a specific amount of reactive end groups or molecular segments by utilizing random

Table 1. Reaction scheme for PA6/PA66 melt blending.

| Polycondensation and hydrolysis | AIRs |
|---|---|
| $A-\text{COOH} + A-\text{NH}_2 \xrightleftharpoons[k_2]{k_2} AA + \text{H}_2\text{O}$ | $AA + AA \xrightarrow{k_{2,5}} AA + AA$ |
| $A-\text{COOH} + B-\text{NH}_2 \xrightleftharpoons[k_2]{k_2} AB + \text{H}_2\text{O}$ | $AA + AB \xrightarrow{k_{2,5}} AA + AB$ |
| $C-\text{COOH} + A-\text{NH}_2 \xrightleftharpoons[k_2]{k_2} AC + \text{H}_2\text{O}$ | $AA + AC \xrightarrow{k_{2,5}} AA + AC$ |
| $C-\text{COOH} + B-\text{NH}_2 \xrightleftharpoons[k_2]{k_2} BC + \text{H}_2\text{O}$ | $AA + BC \xrightarrow{k_{2,5}} AB + AC$ |
| | $AB + AB \xrightarrow{k_{2,5}} AB + AB$ |
| | $AB + AC \xrightarrow{k_{2,5}} AA + BC$ |
| | $AB + BC \xrightarrow{k_{2,5}} AB + BC$ |
| | $AC + AC \xrightarrow{k_{2,5}} AC + AC$ |
| | $AC + BC \xrightarrow{k_{2,5}} AC + BC$ |
| | $BC + BC \xrightarrow{k_{2,5}} BC + BC$ |

numbers to determine reaction probabilities of possible reactions occurred in a reaction system, all variables employed in Monte Carlo simulation relate to a number of molecules or molecular segments. However, the macro-scale reaction rate constants, k_2 , k_2' , and $k_{2.5}$ are based on concentrations of the reactants. Thereby, transformation of the macro-scale reaction rate constants into micro-scale ones, which are based on individual molecular chains or segments, is essential for the Monte Carlo simulation [15]. It is also necessary to reduce the reaction system size by a factor of C:

$$C = \frac{N^0}{N_{MC}^0} \quad (5)$$

in which N^0 is the very large initial number of AA or BC for the PA6/PA66 melt blending. N_{MC}^0 is the initial number of AA or BC adopted in Monte Carlo simulation. Factor C is 1.46×10^{18} in this research.

The probability of the reaction is also needed to describe the simulation scale. Taking the first reaction listed in Table 1 as an example, the macro-scale rate constant is transformed to micro-scale rate constant:

$$\pi_2 = \frac{k_2 C}{\tilde{N} \cdot W} \quad (6)$$

$$\pi_2' = \frac{k_2' C}{\tilde{N} \cdot W} \quad (7)$$

where π_2 and π_2' are the micro-scale rate constants, C is reducing factor, N is the Avogadro constant, W is the weight of the reactant. Therefore, the eqn (1) can be transformed into:

$$\pi_2 = k_2^0 \frac{C}{\tilde{N} \cdot W} + k_2^c N_{COOH} \left(\frac{C}{\tilde{N} \cdot W} \right)^2 \quad (8)$$

Then the probability function of this reaction can be written as:

$$P_{conde,i} = \pi_2 N_{[A-COOH]} N_{[A-NH_2]} / A \quad (9)$$

where A means the overall rate constant:

$$A = \sum_{i=1}^4 P_{conde,i} + \sum_{i=1}^4 P_{hydro,i} + \sum_{i=1}^{10} P_{AIR,i} \quad (10)$$

EXPERIMENTAL

Materials

Two samples, PA6 and PA66, were provided by BASF. Other reagents were supplied commercially and used without further purification.

Relative Viscosity and Number Average Molecular Weight

The relative viscosity of PA6 and PA66 was measured in 95.7 wt% aqueous solutions of sulphuric acid. Temperature of water baths were set at $25 \pm 0.1^\circ\text{C}$ for PA6 and $20 \pm 0.1^\circ\text{C}$ for PA66. Number average molecular weights of both samples were calculated with empirical formulas.

End Group Titration

Concentrations of the amine groups ($-\text{NH}_2$) for the two samples were determined by titration with standard HCl (0.02 N) and concentrations of the carboxyl groups ($-\text{COOH}$) were determined by titration with standard NaOH (0.02 N). The mixture of solvents 2,2,2-trifluoroethanol (TFE) and H_2O was applied in titration. The content of TFE was 85% (volume fraction) for PA6, and 95% (volume fraction) for PA66. A HI9017 pH/mV/ $^\circ\text{C}$ meter was used to record changes in voltage values during the titration.

Amide Interchange Reactions

"Solution-precipitation" strategy was employed to prepare the PA6/PA66 blends in molecular level mixing. TFE was eventually chosen as the solvent of the PA6/PA66 mixtures after trials in acetic acid glacial and sulphuric acid (98 wt%). The structure of the PA6/PA66 blends could be damaged to some extent in cases where acetic acid glacial and sulphuric acid were used. Twelve gram of PA6/PA66 (molar ratio 5:5) was added into a 250-mL flask with 70 mL of pure TFE. Dissolution was carried out at 80°C with vigorous stirring under nitrogen purge. After the admixture was cooled down to room temperature, it was poured into 150 mL of distilled water to obtain co-precipitates of the PA6/PA66 blends. The co-precipitates were collected, washed and dried, and subsequently melt blended using a minimixer. Blending temperatures were varied from 270°C to 290°C . Samples were taken at various AIR time

lengths for DSC measurement.

DSC Measurement

The PA6/PA66 mixtures after melt blending of various AIR time lengths were analyzed on a DuPont 9900 DSC instrument under a nitrogen atmosphere. Heating rate was 20°C/min.

RESULTS AND DISCUSSION

Relative viscosity, molecular weight and concentrations of end groups are calculated as follows:

Number average molecular weight is calculated with Merani's formula [24]:

$$PA6 : \overline{M}_n = 11500(\eta_{0,95.7\%} - 1) \quad (11)$$

$$PA66 : \overline{M}_n = 13870(\eta_{0,95.7\%} - 1.4549) \quad (12)$$

Consequently the relative viscosity, number average molecular weight, and concentrations of the end groups of PA6 and PA66 are:

PA6: $\eta_{0,95.7\%} = 3.405$, $\overline{M}_n = 27660$, $[\text{COOH}] = 36.63$ meq./kg, $[\text{NH}_2] = 39.90$ meq./kg.

PA66: $\eta_{0,95.7\%} = 3.351$, $\overline{M}_n = 26300$, $[\text{COOH}] = 53.41$ meq./kg, $[\text{NH}_2] = 25.31$ meq./kg.

where $[\text{COOH}]$ and $[\text{NH}_2]$ represent the concentrations of carboxyl and amino end groups, respectively. In Monte Carlo simulation, $[\text{COOH}]$ is used to determine k_2 . $[\text{COOH}]$ and $[\text{NH}_2]$ are used as initial simulation conditions. $[\text{COOH}]$ and $[\text{NH}_2]$ are also significant to calculate macro- and micro-scale reaction rates.

From DSC results, the melting point of PA6 is 222.8°C, and that of PA66 is 263.8°C. Two melting peaks are present when the blending time is 0. The two melting points are 213.8°C and 260.0°C, respectively, slightly lower than the melting point of the corresponding homopolymer. As can be seen from Figure 1, with the increase in blending time the melting points of the blends shift to lower temperature, and the melting peaks overlap, indicating AIRs proceed

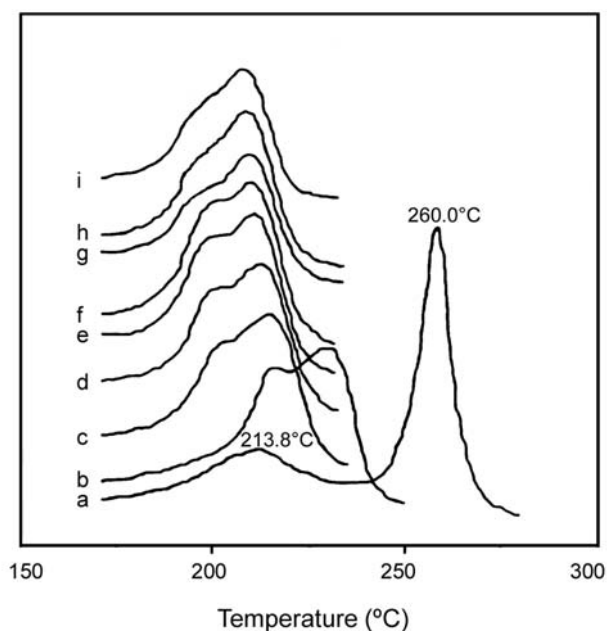


Figure 1. DSC curves of PA6/PA66 blends at various blending times of: (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, (f) 13 h, (g) 14 h, (h) 15 h, and (i) 16 h (blending temperature: 270°C).

further and thus initial homopolymers are changed into block copolymers and block length shortens with blending time as a result of AIRs. Finally the block copolymers convert to random copolymers. Variation of the melting points of the PA6/PA66 melt blends with blending temperature and blending time is summarized in Figure 2. Higher blending temperature results into lower melting points. The melting points

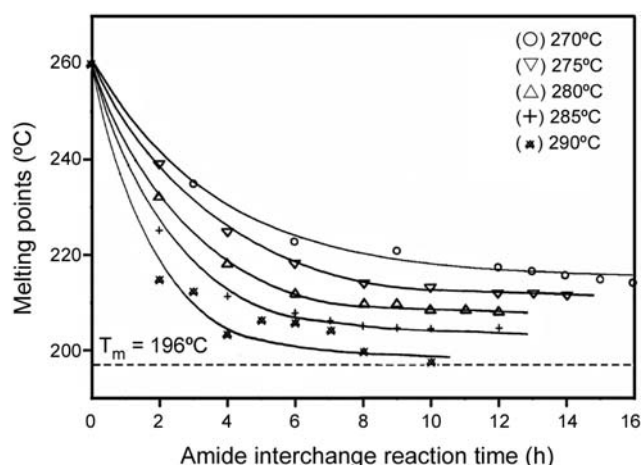


Figure 2. Effect of AIRs on melting points of PA6/PA66 melt blends.

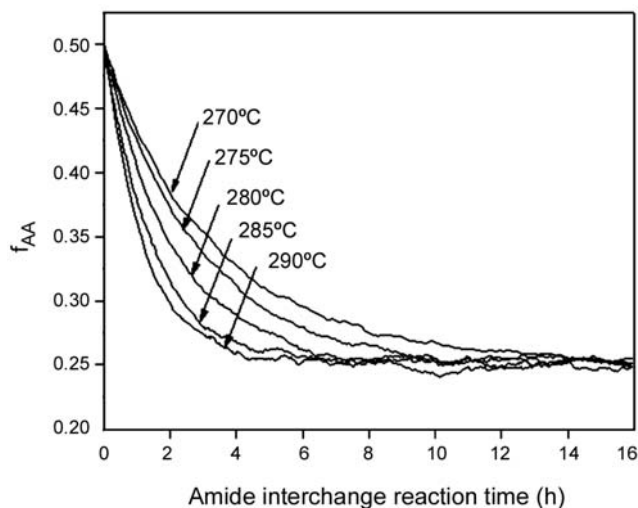


Figure 3. Effect of blending temperature on AIR process.

decrease with duration of blending time. Or, otherwise, the higher blending temperature accelerates AIRs due to improved mobility of the reactive groups, and longer blending time promotes randomization of PA6 and PA66 blocks. Moreover, higher blending temperature corresponds to lower melting points of random copolymers, and thus shorter lifetime of block copolymers. In particular, it takes about 8 h at 285°C to convert block copolyamide into random copolyamide, consistent with the reported value by Allen who quoted two early patents on melting points vs. composition curves for block and random copolymers of PA6 with PA66 [25].

Influence of Blending Temperature

As we reported [15], only AA and BC amido linkages exist at the beginning of blending. When AIRs proceed, AA and BC units are transformed into AB and AC units gradually until chemical equilibrium is reached. Figure 3 presents variation of f_{AA} with blending time and temperature. It should be noted that

f_{BC} is of the same variation as f_{AA} . f_{AA} decreases rapidly at the beginning of blending for various blending temperatures. Finally the same ultimate value of 0.25 is obtained under 5 different blending temperatures. However, the lifetime of block copolymers depends on blending temperature, as listed in Table 2. Compared with the lifetime determined from variation of T_m measured by DSC (Figure 2), the experimental results agree well with those from the Monte Carlo simulation (Figure 3), indicating the improved Monte Carlo model is valid to describe AIRs involved in the PA6/PA66 blend system.

Degree of Transamidation

The degree of transamidation can be easily derived from ^{13}C NMR spectra after molten mixing two homopolyamides [10]. There will be 100% transamidation when all AA and BC units are changed into AB and AC units. A completely random copolymer with a copolymer molar composition of 5:5 is of 50% transamidation, having an equal amount of AA, AB, AC, and BC units. Thus the degree of transamidation (ψ) can be calculated based on the molar fractions of AB and AC binary bond concentrations via the following formula [10]:

$$\psi (\%) = (f_{AB} + f_{AC}) \times 100\% \quad (13)$$

where f_{AB} and f_{AC} are the molar fractions of AB and AC units, respectively.

The degree of transamidation as a function of AIR time and melt blending temperature is shown in Figure 4. Equilibrium value of ψ is 0.5 for the various melt blending temperatures, indicating random copolymers are generated in all cases, although AIR time required to generate random copolymers decreases with the melt blending temperatures as transamidation is speeded up.

Table 2. Lifetime of block copolymers at various blending temperatures.

| Lifetime of block copolymers (h) | Blending temperature (°C) | | | | |
|----------------------------------|---------------------------|------|-----|-----|-----|
| | 270 | 275 | 280 | 285 | 290 |
| Monte Carlo simulation | 14.7 | 11.4 | 9.8 | 8.0 | 5.4 |
| DSC measurement | 14.0 | 12.0 | 9.5 | 8.0 | 6.0 |

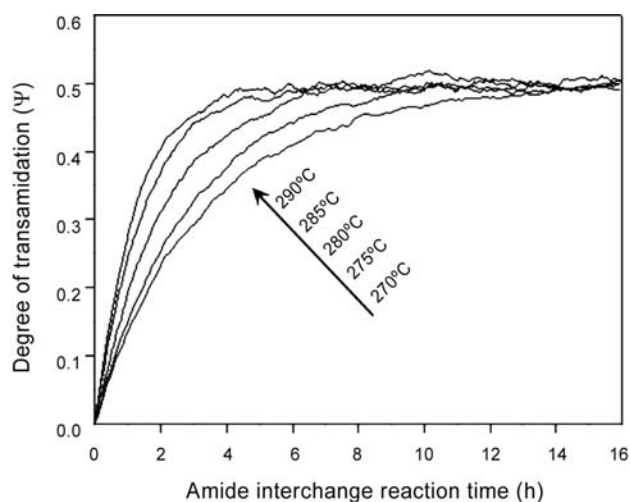


Figure 4. Influence of AIR time on degree of transamidation of PA6/PA66 blends at various temperatures.

Degree of Randomness, Regularity, and Number Average Block Length

Quantification of the degree of randomness and number average block length is defined by several groups for different systems. The statistical model developed by Eersels et al. [10] and Devaux et al. [18] for interchange reactions between two linear polycondensates (AA)_p and (BC)_q is applied in our Monte Carlo model, in which p and q are degrees of polymerization for PA6 and PA66, respectively.

The degree of randomness, χ , is defined by [10]:

$$\chi = \frac{[AB]}{[A][B]} = \frac{[AC]}{[A][C]} \quad (14)$$

So the relation between χ and ψ is derived as:

$$\chi = \frac{\psi}{2f_A f_B} \quad (15)$$

where $f_A = f_{AA} + f_{AC}$, $f_B = f_{AB} + f_{BC}$.

Furthermore, a new concept of degree of regularity, ϕ , is established in this research to describe AIRs well and correlate simulation with experiments. ϕ is calculated as

$$\phi = 1 - \chi \quad (16)$$

The number average block length of AA units, L_{AA} , is:

$$L_{AA} = \frac{I}{P_{AC}} = \frac{[AA]}{[AC]} + I = \frac{f_{AA}}{f_{AC}} + I \quad (17)$$

where P_{AA} represents the probability of finding an A unit followed by another A unit. In the same way, the number average block lengths of AB, AC, and BC units, L_{AB} , L_{AC} , and L_{BC} , respectively, are defined as:

$$L_{AB} = \frac{I}{P_{BC}} = \frac{[AB]}{[BC]} + I = \frac{f_{AB}}{f_{BC}} + I \quad (18)$$

$$L_{AC} = \frac{I}{P_{AA}} = \frac{[AC]}{[AA]} + I = \frac{f_{AC}}{f_{AA}} + I \quad (19)$$

$$L_{BC} = \frac{I}{P_{AB}} = \frac{[BC]}{[AB]} + I = \frac{f_{BC}}{f_{AB}} + I \quad (20)$$

For a completely random copolymer with equal molar ratio of AA and BC, $\psi = 0.5$, $\chi = 1$, and $\phi = 0$. The variations of χ and ϕ with AIR time and melt blending temperature are shown in Figures 5 and 6, respectively.

Block length of block copolymers plays a key role on physical and mechanical properties, such as melting points of copolymers, and tensile strength. Mathematical simulation of block length of block

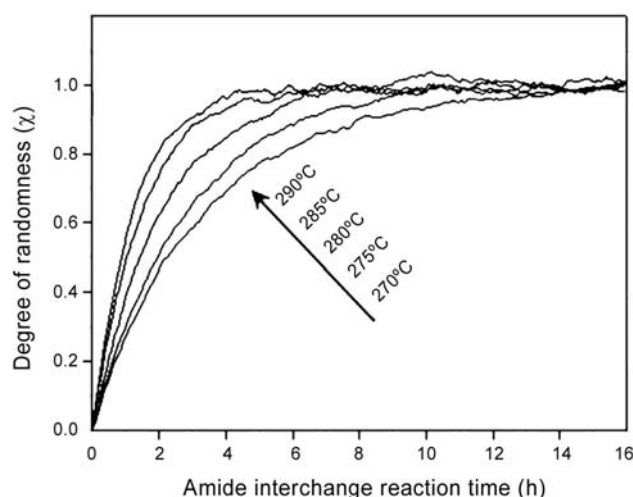


Figure 5. Influence of AIR time on degree of randomness at various blending temperatures.

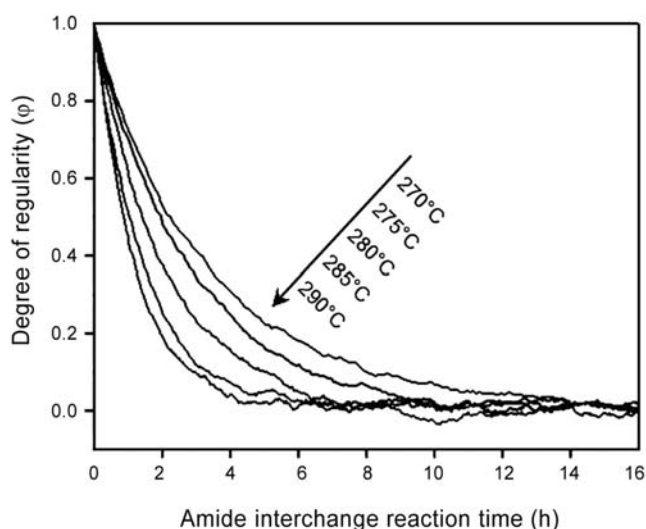
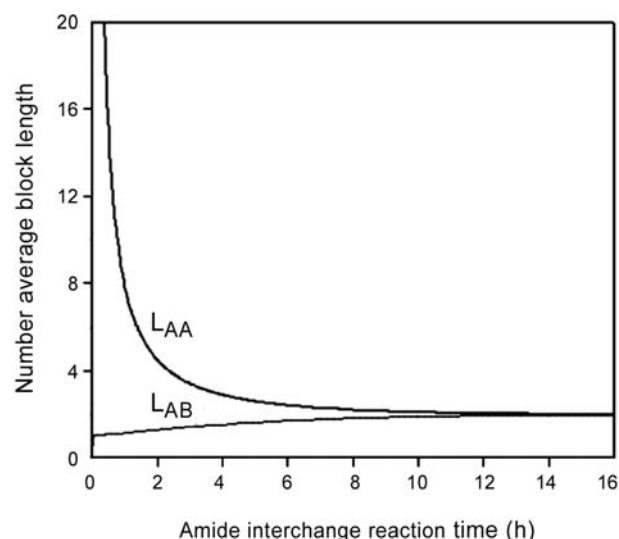


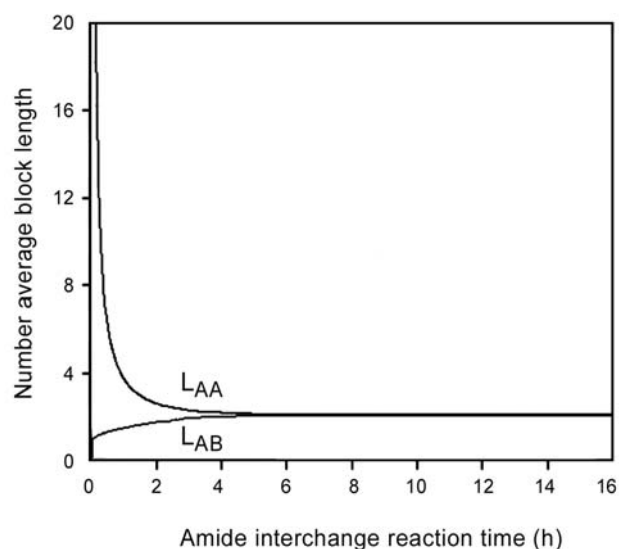
Figure 6. Degree of regularity of PA6/PA66 blends vs. AIR time at various temperatures.

copolymers is an important guide for polymer processing and utilization as we lack direct measurement methods of block length. One or two percent AIRs in a 5:5 PA6/PA66 blends will change the copolymer into the average block length of AA or BC units of 100 and 50, respectively, indicating copolyamides with long block lengths are difficult to prepare. When a copolymer exhibits fully random statistics, $\psi = 50\%$, $f_{AA} = f_{AB} = f_{AC} = f_{BC} = 0.25$, thus $L_{AA} = L_{AB} = L_{AC} = L_{BC} = 2$.

In Figure 7, L_{AA} and L_{AB} are plotted against AIR time for the PA6/PA66 blending systems bearing the initial blending molar ratio 5:5. At the beginning of AIRs, there occurs a strong decrease in L_{AA} till transamidation time of 2 h. In this particular example, L_{AA} is 243 before AIRs. After 2 h transamidation, the average number of AA units next to each other is ~ 4.48 for the blending temperature 270°C, and 2.50 for 290°C. Higher blending temperature leads to shorter AIR time for L_{AA} to reach 2. The AIR time for L_{AA} to reach 2 is 14.7 h for the blending temperature 270°C, and 5.4 h for the blending temperature 290°C, corresponding to their lifetime as listed in Table 1. L_{AB} rises abruptly from 0 to 1, and then a further increase from 1 to 2 is rather slow. The AIR time for L_{AB} to reach 2 is also the lifetime of block copolymer. Variation of L_{BC} is the same as L_{AA} , and variation of L_{AC} is the same as L_{AB} .



(a)



(b)

Figure 7. Number average block length vs. AIR time for blending temperature of: (a) 270°C, and (b) 290°C. Same simulation conditions are as Figure 4.

Relationship Between Melting Points and Degree of Regularity

It is not difficult to find similar variation tendencies between the degree of regularity and the melting points of the PA6/PA66 blends by comparing Figures 2 and 6. Therefore, it is possible to create a function to well describe the relationship between melting point, T_m , and degree of regularity, ϕ , so as to convert calculated ϕ into a theoretical T_m , which could be directly compared to the experimental data with some

possible additional information.

Assuming relationship between T_m and ϕ vs. AIR time, t , obeys one-order exponential decay (Exponential decay 1):

$$T_m = T_{m,e} + (T_{m,0} - T_{m,e}) \exp\left(-\frac{t}{C_1}\right) \quad (21)$$

$$\phi = \exp\left(-\frac{t}{C_2}\right) \quad (22)$$

where $T_{m,0}$ and $T_{m,e}$ are melting points when AIR time is 0 and ∞ , respectively. It should be noted that when $t = 0$, $T_m = T_{m,0}$, $\phi = 1$ and when $t = \infty$, $T_m = T_{m,e}$, $\phi = 0$, the above two equations can be incorporated into:

$$\frac{T_m - T_{m,e}}{T_{m,0} - T_{m,e}} = \phi^{\frac{C_2}{C_1}} = \phi^C \quad (23)$$

For the PA6/PA66 blends, $T_{m,0} = 260.1^\circ\text{C}$, and $T_{m,e} = 196^\circ\text{C}$. By plotting $\ln[(T_m - T_{m,e}) / (T_{m,0} - T_{m,e})]$ against $\ln\phi$, values of C are deduced in the range of 0.45 ± 0.15 and increase with the melt blending temperature, as shown in Figure 8. Relationship between theoretical simulation and experimental measurement is not confined to T_m and ϕ . Even χ , ψ , f_{AA} , f_{AB} , f_{AC} , and f_{BC} correlate with T_m . More accurate functions to

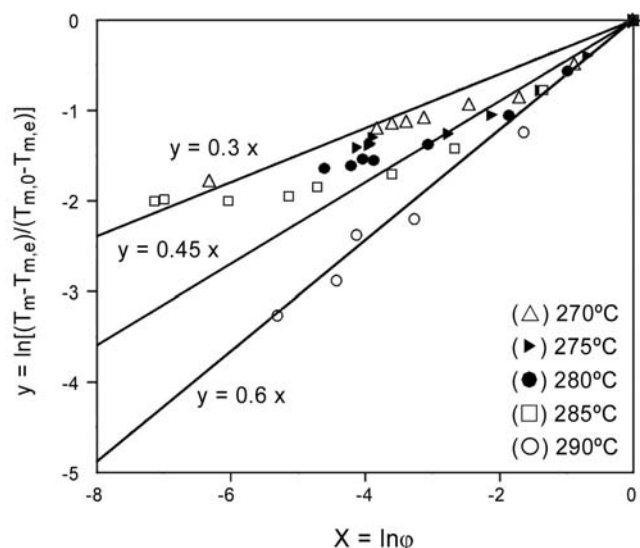


Figure 8. Relationship between melting points and regularity of PA6/PA66 blends at various blending temperatures.

bridge the gap between simulation and experiments are now in progress.

To explain the influence of the blend molar ratio on molar fraction of the resulting AB and AC units, it may be postulated that if two macromolecular chains are involved in an AIR, the resultants are also two new macromolecular chains. So the unit numbers of AB and AC are the same on account of the special features of AIRs in the PA6/PA66 blend system and equal occurrence possibilities of the 10 types of AIRs. Total number of molecular chains in the PA6/PA66 blend system is constant despite several or even infinite time lengths for AIRs are considered. Therefore, molar fractions of AB, f_{AB} , and AC, f_{AC} , are defined as:

$$f_{AB} = \frac{N_{AB}}{N_{AA}^0 + N_{BC}^0} \quad (24)$$

$$f_{AC} = \frac{N_{AC}}{N_{AA}^0 + N_{BC}^0} \quad (25)$$

in which N_{AA}^0 , and N_{BC}^0 are initial numbers of AA, and BC units before AIRs. N_{AB} , and N_{AC} are numbers of the resultants of AB, and AC, respectively. Actually N_{AB} is equal to N_{AC} during AIRs. So f_{AB} is also equal to f_{AC} . Figure 9 shows molar fraction of AB and AC generated from AIRs varies with AIR time for the different blending molar ratios. The same

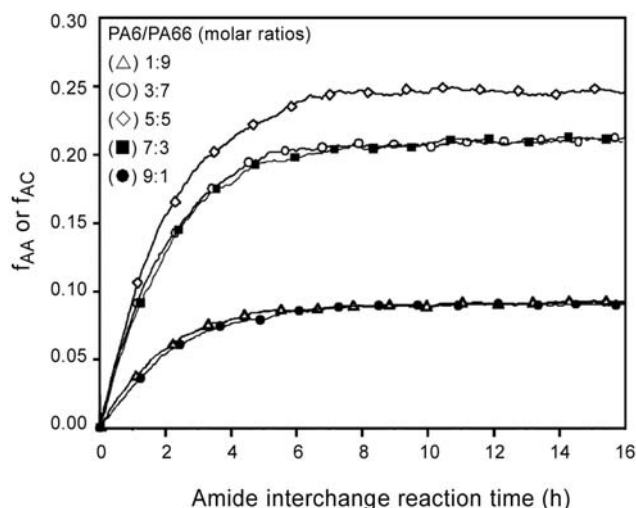


Figure 9. Molar fractions of AB or AC units vs. AIR time at various blend molar ratios (blend temperature: 280°C).

result of f_{AB} or f_{AC} is obtained when the blending molar ratios are 1:9 and 9:1. Similarly, another same result of f_{AB} or f_{AC} is obtained when the molar ratios are 3:7 and 7:3. A maximal equilibrium value of f_{AB} or f_{AC} is observed when the blend molar ratio is 5:5. Actually f_{AB} or f_{AC} is related with occurrence times of AIRs, which is total number of combination of A and B (or C) in the Monte Carlo simulation. The phenomena could be explained by statistics because the total number of combinations of A and B (or C) for the case of the blend molar ratio 3:7 is the same as that for the case of feed molar ratio 7:3. Therefore, it is not strange also to observe the same variation tendency of f_{AB} (or f_{AC}) when the blend molar ratios are 1:9 and 9:1. Moreover, the ultimate or equilibrium values of f_{AB} (or f_{AC}) exhibit some interesting results corresponding to the total numbers of combination of A and B (or C). The ratio of the equilibrium values of f_{AB} or f_{AC} (5:5): f_{AB} or f_{AC} (3:7 or 7:3): f_{AB} or f_{AC} (1:9 or 9:1) being 25:21:9 coincide with the ratio of the total numbers of combination of A and B or C. These results can be used to predict the equilibrium f_{AB} or f_{AC} for the PA6/PA66 blend system with any other feed molar ratio. For example, if the blend molar ratio is 2:8, the equilibrium f_{AB} or f_{AC} is 0.16.

Influence of Blend Molar Ratio on Number Average Block Length

In Figure 10, L_{AA} and L_{AB} are plotted against AIR time for various blending molar ratios. It is found that L_{AA} and L_{AB} are molar ratio dependent, and the equilibrium L_{AA} and L_{AB} , L_{AA}^∞ and L_{AB}^∞ , are $1 + r$. Actually we could provide another theoretical method to compute L_{AA}^∞ and L_{AB}^∞ .

The relationship between equilibrium molar fractions of the four types of amido linkages and the initial blend molar ratios of AB and BC can be obtained theoretically (Appendix):

$$f_{AA}^\infty = (f_{AA}^0)^2, f_{AB}^\infty = f_{AC}^\infty = f_{AA}^0 \cdot f_{BC}^0, f_{BC}^\infty = (f_{BC}^0)^2 \tag{26}$$

The superscripts of 0 and ∞ represent AIR at zero time (at the onset of AIRs) and ∞ (time required for AIR to reach equilibrium), respectively. Therefore, the equilibrium number average block lengths for AA, AB, AC, and BC units are [10]:

$$L_{AA}^\infty = 1 + \frac{f_{AA}^\infty}{f_{AC}^\infty} = 1 + \frac{f_{AA}^0}{f_{BC}^0} = 1 + r \tag{27}$$

$$L_{AB}^\infty = 1 + \frac{f_{AB}^\infty}{f_{BC}^\infty} = 1 + \frac{f_{AA}^0}{f_{BC}^0} = 1 + r \tag{28}$$

$$L_{AC}^\infty = 1 + \frac{f_{AC}^\infty}{f_{AA}^\infty} = 1 + \frac{f_{BC}^0}{f_{AA}^0} = 1 + \frac{1}{r} \tag{29}$$

$$L_{BC}^\infty = 1 + \frac{f_{BC}^\infty}{f_{AB}^\infty} = 1 + \frac{f_{BC}^0}{f_{AA}^0} = 1 + \frac{1}{r} \tag{30}$$

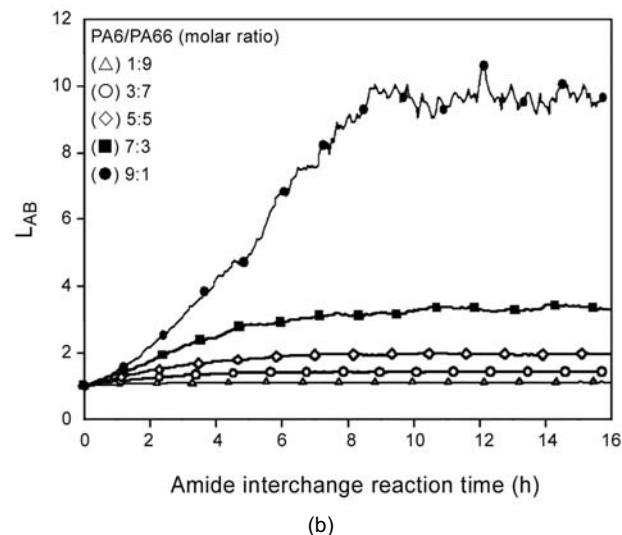
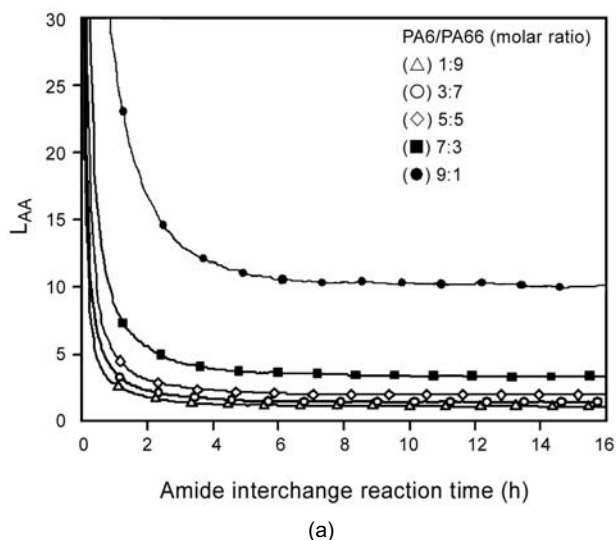


Figure 10. Influence of blending molar ratio on number average block lengths of: (a) L_{AA} , and (b) L_{AB} in PA6/PA66 blends (blending temperature: 280°C).

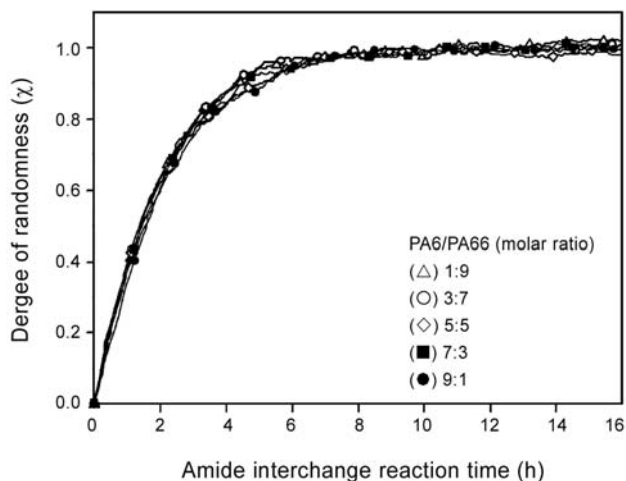


Figure 11. Degree of randomness vs. AIR time at various blending ratios.

where r is blend molar ratio. In this respect the equilibrium number average block length of four types of the amido linkages is able to be determined for any other PA6/PA66 blend system with r .

Influence of Blend Molar Ratio on Degree of Randomness (Irregularity)

We found that degree of randomness, χ , and degree of regularity, ϕ , change with blend temperature for a 5:5 PA6/PA66 blend system. However, χ changes little with various blend molar ratios at blend temperature of 280°C (Figure 11), consistent with the reported results that degree of randomness is independent of blend ratio for copolymerization by ester interchange

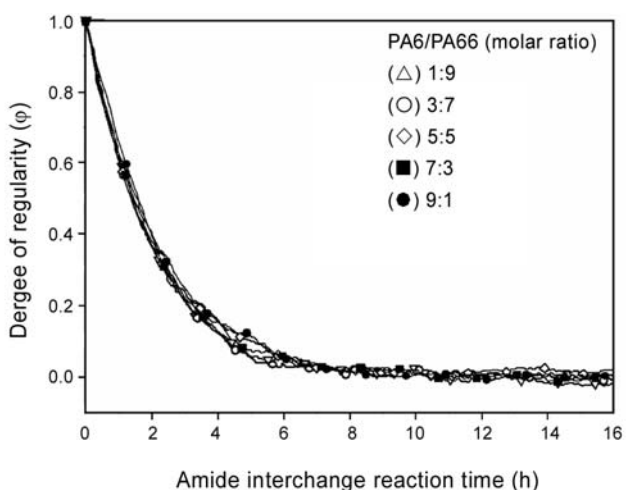


Figure 12. Degree of regularity vs. AIR time at various blending ratios.

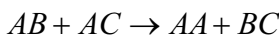
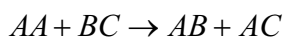
reactions. An equilibrium for the value of 1.0 is observed for χ , indicating randomization is completed by AIRs. Completely random copolymers are virtually generated only in the blend system with the blend molar ratio of 5:5. Nevertheless, block copolymers with the shortest average block length are produced in the blending systems with the blend molar ratios other than 5:5. ϕ decreases from 1.0 to 0 in the same way for the 5 blending systems as $\phi = 1 - \chi$ (Figure 12). It should be stated that the final equilibrium value of ϕ for copolymers with maximal randomization is 0 for the 5 blend systems, corresponding to χ 1.0.

CONCLUSION

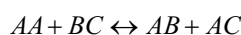
The improved Monte Carlo model was established comprising polycondensation, hydrolysis, and transamidation simultaneously to analyze the influence of AIRs on the degree of transamidation, randomness, regularity and number average block length of each unit. The lifetime of block copolymer derived from the improved Monte Carlo model is in good agreement with that measured by DSC, indicating the improved Monte Carlo model is reliable to describe AIRs during the PA6/PA66 melt blending. Influence of AIRs on degree of transamidation, randomness, regularity, and number average block length of various sequences was achieved with the improved Monte Carlo model. The melting points as expressed in the experimental were fitted with the degree of regularity profile resulted from the Monte Carlo simulation via Exp-decay 1 regression. Maximal equilibrium value 0.25 of molar fractions of AB and AC was observed when the blend molar ratio is 5:5, while the equilibrium molar fractions can be predicted in any other PA6/PA66 blend system. Number average block length of AA, AB, AC, and BC amido linkages is also blend molar ratio dependent. The equilibrium number average block length of AA, AB, and AC units is $1 + r$, in which r is blend molar ratio, while that of BC is $1 + 1/r$. Degree of randomness and regularity are independent of blend molar ratio, consistent with the reported results for copolymerization by ester interchange reactions. The improved Monte Carlo model is also applicable to other polyamide blend systems after minor alteration of reaction parameters.

APPENDIX

In the reaction scheme for PA6/PA66 melt blending, the varieties of the amido linkages are changed before and after AIRs only in the following two reactions, while the varieties and numbers of the four types of the amido linkages are the same after AIRs in the other eight reactions.



The above two reactions can be merged into one reversible reaction.



$$\text{When } t = 0, \quad f_{AA}^0 \quad f_{BC}^0 \quad 0 \quad 0 \quad f_{AA}^0 + f_{BC}^0 = 1$$

$$\text{When } t = \infty, \quad f_{AA}^\infty \quad f_{BC}^\infty \quad f_{AB}^\infty \quad f_{AC}^\infty$$

$$\begin{aligned} \text{Therefore,} \quad f_{AA}^0 - f_{AA}^\infty &= f_{BC}^0 - f_{BC}^\infty = f_{AB}^\infty = f_{AC}^\infty \\ f_{BC}^\infty &= f_{BC}^0 - f_{AA}^0 + f_{AA}^\infty = f_{AA}^0 + f_{BC}^0 - \\ &2f_{AA}^0 + f_{AA}^\infty = 1 - 2f_{AA}^0 + f_{AA}^\infty \\ f_{AA}^\infty &= f_{AA}^0 - f_{AB}^\infty, \quad f_{BC}^\infty = f_{BC}^0 - f_{AB}^\infty \end{aligned}$$

$$\text{When } t = \infty, \quad \frac{df_{AA}}{dt} = -k_{2.5}(f_{AA}^\infty f_{BC}^\infty - f_{AB}^\infty f_{AC}^\infty) = 0$$

$$f_{AA}^\infty f_{BC}^\infty - f_{AB}^\infty f_{AC}^\infty = 0$$

$$f_{AA}^\infty (1 - 2f_{AA}^0 + f_{AA}^\infty) - (f_{AA}^0 - f_{AA}^\infty)^2 = 0,$$

$$\text{so } f_{AA}^\infty = (f_{AA}^0)^2$$

$$(f_{AA}^0 - f_{AB}^\infty)(f_{BC}^0 - f_{AB}^\infty) - (f_{AB}^\infty)^2 = 0,$$

$$\text{so } f_{AB}^\infty = f_{AA}^0 \cdot f_{BC}^0$$

$$\text{In the same way, } f_{BC}^\infty = (f_{BC}^0)^2$$

$$f_{AC}^\infty = f_{AA}^0 \cdot f_{BC}^0$$

SYMBOLS AND ABBREVIATIONS

| | |
|-------------|---|
| AIRs | Amide interchange reactions |
| TFE | 2,2,2-Trifluoroethanol |
| C | Reducing factor of the reaction system |
| f | Molar fractions of various units |
| Ψ | Degree of transamidation |
| χ | Degree of randomness |
| φ | Degree of regularity, $\varphi=1-\chi$ |
| L | Number average block length of various units |
| π | Micro-scale rate constant |
| A | Normalization factor |
| \tilde{N} | Avogadro constant |
| P_{AA} | Probability of finding an A unit followed by another A unit |

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