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Theory of chromatography of ring-shaped block copolymers

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ABSTRACT

A theory is developed for describing liquid chromatography of ring diblock and multiblock copolymers. The chromatographic behavior of ring block copolymers at different adsorption interactions is analyzed theoretically and compared with that of linear block copolymers; typical chromatograms are simulated by using the theory. In particular, it is shown that under the critical interaction condition for one block the chromatographic retention of a ring diblock copolymer is dependent of the length of the 'critical' block; this behavior differs qualitatively from that of a linear diblock copolymer. Ring copolymers are always more retained than linear ones, therefore such copolymers can be separated. Especially good separation of heterogeneous ring and linear block copolymers is predicted at near-critical interaction conditions. According to the theory, ring diblocks and multiblocks can be separated as well, if one component of a copolymer is adsorbing, while the other one is not adsorbing.

1. Introduction

Cyclic polymers are interesting materials with bulk, solution, and surface properties different from those of its linear analogues. A considerable progress is achieved in the synthesis of cyclic polymers [1–6], and many topological forms, such as ring-, eight-, manacle-, theta-shaped, as well as semicyclic and multicyclic macromolecules have been synthesized [7–10].

Cyclic block copolymers [11–16] are of significant interest, because their properties may be considerably different from those of corresponding linear copolymers. In particular, it was shown that cyclization of a block copolymer induces remarkable changes in the morphology of the organized nanostructure [17].

The characterization of cyclic block copolymers and their separation from linear analogues is an important task, since in the result of the synthesis cyclic copolymers are often obtained in the mixture with linear precursors and unwanted by-products. Liquid chromatography has proven to be very efficient method for the characterization of cyclic polymers, as well as for separation of cyclic products from linear precursors [18–24]. Of course, size-exclusion chromatography (SEC) which is a routine tool for studying molar mass and MMD of polymers is as well applicable to the analysis of cyclic polymers. However, SEC is not able to separate polydisperse linear and cyclic polymers. To the other hand, it has been shown that ring homopolymers can by fully separated from linear analogues by the liquid chromatography at the critical condition of adsorption [20–22]. Chromatography has also proven itself as a very useful tool for the analysis of block copolymers. Many reports were published demonstrating a wonderful potential of chromatography in the analysis of block copolymers [25–28].

Development of a theory helps in understanding separation mechanisms, and in finding favorable chromatographic regimes and experimental conditions, (i.e. the combination of stationary and mobile phases as well as the operating temperature) providing for the required separations. A theory of chromatography of linear polymers based on the model of an ideal macromolecule in a slit-like pore has been developed by Gorbunov and Skvortsov [29,30]. This theory, which is more general than the Casassa theory of SEC [31], additionally takes into the account the adsorption interactions between the chain units and pore walls. A similar theory has been developed also for polymer rings [30, 32], and later it has been extended towards eight-shaped, theta-shaped, and even more complex macrocyclic polymers [33, 34].

A considerable progress was achieved in the theory of chromatography of linear and star-shaped block copolymers [35–40]. In particular, an interesting option for separation of linear diblock copolymers by the length of only one block was predicted by theory and proved experimentally. As to the chromatographic behavior of chemically heterogeneous cyclic polymers, only a special case of macromolecules with one or few point-type adsorbing functional groups has been studied theoretically [41].

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The purpose of the present study is to provide a theory describing chromatography of ring-shaped diblock and multiblock copolymers, to analyze the expected chromatographic behavior of these copolymers at various adsorption interaction conditions, and to compare it with that of the corresponding linear block copolymers.

2. Model and mathematical solution: partition coefficients of ring-shaped diblock and multiblock copolymers

To develop a theory of chromatography of a ring diblock copolymer we consider an equilibrium partitioning of its molecule between an unrestricted space and a slit-like pore of a width 2d (Fig. 1).

To account for statistical properties of sub-chains we use like previously [40] a continuum ideal-chain approach [30] which is analogous to describing the motion of a Brownian particle under spatial constraints. Each fragment i ($i = A,B$) of N_i statistical units (Kuhn segments) is modeled as an ideal flexible polymer chain of contour length $N_i b_i$, where b_i is the segment length. The size of every sub-chain is characterized by its statistical radius R_i. For an ideal linear chain in an unrestricted space $R = b\sqrt{N/6}$ is its average radius of gyration.

As in the theories [30, 33, 34, 40] the interaction of polymer chain units with pore walls is accounted for by an interaction parameter c [30]. Negative values of c correspond to effective repulsive forces. The point $c = 0$, at which an adsorption of a chain starts, is referred to as a critical point of adsorption. Positive values of c correspond to the adsorption; c^{-1} has the meaning of an average thickness of the layer formed by an adsorbed macromolecule on the surface.

The chromatographic behavior of a polymer is determined by the partition coefficient K, which is defined as the ratio of the partition functions of a polymer within a pore and in an unrestricted space of the same volume:

$$K = \frac{Z^{(pore)}}{Z^{(0)}} \tag{1}$$

The partition functions $Z^{(pore)}$ and $Z^{(0)}$ for a ring-shaped diblock copolymer are expressible in terms of sub-partition functions $P_i(r',r'')$ of two linear sub-chains A and B having ends at fixed points x',y',z' and x'',y'',z'':

$$Z = \int\limits_{x',x'',y',y''} dx'dx''dy'dy'' \int\limits_{-d}^{d} dz'dz'' P_1(r',r'') \cdot P_2(r',r'') \tag{2}$$

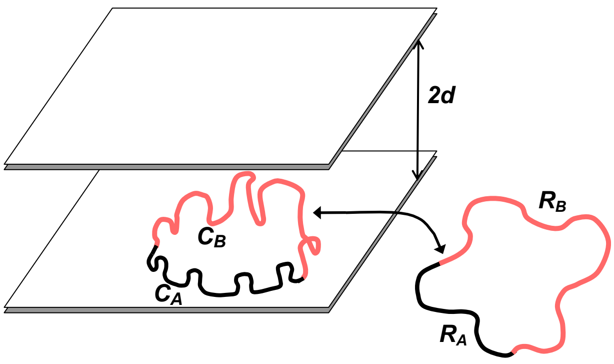

Fig. 1. A diblock copolymer in a slit-like pore with adsorptive walls and in an unrestricted space. Model parameters are indicated: pore width $2d$; statistical radii of sub-chains R_A, and R_B; adsorption interaction parameters c_A and c_B.

In an unrestricted space the sub-partition function $P(r',r'')$ for an ideal linear chain is equal:

$$P(r',r'') = \frac{1}{2\sqrt{\pi R^2}} \exp\left[-\frac{(x'-x'')^2+(y'-y'')^2+(z'-z'')^2}{4R^2}\right] \tag{3}$$

In a slit-like pore $P(r',r'')$ is a solution of the diffusion equation with the boundary condition $\left(P^{-1} \cdot \partial P/\partial z\right)_{\text{on pore walls}} = -c$ [42], which accounts for the adsorption of polymer chain units. This solution has a form [30]:

$$P(r',r'') = \frac{1}{4\pi R^2} \exp\left[-\frac{(x'-x'')^2+(y'-y'')^2}{4R^2}\right] \cdot P(z',z''), \tag{4}$$

$$P(z',z'') = \frac{1}{d}\sum_{k=1}^{\infty} \frac{\cos[\alpha_k \xi - (k-1)\pi/2] \cdot \cos[\alpha_k \xi' - (k-1)\pi/2]}{1 + \lambda/\left(\alpha_k^2 + \lambda^2\right)} \cdot \exp\left[-(g\alpha_k)^2\right] \tag{5}$$

where R is the statistical radius of a free ideal linear chain; $\xi' = (z'-d)/d$ and $\xi'' = (z''-d)/d$ are reduced distances between chain ends and the middle of the slit; $g = R/d$ is macromolecule-to-pore size ratio; $\lambda = -cd$ is dimensionless parameter of a polymer–wall interaction; and α_k are the roots of the equation [29, 32]:

$$\alpha_k = arctg\left(\frac{\lambda}{\alpha_k}\right) + (k-1)\frac{\pi}{2}, \qquad k = 1, 2, \ldots \infty \tag{6}$$

The chain propagator $P(r',r'')$ as given by Eqs. (4), (5) has been used previously to develop an analytical theory of chromatography of linear and cyclic homopolymers [30, 33] and of linear and star-shaped block copolymers [40].

By substituting Eqs. (3), (4), and (5) into the Eqs. (1) and (2), and by integrating, we have obtained the following exact formula for the partition coefficient of a ring diblock (AB):

$$K_{(AB)}(\lambda_A, \lambda_B, g_A, g_B) = \sqrt{\pi} g \cdot \sum_{\substack{k,m=1, \\ (k+m)\ \ even}}^{\infty} C_{k,m}(\lambda_A, \lambda_B) \times \exp\left[-\left(\alpha_k^2 g_A^2 + \beta_m^2 g_B^2\right)\right], \tag{7}$$

wherein

$$C_{k,m} = \frac{4\alpha_k^2 \beta_m^2}{\left(\lambda_A + \lambda_A^2 + \alpha_k^2\right)\left(\lambda_B + \lambda_B^2 + \beta_m^2\right)} \cdot \left(\frac{\lambda_A - \lambda_B}{\alpha_k^2 - \beta_m^2}\right)^2 \tag{8}$$

In Eq. (7) $g = \sqrt{g_A^2 + g_B^2} = \sqrt{R_A^2 + R_B^2}/d$ has a meaning of a molecule-to-pore size ratio of the reference linear copolymer AB. The eigenvalues $\alpha_k^2$and β_m^2 are the roots of the equations of the form of Eq. (6) with corresponding parameters λ_A and λ_B. At negative values of λ some of these eigenvalues are imaginary values [29, 32], however the coefficients $C_{k,m}$ are always real. At some special values of λ and at some eigenvalues the denominator of the Eq. (8) turns zero; however the numerator turns zero as well. Such uncertainties always can be resolved by means of taking corresponding limits. We denote ring diblock copolymers as (AB), to distinguish them from linear ones, AB.

In a similar way we have derived the exact equation for the partition coefficient of a multiblock copolymer $(A_1A_2\ldots A_f)$:

$$K_{(A_1A_2\ldots A_f)}=\sqrt{\pi}g\sum_{\substack{k_1,k_2,\ldots k_f=1\\ \left(f+\sum_{i=1}^{f}k_i\right)\,even}}^{\infty}\left[\prod_{i=1}^{f}\frac{2\alpha_k^2}{\left(\lambda_i+\lambda_i^2+\alpha_{k_i}^2\right)}\right]\times\left[\prod_{i=1}^{f}\frac{\lambda_i-\lambda_{i+1}}{\left(\alpha_{k_i}^2-\alpha_{k_{i+1}}^2\right)}\right]\exp\left(-\sum_{i=1}^{f}\alpha_{k_i}^2g_i^2\right)\tag{9}$$

wherein $g=\sqrt{\sum_i g_i^2}$; the eigenvalues $\alpha_{k_i}^2$ are the roots of the Eq. (6) with the parameter λ_i. The second product in Eq. (9) is the cyclic one, which means that one must substitute the value 1 instead of $f+1$.

Evidently, at $f=2$ Eq. (9) reduces to Eqs. (7) and (8) for a ring diblock copolymer.

Eq. (9) describes rather general ring copolymers ($A_1A_2\ldots A_f$) with blocks which can be all different in their molar mass and chemical nature. In particular, binary multiblock copolymers ($A_1B_1\ldots A_kB_k$) can be also described. In this paper we are discussing the chromatographic behavior of ring-shaped binary block copolymers, (AB) and ($A_1B_1\ldots A_kB_k$).

Apart from the exact equations, approximate asymptotic formulae describing chromatographic behavior in narrow and in wide pores can be also derived as was explained previously [40]. In particular, since at g_A, $g_B >> 1$ the term with $k=m=1$ dominates in the series in Eq. (7), by keeping only this term one can obtain the narrow-pore approximations for $K_{(AB)}$. Similarly, at g_{A1}, g_{A2},…, $g_{Af} >> 1$ the only term with $k_1=k_2=\ldots=k_f=1$ can be left in Eq. (9) in order to obtain asymptotes describing the narrow-pore behavior of a ring multiblock copolymer ($A_1A_2\ldots A_f$). The wide pore asymptotes can be also obtained by using as $P_i(r',r'')$ in Eq. (2) the well-known expression for a chain propagator of an ideal macromolecule near one adsorbing wall [43]. A number of such asymptotic equations for $K_{(AB)}$ at some combinations of interaction conditions for blocks A and B have been obtained; these results will be presented in the next section.

According to Eq. (7), $K_{(AB)}=F(R_A, R_B, c_A, c_B, d)$, and therefore the statistical radii of two blocks, R_A and R_B, and two parameters c_A and c_B (accounting for different interactions of A and B with pore walls) are important. Depending on these parameters, the theory describes a variety of different modes of chromatography of ring-shaped diblock copolymers.

The exact Eqs. (7) and (9) can be used to calculate the partition coefficients $K(R_1,\ldots, R_k, c_1,\ldots, c_k, d)$ of ring block copolymers at different combinations of the parameters, and thus to analyze the behavior of these copolymers. Moreover, one can use these equations for the simulation of chromatograms of compositionally and topologically heterogeneous block copolymers.

In the rest of the paper we give a more detailed analysis of the chromatographic behavior of ring-shaped block copolymers. By using also the previous theoretical results [40], we shall compare the behavior of the corresponding ring-shaped and linear copolymers. A number of interesting simulated chromatograms will be also presented in order to visualize expected separations of heterogeneous block copolymers.

3. Chromatographic behavior of a ring diblock copolymer

3.1. Size exclusion chromatography

In the theory, SEC corresponds to $\lambda_A,\lambda_B\rightarrow\infty$. In this special case Eq. (7) reduces to the well-known result for a non-adsorbing ring [30]:

$$K_{(AB)}^{SEC,\,SEC}\approx\begin{cases}1-\dfrac{\sqrt{\pi}}{2}g, & g<<1\\ \sqrt{\pi}g\cdot\exp\left[-\left(\dfrac{\pi g}{2}\right)^2\right], & g>>1\end{cases},\tag{10}$$

where for a diblock $g=(g_A^2+g_B^2)^{1/2}$, $g_i=R_i/d$ ($i=A,B$).

The SEC behavior of ring polymers is similar to that of linear ones, but differs in a quantitative aspect [30]. In particular, in wide pores (at $g<1$) for both polymers $K\approx 1-s/d$, where s is the effective SEC radius of a macromolecule, which is equal to $2R/\sqrt{\pi}$ for a linear polymer [31], and $\sqrt{\pi}R/2$ - for a ring polymer [30]. Since the SEC radius of a ring polymer is smaller, it elutes later than a linear polymer. This well-known fact is widely used in studies of ring polymers and block copolymers by SEC.

3.2. Behavior at the critical point for one block

This special case is interesting, since the behavior of a linear diblocks at this condition is very simple. The partition coefficient of a linear diblock at $\lambda_B=0$ becomes independent of molar mass of the 'critical' block B, being equal to that of a linear homopolymer A: $K_{AB}=K_A$ [36].

According to the present theory, the behavior of ring diblocks (AB) at the critical condition for B is more complicated. We shall consider two situations.

The first one corresponds to the critical interaction point for B, and SEC for A ($\lambda_B=0$, $\lambda_A=\infty$). Such conditions are often used in the chromatography of high molar mass block copolymers. In this special case ($\lambda_A\rightarrow\infty$, $\lambda_B=0$) $K_{(AB)}^{SEC,cr}$ is approximated as:

$$K_{(AB)}^{SEC,cr}\approx\begin{cases}1-\dfrac{g}{\sqrt{\pi}}\left[\dfrac{2g_Ag_B}{g^2}-arctg\left(\dfrac{g_B^2-g_A^2}{2g_Ag_B}\right)\right], & g<<1\\ \dfrac{8g}{\pi^{3/2}}\exp\left(-\dfrac{\pi^2g_A^2}{4}\right), & g_A,g_B>>1\end{cases}\tag{11}$$

The second interesting situation is the combination of the critical interaction for B and the strong adsorption condition for A ($\lambda_B=0$, $-\lambda_Ag_A>1$). The strong adsorption mode of chromatography is mostly used when the adsorbing polymer chains are short. At $-\lambda_Ag_A>1$, $\lambda_B=0$ the following approximate formulae are obtained:

$$K_{(AB)}^{ads,cr}\approx\begin{cases}K_{(A)}^{ads}, & g_B\rightarrow 0\\ 1+\dfrac{\sqrt{\pi}}{2}g_B+2K_A^{ads}, & g_A<<g_B<<1\\ \sqrt{\pi}g\cdot K_A^{ads}, & g_B>>1\end{cases}\tag{12}$$

where K_A^{ads} and $K_{(A)}^{ads}$ are the partition coefficients of homopolymers - linear, A, and ring, (A), which are of the same molar mass and of the same chemical nature, as the block A in the diblock (AB):

$$K_A^{ads}\approx\frac{2\exp\left(\lambda_A^2g_A^2\right)}{(-\lambda_A)},\quad K_{(A)}^{ads}\approx 2\sqrt{\pi}g_A\exp\left(\lambda_A^2g_A^2\right)\tag{13}$$

The calculated partition coefficients of ring and linear diblocks as functions of g_B at fixed g_A are shown in Figs. 2 and 3. Solid lines – exact Eq. (7) for a ring diblock; dotted lines show Eq. (11) (Fig. 2), and Eq. (12) (Fig. 3); one can see that these approximations are quite reasonable.

As it can be seen in Figs. 2 and 3, at the same values of g_A $K_{(AB)}>K_{AB}$, therefore at the critical point for B ring-shaped copolymers can be separated from linear ones, provided that blocks A are monodisperse.

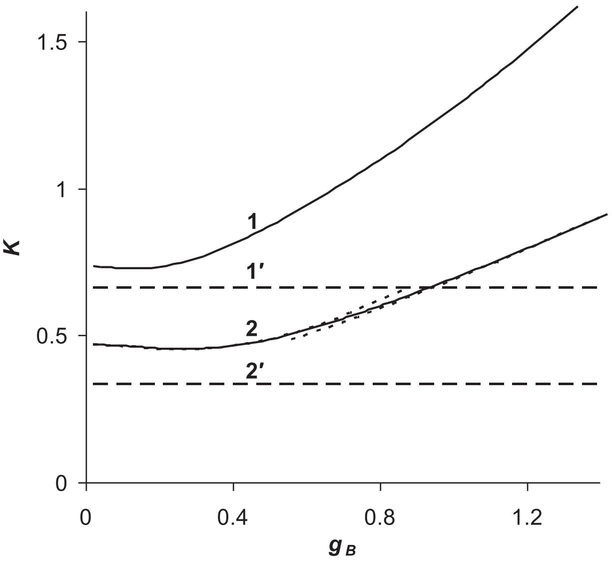

Fig. 2. Dependences of the partition coefficient K of copolymers (AB) and AB on the parameter $g_B = R_B/d$ at the critical point for B and SEC condition for A. Solid lines 1 - 2 – ring diblocks (AB), dashed lines 1′ - 2′– linear diblocks AB; $g_A = 0.3$ (1, 1′), and 0.6 (2, 2′). Dotted lines –Eq. (11).

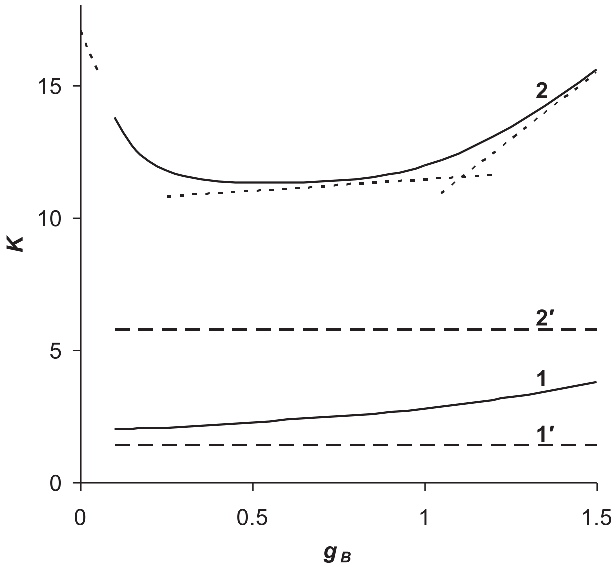

Fig. 3. Dependences of the partition coefficient K of copolymers (AB) and AB on the parameter $g_B = R_B/d$ at the critical point for B and adsorption condition for A (at $\lambda_A = -10$). Solid lines 1 - 2 – ring diblocks (AB), dashed lines 1′–2′ – linear diblocks AB; $g_A = 0.11$ (1, 1′), and 0.18 (2, 2′). Dotted lines – Eq. (12).

It follows from Eqs. (11), (12) and Figs. 2 and 3, that at both SEC and adsorption conditions for A the chromatographic retention of ring diblock copolymers, unlike that of linear diblocks, is dependent of g_B (that is of the length of the 'critical' block). However, at $g_B < 1$ there are intervals of g_B (and hence intervals of the molar mass M_B) where the dependences $K_{(AB)}(M_B)$ are weak, and where the retention of copolymers (AB) will be mostly dependent on the molar mass of A.

3.3. Near-critical conditions

At $|\lambda_A|, |\lambda_B| << 1$ the partition coefficient of a ring diblock copolymer is approximated by the equation:

$$K_{(AB)}(g_A, g_B, \lambda_A, \lambda_B) \approx K_{ring}(g, \bar{\lambda}), \qquad (14)$$

which means that it behaves like a ring homopolymer at some effective interaction parameter

$$\bar{\lambda} = \xi_A\lambda_A + \xi_B\lambda_B,$$

where $\xi_i = g_i^2/g^2 = R_i^2/R^2$, $(i = A,B)$.

Eq. (14) works also quite good in a wider region $|\lambda_A|, |\lambda_B| < 1$, but with $\bar{\lambda}$ defined by a more complicated equation

$$\bar{\lambda} - \frac{\bar{\lambda}^2}{3} = \xi_A\left(\lambda_A - \frac{\lambda_A^2}{3}\right) + \xi_B\left(\lambda_B - \frac{\lambda_B^2}{3}\right)$$

For the narrow-pore situation g_A, $g_B >> 1$ one more simple equation relating partition coefficients of ring and linear diblock copolymers is obtained:

$$K_{(AB)} \approx \sqrt{\pi} g \cdot K_{AB} \qquad (15)$$

Linear diblock copolymers at $|\lambda_A|, |\lambda_B| < 1$ also behave like corresponding linear homopolymers at the effective interaction parameter $\bar{\lambda}$, which is the just the same function of λ_A, λ_B, and the copolymer composition (similar equations for a linear diblock were reported in [40]).

Dependences of K on the parameter $g = (R_A^2 + R_B^2)^{1/2}/d$ for ring and linear diblock copolymers of different composition are given in Fig. 4. The composition of diblocks is characterized by a parameter $\xi_A = R_A^2/(R_A^2 + R_B^2)$. Since R_A and R_B are defined as the parameters of the reference linear chains A and B (which are identical to the

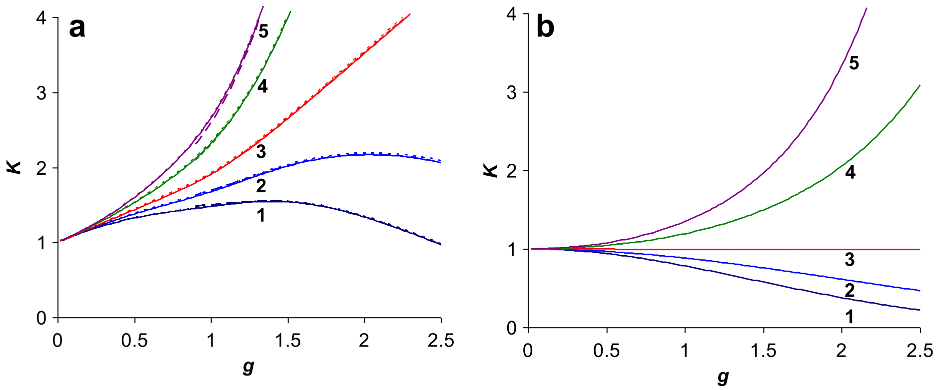

Fig. 4. Dependences of K on g for ring (a), and linear (b) diblock copolymers of different composition at $\lambda_A = -0.3$, $\lambda_B = 0.3$. The values of ξ_A: 0.05 (1), 0.25 (2), 0.45 (3), 0.75 (4), and 0.95 (5). Eqs. (14) and (15) are shown by dotted and dashed lines.

blocks A and B of a diblock copolymer), ring and linear diblocks with equal g and with equal ξ_A are of the same molar mass and of the same composition.

Solid lines in Fig. 4a represent exact Eqs. (7), (8), dotted lines correspond to Eq. (14), dashed lines — Eq. (15). Fig. 4 shows that Eqs. (14) and (15) are very good approximations at $|\lambda_A|, |\lambda_B| < 1$; Eq. (14) being quite good practically at all g.

As it follows from the theory (Eq. (15)), Fig. 4), if the interaction conditions for both A and B are close to the critical level, it is possible to separate linear and ring-shaped diblock copolymers of the same molar mass and composition. What is important, at some combinations of λ_A and λ_B such separations can be possible even if both linear and cyclic diblock copolymers are polydisperse.

An example of a good separation condition is given in Fig. 5. This figure shows the partition coefficients of linear and cyclic copolymers at λ_A and λ_B which are both shifted from the critical interaction point to the exclusion side.

As can be seen in Fig. 5, at $g < 1$ the dependences of K on g for both linear and cyclic copolymers of different composition are rather weak, while there is a considerable gap between K values of linear and cyclic copolymers. The theory thus predicts a very good separation of heterogeneous linear and ring copolymers in wide pores, under the conditions similar to that of Fig. 5.

It was shown previously [40] that at $|\lambda_A|, |\lambda_B| < 1$ there is practically no separation between linear diblock and multiblock copolymers of the same overall composition. As it follows from the present theory, the same is also true for ring block copolymers.

3.4. Strong adsorption conditions for both components

At $-\lambda_A g_A,\ \ -\lambda_B g_B >> 1$ the partition coefficient is approximated as:

$$K^{ads,\ ads}_{(AB)} \approx \sqrt{\pi} g \frac{8\lambda_A\lambda_B}{(\lambda_A+\lambda_B)^2} \cdot \exp\left(\lambda_A^2 g_A^2 + \lambda_B^2 g_B^2\right) \qquad (16)$$

At $\lambda_A = \lambda_B$ Eq. (16) reduces to the well-known equation for an adsorbing ring $K^{ads}_{ring} \approx 2\sqrt{\pi} g \cdot \exp(\lambda^2 g^2)$ [30].

If the adsorption interactions of components A and B are different, $K_{(AB)}$ depends on the copolymer composition, and increases exponentially with g_A^2 and g_B^2 (that is with molar masses of both blocks A and B). This is similar to the behavior of a linear diblock copolymer at strong adsorption conditions [40].

Fig. 6 shows the dependences K on g for ring and linear diblock copolymers of different composition at the adsorption condition. As can be seen, in adsorption chromatography ring and linear copolymers behave quite similar: its retention depends on both g and ξ_A, that is on both molar mass and composition. As it follows from the theory (Fig. 6), there is a principle possibility to separate block copolymers of the same molar mass by both composition and topology. However, since the molar mass dependences are very sharp, such separations will be possible only for copolymers with narrow molar mass distributions.

3.5. One component – at strong adsorption, the second one – at SEC condition

The mode of chromatography, in which one block B of a linear diblock copolymer is at the SEC condition while A is adsorbing, was realized by Trathnigg and co-workers, and was extensively studied [44, 45]. In this mode copolymers typically are highly retained, as in adsorption chromatography, but the order of retention of copolymers by molar mass of B is as in SEC; this results in improved resolution of peaks in chromatography of oligomeric block copolymers.

In the theory, the adsorption–SEC combination of the interaction conditions corresponds to $\lambda_B >> 1$, $-\lambda_A g_A >> 1$. In this situation the present theory results in:

$$K^{ads,\ SEC}_{(AB)} \approx \begin{cases} K^{ads}_{(A)}, & g_B \to 0 \\ 1 - \dfrac{\sqrt{\pi}}{2} g + \dfrac{K^{ads}_A}{\lambda_A^2 g_B^2}, & g_B << 1 \\ K^{ads}_A \cdot \left(\dfrac{\lambda_A}{\pi} + \dfrac{\pi}{4\lambda_A}\right)^{-2} \cdot \dfrac{\sqrt{\pi}}{2} g \cdot \exp\left(-\pi^2 g_B^2/4\right), & g_B >> 1 \end{cases} \qquad (17)$$

where K^{ads}_A and $K^{ads}_{(A)}$ - (Eq. (13)).

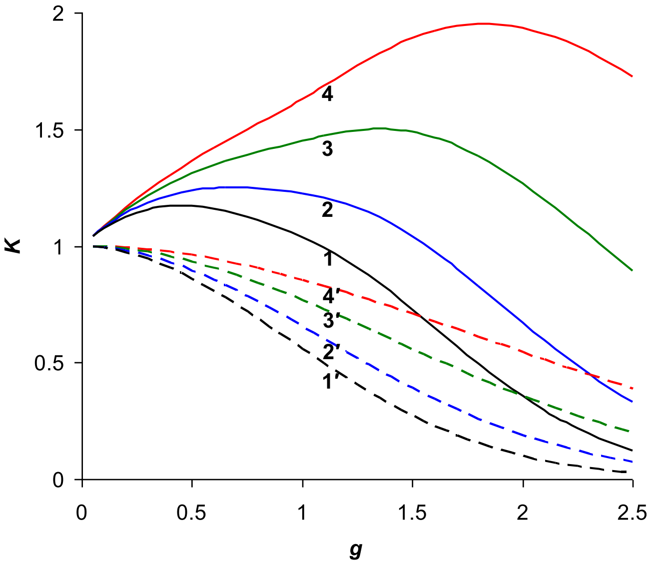

Fig. 5. Dependences of K on g for ring (solid lines 1–4), and linear (dashed lines 1′–4′) diblock copolymers of different composition at $\lambda_A = 0.1$, $\lambda_B = 0.8$. The values of ξ_A: 0.1 (1, 1′), 0.4 (2, 2′), 0.7 (3, 3′), and 0.9 (4, 4′).

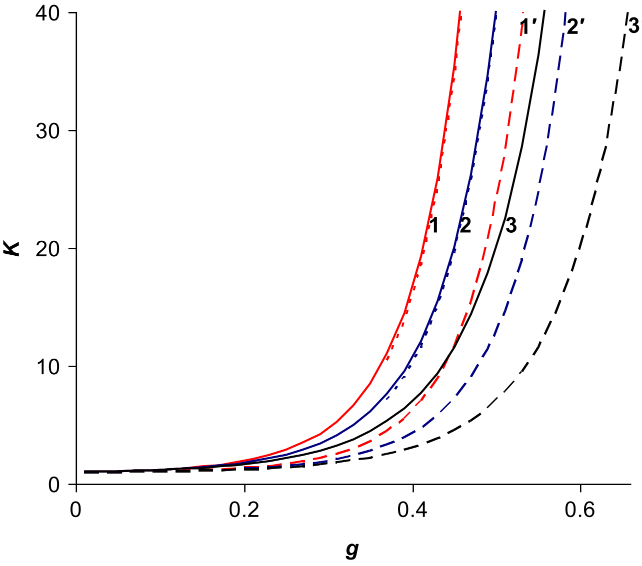

Fig. 6. Dependences of K on g for ring (solid lines 1–3), and linear (dashed lines 1′–3′) diblock copolymers of different composition at $\lambda_A = -3$, $\lambda_B = -4$. The values of ξ_A: 0.1 (1, 1′), 0.5 (2, 2′), and 0.9 (3, 3′). Dotted lines – Eq. (16).

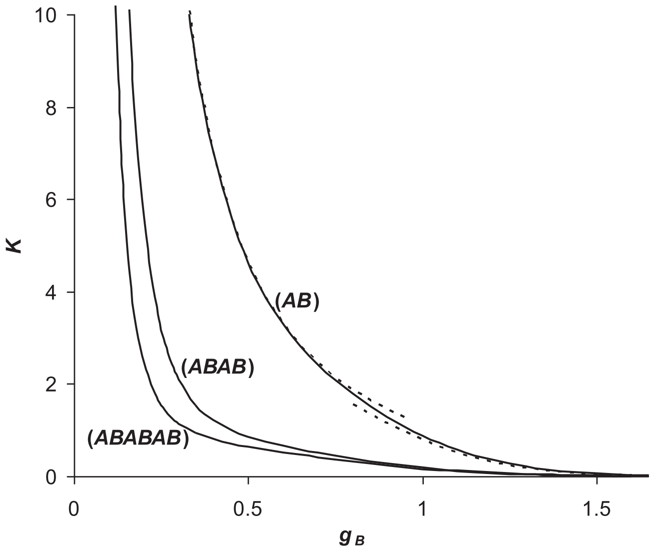

Fig. 7. Dependences of K on g_B for ring block copolymers (AB), ($ABAB$), and ($ABABAB$) at adsorption condition for A, SEC – for B. $\lambda_A = -10$;$g_A = 0.25$. Dotted lines – Eq. (17).

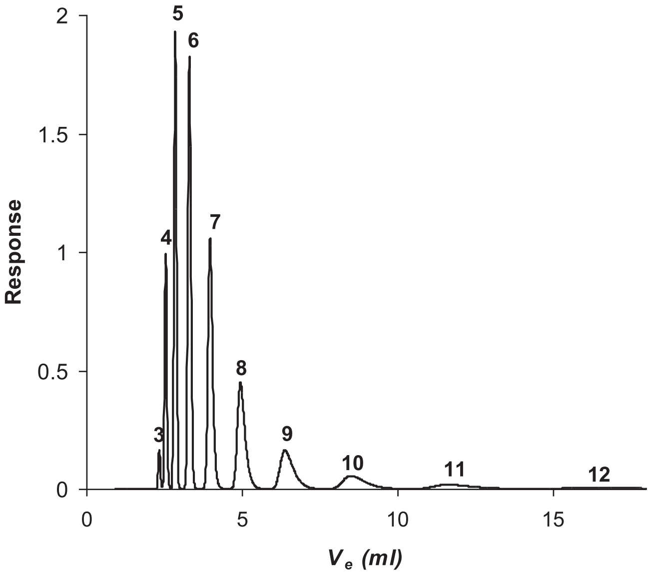

Fig. 8. Virtual chromatogram of a heterogeneous ring diblock copolymer (AB) under the critical condition for block B and strong adsorption for A. Simulation parameters: $(M_w)_A = 300$, $(M_w/M_n)_A = 1.09$; $(M_w)_B = 1000$, $(M_w/M_n)_B = 1.5$; $\lambda_A = -27$. Numbers of repeat units of A are indicated.

These approximate equations are qualitatively similar to those of the linear diblock theory [40,44a], and thus the behavior of ring diblock copolymers at the adsorption–SEC conditions is similar to that of linear diblocks.

This mode of chromatography is also interesting, because of the difference in the behavior of diblock and multiblock copolymers. In Fig. 7 we compare copolymers (AB), ($ABAB$), and ($ABABAB$) at the adsorption–SEC condition; the partition coefficient K is calculated by using Eqs. (7)–(9), and plotted *versus* $g_B = \sqrt{\sum R^2_{B_i}}/d$ at fixed $g_A = \sqrt{\sum R^2_{A_i}}/d$ (that is at equal total molar mass of the component A). As it can be seen in Fig. 7, in the wide-pore situation (at about $0.3 < g_B < 1$) there is a considerable difference between the partition coefficients of ring diblocks and multiblocks of the same molar mass and composition. Therefore, a separation of ring diblock and multiblock copolymers may become possible.

4. Simulating chromatograms of heterogeneous ring block copolymers

In order to simulate chromatograms of heterogeneous polymers we use the virtual chromatography technique, which was described previously [46]. Heterogeneous polymers are considered as ensembles of macromolecules. For example, a homopolymer represents an ensemble of linear molecules of different molar mass. A heterogeneous diblock copolymer represents a more complex ensemble with molar mass distribution in both blocks. The chromatographic elution volume $V_e = V_i + V_p K$ is determined by the partition coefficient K (the interstitial volume V_i and the pore volume V_p are the parameters of the chromatographic system, which can be assumed as constants). By calculating partition coefficients for the members of a given ensemble of macromolecules one can construct a theoretical chromatogram of a heterogeneous polymer [46].

This theoretical approach was already used to simulate the chromatography of homopolymers and linear block copolymers; the simulation results have proven to be very similar to real chromatograms [40, 44, 46, 47]. The virtual chromatography technique was also used to predict separations of polydisperse complex polymers [33, 34, 40, 41].

Since the qualitative chromatographic patterns are not influenced by V_i and V_p, we shall assume $V_i = V_p = 1$ ml. A porous material of the pore diameter 20 nm, and a column of the plate

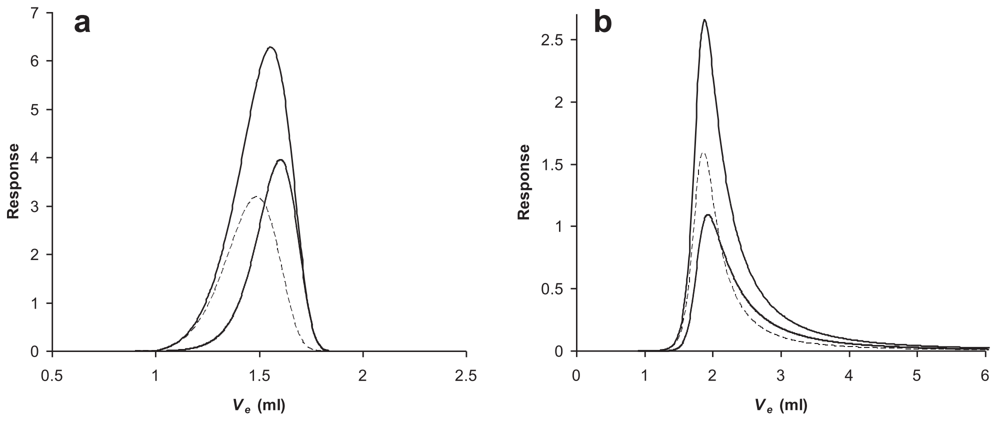

Fig. 9. Simulated chromatograms of a mixture of heterogeneous linear and ring copolymers AB and (AB). Parameters of copolymers: $(M_w)_A = 16\,000$, $(M_w)_B = 8000$, $(M_w/M_n)_A = (M_w/M_n)_B = 1.5$. Interaction conditions: a: SEC for both A and B; b: A – adsorption ($\lambda_A = -2$), B – SEC.

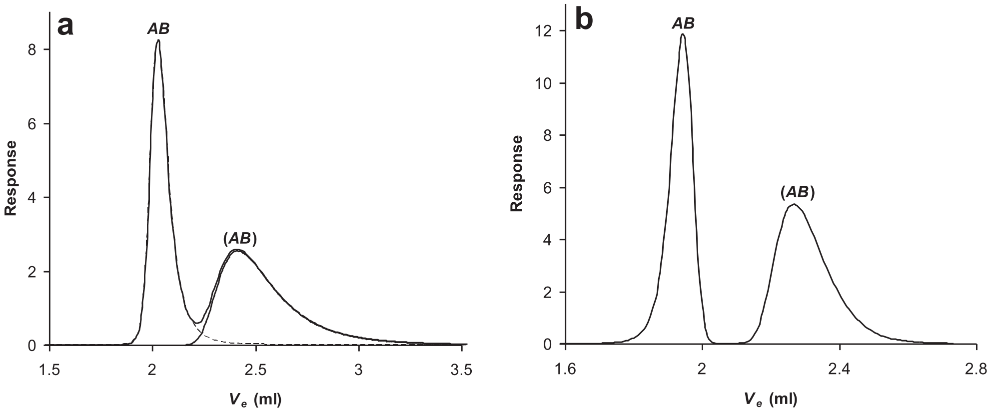

Fig. 10. Chromatograms for a sample of Fig. 9 simulated at near–critical interaction conditions. Interaction parameters: *a*: $\lambda_A = -0.4$, $\lambda_B = 0.4$; *b*: $\lambda_A = 0.1$, $\lambda_B = 0.8$.

count 3000 will be assumed. The chromatographic behavior of polymers is highly universal, and our study will be focused on the qualitative aspects chromatography of block copolymers. Just to bind the simulations to familiar polymers, we are assuming that *A* is poly(ethylene oxide) with R_A (nm) = 0.034 $M^{0.5}$, *B* is poly (propylene oxide) with R_B (nm) = 0.031 $M^{0.5}$, while (*AB*) is the corresponding ring diblock copolymer PEO–PPO.

Fig. 8 shows a simulated chromatogram for a model ring copolymer (*AB*), in which block *B* is very polydisperse, while *A* has a moderate polydispersity. The chromatogram of Fig. 8 is simulated at strong adsorption interaction for *A* and critical condition for *B*. There is a series of completely separated peaks in this simulated chromatogram. Each individual peak corresponds to co-oligomers with all possible numbers of repeat units of the component *B*, but with the same fixed number of *A* units.

Thus the theory predicts possibility of separation of polydisperse low-molar mass ring diblock copolymers by the length of strongly adsorbing block *A* at the critical condition for the other block *B* (like it is the case with linear diblocks). However, unlike linear diblock, now peak positions are not identical to those of an individual adsorbing polymer *A*. Therefore the identification of peaks in such chromatogram can not be made by comparing the result with that for a homopolymer *A*. If however some ring copolymer with monodisperse block *A* is available and the molar mass of this block is exactly known, the identification will become possible.

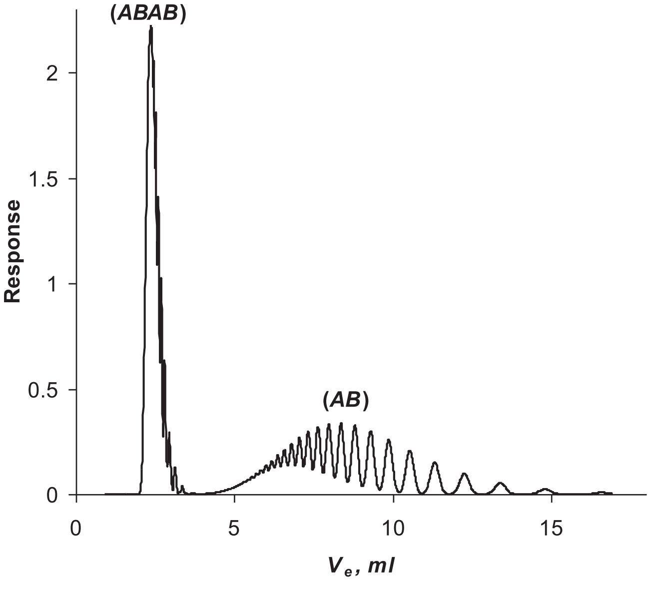

Fig. 11. Simulated chromatogram for a mixture of (*AB*) and (*ABAB*) at the adsorption–SEC condition. In a diblock copolymer adsorbing block *A* is monodisperse chain of $n_A = 10$ repeat units; non-adsorbing block *B* is of $M_w = 1000$ and $M_w/M_n = 1.1$. In a tetrablock copolymer there are two adsorbing *A* blocks (each of $n_B = 5$), and two non-adsorbing *B* blocks (each of $M_w = 500$ and $M_w/M_n = 1.1$). Adsorption interaction parameter: $\lambda_A = -38$.

Figs. 9 and 10 show simulated chromatograms for a mixture of linear and ring diblock copolymers *AB* and (*AB*). In the modeled linear and ring copolymers blocks *A* and *B* were highly polydisperse (both having the heterogeneity index $M_w/M_n = 1.5$).

Fig. 9*a* corresponds to the SEC condition for both *A* and *B*. Cyclic copolymers are eluted later than their linear analogues. However, because of the polydispersity the peaks corresponding to cyclic and linear copolymers (shown by thin solid and dashed lines) are wide and the resulting chromatogram appears as a single peak. The separation is even poorer at the adsorption condition for *A* and SEC for *B* (Fig. 9*b*). Similarly, no separation between ring and linear copolymers was achieved under the critical condition for *B* and either SEC or adsorption condition for *A*, as well as at the adsorption condition for both *A* and *B*.

Fig. 10*a*,*b* correspond to chromatographic conditions where the interactions for *A* and *B* are both close to the critical interaction point. A chromatogram for a case where these interactions are shifted from the critical point to the opposite directions is given in Fig. 10*a*, while Fig. 10*b* corresponds to both pre-critical interactions. As it follows from the theory (Fig. 10*a*,*b*), a considerable chromatographic separation between linear and ring copolymers can be achieved at such conditions even if these polymers are very polydisperse. The theory predicts especially good separation if interactions (which are both close to the critical point) are shifted to the exclusion side (Fig. 10*b*). The reason of excellent separation in Fig. 10*b* is clear from Fig. 5.

Fig. 11 shows a virtual chromatogram of a mixture of low-molar mass ring-shaped diblock and tetrablock copolymers of the same M_w and of the same average composition at the strong adsorption condition for blocks *A*, and SEC for *B*. These diblock and tetrablock copolymers are completely separated from each other, tetrablocks being eluted first. Within each zone copolymers with short blocks *B* are retained stronger; and even there is partial separation of individual co-oligomers (*AB*). Such impressive separation of diblocks from multiblocks can be expected, however, only if the strongly adsorbable blocks *A* are monodisperse.

5. Conclusion

The main result of this work is a new theory for describing the chromatographic behavior of ring-shaped block copolymers. This theory is based on the ideal-chain model, the advantages and drawbacks of which in describing chromatography of complex polymers were discussed previously [30,33,40]. We just point out two disadvantages: (i) this theory does not account for the excluded volume effects and intramolecular chain unit interactions (and hence in the systems where such interactions are significant one may expect deviations from the ideal-chain theory); (ii) the ring topology of a polymer chain is accounted only partially (in fact, a ring macromolecule in this model is represented by an ensemble of unknotted and knotted rings). To the other hand, nowadays only ideal-chain theories are available to describe analytically chromatography of polymers, and exact solutions are obtainable even for complex macromolecules. Despite the above mentioned disadvantages, ideal-chain theories have proven to describe quite reasonably chromatography of real linear and cyclic homopolymers, as well as of linear block copolymers [23, 25, 30, 33b, 34, 40, 44–47]. We could not find in the literature experimental data on the behavior of ring block copolymers in various modes of interactive chromatography, in order to check the predictions of the present theory. We hope that such experiments will be reported in the future.

In particular, this theory predicts the following. (i): In the contrast to the behavior of linear diblocks, the chromatographic retention of ring diblock copolymers will be dependent of the length of the ‘critical’ block (Figs. 2 and 3). (ii): At the conditions of Fig. 3 the separation of ring diblock co-oligomers according to molar mass of one block can be possible (Fig. 8). (iii): At the conditions of adsorption for one component *A* and SEC for *B* it can be possible to separate ring copolymers having the same average molar mass and the same average composition, but differing in the number of blocks; it is expected that diblocks will be more retained than multiblocks (Figs. 7 and 11). (iv): Full separation of polydisperse ring block copolymers from the linear ones (Fig. 10*b*) is expected at the conditions of Fig. 5; the number of blocks and its sequence in both ring and linear copolymers being of no importance. The question is whether such conditions can be realized in chromatographic experiments.

There are relevant interesting problems to be addressed in the future. We just mention that this theory can be used to analyze features of two-dimensional chromatography of ring-shaped diblock copolymers. It seems that analogous theories can be developed also for topologically more complex copolymers, such as linear–cyclic and eight-shaped block copolymers, etc.

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