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How Well Can One Separate Copolymers According to Both Chemical Compositions and Sequence Distributions?

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ABSTRACT: Partitioning of statistical AB type copolymer chains into a slit pore was studied with Monte Carlo simulations on a simple cubic lattice with self-avoiding walk models. Only one of the monomer types, B monomers, has attractive interaction with the surface, while the A monomers have no interaction with the surface. The critical adsorption point (CAP) of the copolymer at a given chemical composition f_B and sequence order parameter λ, which characterizes the degree of blockiness in the copolymer, was determined. The CAP's obtained in the simulations were compared with theoretical predictions proposed by Brun [*J. Liq. Chromatogr. Relat. Technol.* **1999**, *22*, 3027−3065]. Most simulation data agree well with Brun's theoretical equation except for sequences at the two extreme of sequence types (i.e., extremely blocky or nearly perfectly alternating). The potential separation of copolymers according to chemical composition in interactive chromatography was examined by examining the partition of copolymers at chosen surface interaction energies. Simulation results show that one can separate the copolymers according to the chemical composition only when the sequence order parameter λ is fixed or has a narrow distribution. The separation will be impaired if there is also a distribution in λ. Separation of copolymer samples according to sequence order parameter at a given chemical position is of limited resolution.

1. Introduction

Copolymers consist of two or more chemically different monomers linked together, as opposed to homopolymers where only one monomer type is present. The benefits of linking different monomers together are the possibility to obtain new and desirable properties that are otherwise absent from their parent homopolymers. Various copolymers are industrially produced, and these materials, for example, ethylene/propylene copolymers, are widely used in everyday life. The properties of copolymers are strongly influenced by both the chemical composition of the monomers and the molecular weight of the polymers. This therefore requires researchers to analyze not only the molecular weight distribution in a given sample but also the chemical composition distribution present in the copolymers. In addition to the overall chemical composition, the exact sequences of connection of monomers can also dramatically influence the properties of copolymers. At the extremes, monomer placements along the chain can be completely random, perfectly alternating, or in blocks such as diblock, triblock, or multiblock copolymers. Block copolymers in particular have fascinated the researchers for decades due to their special ability to self-assemble into various nanostructures.[1−3]

Analysis and characterization of copolymers is a more challenging task than analysis of homopolymers. Spectroscopic methods such as NMR and FT-IR can provide average chemical composition of the sample but are unable to provide information on its distribution. Temperature rising elution fractionation (TREF) or crystallization analysis (CRYSTAF) can characterize the chemical composition distribution for many polyolefin copolymers, but only if they are crystallizable. Size exclusion chromatography (SEC) separates polymers according to hydrodynamic volume and is often used to obtain the molecular weight distribution, but when this is applied to analysis of copolymers, it often encounters problems because the hydrodynamic volume of a copolymer depends on both molecular weight and chemical composition.[4] In recent years, new liquid chromatography methods with elution modes other than SEC, generally referred as interactive liquid chromatography, have been developed for polymers soluble at room temperature[5] as well as polymers soluble at high temperature.[6−8] In particular, liquid chromatography at the critical condition (LCCC) and liquid adsorption chromatography (LAC) in isocratic or gradient modes have attracted great attention for their potential use in analyzing complex polymer systems. Unlike SEC, in which separation is based on larger polymer chains being entropically excluded from column pores, the separation mechanism in these latter chromatographic techniques also depends on attractive enthalpic interactions between polymers and porous surfaces. In LAC, the enthalpic interaction dominates entropic exclusion, and polymer chains with higher molecular weights are increasingly retained. LCCC marks the transition from SEC to LAC and refers to a set of conditions at which entropy and enthalpy are counterbalanced so that elution may become independent of molecular weight. Theoretically, this critical condition is shown to be the critical adsorption point (CAP)[9−12] of a polymer chain above a surface, and the exact location of the CAP depends on the chemical nature of polymer, solvent, temperature, and other conditions. Locating the experimental conditions needed to reach the critical condition for a given system is a challenge, but researchers in recent years have developed several efficient ways to find the critical condition.[13−16] In experimental studies, the critical condition is also referred as critical eluent composition when eluent composition is used to adjust the adsorption strength. The CAP here should be understood as the critical interaction energy at the critical eluent composition.

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The existence of the CAP of homopolymer chains is well established. The existence of the CAP of copolymer chains however is not obvious. For block copolymers, each block has its own CAP. This property has been utilized in experiments using LCCC method to characterize individual block lengths in diblock or triblock copolymers.[17−22] For statistical copolymers, Brun[14,23,24] suggested that statistical copolymers with a narrow chemical composition distribution have a CAP that depends on chemical composition and sequence order (more explanation of sequence order will be given later). The proof of the existence of a single CAP for statistical copolymers is theoretically challenging and makes use of several approximations.[24] For the practical purpose of analysis of copolymer samples, if a CAP indeed exists for statistical copolymers with a given chemical composition and sequence order, then one may use LCCC or gradient LAC to separate statistical copolymers according to both chemical composition and sequence order. Several research groups have experimentally demonstrated the feasibility of separating statistical copolymers according to chemical composition using gradient elution with interactive chromatography.[6,23,25,26] However, the possibility to separate according to sequence order distributions remains elusive.

Earlier our group investigated the dependence of the CAP on copolymer chemical composition for statistical random copolymer adsorption above a homogeneous surface using Monte Carlo simulations.[27] The simulation results were found to fit an analytical equation that had been proposed by Brun earlier.[24] However, the previous studies only focused on statistical random copolymers and did not consider statistical copolymers with nonrandom sequence distribution. In this study, we first examine the possible sequence distributions of all statistical copolymers and examine the location of CAP for statistical copolymers with nonrandom sequence distributions. We also examine how the copolymer samples with a given chemical composition and nonrandom sequence distributions may elute at a given surface interaction energy so we may get a better understanding of the potential separation of copolymers according to chemical composition and sequence distributions by interactive chromatography.

2. Monte Carlo Simulation Methods

In our simulations, polymer chains are modeled as self-avoiding walks (SAW) in a simple cubic lattice of dimensions $250a \times 250a \times 30a$, representing a slit pore, where a is the lattice unit length. Each vertex of the SAW represents a monomer of the polymer chain, which could of type A or type B. The chain lengths here are varied from 40 to 200. Periodic boundary conditions were applied in the X and Y directions. There are two impenetrable walls in the $Z = a$ and $Z = 30a$ planes representing the slit pore surfaces.

We used the biased chain insertion method to evaluate the chemical potential of the chain. First, we randomly selected one monomer from the chain and randomly placed it on a site in a slit pore (between $Z = 2a$ and $Z = 29a$ planes). The remaining monomers of the chain are then grown using the biased chain insertion method.[28] Monomers on the planes of $Z = 2a$ and $Z = 29a$ are considered to be adsorbed on surfaces. For all adsorbed monomers, the polymer−surface interaction energies, ε_w^A and ε_w^B, are applied for A and B monomers, respectively. The polymer−surface interaction energies in the simulation can be varied. In the current study, we set $\varepsilon_w^A = 0$ and ε_w^B as a negative value, indicating that the B type monomer has attractive interaction with the surfaces.

The standard chemical potential of the chain, μ^0, is calculated from the Rosenbluth−Rosenbluth weighting factor, $W(N)$, which is given by the following equation:[27,28]

$$\beta\mu^0 = -\ln\langle W(N)\rangle = -\ln\langle \prod_{i=1}^{N} w_i\rangle \quad \text{and}$$

$$w_i = \frac{\sum_{j=1}^{z} \exp(-\beta E_j)}{z} \tag{1}$$

where z is the lattice coordination number ($z = 6$ for simple cubic lattice), E_j is the energy of ith inserted monomer in the jth potential direction, and $\langle\rangle$ refers to ensemble average over all possible conformations. μ^0 is the standard free energy per chain. $\beta = 1/k_BT$, where k_B is the Boltzmann constant and T is the temperature. The details of the chain insertion method have been reported previously.[10]

We determined the standard chemical potentials of a chain in the pore, μ^0_{ads}, as well as a chain grown in a bulk solution, μ^0_{bulk}. The bulk solution is modeled in a $100a \times 100a \times 100a$ lattice with no walls and periodic boundary conditions applied in all three directions. All chemical potentials calculated are reduced by the Boltzmann factor, $\beta = 1/k_BT$. The partition coefficients, K, were then given by $K = \exp(-\beta\Delta\mu^0)$, where $\Delta\mu^0 = \mu^0_{ads} - \mu^0_{bulk}$. The partition coefficient determined in the simulation can be related to the retention volume of polymers, V_R, in the column in the experiment through the following equation: $V_R = V_0 + KV_P$, where V_0 is the volume of the mobile phase and V_P is the volume of the pore region in the column. The elution volume of a solute V_R may be compared with elution volume of solvent V_S to determine whether the solute is less likely or more likely to enter the pore. When $V_R < V_S$, solutes are less likely to enter the pore, which is corresponding to $K < 1$; when $V_R > V_S$, solutes are more likely to enter the pore and $K > 1$. The typical chain length N examined here ranges from 40 to 200. The corresponding ratio of pore radius to polymer size, measured by $D/2R_{g0}$, ranges from 3.8 to 1.5, where R_{g0} is the radius gyration of the chain in the bulk solution. This range corresponds to wide pore limit (i.e., $D/2R_{g0} > 1$) and is typical of experimental conditions.

3. Results and Discussion

3.1. Distributions of Number of Sequences of Copolymer. In analyzing AB type copolymers, one is typically concerned with two questions: what is the fraction of each monomer type present, and how are the two monomer types arranged along the chain? The answer to the first question is given by the chemical composition of the two types, f_A and f_B. The answer to the second question however can only be partially obtained. Given an AB type of copolymer of length N and with a monomer fractions, f_A, and f_B, the total number of possible sequences is given by

$$\Omega(N, f_B) = \frac{N!}{N_B!(N - N_B)!} \tag{2}$$

where $N_B = f_BN$. Here, the sequences considered have direction (i.e., AAABB and BBAAA are considered different). Among these possible sequences, the arrangement of monomers along the chain could be completely blocky or completely alternating. Random copolymers are a special type in which there is no statistical correlation between two consecutive monomers along the chain. One can define a sequence order parameter λ to partially characterize the sequence distribution of copolymers, as follows:

$$\lambda = 1 - P_{AB} - P_{BA} \tag{3}$$

where P_{ij} is the nearest-neighbor transition probability which is the probability that a monomer of type i is followed

Table 1. Values of N_{AA}, N_{BB}, N_{AB}, N_{BA}, A_{number}, and B_{number} for the Copolymer with the Specified N, λ, and f_B

	A(...)B	B(...)A	A(...)A	B(...)B
N_{AA}	$Nf_A - Nf_Af_B(1-\lambda)$	$Nf_A - Nf_Af_B(1-\lambda)$	$Nf_A - Nf_Af_B(1-\lambda) - 1$	$Nf_A - Nf_Af_B(1-\lambda)$
N_{BB}	$Nf_B - Nf_Af_B(1-\lambda)$	$Nf_B - Nf_Af_B(1-\lambda)$	$Nf_B - Nf_Af_B(1-\lambda)$	Nf_B- $Nf_Af_B(1-\lambda) - 1$
N_{AB}	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda) - 1$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$
N_{BA}	$Nf_Af_B(1-\lambda) - 1$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$
A_{number}	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda) + 1$	$Nf_Af_B(1-\lambda)$
B_{number}	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda)$	$Nf_Af_B(1-\lambda) + 1$

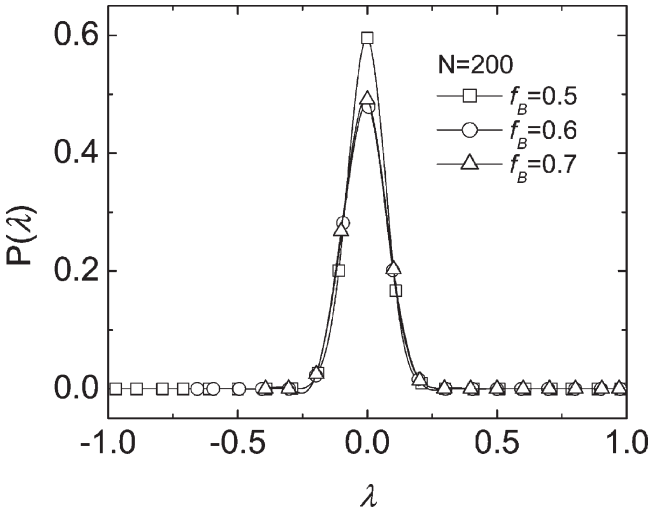

Figure 1. Distribution of normalized possible number of monomer sequences as a function of sequence order parameter λ at several different f_B.

by a monomer of type j. Here, the transition probabilities P_{AB} and P_{BA} can be calculated as

$$P_{AB} = \nu_{AB}/f_A \tag{4}$$

$$P_{BA} = \nu_{BA}/f_B \tag{5}$$

where ν_{AB} and ν_{BA} are probabilities of finding the diads AB and BA, respectively, along the chain. The transition probabilities relate to relative monomer reactivity in copolymerizations. For random copolymers, $P_{AB} = f_B$ and $P_{BA} = f_A$, which leads to $\lambda = 0$ since $f_A + f_B = 1$. When $\lambda > 0$, this implies that the copolymers are more blocky, while $\lambda < 0$ means the copolymers are more alternating compared with that of random copolymers. However, the parameter λ considers only correlation between nearest neighbors. Hence, a copolymer chain with sequence such as AABBAABB will also have $\lambda = 0$, but it is certainly not a random copolymer. In another word, parameter λ is useful to differentiate different types of copolymers only if copolymer statistics follow first-order Markov chain.

There are still a large number of sequences for statistical copolymers with a given λ and f_B. Consider the probability distribution, $P(\lambda,f_B,N) = W(f_B,\lambda,N)/\Omega(N,f_B)$, where $W(f_B,\lambda,N)$ is the number of sequences with given λ and f_B. The Appendix presents the math that treats this problem. The final result is

$$W(\lambda,f_B,N) = \frac{(N_A-1)!}{(N_A-A_{number})!(A_{number}-1)!}\frac{(N_B-1)!}{(N_B-B_{number})!(B_{number}-1)!} \tag{6}$$

where A_{number} and B_{number} are the numbers of A and B blocks, respectively. The corresponding N_{AA}, N_{BB}, N_{AB}, A_{number} and B_{number} (N_{AA}, N_{BB} and N_{AB} will be discussed in the Appendix.) for the copolymer with the specified N, λ, and f_B are determined by the equations presented in the Table 1. Figure 1 presents a plot of this distribution as a function of λ for several different f_B values with chain length $N = 200$. The Y value of each data point represents the sum of the probability of all the copolymers within $[\lambda - 0.05, \lambda + 0.05]$, while the X value is the mean value of the λ of all the copolymers within the same region. The random sequences $\lambda = 0$ would always be the most abundant type. For example, the probability of the monomer sequence at $f_B = 0.5$ with the λ within the region of [0.05, 0.05] is up to 60%.

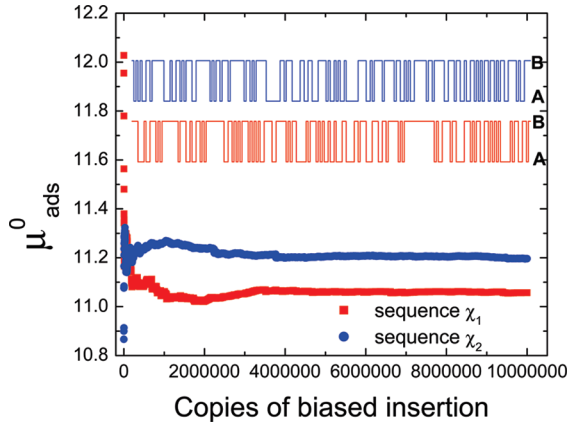

Figure 2. Determined chemical potentials for two specific sequences, χ_1 and χ_2, as a function of number of configurations. The inset presents the actual sequences. $f_B = 0.6$, $\lambda = 0.003$, and $\varepsilon_w = -0.49$.

3.2. Influence of Sequences on the Determined Chemical Potential. From the above section, we see that there are still a large number of sequences with a given chemical composition f_B and sequence order parameter λ. The question then remains how these sequences may affect the determined chemical potential and thus the partition coefficient. We will use $W(N,\chi)$ to denote the Rosenbluth weighting factor for a defined sequence χ, which has a specified f_B and λ, i.e., $\chi(f_B,\lambda)$. In order to determine the chemical potential of the copolymers with a given composition and sequence order parameter, we are faced with determining how to sample a large number of sequences and how the reported chemical potentials should be averaged over different sequences. We first show that the determined chemical potential varies with sequences which have the same given f_B and λ. Figure 2 presents the determined chemical potentials for two specific sequences, χ_1 and χ_2, as a function of number of configurations being sampled. The polymer/surface interaction ε_w is set as -0.49. Both sequences have the same $f_B = 0.6$ and $\lambda \cong 0.0$ ($\lambda = 0.003$) but are two distinct sequences, as shown in the inset of the figure. Clearly the determined chemical potential converges to a defined value as the number of configurations increases, but the final converged values for the two sequences differ by more than the estimated error bars. On the other hand, different runs with different seeds but with the same sequence yield the final values within the error bars as long as the number of configurations sampled is sufficient. These two sequences have the same λ,

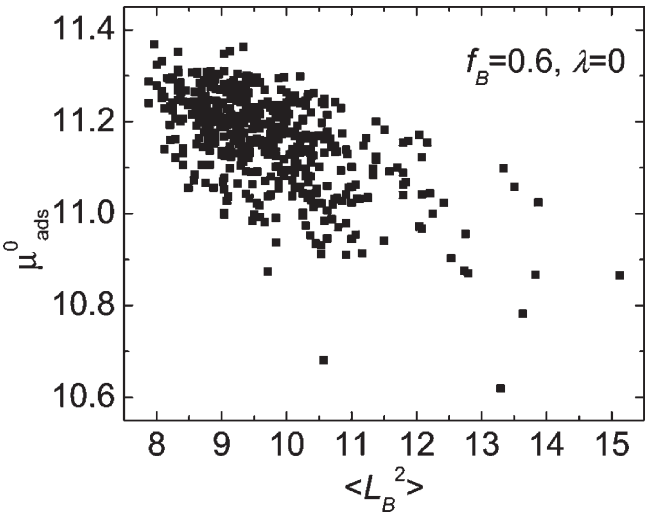

Figure 3. Plot of determined chemical potentials, μ^0_{ads}, for 500 sequences with the same λ and f_B as a function of mean square of B block length. $\lambda = 0$, $f_B = 0.6$, and $\varepsilon_w = -0.49$. Each sequence is used in biased insertion for 1 000 000 times to obtain the chemical potential. The average error bar for each μ^0_{ads} is 0.06.

however one can visually tell from the inset that the two sequences differ in their blockiness. The sequence χ_1, which has a lower chemical potential, possesses more long B blocks than sequence χ_2, which correspondingly has a higher chemical potential.

To further investigate what additional factors other than f_B and λ may affect the determined chemical potentials, we generated 500 sequences ($\chi_1, \chi_2, ..., \chi_{500}$) for a given f_B and λ. These 500 sequences may contain redundant ones, but the probability of getting a redundant one is small. Each sequence is then used in biased insertion 1 000 000 times to obtain the chemical potential, μ^0_{ads}, for that particular sequence. In addition, we characterize the blockiness of each sequence by defining two additional parameters:

$$\langle L_B \rangle = \frac{\sum_{k=1}^{m} l_k}{m} \tag{7}$$

$$\langle L_B^2 \rangle = \frac{\sum_{k=1}^{m} l_k^2}{m} \tag{8}$$

Here l_k is the length of uninterrupted B blocks, and m is the total number of B blocks on a given sequence. $\langle L_B \rangle$ and $\langle L_B^2 \rangle$ are the first and second moment mean of B block length of a given sequence, respectively. When f_B and λ are specified, $\langle L_B \rangle$ are the same for all the sequences, but $\langle L_B^2 \rangle$ is not. In fact, $\langle L_B \rangle \approx 1/((1 - f_B)(1 - \lambda))$. For example, the determined $\langle L_B^2 \rangle$ for the two sequences, χ_1 and χ_2, in Figure 2 are 12.2 and 8.8, respectively, while $\langle L_B \rangle = 2.45$ for both sequences. The larger the $\langle L_B^2 \rangle$ is, the more long B blocks the copolymer possesses. Figure 3 presents the plot of determined chemical potentials against the corresponding $\langle L_B^2 \rangle$ for the 500 sequences generated with $f_B = 0.6$ and $\lambda = 0$ and with polymer/surface interaction ε_w at -0.49. Clearly, the chemical potential of copolymer decreases with an increase in $\langle L_B^2 \rangle$.

The above discussion demonstrates that the chemical potential, μ^0_{ads}, and hence the partition coefficient K for a copolymer sample with a specified f_B and λ will still have a distribution caused by difference in $\langle L_B^2 \rangle$. This distribution will hence interfere or limit how well one might separate copolymer samples according to chemical composition and sequence order distributions. We will further discuss this issue in section 3.4.

3.3. Dependence of CAP on Chemical Composition and Sequence Order Parameters. The critical conditions of copolymers depend on copolymer's chemical composition and also the sequence order parameters. Hence, the critical interaction energy (CAP) of a copolymer sample will depend on those parameters. Brun[24] discussed the existence of the CAP of the statistical copolymer when the copolymer has a narrow chemical composition distribution. He derived an equation that describes the dependence of the critical adsorption energy (the CAP) on the chemical composition and order parameter λ for statistical copolymers, which is shown as follows:

$$\begin{aligned}[\exp(-\varepsilon_w^h(cc))]^2 + \exp(-\varepsilon_w^A)\exp(-\varepsilon_w^B)(1 - P_{AB} - P_{BA}) \\ = \exp(-\varepsilon_w^h(cc))[\exp(-\varepsilon_w^A) + \exp(-\varepsilon_w^B) \\ - (P_{AB} + P_{BA})(\exp(-\varepsilon_w^A)f_B + \exp(-\varepsilon_w^B)f_A)]\end{aligned} \tag{9}$$

where the $\varepsilon_w^h(cc)$ is the critical interaction energy for the homopolymers (assuming homopolymer of B), and ε_w^A and ε_w^B are the surface energy of A and B monomers interacting with the surface at the CAP for the copolymers. Since we have set $\varepsilon_w^A = 0$, we will denote the CAP determined for the copolymers as $\varepsilon_w^B(cc)$, and using $\lambda = 1 - P_{AB} - P_{BA}$, eq 9 can now be expressed in the form

$$\begin{aligned}[\exp(-\varepsilon_w^h(cc))]^2 + \exp(-\varepsilon_w^B(cc))\lambda \\ = \exp(-\varepsilon_w^h(cc))[1 + \exp(-\varepsilon_w^B(cc)) \\ - (1 - \lambda)(f_B + \exp(-\varepsilon_w^B(cc))f_A)]\end{aligned} \tag{10}$$

For the random copolymer, $\lambda = 0$, and eq 10 can be simplified as follows:

$$\exp(-\varepsilon_w^h(cc)) = f_A + \exp(-\varepsilon_w^B(cc))f_B \tag{11}$$

Here $\varepsilon_w^h(cc)$ in eqs 10 and 11 are the same as in eq 9; it is the critical interaction energy of a homopolymer B at the critical condition. $\varepsilon_w^B(cc)$ is the critical interaction energy of statistical AB copolymers. When the fraction of B monomers f_B in copolymers decreases, the corresponding adsorption strength for the copolymer samples have to be stronger than the homopolymer samples in order to reach the critical condition. Equation 11 had been presented in our earlier work and the equation was found to fit the computational data very well.[27] However, in our previous study, the averaged chemical potential $\mu_{ads}(f_B)$ is averaged over an ensemble of sequences that has a distribution in λ. Here we will obtain the averaged chemical potential over the ensemble of sequences with a given f_B and λ and examine how the determined $\varepsilon_w^B(cc)$ at the given f_B and λ may be compared against eq 10.

For each specified f_B and λ, we randomly generated 5000 sequences, and each sequence was used in biased insertion for 5000 times. Afterward, the chemical potential of these sequences are averaged. Two average methods concerning sequence distributions in copolymers are discussed in the literature; one is called the quenched average, and the other is the annealed average. In the quenched average, one obtains chemical potential for each specific sequence first, $\mu(\chi,N) = -\ln\langle W(\chi,N)\rangle$, where $\langle\,\rangle$ stands for ensemble average over the conformation only. Afterward, the averaged chemical potential, which is the quenched average, $\mu_{quenched} = \langle\mu(\chi,N)\rangle$ is performed over the ensemble of the sequence. In the

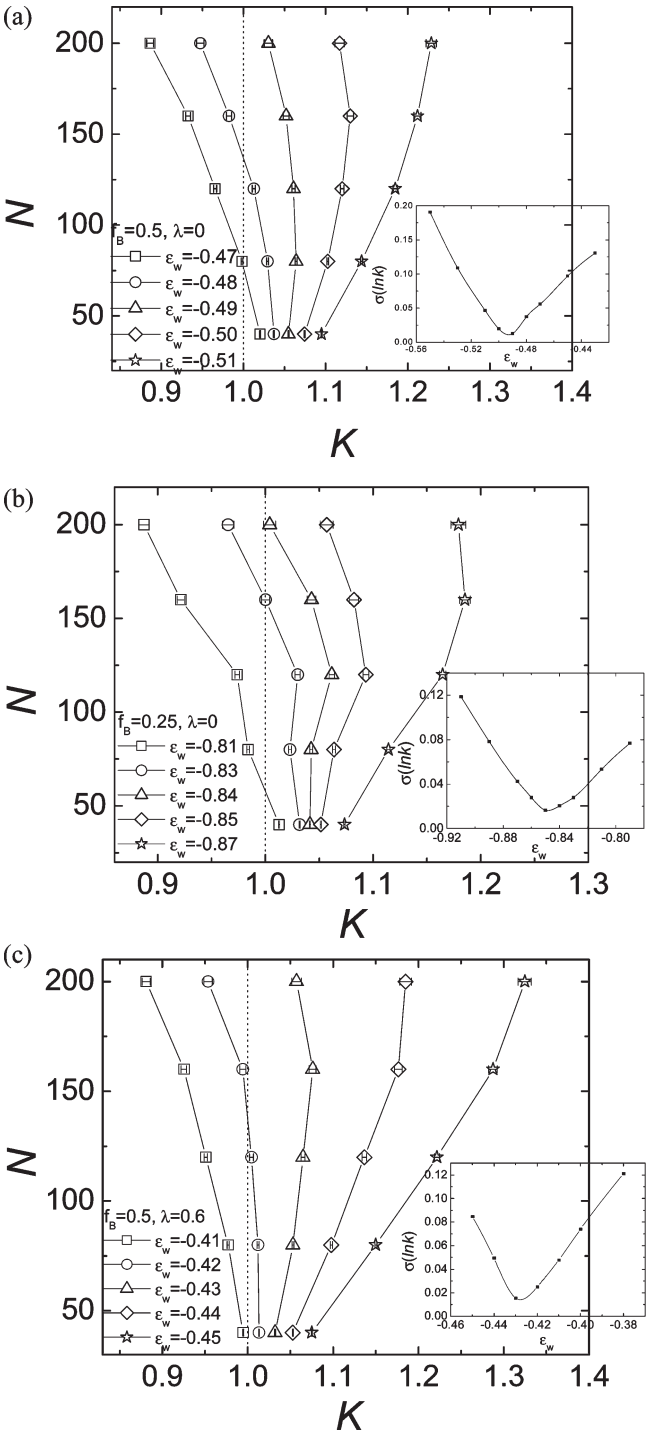

Figure 4. Variation in the average partition coefficient K with the chain length N at different polymer/surface interaction ε_w^B. Insets are the plots of deviation in ln K vs ε_w^B for the given range of N in the corresponding figures. The mimimum in the insets identifies the CAP. The vertical dotted line in the figure shows the location of $K = 1$. The λ and f_B are varied. (a) $f_B = 0.5, \lambda = 0$; (b) $f_B = 0.25, \lambda = 0$; (c) $f_B = 0.5, \lambda = 0.6$.

annealed average, the Rosenbluth weight factor $\langle W(\chi,N)\rangle$ is averaged over the ensemble of sequences as well as the conformations, and then the chemical potential is determined from that Rosenbluth weighting factor directly. It has been discussed in the literature that the two average methods do not differ a lot before the critical adsorption point, but they may differ beyond the critical adsorption point.[29] Here we have used the quenched average since this is more relevant to experimental conditions.

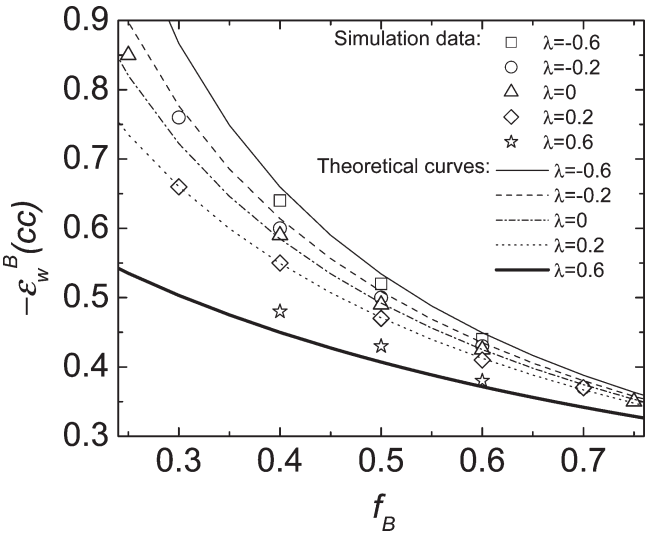

Figure 5. Plot of CAP, $-\varepsilon_w^B(cc)$, of copolymers against the f_B for the copolymers at different λ. The symbols are the CAP determined by the simulation, while the lines are the plots according to eq 10 by taking $\varepsilon_w^A = 0$ and $\varepsilon_w^h(cc) = -0.276$, while -0.276 is the CAP of the linear SAW homopolymer of B in the slit pore. The error bar for simulation data is ± 0.01.

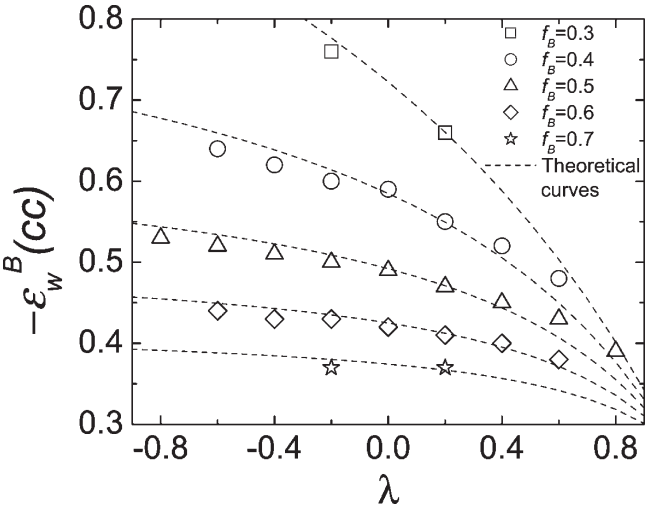

Figure 6. Plot of CAP, $-\varepsilon_w^B(cc)$, of copolymers against the λ for the copolymers at different f_B. The symbols are the CAP determined by the simulation, while the lines are the plots according to eq 10 with taking $\varepsilon_w^A = 0$ and $\varepsilon_w^h(cc) = -0.276$. The error bar is ± 0.01.

In Figure 4a−c, we present representative plots of the average partition coefficient K vs N for the statistical copolymer at specified λ and f_B while varying ε_w to locate the critical condition. Here the chains are inserted in a slit pore with width $D = 30a$. As shown in a previous study, the CAP identified in a slit geometry does not shift when D changes.[11] We identified the CAP as the point when K varies least with N, as shown in the insets of these figures (Figure 4a−c). The determined CAP is $\varepsilon_w^B(cc)$ since ε_w^B has been varied to reach critical condition. The $\varepsilon_w^B(cc)$ for the three cases were $\varepsilon_w^B(cc) = -0.35 \pm 0.01$, -0.49 ± 0.01, and -0.43 ± 0.01. In all cases, K is not entirely independent of the chain length at the critical condition since we have used SAW models for the chain. Also observable from Figure 4b, when the percentage of interacting monomers are less ($f_B = 0.25$), the fluctuations in the determined K values are larger.

Figures 5 and 6 present the dependence of determined CAP, $\varepsilon_w^B(cc)$, on f_B and λ, respectively. For the purpose of

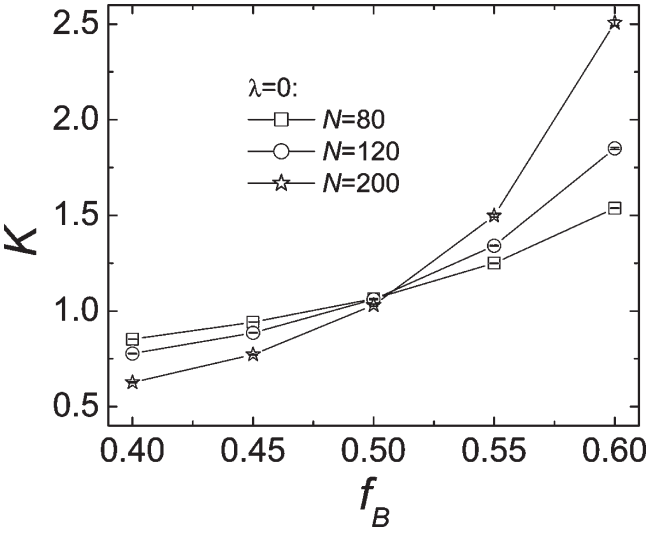

Figure 7. Plot of K against the f_B for the random copolymers at different N. $\lambda = 0$ and $\varepsilon_w = -0.49$.

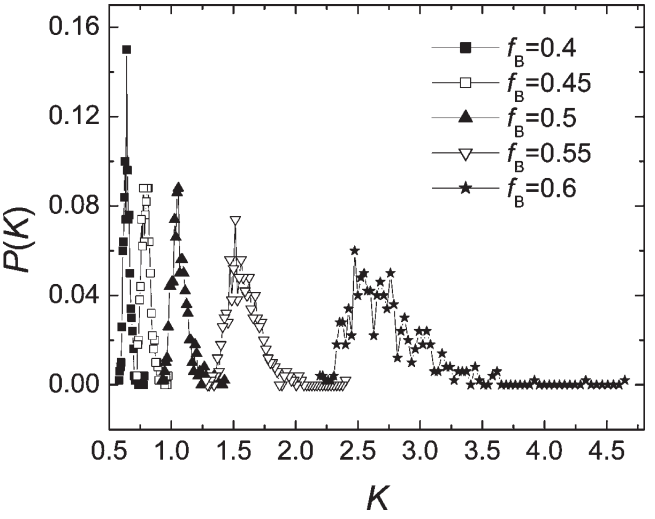

Figure 8. Historgram distribution of partition coefficient K from 500 copies of sequences generated for the given f_B and $\lambda = 0$. $N = 200$ and $\varepsilon_w = -0.49$. Each sequence is used in biased insertion for 1 000 000 copies to obtain the Rosenbluth−Rosenbluth weighting factor.

comparison, the corresponding theoretical curves from eq 10 are plotted in the figures as well. Overall, the simulation data fit very well with theoretical prediction although small deviations can be observed at two extreme values of λ. Simulation data are slightly above theoretical prediction at large positive λ such as $\lambda = 0.6$ and 0.8 and are slightly below theoretical prediction at large negative value of λ. The deviation at the two extreme values of λ is to be expected since the Brun used several approximations that will fail in these extremes, as discussed in a recent paper.[30] For example, when $\lambda = 1$, eq 10 can be simplified as follows:

$$[\exp(-\varepsilon_w^h(cc))]^2 + \exp(-\varepsilon_w^B(cc)) = \exp(-\varepsilon_w^h(cc))[1 + \exp(-\varepsilon_w^B(cc))] \quad (12)$$

This equation predicts that $\varepsilon_w^B(cc) = \varepsilon_w^h(cc) = -0.276$ when $\lambda = +1$. This implies that the CAP of block copolymer is always equal to the CAP energy of homopolymer chain and is independent of A block fraction. This prediction however was obtained under several approximations used by Brun. Detailed discussions on why these approximations fail at the two extremes can be found in ref 30. Physically one can also easily understand that this prediction will not hold for realistic block copolymers. When a block copolymer has a long nonadsorbing block, it will be a lot harder to attach the adsorbing block on the surface compared with the corresponding homopolymer. The nonadsorbing blocks will influence the adsorption capability of the adsorbing blocks.[31,32] In our previous study,[27] the determined $\varepsilon_w^B(cc)$ for the block copolymer at $f_B = 0.5$ is -0.30, which is slightly higher than the CAP of the hompolymer, which is at -0.276. Therefore, slight deviation from Brun's analytical equation is to be expected when the copolymer chain is very blocky. Brun's equation is not applicable for very blocky or alternating copolymers. Overall, the simulation data fits the theoretical equation derived by Brun fairly well except for some sequences with large positive or negative λ values.

3.4. Possibilities of Separate Copolymers According to Chemical Composition. The above section shows that critical condition exists for a given copolymer sample with a given f_B and λ. We further examine how well one may separate copolymers according to chemical composition f_B and sequence order parameter λ. For this purpose, we will examine

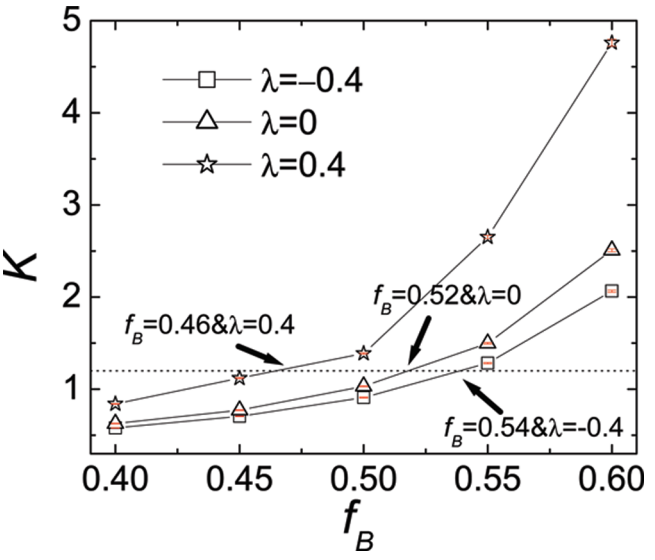

Figure 9. Plot of K against the f_B for statistical copolymers with different λ. $N = 200$ and $\varepsilon_w = -0.49$.

how the partition coefficient K for a copolymer sample depends on these two parameters at a chosen CAP. In addition, recall in section 3.2 the determined chemical potential, and therefore K is an average over different sequences and hence K has an inherent distribution caused by sequence distribution with a given f_B and order parameter λ. We will examine how this inherent distribution may interfere with the separation.

Figure 7 presents a plot of average partition coefficient K against f_B for the copolymers with chain length $N = 80$, 120, and 200 when ε_w is set at -0.49, which is the CAP for copolymer with $f_B = 0.5$ and $\lambda = 0$. Here the average K is obtained from 5000 different sequences. K grows monotonically with f_B for all chain lengths but is steeper when chain length N is large. Also curves for different N intersect at $f_B = 0.5$ since we are setting ε_w at the CAP of copolymer with $f_B = 0.5$. Data in Figure 7 indicate that if one wants to resolve copolymers according to chemical composition, it is important that the sample should be first resolved according to molecular weight before it is subjected to interactive

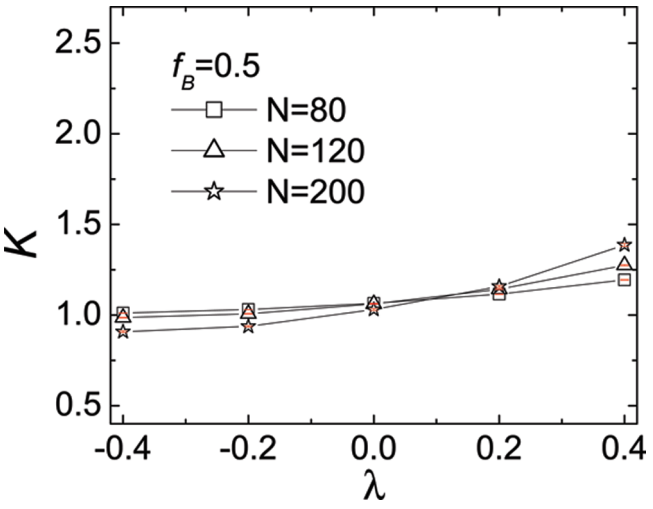

Figure 10. Plot of average K against the λ for statistical copolymers at different N. $f_B = 0.5$ and $\varepsilon_w = -0.49$.

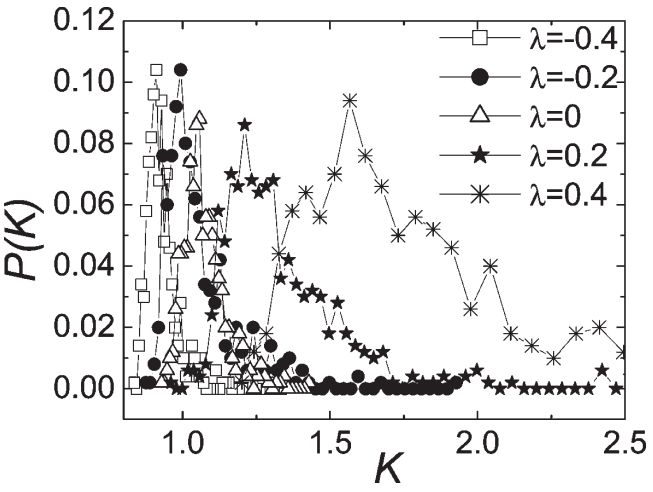

Figure 11. Histogram distributions of partition coefficient obtained from 500 copies of sequences generated with fixed $f_B = 0.5$ but varying λ. $N = 200$ and $\varepsilon_w = -0.49$. Each sequence is used in biased insertion for 1 000 000 copies to obtain the Rosenbluth−Rosenbluth weighting factor.

chromatography (IC). If the sample containing different molecular weights is subjected to IC first, then peaks resolved in IC will be a mixture of long chains with small f_B and short chains with high f_B except at the composition $f_B = 0.5$. We notice that the general trends shown in Figure 7, i.e., the retention increases with increasing the attractive B percentage, are in agreement with the experimental results.[33] Mori et al.[33] observed that the styrene−methyl methacrylate random copolymers with lower methyl methacrylate content (methyl methacrylate units are adsorbed, while styrene units are not adsorbed) are eluted earlier than those with higher methyl methacrylate content.

Recall that there are still a large number of sequences even when λ and f_B are specified; hence, the determined K at given λ and f_B has an inherent distribution. We therefore examine how the inherent distribution in sequences will affect the separation. We selected 500 sequences for each copolymer sample at a given f_B ($\lambda = 0$ and $N = 200$) and obtained chemical potential for each sequence with 1 000 000 insertion trials. Then the histogram distributions of K are obtained and are presented in Figure 8 for f_B from 0.40 to 0.60 at increment of 0.05. The histogram distribution obtained at each f_B might vary somewhat if we increase the number of sequences or number of insertion trials and we do not have a numerical way to obtain the exact distributions. These distributions presented serve as a guide to reflect the potential fluctuations in K inherent due to sequence distributions. It is clear that copolymer samples with different f_B can be resolved down to 0.05 increments despite the fluctuations in K.

Figure 9 presents the average K against f_B for the copolymers with different λ for $N = 200$ at the same $\varepsilon_w = -0.49$. The presence of λ distributions will make the separation of copolymer mixtures according to f_B become more difficult because different copolymers with different f_B and λ may correspond to the same K. For example, when $\varepsilon_w = -0.49$, the copolymers with $f_B = 0.46, \lambda = 0.4$ or $f_B = 0.52, \lambda = 0.4$ or $f_B = 0.54, \lambda = -0.4$ will be eluted at the same time because they have the same K value (see the dotted line in Figure 9).

Lastly, we examine if one can separate copolymers according to sequence order parameter λ if chemical composition is narrowly controlled. Figure 10 presents average partition coefficient K against λ for the copolymers at $N = 80$, 120, and 200 (f_B is fixed at 0.5). K increases very little with λ, which implies it is difficult to further separate copolymers with respect to λ. The histogram distributions of K at different λ are presented in Figure 11 for the copolymers at $N = 200$, $f_B = 0.5$. It is clear that the adjacent K curves overlap with each other, which implies that we cannot effectively separate copolymer mixtures according to sequence order λ at resolution of 0.2. The possibility of separation according to λ probably can only be achieved at a resolution of 0.4 or higher. These data indicate that separation of copolymers according to sequence order parameter λ will be limited. However, separation of random copolymers from block copolymers should be possible since their order parameter λ differs more than 0.4.

4. Conclusions

Statistical copolymers, for example, styrene−methyl methacrylate, ethylene−propene copolymers, etc., are important, industrially produced materials. Physical properties of such polymers depend on both the average chemical composition and the distribution of monomers sequences along the chains. Hence, separation and characterization of statistical copolymers according to both chemical composition and sequence distributions is an important subject. We investigated potential separation of statistical copolymers according to chemical composition and sequence order parameters with interactive chromatography through lattice Monte Carlo simulations. The chief purpose of this work is to examine the influence of monomer sequence distributions on the separation of copolymers in liquid chromatography. When the sequence order parameter λ is fixed or with a narrow distribution, it is possible to separate the statistical copolymers with respect to their chemical compositions by using interactive chromatography such as gradient separations at CAP or LCCC techniques. However, when the sequence order parameter λ also has a wide distribution, it will be difficult to separate the statistical copolymers according to chemical composition without interference from the sequence distribution of λ. We also compared the CAP of statistical copolymers obtained with Monte Carlo simulations with the theoretical prediction proposed by Brun.[24] It was found that simulation data agree well with the theoretical curves except for copolymers with high degree of blockiness or extremely alternating sequences.

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Appendix

Let us consider a copolymer chain with length N and f_A and f_B fractions of A and B monomer types ($f_A + f_B = 1$). The total number of possible sequences not differentiating their sequence order parameter λ is given by eq 2. In order to find the number of sequences with given λ, $W(N,f_B,\lambda)$, we note that the probability of finding diads ν_{AB} is equal to ν_{BA}. Therefore, by rearranging eqs 3−5, ν_{AB} can be written as

$$\nu_{AB} = f_A f_B(1-\lambda) \tag{13}$$

Fixing λ therefore fixes the probability of finding the dyads, and hence N_{AA}, N_{BB}, N_{AB}, and N_{BA}, which represent the total numbers of AA, BB, AB, and BA diads present in a sequence, respectively. For example, $N_{AB} = \nu_{AB}N_{tot}$ where N_{tot} is the total number of dyads, which is given by $N_{tot} = N$ (ignoring the end effect). Since $N_{AB} + N_{AA} = Nf_A$, therefore $N_{AA} = Nf_A - Nf_Af_B(1-\lambda)$ and so on. In addition, the number of consequentive A blocks present on a chain is determined by the number AB dyad. Every time you have AB dyad, you switch from an A block to B block. So the number of A blocks $A_{number} = Nf_Af_B(1-\lambda)$ with an equal number of B blocks. The only little complication we ran into here is that we did not account for the chain end effects (the last monomer has no dyad). In order to correct for the chain end effect, we need to differentiate four situations: a copolymer begin with a A monomer and end with a B monomer denoted as A(...)B, a copolymer begin with a B monomer and end with a B monomer denoted as B(...)B, and so on. In each case, there will a correction on N_{AA}, N_{AB}, N_{BA}, N_{BB}, A_{number}, and B_{number}. Table 1 tabulates these numbers for four types of copolymers.

Different sequences that satisfy fixed N_{AA}, N_{BB}, N_{AB}, N_{BA}, A_{number}, and B_{number} are realized by sorting N_A number of A monomers to A_{number} groups with minimum number of monomers in each group being one, and the same applies to B monomers. This is equivalent to the combination statistics about sorting n number of indistinguishable balls to m distinguishable boxses with each box having at least one ball. The latter is given by

$$\binom{n-1}{n-m} = \frac{(n-1)!}{(n-m)!(m-1)!}$$

By making use this combination statistics, we obtain the number of possible monomer sequence, $W(\lambda,f_A,N)$, by the following:

$$W(\lambda,f_B,N) = \frac{(N_A-1)!}{(N_A-A_{number})!(A_{number}-1)!}\frac{(N_B-1)!}{(N_B-B_{number})!(B_{number}-1)!} \tag{14}$$

We calculate the $p(\lambda)$ for the copolymer at different specified λ and f_B and present the variation of $p(\lambda)$ vs λ in Figure 1. The normalized possible monomer sequence number exhibits a Gaussian distribution with zero mean of λ at different f_B. The minimum λ value of the copolymers with a specified f_B is $-\mathrm{Min}(f_A,f_B)/\mathrm{Max}(f_A,f_B)$, where $\mathrm{Min}(f_A,f_B)$ and $\mathrm{Max}(f_A,f_B)$ are the minimum and maximum values of f_A and f_B, respectively. As a result, the curves for the copolymer at $f_B \neq 0.5$ are not symmetric in Figure 1.

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