



Discrimination of block structures in liquid adsorption chromatography of polymers. Simulation and experiment



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ABSTRACT

Di- and triblocks can be separated from each other under adsorption conditions for the outer block and critical or exclusion conditions for the inner block. If the center block is uniform, even a separation according to symmetry can be achieved. This behavior is studied in much detail by theory and simulations as well as in the chromatographic experiments with block copolymers of ethylene oxide and ϵ -caprolactone.

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1. Introduction

Polymers and oligomers with a block structure are used in many fields: if they contain blocks with different solubility they may be used as surfactants or emulsifiers, if they contain functional end groups, they may serve as building blocks, etc.

Typical examples for diblock structures are fatty alcohol ethoxylates (FAE), which are commonly used as surfactants. Typical examples of triblock structures are diesters of polyethylene glycol (PEG) with fatty acids, block copolymers of ethylene oxide with propylene oxide (often called poloxamers) and the reaction products of oligoethylene glycols with lactones (such as ϵ -caprolactone, lactide, glycolide). For example, caprolactone-diols are typically produced by polymerization of ϵ -caprolactone with a lower oligomer of ethylene oxide (EO), such as diethylene glycol (DEG).

All of these products typically contain side products: FAE may contain residual fatty alcohol, and PEG, triblocks may contain the homopolymers as well as the diblocks and unreacted starting materials: PEG esters contain not only the monoesters, but also diesters and PEG.

Obviously, these impurities may seriously affect the properties of the product. As di- and triblocks have quite different properties,

it is also important to determine the amount of diblocks in a triblock copolymer.

The homopolymers can be separated from the block copolymers by liquid chromatography at critical conditions (LCCC), hence their content in a sample can easily be determined.

This is, however, much more complicated for diblocks in triblock copolymers. In special cases such a separation can be achieved, as is the case for PEG esters with pure fatty acids, but products based on technical fatty acids typically require a two-dimensional separation [1–4].

An additional complication is caused by the fact that triblocks may also differ in symmetry: the arms of a triblock may have equal or different length: the highest asymmetry corresponds to the diblock, and there may be symmetric and asymmetric triblocks with degree of asymmetry.

In the case of diesters with fatty acids the diblocks (monoesters) with different fatty acids can easily be separated according to the chain length of the fatty acid by LCCC. A separation of the diesters according to the total number of carbon atoms in the fatty acids can also be achieved, but the degree of asymmetry in the diesters is typically not high enough to allow a separation of e.g. C12-PEG-C16 esters from C14-PEG-C14 esters.

The situation becomes even more complicated with triblocks, where the arms have a higher polydispersity, as is the case with poloxamers or caprolactone-diols.

Consequently, the characterization of such block copolymers is a difficult task: considerable advances could be achieved by different modes of liquid chromatography and mass spectroscopy (mainly MALDI-TOF-MS). Anyway, MALDI-TOF-MS is not capable

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to discriminate molecules with the same molar mass, but different architecture.

This should (at least in principle) be possible with a chromatographic separation. Indeed such separations have been described in the literature: Lee and Chang have analyzed block copolymers of EO and lactide [5,6], Park et al. have described the separation of styrene-butadiene block copolymers with different architecture [7].

A separation of diblock and triblock copolymers of poly(ethylene oxide) (PEO) and poly(ϵ -caprolactone) (PCL) by liquid chromatography has been recently reported [8]. In this study it turned out possible to separate not only diblocks and triblocks of the same chemical composition, but also symmetric and asymmetric triblocks PCL-PEO-PCL. It could be shown by MALDI-TOF-MS, that species with the same molar mass eluted as well resolved peaks.

In principle, their identification with respect to architecture would have been possible by NMR spectroscopy, but because of the low concentration of the individual oligomers this could not be achieved.

From theoretical considerations it was concluded, that the symmetric products should elute earlier than the asymmetric one (i.e. the diblock). A theory of chromatography of block copolymers [9] has predicted the principle possibility to separate block copolymers by the architecture. However, the chromatographic conditions and parameters, which will provide good separations, have not been theoretically investigated.

In this study, basing on the results of the theory [9], we present now a detailed analysis of the influence of molecular and chromatographic parameters on the separation of block copolymers. This will be helpful for finding chromatographic conditions, which allow a discrimination of block copolymers according to symmetry. By using the previously developed ‘virtual chromatography’ technique [10], we simulate possible chromatographic separations of diblocks and symmetric and asymmetric triblocks, and compare these theoretical chromatograms with the experimental ones obtained with PCL-PEO and PCL-PEO-PCL copolymers.

2. Separation mechanisms in liquid chromatography of polymers: a theoretical description

The elution of a polymer in liquid chromatography is commonly described by the following relation:

$$V_e = V_i + K \cdot V_p \quad (1)$$

wherein V_e is the elution volume, V_i is the interstitial volume, V_p is the pore volume, and K is the distribution coefficient – a parameter which characterizes the partitioning of a polymer between the flowing and the stagnant part of the liquid phase. If a theory for the distribution coefficient of various types of polymers is available, one can predict and simulate possible separations.

2.1. Homopolymers

A theory of chromatography of homopolymers is quite well developed [11–13]. The results are well-known, and here we give only the basic equations, which will be necessary for the analysis of the behavior of block copolymers.

The theory [11–13] is based on the continuum model of an ideal polymer chain in a pore. The model parameters are: $R \sim M^{1/2}$ – the radius of gyration of a polymer, $2d$ – the width of a slit-like pore, and an adsorption interaction parameter c . Negative c values correspond to effective repulsive forces. The point $c = 0$ is usually referred to as a critical adsorption point (CAP). Positive c corresponds to adsorption. At $c > 0$, a macromolecule forms an adsorption layer on the surface; and the average thickness of this layer is equal to c^{-1} .

In liquid chromatography of homopolymers, the most common technique to determine molar mass distributions (MMD) is size exclusion chromatography (SEC), which separates according to molecular size. In ideal SEC, c is strongly negative ($-c \rightarrow \infty$). The well-known approximations of the SEC-mode distribution coefficient $K^{(SEC)}$ in wide and in narrow pores are the following [11]:

$$K^{(SEC)} \approx \begin{cases} 1 - \frac{2}{\sqrt{\pi}} \frac{R}{d}, & R/d < 0.46 \\ \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 R^2}{4d^2}\right), & R/d > 0.46 \end{cases} \quad (2)$$

According to Eq. (2), in SEC, K can assume values between 0 and 1, and a polymer elutes in between V_i and $V_i + V_p$; the elution volume in SEC decreases with R (and hence, with molar mass M).

Liquid adsorption chromatography (LAC) separates according to the number of structural units, which may interact with the stationary phase, and the strength of this interaction. In LAC, at $c > 0$, $K^{(ads)} > 1$ and increases with M . At strong adsorption condition (i.e. $cR > 1$), $K^{(ads)}$ for a polymer of n chain units can be approximated by

$$K^{(ads)} \approx 1 + \frac{2}{cd} \left[\exp(c^2 R^2) - \frac{cR}{\sqrt{\pi}} \right] \approx 1 + \frac{2 \exp(c^2 R^2)}{cd} \approx 1 + \frac{2 \exp(c^2 nb^2/6)}{cd} \quad (3)$$

Liquid chromatography under critical conditions (LCCC) is the limiting case between size exclusion and adsorption. In LCCC (at $c = 0$), $K^{(cr)} = 1$ [12,13], which corresponds to the elution at the void volume $V_0 = V_i + V_p$. At the CAP all chains with the same repeat unit elute at the same position (regardless their molar mass), in other words, a polymer chain at the CAP becomes ‘‘chromatographically invisible’’.

2.2. Block copolymers AB and ABA

A theory of chromatography of block copolymers AB and ABA has been also developed in much detail [9,14–19]. In block structures containing two different repeat units (of A and B types), two interaction parameters (c_A and c_B) must be taken into account.

For a diblock AB , depending on c_A and c_B , the following situations can be possible:

1. c_A and c_B are negative: the diblock elutes in SEC mode.
2. c_A and c_B are positive: the diblock elutes in LAC mode.
3. $c_A < 0$; $c_B = 0$: B is invisible, separation according to A in SEC mode.
4. $c_A > 0$; $c_B = 0$: B is invisible, separation according to A in LAC mode.
5. $c_A > 0$; $c_B < 0$. The copolymers AB are strongly retained, like in the LAC mode, but the individual homologues of B elute in SEC order. This is utilized in liquid exclusion adsorption chromatography (LEAC) [20].

Evidently, other possible situations $c_A = 0$; $c_B < 0$, $c_A = 0$; $c_B > 0$, and $c_B > 0$; $c_A < 0$ are just the situations 3, 4, and 5 (with A and B interchanged).

It must be mentioned, that the behavior of triblocks ABA is somewhat different from that of a diblock AB ; the differences are more pronounced in the cases 3, 4 and 5. In particular, as has been mentioned in previous papers [2,7,9], the block B in an ABA triblock does not become invisible at the CAP for B (as it would do in an AB diblock)! This offers a chance to discriminate di- and triblocks with the same number of repeat units in the A blocks.

Here we shall focus on the situations where the strong adsorption condition is realized for block(s) A ($c_A \equiv c \gg 1/R_A$). Furthermore,

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