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Can the individual block in block copolymer be made chromatographically “invisible” at the critical condition of its corresponding homopolymer?

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ABSTRACT

Liquid chromatography at the critical condition (LCCC) method has been proposed as an attractive method to characterize individual blocks in block copolymers because it can make one block chromatographically “invisible” at the critical condition of its corresponding homopolymer. However, observable dependence of retention time on the “invisible” block length was reported in LCCC experimental studies of diblock copolymer [Macromolecules 2001;34:2353–2358; Anal Chem 2001;73:3884–3889.]. In this study, we re-examined the validity of the LCCC method for AB, BAB and ABA block copolymers by the lattice Monte Carlo simulation method with using random walk (RW) and self-avoiding walk chain (SAW) models. In the current study, the A block is set in the size exclusion mode and is chromatographically “visible”. The interaction between the B type monomer and the column surface are varied to identify the critical condition of B block in the block copolymer. Our simulation results establish that individual block, i.e. B block in the current work, from the block copolymer has its own critical condition for the first time. However, it was also found that the critical condition of B block might be different from the critical condition of B homopolymer. The critical condition of B block in the AB diblock is exactly equal to the critical condition of B homopolymer only when the chain is modeled by RW model. However, deviations of the critical condition of B block away from that of the B homopolymer are observed for AB copolymer using SAW model, and also for BAB and ABA copolymers whether the chain is modeled by RW or SAW models. Moreover, under the critical condition of B homopolymer, no dependence of the partition coefficient on the “invisible” B block length was observed for the AB and BAB copolymers when the copolymer chains were modeled by RW model. Distinct dependence of the partition coefficient of these two types’ copolymers on the B block length was found when the chain was modeled by SAW model. For the ABA triblock copolymer, slight dependence of the partition coefficient on B block length was observed even for the RW model while this dependence became much stronger when the chain was modeled by SAW model. Moreover, it was also found that the partition coefficient of ABA copolymer is much smaller than those of AB and BAB copolymers under the critical condition of B homopolymer because of the chain architecture effect. The current study confirms that the block in the block copolymer is hard to be made completely chromatographically “invisible” because the intrinsic nature of the excluded volume interaction existed in real polymer system.

1. Introduction

Block copolymer is a special type of copolymer that comprises two or more chemically distinct, and frequently immiscible, polymer blocks covalently linked together. The special structure of block copolymer leads to a variety of unique properties unpossessed by the homopolymers. For example, block copolymers can self-assembled into micelles that can be used for drug delivery and other applications [1,2]. Block copolymers are also frequently added into immiscible polymer blends as compatibilizers to improve the compatibility of the blends [3–5].

It is known that the properties of the block copolymers depend on not only the chemical properties of repeat units but also the architectural arrangements of the repeat units [6–10]. For example, self-assembled morphologies from diblock copolymer in selective

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solution depend critically on the relative length of the two incompatible blocks [6]. The domain size and morphological boundaries in the self-assembly of diblock copolymers are dramatically influenced by the dispersity in the block lengths [10]. Therefore, effective separation and analysis of block copolymers according to chemical composition are essential for the better control in the application of block copolymers. It is clear that block copolymers not only have molecular weight distribution of the overall chain but also have molecular weight distribution for the individual blocks. Size exclusion chromatography (SEC) cannot provide the information on the block length distribution since the hydrodynamic volume of a copolymer chain is affected by both the overall molecular weight and the chemical composition, i.e. the relative length of individual blocks [11]. Liquid chromatography at the critical condition (LCCC) is an attractive method for the characterization of individual blocks in block copolymers [12–26]. This technique is based on the assumption that a block can be made chromatographically "invisible" at the critical condition of the corresponding homopolymer and the retention of the block copolymer is supposed to be determined solely by the other block (i.e. the "visible" block) in the block copolymer [27–29].

The LCCC analysis of block copolymer can be divided into two categories according to the elution mode of the "visible" block. One is to elute the "visible" block in the liquid adsorption chromatography (LAC) mode which means the "visible" block is more attractive with the stationary phase surfaces than the "invisible" block. For this separation mode, the retention of the "visible" block is supposed to be exponentially increases with "visible" block length since the LAC mode is dominated by the enthalpic interaction. As a result, this LCCC analysis mode is limited to end group analysis or to rather short oligomers due to the exponential dependence of the retention on the "visible" block length (Martin's rule) [12,13,15,21,23]. The other separation mode is to elute the "visible" block in a size exclusion mode that means the "visible" block is less attractive on the stationary phase surfaces than the "invisible" block. In this elution mode, the retention of the copolymer decreases with increasing in the "visible" block length because the elution is governed by the entropic exclusion. Up to now, most of the LCCC applications to the characterization of block copolymers have been made in this elution mode [14,16–20,22,24–26]. In this elution separation mode, the block length distribution of the "visible" block can be easily determined by using the standard calibration method that is commonly used in the SEC.

The principle of LCCC analysis of block copolymer is based on the assumption that one of the blocks in the block copolymer can be made chromatographically "invisible" at the critical condition of its corresponding homopolymer and the retention of block copolymer becomes independent of "invisible" block length. This assumption is supported by many experimental results [27–29]. However, Lee et al. observed some dependence of retention on "invisible" block length in the LCCC analysis of block copolymer [24,25]. Their results show that the retention of "visible" block gradually increases with increasing length of the "invisible" block when the length of the "visible" block was fixed. Computationally, Jiang et al. applied lattice Monte Carlo method to examine retention of AB diblock copolymer at the critical condition of B type homopolymer, while there is no interaction between A block and column surface which means the A block is in the SEC regime [30]. In that work, a similar dependence in the partition coefficient K was observed for the AB diblock copolymer with the same "visible" A block length but different "invisible" B block lengths.

The current study expands on the earlier computational study [30] in that we investigated LCCC analysis of block copolymer by using two different chain models, random walks (RW) where excluded volume interaction is absent and the self-avoiding walks where the excluded volume interaction is present as in real polymeric chain. The excluded volume interaction present in any real polymeric chain is ignored in theoretical investigations of polymer LCCC analysis because of the difficulty to consider this effect. In experiments, LCCC is often performed with a poor solvent close to a theta-solvent. Although it is understood that the manifestation of excluded volume interaction is minimized in a theta-solvent, for polymers partitioning into pores, the excluded volume interaction is still present and cannot be ignored even in the theta-solvent. This has been discussed in another of our previous study [31]. Clarification of effect of excluded volume interaction on LCCC analysis of block copolymer is important. Our earlier theoretical study [30] on the LCCC analysis of block copolymer did not include a comparison between RW model versus SAW model. The main purpose of the current study is to clarify if the dependence seen earlier both in experiments and simulations is due to the excluded volume effect or some other trivial effects. In addition, we would like to clarify if block copolymer can have its own critical adsorption point (CAP) and if it does, whether it will be the same as the corresponding homopolymers or it can be something different.

2. Monte Carlo simulation methods

In this study, polymer chains are modeled as RW chains and SAW chains in a simple cubic lattice with a coordination number $Z = 6$. In RW model, monomers on a polymer chain may occupy the same site on the lattice, while no two monomers may occupy the same site in SAW model. In this simulation, we investigated the LCCC separation of block copolymer into slit pores. The slit pore is modeled as a cubic lattice with dimensions of $250a \times 250a \times 30a$, where a is the lattice unit length. Periodic boundary conditions were applied in the X and Y directions, while there are impenetrable walls in the $Z = a$ and $Z = 30a$ planes representing the slit pore surfaces.

The standard chemical potential of block copolymer in the slit is determined by the biased chain insertion method. First, we randomly place the first monomer from the block chain on a site in the slit pore between $Z = 2a$ and $Z = 29a$ planes. Then, the remaining monomers of the chain are then grown using the biased chain insertion method [32]. When the monomers are on the planes of $Z = 2a$ and $Z = 29a$, we consider them as being adsorbed on pore surfaces. For all adsorbed monomers, the polymer-surface interaction energies, $\varepsilon_w(A)$ and $\varepsilon_w(B)$, are applied for A and B monomers, respectively. In this work, we set A block as the visible block(s) and it is in an ideal size exclusion mode. As a result, A type monomer does not have any interactions with the wall ($\varepsilon_w(A) = 0$). For the B block, it was already reported that it cannot be completely "invisible" at the critical condition of B homopolymer [24,25,30]. One possible reason might be because the critical condition of individual block is different from the critical condition of its corresponding homopolymer if the block copolymer really possesses its own critical condition. Therefore, we varied the interaction between B monomers and wall surface to determine the location of critical condition of B block. The determined critical condition of B block was further compared to that of B homopolymer.

Three typical types of block copolymers, i.e. AB (A_NB_M) diblock copolymers, ABA ($A_{N/2}B_MA_{N/2}$) triblock copolymers, and BAB ($B_{M/2}A_NB_{M/2}$) triblock copolymers, were investigated in the current study. Typically N ranges from 20 to 100 while M ranges from 20 to 200. The standard chemical potential of the overall block copolymer chain inside the slit, reduced by the Boltzmann factor, μ_{in}^0, is determined by biased chain insertion method. Detailed descriptions of the chain insertion method can be found in Refs. [32–39]. The partition coefficient K is calculated by the equation of $\text{In}K = -(\mu_{\text{in}}^0 - \mu_{\text{bulk}}^0)$, μ_{bulk}^0 is the standard chemical potential of the