

Theory of chromatographic separation of linear and star-shaped binary block-copolymers

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Abstract

Equations for the distribution coefficient of heteroarm stars are derived by using a model of an ideal chain in a slit-like pore; these equations together with those previously reported for linear block-copolymers are applied to describe chromatography of such copolymers. According to the theory, the retention generally depends on molar mass, composition, and architecture (microstructure and topology) of copolymers, on pore size and on adsorption interaction of chain units *A* and *B*. Three special modes of chromatography are studied in detail. (i) If interactions for *A* and *B* are close to the critical point of adsorption (CPA), the retention practically does not depend on architecture, and high molar mass copolymers can be separated by composition. (ii) At SEC condition for *B* and strong adsorption for *A*, copolymers in principle can be separated by architecture; better separation is expected in wide pores. Retention of linear block-copolymers decreases with increasing of the number of blocks; for heteroarm stars the theory predicts retention decreasing as: $AB > StarAAB > StarABB$; $StarAAAB > StarABBB > StarAABB$; $StarAAAAB > StarABBBB > StarAAABB > StarAABBB$. (iii) At the CPA for *B* copolymers *AB*, *BAB* and heteroarm stars regardless molar mass of *B*, M_B , can be separated by M_A . The same is true for *ABA* and *ABAB*. . . *A* in narrow pores. While the retention of *AB*, *BAB*, . . . *B* and *Star AB*. . . *B* is the same, copolymers *AB*, *ABA* and linear multiblock-copolymers can be separated, as well as symmetric and very asymmetric triblock-copolymers *ABA*.

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1. Introduction

Block-copolymers are constituents of many practically important materials. Properties of copolymers depend not only on average molar mass and polydispersity, but also on average chemical composition and compositional heterogeneity. Generally, the heterogeneity of a diblock-copolymer *AB* may be characterized by a two-dimensional distribution function (which can be a distribution either by molar mass and composition or by molar mass of blocks *A* and *B*). The determination of two-dimensional molar mass–composition distribution is, therefore, an important step in the copolymer characterization.

Both size-exclusion and adsorption chromatography has proven itself as useful tools for analysis and separation of copolymers. It turned, however, to be a matter of difficulty that chromatographic retention is generally influenced by both molar mass and composition of copolymers. Therefore, in order to succeed in the analysis of copolymers by chromatography, it is important to find such conditions at which retention is mainly governed by only one of these factors. If such conditions are available, stage-by-stage strategies of analysis of copolymers become possible. For example, one can first separate diblock-copolymers by composition, and then subject fractions to the second chromatographic process at changed conditions, thus further separating these with respect to molar mass. Another possibility is to separate diblock-copolymers according first to the length of block *B*, and then, to the length of the other block *A*. Both schemes

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result in getting two-dimensional function of a distribution on composition and molar mass. Many reports on experimental studies were published demonstrating a wonderful potential of chromatography in the analysis of copolymers [1–29].

Along with molar mass and composition of importance is the molecular architecture (microstructure and topology) of copolymers. Therefore, such goals are challenging as, for example, separation of di- and triblock-copolymers; linear and branched copolymers; block- and statistical copolymers. The question is whether these separations can be achieved by chromatography. For all that of special interest are regimes of chromatography which allow separation of copolymers of the same molar mass and composition, but of different architecture.

Experimental selection of optimum regimes for separation of copolymers is very laborious, material- and time-consuming way; generally, it requires sets of well-defined copolymeric standards. A theory could provide a more efficient way to the goals of optimization.

A molecular-statistical theory of interactive chromatography of copolymers has been originated by Skvortsov and Gorbunov [30–32]; mostly the case of narrow-pore adsorbents and high molar mass diblock-copolymers was considered in those papers. Brun [33] and Brun and Alden [34] has applied a theory to describe features of gradient chromatographic separation of statistical copolymers by composition. DiMarzio et al. [35] and Guttman et al. [36] have developed a lattice-model-based theory and performed calculations of the distribution coefficient of copolymers of various architectures. Ennis and Jönsson [37] have derived equations for the distribution coefficient of a linear multiblock-copolymer; these equations, however, were not used to analyze features of chromatography. Kosmas et al. [38] have obtained some theoretical results, which are relevant to chromatography of star-block-copolymers on wide pore adsorbents. Although a considerable progress in the theory of chromatography of copolymers was achieved, a problem of separation of copolymers by architecture is far from being thoroughly understood.

The main objective of the present paper is a theoretical analysis of chromatographic behavior of binary block-copolymers of different architecture. We shall consider linear di-, tri- and multiblock-copolymers, as well as star-shaped copolymers. By using a continuum model of a macromolecule in a slit-like pore, we shall derive exact equations for the distribution coefficient of star-shaped block-copolymers; we shall use also the exact results previously obtained for homopolymer and linear block-copolymers. Our analysis will be focused on the chromatographic behavior of binary block-copolymers at three special modes of interactive chromatography.

We shall first revisit the situation which is relevant to the analysis and separation of block-copolymers by liquid chromatography at the critical conditions (LCCC), where the CPA is realized for one of the components, B . These special condi-

tions are important because it is known that retention of linear diblock-copolymers AB under such conditions becomes independent of M_B , and such copolymers can be separated by molar mass of the other component A , M_A . We shall analyze the behavior of binary copolymers of different architecture under these special conditions.

Then, we shall proceed to another interesting situation where interaction parameters for A and B , being of different sign, are close to the CPA. As it will be shown, under these conditions the chromatographic behavior of binary copolymers practically does not depend on architecture.

Finally, we shall study the chromatographic behavior at the SEC condition for B and strong adsorption for A . This mode of chromatography has proven to be very convenient for separating oligomeric block-copolymers [24–27,39–41]. We shall discuss the possibility for separation of binary linear and star-shaped block-copolymers by architecture by using this special mode of chromatography.

2. Distribution coefficient of linear and star-shaped binary block-copolymers

In order to analyze the chromatographic behavior of block-copolymers we use a theory for the distribution coefficient, which is based on the continuum model of an ideal polymer chain in a slit-like pore. We shall consider binary block-copolymers, which include chain fragments of two different types, A and B .

Fig. 1 shows two families of binary block-copolymers under the consideration: linear block-copolymers and heteroarm stars. A diblock-copolymer AB can be considered as the simplest member of both series. Only the basic topological structures are shown in Fig. 1, but we shall distinguish some of the topological analogues, such as e.g. ABA and BAB or $StarABB$ and $StarAAB$, etc., since the blocks A and B are assumed as being chemically different, and one may expect that such analogues would behave in chromatography in a different way.

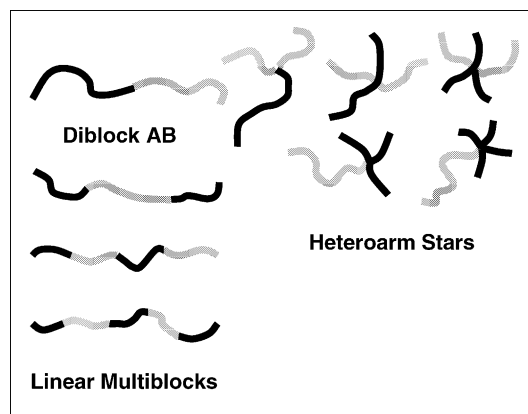


Fig. 1. Two families of binary block-copolymers.

2.1. Linear homopolymer and block-copolymers

An exact equation for the distribution coefficient K of a linear homopolymer has a form [42,43]:

$$K_{ABA} = \sum_{k,l,m=1}^{\infty} \frac{8\lambda_A^2 \beta_l^2 (\lambda_A - \lambda_B)^2 \exp(-\alpha_k^2 g_{A1}^2 - \beta_l^2 g_B^2 - \alpha_m^2 g_{A2}^2)}{(\lambda_A + \lambda_A^2 + \alpha_k^2)(\lambda_B + \lambda_B^2 + \beta_l^2)(\lambda_A + \lambda_A^2 + \alpha_m^2)(\alpha_k^2 - \beta_l^2)(\alpha_m^2 - \beta_l^2)} \quad (4)$$

$$K_{\text{lin}} = \sum_{k=1}^{\infty} \frac{2\lambda^2 \exp(-\alpha_k^2 g^2)}{\alpha_k^2 (\lambda + \lambda^2 + \alpha_k^2)} \quad (1)$$

where $g = R/d$ is macromolecule-to-pore size ratio ($R \propto \sqrt{M}$ is the radius of gyration of a free ideal linear chain); $\lambda = -cd$; and α_k are the roots of the equation:

$$\alpha_k \operatorname{tg}(\alpha_k) = \lambda, \quad k = 1, 2, \dots, \infty \quad (2)$$

A parameter c serves in the theory as the adsorption interaction parameter. The interaction is assumed to be short-ranged. Negative c values correspond to effective repulsive forces. The point $c = 0$, at which the adsorption of an infinitely long chain starts is usually referred to as an adsorption threshold point or as a critical point of adsorption. Positive values of c correspond to adsorption. At $c > 0$, a sufficiently long macromolecule forms an adsorption layer on the surface; the average thickness of this layer is equal to c^{-1} .

Simpler asymptotic equations describing chromatographic behavior of a homopolymer at both $R > d$ and $R < d$, and at various interaction conditions have been also reported [42].

In the theory for a diblock-copolymer [31], two interaction parameters c_A and c_B were introduced to account for different interaction of blocks A and B with pore walls. According to [31], an exact equation for the distribution coefficient of a linear diblock-copolymer has a form:

$$K_{\text{lin}}^{(A,B)} = \sum_{k,l=1}^{\infty} \frac{4\lambda_A \lambda_B (\lambda_A - \lambda_B) \exp(-\alpha_k^2 g_A^2 - \beta_l^2 g_B^2)}{(\lambda_A + \lambda_A^2 + \alpha_k^2)(\lambda_B + \lambda_B^2 + \beta_l^2)(\alpha_k^2 - \beta_l^2)} \quad (3)$$

where α_k , and β_l are roots of the Eq. (2) with corresponding parameters λ_A and λ_B ;

$$g_i = \frac{R_i}{d}; \quad \lambda_i = -c_i d \quad (i = A, B).$$

A set of simpler asymptotic equations for the narrow-pore situation ($R_A, R_B \gg d$) at various interaction conditions was presented in [31]. We have derived approximate formulae for the wide-pore situation $R_A, R_B \ll d$. These equations are given in the Appendix A. There can be even more regimes of specific chromatographic behavior of diblock-copolymers if R_A and R_B are very different. For example, if $R_A \gg R_B$, apart from narrow-pore ($R_A, R_B \gg d$) and wide-pore ($R_A, R_B \ll d$)

situations there can be a situation of $R_A \gg d$ and $R_B \ll d$. Of course, all these situations are covered by the general Eq. (3).

An equation describing multi-block linear copolymers has been derived by Ennis and Jönsson [37]. In particular, the result for a binary triblock-copolymer ABA can be written down in a form:

where α_k and α_m are the k -th and the m -th roots of the Eq. (2) with a parameter λ_A ; and β_l is the l -th root of this equation with the parameter λ_B ; $g_{A1} = R_{A1}/d$; $g_{A2} = R_{A2}/d$; $g_B = R_B/d$; $\lambda_A = -c_A d$; $\lambda_B = -c_B d$.

Equations for linear copolymers with four, five and more blocks are rather complicated, but suitable for numerical calculation.

2.2. Star-block-copolymers

The distribution coefficient K_{star} of a star-block-copolymer with f arms of different length and chemical nature, which is equal to the ratio of the partition functions for this copolymer within a slit-like pore of a width $2d$ and in an unrestricted space of the same volume, is equal

$$K_{\text{star}} = (2d)^{-1} \int_{-d}^d dx \prod_{i=1}^f P_i(x) \quad (5)$$

where $P_i(x)$ is a sub-partition function of a polymer chain i (i -th arm of a star), having one end at the distance x from the plane corresponding to the middle of the slit. According to [42], the expression for $P_i(x)$ has a form

$$P_i(x) = \sum_{k_i=1}^{\infty} \frac{2\lambda_i \cos(\alpha_{i,k_i} x/d) \operatorname{sec}(\alpha_{i,k_i})}{\lambda_i + \lambda_i^2 + \alpha_{i,k_i}^2} \exp(-\alpha_{i,k_i}^2 g_i^2) \quad (6)$$

where $g_i = R_i/d$, $\lambda_i = -c_i d$, and an eigenvalue α_{i,k_i} is the k_i -th root of Eq. (2).

After the substitution of functions $P_i(x)$ as given by Eq. (6) into the Eq. (5), one obtains the general formula for the distribution coefficient of a star-block-copolymer:

$$K_{\text{star}} = 2^f \sum_{k_1, k_2, \dots, k_f=1}^{\infty} I_{k_1, k_2, \dots, k_f} \prod_{i=1}^f \frac{\lambda_i \operatorname{sec}(\alpha_{i,k_i})}{\lambda_i + \lambda_i^2 + \alpha_{i,k_i}^2} \times \exp\left(-\sum_{i=1}^f \alpha_{i,k_i}^2 g_i^2\right), \quad (7)$$

where

$$I_{k_1, k_2, \dots, k_f} = \int_0^1 \cos(\alpha_{1,k_1} \varphi) \cos(\alpha_{2,k_2} \varphi) \dots \cos(\alpha_{f,k_f} \varphi) d\varphi$$

For specified number of arms ($f = 1, 2, 3$, etc.), the integration can be completed. The integration with $f = 1$ and 2

of course results in Eq. (1) for a homopolymer and in Eq. (2) for a diblock-copolymer. The exact results obtained for stars with $f=3$ and 4 are presented in Appendix B. Even more lengthy equations are obtained for star-copolymers with five arms.

At some special values of λ and at some eigenvalues the denominators of the Eqs. (1), (3) and (4), (B.1) and (B.2) turn zero; however, the numerators turn zero as well. Such uncertainties always can be resolved by means of taking corresponding limits.

The theory describes stars generally having different arms. Stars with arms of the same chemical nature and binary stars that are shown in Fig. 1 are important special cases, which are covered by the theory.

We shall use the Eqs. (3)–(7) and (B.1), (B.2) to analyze chromatographic behavior of binary block-copolymers and to predict separation of these polymers by chromatography.

3. Analysis of the chromatographic behavior of linear and star-shaped binary block-copolymers

Theory covers a variety of physically different regimes of chromatography, those corresponding to various interactions of components A and B with the adsorbent, as well as to the narrow- and wide-pore situations. In the present study, we are especially interested in the conditions, at which the retention becomes practically independent of one of the parameters of the structure of a copolymer (for example, of the length of one of the blocks, of molar mass, or of architecture). At our focus will be also the conditions, at which copolymers differing only in architecture could be separated from each others.

3.1. Critical interaction condition for one of the components

It has been found previously [31,32] that for many types of binary block-copolymers the separation by molar mass of one component can be achieved at the CPA condition for the other component. For example, at the CPA for a block (blocks) B the retention of the copolymers AB , BAB , and heteroarm stars $Star AB \dots B$ and $Star AAB \dots B$ (with f arms of the type B) will be determined by the contour length of a chain A (that is by M_A) and will not depend on M_B . For these copolymers at the CPA for B (at $c_B=0$) in both narrow and wide pores K is equal:

$$K_{\text{copolymer}} = K_A, \quad (8)$$

where K_A is the distribution coefficient of a linear homopolymer A of the same contour length as the chains of a copolymer.

Eq. (8) stays also valid for block-copolymers $Star A \dots AB \dots B$. However, now K_A in Eq. (8) has a meaning of that of a star-homopolymer $Star A \dots A$. For these copolymers, K also does not depend on M_B , but is different to some

extent from that of the copolymers of the first group (see Fig. 2). The reason is in the difference in the distribution coefficients of linear and star-shaped homopolymers of equal contour length.

At high values of g_B , the distribution coefficient of a triblock-copolymer ABA also does not depend on g_B , being approximately equal [32]:

$$K_{A_1 B A_2} \approx K_{A_1} K_{A_2}, \quad (9)$$

while for a linear copolymer $ABAB \dots A$ with n blocks of the type A at the situation where all $g_{B_i} \gg 1$, the result is [32]:

$$K_{A_1 B_1 A_2 B_2 \dots A_n} \approx K_{A_1} K_{A_2} \dots K_{A_n} \quad (10)$$

At small values of g_B the chromatographic behavior of linear copolymers ABA and $ABAB \dots A$ at the CPA condition for B is different from that of a diblock-copolymer and of the above mentioned star-block-copolymers. Fig. 2a and b

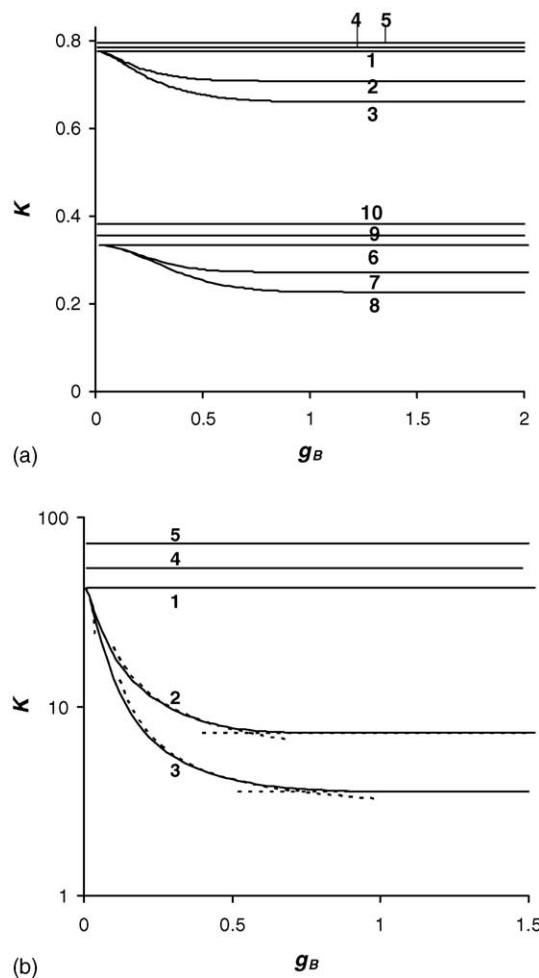


Fig. 2. Dependences of K on $g_B = R_B/d$ for several types of symmetric block-copolymers at the critical interaction for ($\lambda_B = 0$). (a) Condition of SEC for A ($\lambda_A = 1000$); $g_A = 0.2$ (1–5) and 0.6 (6–10). (b) Condition of strong adsorption for A ($\lambda_A = -25$); $g_A = 0.1$. (1, 6) Block-copolymers AB , BAB , $StarAB \dots B$ and $StarAAB \dots B$; (2, 7): ABA ; (3, 8): $ABABA$; (4, 9): $StarAAAAB \dots B$; (5, 10): $StarAAAAAB \dots B$. Dotted lines represent approximate Eqs. (9)–(12).

show the dependences of K on g_B for AB , ABA and $ABABA$ copolymers at the CPA for B . Fig. 2a corresponds to the SEC condition for blocks A ; the case of strong adsorption for A is shown in Fig. 2b. In both cases symmetrical tri- and multiblock-copolymers are considered (if there are several blocks of the same type, these blocks are assumed of equal length). In Fig. 2, the distribution coefficient is plotted versus $g_B = \sqrt{\sum R_{B_i}^2/d}$; we compare copolymers at fixed $g_A = \sqrt{\sum R_{A_i}^2/d}$ (that is at equal M_A).

Fig. 2 shows that in wide pores or at low M_B (at $g_B < 1$) K_{ABA} depends on g_B (being a decreasing function of g_B). A similar dependence has been previously reported by Guttman et al. in their lattice-model-based study [36]. A very similar effect for polymers with adsorption-active end groups has been predicted and was extensively discussed in [44–48]. This effect was really observed for difunctional oligomers of PEG [46]. Recently, Park et al. [28] have observed a difference in the retention of di- and tri-blocks of polystyrene (PS) and polybutadiene (PB). They found that at the CPA for PB and at SEC condition for PS retention of SBS triblock-copolymers is lower than that of SB and BSB copolymers, which agrees well with the theory.

By using the analogy between the chromatographic behavior of a difunctional macromolecule and a copolymer ABA [41], we have obtained the following approximate equation for the distribution coefficient of a triblock-copolymer at $c_B = 0$, $c_A \gg R_A^{-1}$, and $c_A^{-1} \ll R_B \ll d$:

$$K_{A_1BA_2} \approx 1 + (K_{A_1} - 1) + (K_{A_2} - 1) + \frac{(K_{A_1} - 1)(K_{A_2} - 1)}{\sqrt{\pi}g_B} \quad (11)$$

At $R_B \ll c_A^{-1}$ the distribution coefficient of a triblock-copolymer tends to that of a corresponding homopolymer A_1A_2 as $K_{A_1BA_2} \approx K_{A_1A_2}(1 - \lambda_A^2 g_B^2)$.

According to the theory, the behavior of linear multiblock-copolymers at small g_B is qualitatively similar to that of a triblock-copolymer. In particular, in the situation of wide pores and strong adsorption of A , the distribution coefficient of a copolymer $A_1B_1A_2B_2$ can be approximated by the Eq. (11) with g_B changed to g_{B_2} , while for a pentablock-copolymer, we have obtained the following approximation:

$$K_{A_1B_1A_2B_2A_3} \approx 1 + (q_1 + q_2 + q_3) + \frac{1}{\sqrt{\pi}} \left(\frac{q_1q_2}{g_{B_1}} + \frac{q_2q_3}{g_{B_2}} + \frac{q_1q_3}{g_{B_1A_2B_2}} \right) + \frac{q_1q_2q_3}{\pi g_{B_1}g_{B_2}} \quad (12)$$

where $q_i = K_{A_i} - 1$, $i = 1, 2, 3$; and $g_{B_1A_2B_2} = \sqrt{g_{B_1}^2 + g_{A_2}^2 + g_{B_2}^2}$.

Dotted lines in Fig. 2b correspond to the approximate Eqs. (9)–(12). As it can be seen, these approximations are quite reasonable.

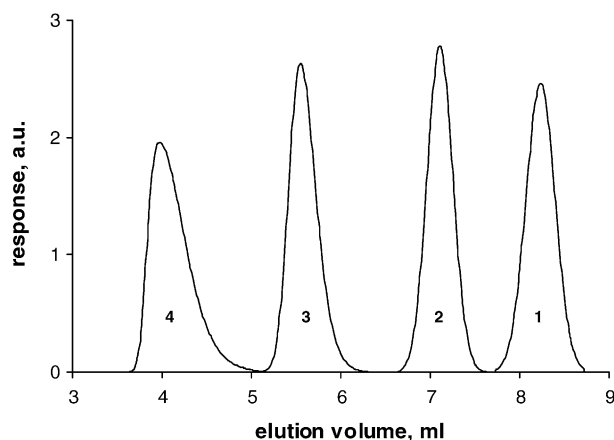


Fig. 3. A chromatogram simulated for a model mixture of AB , asymmetric and symmetric ABA copolymers at the CPA for polyoxyethylene block B and strong adsorption condition for hydrocarbon block(s) A . Components of the mixture are copolymers of equal average molar mass and composition (each consisting of monodisperse block(s) A of total $M = 252$ and block B with $M_w = 5000$ and $M_w/M_n = 1.5$): (1) diblock-copolymer AB ; asymmetric triblock-copolymers A_1BA_2 with (2) $M_{A_1} : M_{A_2} = 1 : 17$ and (3) $M_{A_1} : M_{A_2} = 3 : 15$, (4) symmetric triblock-copolymer ABA . Simulation parameters: $c_A = 3$; $2d = 12$ nm; pore volume, $V_p = 1$ ml; interstitial volume, $V_i = 1$ ml.

So, according to the theory, at the CPA condition for a component B linear copolymers AB , BAB and heteroarm stars $Star AB \dots B$ and $Star AAB \dots B$ regardless their molecular architecture and M_B can be separated by M_A .

As it follows from Fig. 2 and Eqs. (9)–(12), there is a difference in the retention of AB , ABA and linear multiblock-copolymers at the CPA for B . This difference is rather small in the case of SEC condition for A (Fig. 2a), but becomes quite pronounced if blocks A are strongly adsorbable (Fig. 2b). Therefore, one may expect that copolymers AB , ABA and multiblock-copolymers having the same M_A but polydisperse in M_B can be efficiently separated from each other at the latter conditions. The theory predicts that it is even possible to separate symmetric and very asymmetric copolymers, such as, e.g. symmetric and asymmetric triblock-copolymers.

In order to visualize the expected separations of copolymers we apply a ‘virtual chromatograph’ [49], a special software for the computer-assisted simulation of chromatograms of polymers, which is based on the theory of the distribution coefficient. The virtual chromatography technique has been already used to predict separations of polydisperse polymers of various types [24,25,41]; in those studies, simulated chromatograms have proven to be very similar to the real ones. By using the exact Eqs. (3) and (4), we have simulated chromatograms for a mixture of copolymers AB with symmetric and asymmetric ABA ; one example is shown in Fig. 3. Fig. 3 presents a chromatogram simulated for block-copolymers with poly(ethyleneoxide) block B and hydrocarbon chain in block(s) A (copolymers such as fatty alcohol ethoxylates or fatty acid polyglycolesters and chromato-

graphic conditions reported in the papers on the analysis of these copolymers by LCCC [25,27,41] can be imagined for a reference to real-life systems). As can be seen, quite good separation may be expected for symmetric and very asymmetric ABA copolymers, even if they have a polydisperse block B.

3.2. Interaction conditions for A and B are close to the critical point

It has been shown previously [30,31] that in the situation where the interaction parameters c_A and c_B are of different sign it is possible to separate diblock-copolymers by composition. From the practical standpoint, the conditions are of interest at which separation by composition is not affected by architecture.

At $|\lambda_A|, |\lambda_B| \ll 1$, Eq. (3) for a diblock-copolymer reduces to the following approximate formula:

$$K \approx \exp(-\bar{\lambda}g^2) \quad (13)$$

where $g^2 = g_A^2 + g_B^2$, and

$$\bar{\lambda} = \xi_A \lambda_A + \xi_B \lambda_B \left(\xi_i = \frac{R_i^2}{R^2}; i = A, B \right). \quad (14)$$

According to Eqs. (13) and (14), the distribution coefficient depends on both molar mass and composition of a copolymer.

Eq. (13) has the same form as that for a homopolymer with an effective interaction parameter $\bar{\lambda}$ (at $|\bar{\lambda}| \ll 1$) [43]. It follows from Eq. (14), that if λ_A and λ_B are of different sign, for example, if $\lambda_A < 0, \lambda_B > 0$ (this situation corresponds to weak adsorption interaction for A and pre-critical interaction for B), then at some special composition of a copolymer, namely at $\xi_A^* \approx \lambda_B / (\lambda_B - \lambda_A)$, $\bar{\lambda}$ turns zero, and the distribution coefficient of a copolymer of this special composition becomes independent of both molar mass and pore size, being equal unity, like it happens with a homopolymer at the CPA (at $\lambda = 0$).

For all copolymers with $\xi_A > \xi_A^*$ $K > 1$ and exponentially increases with M at high $g = R/d$. At $g > 1$ (that is, at high M or in narrow pores), all such copolymers are strongly retained. To the other hand, copolymers with $\xi_A < \xi_A^*$ at high g possess exponentially small values of the distribution coefficient. Thus, it follows from the theory that high molar mass copolymers with $\xi_A > \xi_A^*$ and $\xi_A < \xi_A^*$ can be efficiently separated by using the narrow-pore adsorbents.

An important theoretical result is that at $|\lambda_A|, |\lambda_B| \ll 1$, K of all considered copolymers is described by the same Eq. (13) with

$$\bar{\lambda} = \sum \xi_i \lambda_i \quad (15)$$

This implies that under such conditions the considered block-copolymers (regardless of architecture) have the same dependence of K on molar mass and composition.

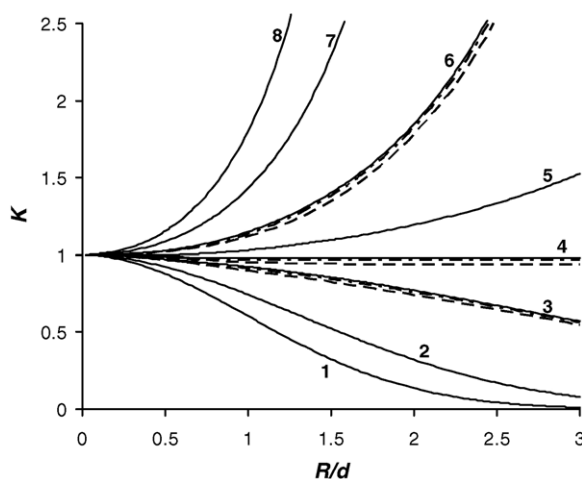


Fig. 4. Dependences of K on R/d (where $R = \sqrt{R_A^2 + R_B^2}$) for copolymers AB (solid lines), ABA (dash-dotted) and ABABA (dashed) of various composition. Values of the parameter $\xi_A = R_A^2/R^2$: 0 (1); 0.2 (2); 0.4 (3); 0.455 (4); 0.5 (5); 0.6 (6); 0.8 (7); and 1 (8).

This type of chromatographic behavior and its practical independence on architecture of copolymers holds also good in broader region of interaction conditions, namely, at $|\lambda_A|, |\lambda_B| < 1$.

Fig. 4 shows the dependences of K on the ratio R/d calculated by using the exact equations of Section 2 at $\lambda_A = -0.5, \lambda_B = 0.6$.

Each curve in Fig. 4 corresponds to a copolymer of fixed composition. One can see that at the threshold composition $\xi_A^* \approx \lambda_B(1 + \lambda_A/3)/(\lambda_B - \lambda_A) \approx 0.455$, K practically does not depend on g , while at $\xi_A > \xi_A^*$ or $\xi_A < \xi_A^*$, there is either increase or decrease of K with g .

Solid lines in Fig. 4 correspond to a copolymer AB; dash-dotted and dashed lines show the results for the copolymers ABA and ABABA at $\xi_A \approx 0.4, \xi_A \approx 0.455$ and $\xi_A \approx 0.6$. The calculated data for the other considered copolymers (these curves are not shown in Fig. 4) have turned to be even closer to the results for a diblock-copolymer than those for ABABA.

Since ξ_A^* depends on λ_A and λ_B , one can use gradient chromatography in order to move ξ_A^* by changing interaction conditions, thus gradually separating diblock-copolymers according to composition. As it follows from the theory, one may expect that the separation of high molar mass copolymers by composition in narrow pores will not depend on the copolymer molar mass.

It has been shown by Brun [33] that equations practically coinciding with Eqs. (13) and (14) describe also chromatography of statistical copolymers at the interactions of the components in the vicinity of the CPA. This allows the use of gradient chromatography for separation of such copolymers by composition [33,34].

Thus, it follows from the theory, that it is possible to separate binary copolymers by composition regardless of molar mass and architecture by using narrow-pore adsorbents and

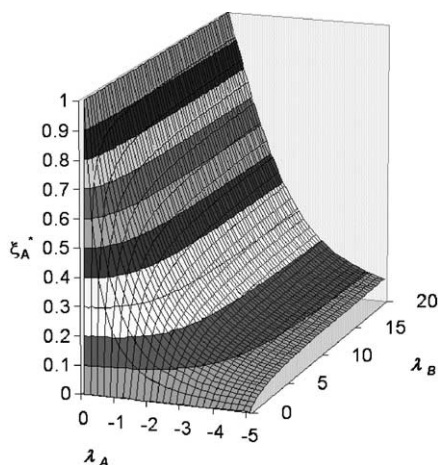


Fig. 5. Dependence of the threshold composition ξ_A^* of high molar mass binary block-copolymers on the interaction parameters λ_A and λ_B .

specially selected conditions corresponding to weak near-critical interactions.

3.3. Separation diagram and chromatographic behavior at very different λ_A and λ_B

It follows from Eqs. (3) and (4), (B1) and (B2) that the threshold composition ξ_A^* for binary copolymers of considered types is determined by a general formula:

$$\xi_A^*(\lambda_A, \lambda_B) = \frac{\beta_1^2}{\beta_1^2 - \alpha_1^2} \quad (16)$$

where $\alpha_1 = \alpha_1(\lambda_A)$ and $\beta_1 = \beta_1(\lambda_B)$ are the principal roots of the Eq. (2); λ_A and λ_B are of different sign. Assuming negative values of λ_A (adsorption interaction for A) and positive λ_B (effective repulsion for B), we have calculated ξ_A^* as a function of λ_A and λ_B (Fig. 5).

Fig. 5 represents a separation diagram for high molar mass binary copolymers. At given λ_A and λ_B copolymers with $\xi_A > \xi_A^*(\lambda_A, \lambda_B)$ are strongly adsorbed and retained in the column package, while those with $\xi_A < \xi_A^*(\lambda_A, \lambda_B)$ are not adsorbed and moving along the column.

It follows from Fig. 5 that separation of copolymers of different composition is also possible, when components A and B are very different in their adsorption properties. However, the chromatographic behavior of block-copolymers at very different λ_A and λ_B becomes more complicated than at interactions close to the CPA.

Fig. 6 is similar to Fig. 4, but calculated at quite different λ_A and λ_B . Solid lines correspond to diblock-copolymers of various compositions. The behavior of *StarAAB*, *ABA* and *ABABA* block-copolymers is also shown in Fig. 6 at several selected values of composition.

As it follows from the theory (see the results given in the Appendix A), at very different λ_A and λ_B , the behavior of a diblock-copolymer of a given composition is no longer

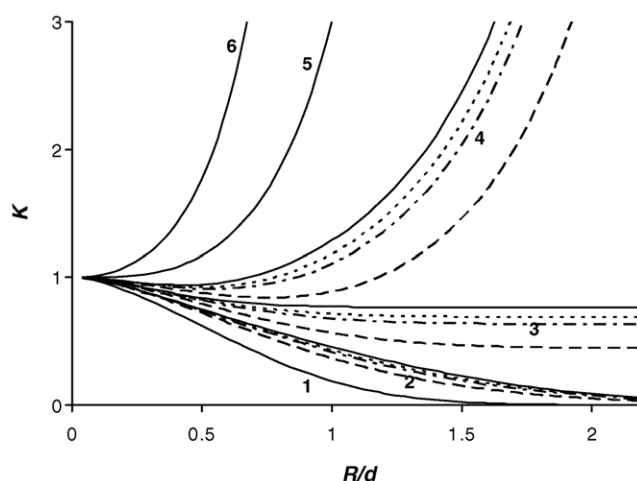


Fig. 6. Dependences of the distribution coefficient of binary block-copolymers *AB* (solid lines), *StarAAB* (dotted), *ABA* (dash-dotted) and *ABABA* (dashed) on the parameter $g = R/d$. $\lambda_A = -1.5$, $\lambda_B = 4$; $\xi_A = 0$ (1), 0.25 (2), 0.378 (3), 0.5 (4), 0.7 (5) and 1 (6).

exactly equivalent to that of a homopolymer with some effective interaction parameter. However, as it can be seen in Fig. 6 at high values of g features of chromatographic behavior of diblock-copolymers at varying adsorption interaction are still similar to some extent to that of homopolymers: K exponentially increases or decreases with g at high g , depending on whether $\xi_A > \xi_A^*$ or $\xi_A < \xi_A^*$. The distribution coefficient of a diblock-copolymer of the threshold composition ξ_A^* still stays independent on M at high M or in narrow pores (at $g > 1$). The threshold value of the distribution coefficient K^* is, however, less than unity now; K^* decreases with g at $g < 1$. According to the theory, this decrease is more pronounced at big difference in interaction parameters of the components.

Fig. 6 demonstrates that at very different λ_A and λ_B copolymers of *AB*, *ABA*, *ABABA* and *StarAAB* types behave in a similar way, but some quantitative differences appear now.

3.4. Condition of SEC for B and adsorption for A

Since the difference in K due to the molecular architecture of copolymers increases with the increase of the difference between λ_A and λ_B (Figs. 4 and 6), one may expect a considerable separation of block-copolymers of different type under the conditions of size-exclusion chromatography for one component of a copolymer and of strong adsorption, for the other one.

At $-\lambda_A g_A = c_A R_A \gg 1$, $\lambda_B g_B \gg 1$, the distribution coefficient of a high molar mass diblock-copolymer with $R_B \gg d$ can be approximated by the following equation:

$$K_{AB} \approx 4 \left(\lambda_A^2 + \frac{\pi^2}{4} \right)^{-1} \exp \left(\lambda_A^2 g_A^2 - \frac{\pi^2}{4} g_B^2 \right), \quad (17)$$

while (as it follows from the Appendix A) for lower diblock-copolymers at $c_A^{-1} \ll R_B \ll 1$

$$K_{AB} \approx 1 - \frac{2}{\sqrt{\pi}}g + \frac{2}{\sqrt{\pi}} \frac{\exp(\lambda_A^2 g_A^2)}{\lambda_A^2 g_B} \approx K^{(\text{SEC})} + \frac{K_A^{(\text{ads})}}{\sqrt{\pi}(-\lambda_A)g_B} \approx \frac{K_A^{(\text{ads})}}{\sqrt{\pi}c_A R_B} \quad (18)$$

where

$$K^{(\text{SEC})} \approx 1 - \frac{2}{\sqrt{\pi}} \frac{R}{d}$$

and

$$K_A^{(\text{ads})} \approx K_A^{(\text{SEC})} + \frac{2 \exp(\lambda_A^2 g_A^2)}{-\lambda_A} \approx \frac{2 \exp(c_A^2 R_A^2)}{c_A d}$$

is the distribution coefficient of a homopolymer A in the regime of adsorption.

Eq. (18) is not applicable to oligomers with very small R_B . The theory results in another asymptote for K_{AB} at $R_B \ll c_A^{-1}$:

$$K_{AB} \approx K_A^{(\text{ads})} \left(1 - \frac{2}{\sqrt{\pi}} c_A R_B \right) \quad (19)$$

Eq. (19) gives a correct limit of $K_{AB} \rightarrow K_A^{(\text{ads})}$ at $R_B \rightarrow 0$. At very strong adsorption of a block A , the interval of $R_B < c_A^{-1}$ is, however, very narrow, and Eqs. (17) and (18) cover almost the entire range of R_B .

Approximate equations that are similar to Eq. (17) are obtained also for some of the other considered block-copolymers. At high g_B , the result can be presented in a general form

$$K_{\text{block-copolymer}} \approx S \exp \left(\lambda_A^2 g_A^2 - \frac{\pi^2}{4} g_B^2 \right) \quad (20)$$

with coefficients S depending on chain architecture. In particular, for triblock-copolymers

$$S_{ABA} \approx 2\pi^2 \left(\lambda_A^2 + \frac{\pi^2}{4} \right)^{-2};$$

$$S_{BAB} \approx 8(-\lambda_A) \left(\lambda_A^2 + \frac{\pi^2}{4} \right)^{-2};$$

$$S_{\text{StarAAB}} \approx 2 \left(\lambda_A^2 + \frac{\pi^2}{16} \right)^{-1};$$

$$S_{\text{StarABB}} \approx 16(-\lambda_A)^{-1} (\lambda_A^2 + \pi^2)^{-1}.$$

In the approximation which is similar to that of Eq. (18), we have obtained for copolymers BAB and ABA with terminal blocks of equal length the following formulae:

$$K_{BAB} \approx 1 - \frac{2}{\sqrt{\pi}}g + \frac{4}{\pi(-\lambda_A)^3 g_{B1}^2} \exp(\lambda_A^2 g_A^2) \approx K_{\text{SEC}} + \frac{2K_A^{(\text{ads})}}{\pi(c_A R_{B1})^2} \quad (21)$$

$$K_{ABA} \approx K_{\text{SEC}} + \frac{2K_A^{(\text{ads})}}{\sqrt{\pi}(c_A R_B)} + \frac{K_{2A}^{(\text{ads})}}{\sqrt{\pi}(c_A R_B)^3} \quad (22)$$

where the index B_1 in Eq. (21) corresponds to one of two equal blocks of type B , $K_A^{(\text{ads})}$ corresponds to a homopolymer which is the same as block A , and $K_{2A}^{(\text{ads})}$ is that for a homopolymer of type A with doubled contour length.

Analogous equations for symmetric star triblock-copolymers are the following:

$$K_{\text{StarAAB}} \approx K_{\text{SEC}} + \frac{K_A^{(\text{ads})}}{2\sqrt{\pi}(c_A R_B)} \quad (23)$$

$$K_{\text{StarABB}} \approx K_{\text{SEC}} + \frac{4K_{2A}^{\text{ads}}}{\pi(c_A R_{B1})^2} \quad (24)$$

Eqs. (21)–(24) are applicable at $R_{B1}, R_B \gg c_A^{-1}$. The distribution coefficient of block-copolymers with shorter block(s) B , of course, tends to $K_A^{(\text{ads})}$ (for BAB and Star ABB) or to $K_{2A}^{(\text{ads})}$ (for ABA and StarAAB).

Fig. 7a and b shows the results of calculation by using Eqs. (1)–(7) in the form of the dependences of K on $g_B = R_B/d$ for various symmetric copolymers under the SEC condition for B and strong adsorption for A . Here, $R_B = (\sum R_{B_i}^2)^{1/2}$ and R_A is defined in a similar way. Parameter $g_A = R_A/d$ is taken constant, which means the same M_A in all considered copolymers. Approximations (17), (18), (20)–(24) are also shown in Fig. 7. As can be seen, at chosen conditions, these approximations work quite satisfactory.

In Fig. 7, the distribution coefficients at fixed g_B correspond to copolymers of the same molar mass and composition but of different architecture. One can see that at given conditions and at g_B in the interval of 0.1–0.5 curves for many of the considered types of copolymers are more or less separated. In the family of linear multiblock-copolymers retention decreases with increasing the number of blocks (Fig. 7a). Some results for heteroarm stars are shown in Fig. 7b. While the retention of StarAAB , StarAAAB and StarAAAAB is about the same, for other stars it differs considerably. The theory predicts the order of retention for stars of three arms: $\text{StarAAB} > \text{StarABB}$; for stars of four arms the order is: $\text{StarAAAB} > \text{StarABBB} > \text{StarAABB}$; the following order is obtained for stars of five arms: $\text{StarAAAAB} > \text{StarABBBB} > \text{StarAAABB} > \text{StarAABBB}$.

Examples of expected chromatographic separations are shown in Figs. 8 and 9. Fig. 8 presents a simulated chromatogram for a mixture of symmetrical oligomeric block-copolymers of ABA , BAB , StarAAB and AB types with poly(ethyleneoxide) block(s) B and hydrocarbon chain in block(s) A . Copolymers are assumed of the same average molar mass and composition with polydisperse non-adsorbing blocks B and monodisperse adsorbing blocks A .

Four series of peaks in Fig. 8 correspond to four types of copolymers in the mixture. Each series consists of partially

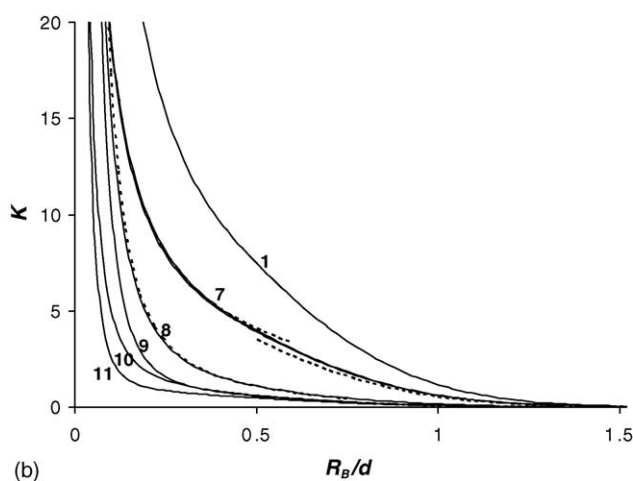
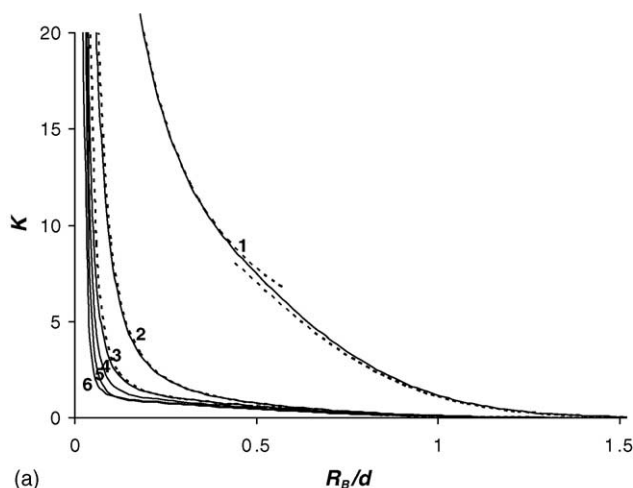


Fig. 7. Dependences of K on $g_B = R_B/d$ for two families of binary copolymers: (a) linear block-copolymers AB (1), BAB (2), ABA (3), $ABAB$ (4), $BABAB$ (5) and $ABABA$ (6); (b) star-block-copolymers $StarAAB$, $StarAAAB$ and $StarAAAAB$ (7), $StarABB$ (8); $StarABBB$ (9); $StarAABB$ (10) and $StarAABBB$ (11). Interaction conditions: SEC for B , strong adsorption for A ; $\lambda_A = -50$; $g_A = 0.06$. Dotted lines correspond to Eqs. (17), (18), and (20)–(24).

separated individual oligomeric homologues; within the series retention decreases with increase in the number of EO units. Fig. 8 shows a good expected chromatographic separation of these four block-copolymers.

It follows from the theory, that even separation of symmetric and very asymmetric block-copolymers is possible, in principle. Fig. 9a and b demonstrate expected patterns of separation of symmetric and asymmetric stars ABB , and diblock-copolymers AB . Here we model the mixture of PPO–PEO copolymers of equal average M and composition. Fig. 9 shows better separation in wider pores. According to the theory (Fig. 7), better separation of block-copolymers by architecture in the SEC-adsorption mode is generally expected at values of R_B/d of order of 0.1–0.5.

It should be noted, that in the SEC-adsorption mode separation of block-copolymers by architecture is possible if

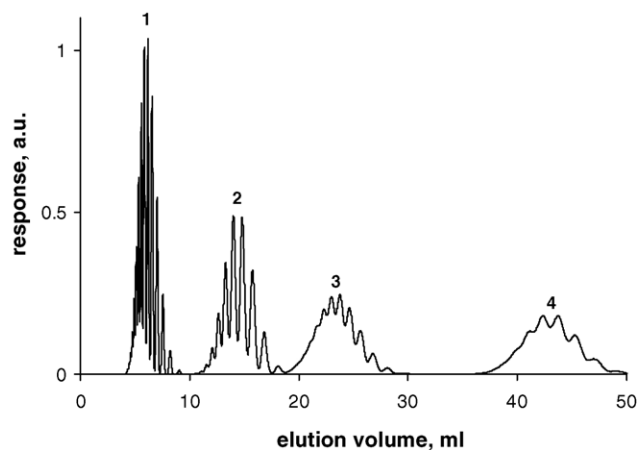


Fig. 8. Simulated chromatogram for a mixture of copolymers ABA (1), BAB (2), $StarAAB$ (3) and AB (4) under the condition of SEC for polyoxyethylene block(s) B and strong adsorption for hydrocarbon block(s) A . Parameters of simulation: $M_A = 280$; $(M_w)_B = 600$, $(M_w/M_n)_B = 1.03$; $c_A = 4 \text{ nm}^{-1}$; $V_p = 1 \text{ ml}$, $V_i = 1 \text{ ml}$; $2d = 12 \text{ nm}$.

blocks are monodisperse or possess narrow molar mass distributions. In simulations we achieved good separation results for copolymers with monodisperse adsorbing blocks and non-adsorbing blocks of $M_w/M_n < 1.05$.

4. Concluding remarks

We apply the molecular-statistical theory for studying possibilities of chromatography to analyze and to separate linear and star-shaped binary block-copolymers. The theory is based on the model of an ideal chain in a slit-like pore, and is developed in the similar manner for block-copolymers of various structures.

Three special types of chromatographic conditions and consequently three special modes of chromatography are in the focus of our study.

According to the theory, at the CPA for one of the components, B , the distribution coefficient K of linear copolymers AB , BAB and star-block-copolymers is independent of M_B , and (at equal M_A) coincides for most of these copolymers. All these copolymers regardless their architecture and M_B can be separated by M_A .

Under the same conditions the chromatographic behavior of linear copolymers ABA and $ABAB$. . . A is considerably different in both qualitative and quantitative aspects from that of a diblock-copolymer. While being independent of M_B at high M_B , K increases at low M_B for these polymers. We gave simple approximate equations to describe this effect. It is shown that at the CPA for B not only the separation of AB , ABA and multiblock-copolymers can be possible, but the same is also true for symmetric and very asymmetric copolymers ABA .

If the interaction conditions for A and B are close to the CPA the retention of the considered binary copolymers prac-

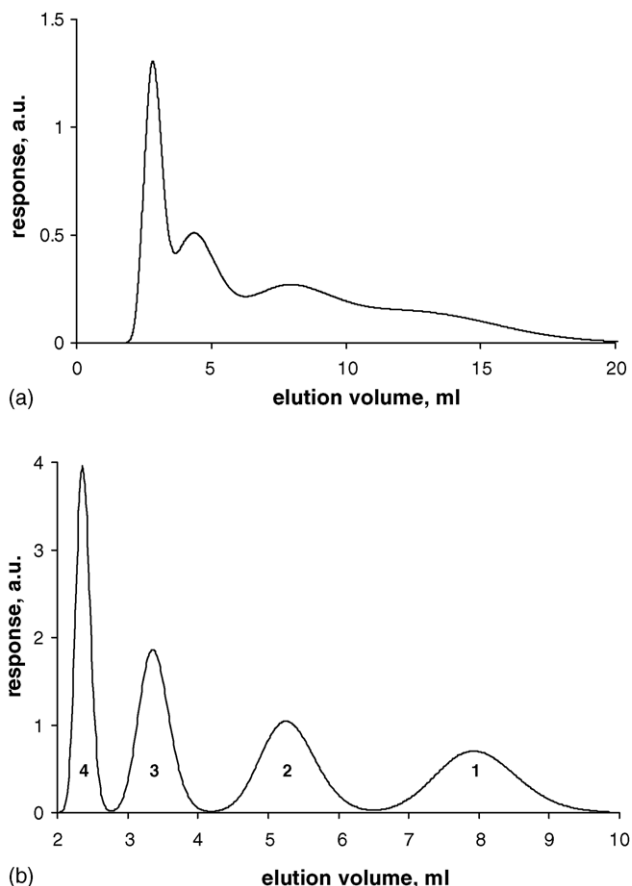


Fig. 9. Simulated chromatograms for a mixture of AB with symmetric and asymmetric $StarABB$ copolymers under the condition of SEC for polyoxyethylene block(s) B and strong adsorption for polyoxypropylene block A . Components of the mixture are copolymers of equal average molar mass and composition (each consisting of monodisperse block A of $M = 1000$ and block(s) B of total $M_w = 40 \times 10^3$ with $M_w/M_n = 1.03$): (1) diblock-copolymer AB ; triblock-copolymers $StarAB_1B_2$ with (2) $M_{B1}:M_{B2} = 39.8:0.2$, (3) $M_{B1}:M_{B2} = 38.5:1.5$ and (4) $M_{B1}:M_{B2} = 20:20$. Simulation parameters: $c_A = 3.1$; $V_p = 1$ ml, $V_i = 1$ ml. Pore dimension: $2d = 18$ nm (a); $2d = 50$ nm (b).

tically does not depend on their architecture and is the same as that of a homopolymer with an effective interaction parameter $\bar{\lambda} = \xi_A \lambda_A + \xi_B \lambda_B$. At weak adsorption interaction for A and pre-critical interaction for B , there is a threshold composition of a copolymer ξ_A^* (the same for all considered copolymers), at which the retention becomes independent of M like it happens with a homopolymer at $\lambda = 0$. In the limit of $R/d \gg 1$, K tends either to zero or to infinity, depending on whether $\xi_A < \xi_A^*$ or $\xi_A > \xi_A^*$. One can make use of this fact by applying a gradient technique and narrow-pore adsorbents in order to gradually separate high molar mass binary copolymers by composition. For the considered types of copolymers, the result will not depend on architecture.

According to the theory, at SEC condition for B and strong adsorption for A block-copolymers of equal average molar mass and composition but of different architecture, in principle, can be separated from each others; it seems

even possible to separate symmetric and very asymmetric block-copolymers. The theory predicts better separation by architecture in wide pores. Obviously, because of the strong dependence of K on both M_A and M_B , separation by architecture at these conditions will be only possible if blocks A and B are monodisperse or have narrow MMD. It is also evident that this approach can be mostly applied to oligomers with functional groups or to copolymers with rather short adsorbing blocks since copolymers with large enough blocks A will be practically fully retained within a column.

Three-dimensional strategies based on combinations of the above discussed modes of chromatography can be developed for the analysis and separation of binary copolymers. According to the theory, in some cases full separation by molar mass, composition and architecture is possible, in principle. For example, polydisperse copolymers AB , $StarAAB$ and $StarABB$ can be separated by M_A at the CPA for B , then by M_B at the CPA for A , and then by architecture at the SEC-adsorption mode. High molar mass copolymers AB and BAB , in principle, can be separated by composition by using narrow-pore adsorbents and gradient chromatography at the close-to-critical interaction conditions, then by M_A at the CPA for B , and finally by architecture either at the CPA for A or at the SEC-adsorption mode.

In the theory, it is assumed that both chains A and B are flexible (and of equal flexibility). If this is not the case (for example, if B is flexible, while A is semiflexible, or if both A and B are semiflexible), one may expect considerably different chromatographic behavior of such copolymers (especially in narrow pores).

An ideal chain model does not take into account interactions between chain units. We think that interactions of repulsive type with the short-ranged potential would hardly change the features of chromatographic behavior of block-copolymers; deviations may be expected for stars with many arms, for which the excluded volume effects are important. If, however, the attraction takes place (for example, the attraction of blocks A in ABA), one may expect more rich and complicated behavior of such polymers in chromatography. Similarly, one may expect some effect of the attraction between A and B on the chromatographic behavior of a diblock-copolymer AB . Numerical studies of the behavior of block-copolymers in pores with a proper account of chain unit interactions (similar to those performed by Cifra and Bleha [50] for linear polymers) could help in understanding these effects.

In many papers on chromatography of binary block-copolymers at the conditions of CPA for one of the components [7–10,12–17,28], experimental results were reported which are fully consistent with the theory. In particular, it was shown that a block-copolymer AB at the CPA for B behaves as a homopolymer identical to a block A . Some deviations from this behavior were observed by Lee et al. [20] who found somewhat higher retention of AB and its weak increase with molar mass of B at the conditions of SEC for A and CPA for B ; the reason of these deviations was not understood.

End groups in polymers may differ considerably from the repeating ones in the aspect of adsorption interaction. This is the well-known fact that the presence of such groups influences the chromatographic behavior of homopolymers [44–48]; similar effects are expected in block-copolymers. In particular, it is evident that the presence of an adsorbing group on the end of the block B of a copolymer AB may result in the chromatographic behavior which is typical for a triblock-copolymer. At the CPA for B , the retention of such copolymer will be different from that of a corresponding homopolymer A and will depend on M_B . If block A is adsorbing, one may expect a triblock-like behavior of Fig. 2b. However, as it follows from the theory, at SEC condition for A and CPA for B the retention of AB with an adsorbing group at the end of B should be somewhat higher than that of a homopolymer A ; and one may expect for such copolymer the increase of K with M_B in wide pores. Similarly, adsorbing end-groups may also influence the chromatographic behavior of star-shaped block-copolymers.

In this paper, we have focused mostly on the chromatographic behavior of block-copolymers with fixed regular structures under three special types of chromatographic conditions. Of course, a more detailed analysis could be done for other chromatographic regimes. Another interesting

$$K_{AB} \approx 1 - \frac{2}{\sqrt{\pi}}g + \frac{2}{\pi} \left(\frac{\arctg(\sqrt{\xi_A/\xi_B})}{\lambda_A} + \frac{\arctg(\sqrt{\xi_B/\xi_A})}{\lambda_B} \right) - \frac{Y(\Gamma_A)Y(\Gamma_B) + (\lambda_B/\lambda_A)Z(\xi_A, \Gamma_A) + (\lambda_A/\lambda_B)Z(\xi_B, \Gamma_B)}{\lambda_A + \lambda_B} \quad (\text{A.2})$$

problem is a chromatographic behavior of random and disordered heteropolymers which could serve as models for biomimetic polymers [52]. There are several physical approaches to describe adsorption of such heteropolymers [33,53–56]; these approaches may be useful for future extensions of the theory of chromatography of copolymers.

Acknowledgements

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$$Z(\xi, t) \approx \begin{cases} \frac{\sqrt{\xi}}{t\sqrt{\pi}} & t \gg 1 \\ \frac{2}{\pi} \arctg \left(\sqrt{\frac{\xi}{1-\xi}} \right) - \frac{2(1-\sqrt{1-\xi})}{\sqrt{\pi\xi}}t + \frac{2}{\pi\sqrt{\xi}} \left[\arctg \left(\sqrt{\frac{\xi}{1-\xi}} \right) - \sqrt{\xi(1-\xi)} \right] t^2 & |t| \ll 1 \\ 2 \exp(t^2)Y \left(-t\sqrt{\frac{1-\xi}{\xi}} \right) & -t \gg 1 \end{cases} \quad (\text{A.4})$$

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Appendix A. Diblock-copolymer AB: wide-pore approximation

In order to obtain the asymptotes at $R_A, R_B \ll d$, it is more convenient to use as the function P in Eq. (5) the Green's function for a semi-infinite space near one wall, which has a form [43,51]:

$$P = 1 + \exp(-\eta^2)[Y(\Gamma + \eta) - Y(\eta)] \quad (\text{A.1})$$

where $\eta = z/2R$, $\Gamma = -cR$, and

$$Y(x) = \exp(x^2)\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(x^2 - t^2)dt$$

By substituting $P_A = P(c_A, R_A)$ and $P_B = P(c_B, R_B)$, as given by Eq. (A.1) into Eq. (5) and by taking some of the integrals, we obtain the following equation for the distribution coefficient of a diblock-copolymer at $R_A, R_B \ll d$:

$$\text{where } \xi_i = R_i^2/R^2 (i = A, B); \quad R^2 = R_A^2 + R_B^2; \quad \text{and} \\ Z(\xi_i, \Gamma_i) = 2\sqrt{\xi_i/\pi} \int_0^\infty \exp(-t^2)Y(t\sqrt{1-\xi_i} + \Gamma_i)dt.$$

By making use of the asymptotic expansions for the functions Y and Z

$$Y(t) \approx \begin{cases} \frac{1}{\sqrt{\pi}} \left(\frac{1}{t} - \frac{1}{2t^3} + \dots \right) & t \gg 1 \\ 1 - \frac{2}{\sqrt{\pi}}t + t^2 - \dots & |t| \ll 1 \\ 2 \exp(t^2) & -t \gg 1 \end{cases} \quad (\text{A.3})$$

one can obtain more simple approximate equations for a number of special chromatographic regimes. These formulae are listed in Table 1.

Table 1
Distribution coefficient of a diblock-copolymer K_{AB} (wide-pore approximation)

Chromatographic regime, parameters	Distribution coefficient
Size-exclusion type for A and B, $\Gamma_A \gg 1, \Gamma_B \gg 1$	$1 - \frac{2}{\sqrt{\pi}}g + \frac{2}{\pi} \left[\lambda_A^{-1} \operatorname{arctg} \left(\sqrt{\frac{\xi_A}{\xi_B}} \right) + \lambda_B^{-1} \operatorname{arctg} \left(\sqrt{\frac{\xi_B}{\xi_A}} \right) \right]$
Critical type, $ \Gamma_A \ll 1, \Gamma_B \ll 1$	$1 - g^2(\xi_A \lambda_A + \xi_B \lambda_B)$
Adsorption type, $-\Gamma_A \gg 1, -\Gamma_B \gg 1$	$1 - \frac{2}{\sqrt{\pi}}g + \frac{2}{\sqrt{\pi}} \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_B} \right) \left[\frac{\exp(\Gamma_A^2)}{\lambda_A g_B} - \frac{\exp(\Gamma_B^2)}{\lambda_B g_A} \right] + 4 \frac{\exp(\Gamma_A^2 + \Gamma_B^2)}{ \lambda_A + \lambda_B }$
Critical type for A; SEC-type for B, $ \Gamma_A \ll 1, \Gamma_B \gg 1$	$1 - \frac{2}{\sqrt{\pi}}g_B + \frac{1}{\lambda_B} - \frac{2}{\pi} g^2 \lambda_A \left[\operatorname{arctg} \left(\sqrt{\frac{\xi_A}{\xi_B}} \right) - \sqrt{\xi_A \xi_B} \right]$
Adsorption for A; critical type for B, $-\Gamma_A \gg 1; \Gamma_B \ll 1$	$1 - \frac{2}{\sqrt{\pi}}g_A + \frac{2}{ \lambda_A } \exp(\Gamma_A^2) - \frac{2}{\pi} g^2 \lambda_B \left[\operatorname{arctg} \left(\sqrt{\frac{\xi_B}{\xi_A}} \right) - \sqrt{\xi_A \xi_B} \right]$
Adsorption for A; SEC for B, $-\Gamma_A \gg 1; \Gamma_B \gg 1$	$1 - \frac{2}{\sqrt{\pi}}g + \frac{2}{ \lambda_A } \exp(\Gamma_A^2) Y \left(-\Gamma_A \sqrt{\frac{\xi_B}{\xi_A}} \right)$

The equation in the last row of the table can be further simplified at $c_A R_B \gg 1$ and at $c_A R_B \ll 1$. This results in approximate Eqs. (18) and (19).

Appendix B. Distribution coefficient of star-block-copolymers with $f=3$ and $f=4$

For a star-block-copolymer with three arms A, B and C ($f=3$), we have obtained:

$$K_{starABC} = \sum_{k,l,m=1}^{\infty} S_{klm} \exp(-\alpha_k^2 g_A^2 - \beta_l^2 g_B^2 - \gamma_m^2 g_C^2) \quad (\text{B.1})$$

where α_k, β_l , and γ_m are the roots of Eq. (2) with corresponding parameters λ_A, λ_B and λ_C ;

$$S_{klm} = \frac{8\lambda_A \lambda_B \lambda_C [2\lambda_A \lambda_B \lambda_C + \lambda_A(F - 2\alpha_k^2) + \lambda_B(F - 2\beta_l^2) + \lambda_C(F - 2\gamma_m^2)]}{(\lambda_A + \lambda_A^2 + \alpha_k^2)(\lambda_B + \lambda_B^2 + \beta_l^2)(\lambda_C + \lambda_C^2 + \gamma_m^2)(4E - F^2)};$$

$$F = \alpha_k^2 + \beta_l^2 + \gamma_m^2; E = \alpha_k^2 \beta_l^2 + \beta_l^2 \gamma_m^2 + \gamma_m^2 \alpha_k^2$$

It turned out also possible to obtain an exact result for a star with four different arms:

$$K_{starABCD} = \sum_{k,l,m,n=1}^{\infty} S_{klmn} \exp(-\alpha_k^2 g_A^2 - \beta_l^2 g_B^2 - \gamma_m^2 g_C^2 - \delta_n^2 g_D^2) \quad (\text{B.2})$$

where eigenvalues $\alpha_k, \beta_l, \gamma_m$, and δ_n are the roots of the Eq. (2) with corresponding parameters $\lambda_A, \lambda_B, \lambda_C$ and λ_D ;

$$S_{klmn} = \frac{s[2(\lambda_A \lambda_B \lambda_C \nu_4 + \lambda_B \lambda_C \lambda_D \nu_1 + \lambda_C \lambda_D \lambda_A \nu_2 + \lambda_D \lambda_A \lambda_B \nu_3) + \lambda_A w_1 + \lambda_B w_2 + \lambda_C w_3 + \lambda_D w_4]}{u^2 - 64\alpha_k^2 \beta_l^2 \gamma_m^2 \delta_n^2}$$

$$s = \frac{16\lambda_A \lambda_B \lambda_C \lambda_D}{(\lambda_A + \lambda_A^2 + \alpha_k^2)(\lambda_B + \lambda_B^2 + \beta_l^2)(\lambda_C + \lambda_C^2 + \gamma_m^2)(\lambda_D + \lambda_D^2 + \delta_n^2)};$$

$$u = u_1 \alpha_k^2 + u_2 \beta_l^2 + u_3 \gamma_m^2 + u_4 \delta_n^2;$$

$$u_1 = -\alpha_k^2 + \beta_l^2 + \gamma_m^2 + \delta_n^2; \quad \nu_1 = u - 4u_1 \alpha_k^2; \quad w_1 = uu_1 - 16\beta_l^2 \gamma_m^2 \delta_n^2;$$

$$u_2 = +\alpha_k^2 - \beta_l^2 + \gamma_m^2 + \delta_n^2; \quad \nu_2 = u - 4u_2 \beta_l^2; \quad w_2 = uu_2 - 16\gamma_m^2 \delta_n^2 \alpha_k^2;$$

$$u_3 = +\alpha_k^2 + \beta_l^2 - \gamma_m^2 + \delta_n^2; \quad \nu_3 = u - 4u_3 \gamma_m^2; \quad w_3 = uu_3 - 16\delta_n^2 \alpha_k^2 \beta_l^2;$$

$$u_4 = +\alpha_k^2 + \beta_l^2 + \gamma_m^2 - \delta_n^2; \quad \nu_4 = u - 4u_4 \delta_n^2; \quad w_4 = uu_4 - 16\alpha_k^2 \beta_l^2 \gamma_m^2.$$

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