



Theory of chromatography of partially cyclic polymers: Tadpole-type and manacle-type macromolecules



Andrey V. Vakhrushev, Alexei A. Gorbunov*

Institute for Highly Pure Biopreparations, 7 Pudozhskaya, 197110 St. Petersburg, Russia

ARTICLE INFO

Article history:

Received 6 November 2015

Received in revised form

14 December 2015

Accepted 15 December 2015

Available online 19 December 2015

Keywords:

Partially cyclic polymers

Chromatography

Theory

Separation by topology

Size-exclusion

Critical adsorption interaction

ABSTRACT

A theory of chromatography is developed for partially cyclic polymers of tadpole- and manacle-shaped topological structures. We present exact equations for the distribution coefficient K at different adsorption interactions; simpler approximate formulae are also derived, relevant to the conditions of size-exclusion, adsorption, and critical chromatography. Theoretical chromatograms of heterogeneous partially cyclic polymers are simulated, and conditions for good separation by topology are predicted. According to the theory, an effective SEC-radius of tadpoles and manacles is mostly determined by the molar mass M , and by the linear-cyclic composition. In the interactive chromatography, the effect of molecular topology on the retention becomes significant. At the critical interaction point, partial dependences $K(M_{\text{lin}})$ and $K(M_{\text{ring}})$ are qualitatively different: while being almost independent of M_{lin} , K increases with M_{ring} . This behavior could be realized in critical chromatography—for separation of partially cyclic polymers by the number and molar mass of cyclic elements.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Since the topological structure of macromolecules has a significant impact on the polymeric properties [1–3], the creation of polymers with predetermined molecular topology is becoming more urgent. In particular, in recent years, great progress has been achieved in the synthesis of topologically complex macrocyclic polymers [4–9]; examples of the precision synthesis of complex polymers of even tetra- and pentacyclic topologies have been recently reported [10–13].

For the identification and characterization of the synthesized polymers and for separating the target macromolecules from their precursors and by-products the chromatographic methods are successfully used [14–16]. Most commonly, the size-exclusion chromatography (SEC) is applied, which allows to separate molecules according to their size. However, for complex polymers the possibilities of SEC are limited, since molecular sizes of these macromolecules are determined not only by the length of the polymeric chain, but also by the chain topology.

In such cases, along with the SEC, other modes of chromatography are used, which are based on the adsorption of macromolecules. In order to achieve good separation results, it is

important to choose optimal conditions of adsorption interaction (that is to select a proper combination of stationary and mobile phases as well as the operating temperature). Method development in chromatographic separation of polymers can be facilitated by using approaches based on the molecular theory.

The molecular theories of chromatography have been developed for linear and ring polymers [17–20]. Like the well-known Casassa theory of SEC [21,22], these theories were based on the model of an ideal macromolecule in a slit like pore, but adsorption interactions were additionally taken into account. These theories have proven to describe very reasonably both SEC and adsorption chromatography of real linear and ring polymers and were used to predict new chromatographic techniques for separation of polymers. In particular, a possibility of a very efficient separation of linear and ring polymers has been predicted at the critical interaction conditions, intermediate between the conditions of SEC and adsorption chromatography [13,15,16]. Now the method of liquid chromatography at the critical conditions (LCCC) has become a recognized technique in separation and characterization of macrocycles [23].

Analogous theories have been developed also for star-shaped polymers [24,25], for ring-shaped block-copolymers [26], and for more complex cyclic polymers, such as eight-shaped and theta-shaped macromolecules [27,28]. Some results of these theories also found the experimental confirmation [24,29].

In this paper, we consider partially cyclic polymers: tadpole-type structures (Fig. 1A and B), which are also called as ring-with-branches [30], and manacle-type structures (Fig. 1C–E),

* Corresponding author. Fax: +7 8122304948.

E-mail addresses: AlexeiGorbunov@hotmail.com, aagorbunov@live.ru (A.A. Gorbunov).

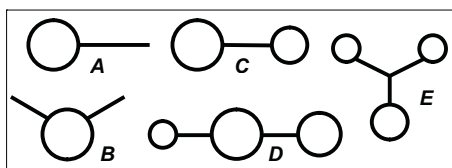


Fig. 1. Partially cyclic macromolecules. (A) a tadpole LR; (B) a ring with two branches LRL; (C) a manacle-shaped polymer R_1LR_2 ; (D) a linearly-bridged tricyclic chain, (E) a star-bridged tricyclic polymer.

also referred to as bridged multi-cyclic polymer topologies [7]. Many representatives of these families have been synthesized, both SEC and interactive chromatography were applied for their separation and characterization [26,31]. The SEC behavior of some partially cyclic polymers in wide pores can be understood basing on the mean span dimension theory elaborated by Wang and co-authors [32]. However, there is no theory covering both SEC and interactive chromatography of these polymers.

We have developed such a theory, and we are presenting it here. Basing on the theory, the behavior of these polymers in size-exclusion, adsorption, and critical chromatography will be discussed. In order to visualize the expected separations, and to analyze the molar mass heterogeneity effects, we use the theory for simulating chromatograms of heterogeneous tadpole- and manacle-shaped polymers.

2. Model and theory: distribution coefficient of partially cyclic polymers

In this study, we use an ideal-chain model to obtain exact analytical equations describing chromatography of partially cyclic polymers (Fig. 1 shows some members of this family).

The chromatographic retention is determined by the distribution (or partition) coefficient K that can be expressed in terms of the ratio of the partition functions for a polymer within a pore and in an unrestricted space of the same volume:

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

Like in the previous papers [13,14,16,23,24], we use here the continuum approach, which is analogous to describing the motion of a Brownian particle under spatial constraints, and consider a slit-like pore as the space between two planar surfaces (pore walls) which are situated at $z = -d$ and $z = d$. The scopes of this approach and its capability to describe real-life systems were discussed previously [13,14,23].

We consider a chain of N segments with contour length Nb , where b is the segment length. In the continuum approach all possible conformations of an ideal chain are described by the diffusion equation, while the de Gennes' boundary condition [33] is applied on the pore walls to account for the adsorption interaction. A parameter c entering into the boundary condition, serves in the theory as the adsorption interaction parameter. Negative c values correspond to effective repulsive forces. The point $c = 0$, is referred to as a critical interaction point (CIP). At $c = 0$, for a linear ideal-chain homopolymer of any N , adsorption enthalpic interaction is compensated by the steric entropic effects. Positive values of c correspond to adsorption and therefore c may be considered as an adsorption parameter. Its inverse $1/c$ is the average thickness of the layer formed by an adsorbed macromolecule on the surface.

Let us consider a tadpole-shaped polymer LR, which is characterized by the sizes of its linear and ring parts $R_{\text{Lin}} = b\sqrt{N_{\text{Lin}}/6}$, and $R_{\text{Ring}} = b\sqrt{N_{\text{Ring}}/6}$ Fig. 2. Please, note, that while R_{Lin} has a meaning of the radius of gyration of an unconfined linear chain L , R_{Ring} is

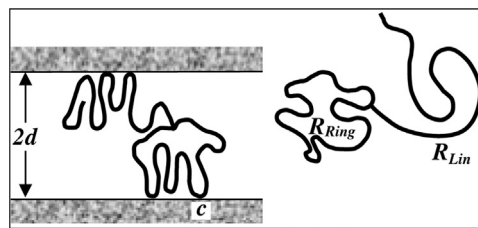


Fig. 2. A flexible tadpole-shaped polymer LR in the equilibrium with a slit-like pore. Model parameters: the sizes of linear and ring fragments, R_{Lin} , and R_{Ring} , pore size parameter d , and adsorption interaction parameter c .

not that of a ring R . R_{Ring} is the radius of gyration of a reference linear chain, having the same contour length (the same molar mass) as the ring R .

The partition functions $Z_{\text{LR}}^{(\text{pore})}$ and $Z_{\text{LR}}^{(0)}$ for a tadpole-shaped macromolecule are expressible in terms of a sub-partition function $P(r', r'')$ of a chain having ends at fixed points x', y', z' and x'', y'', z'' :

$$Z_{\text{LR}} = \iint_{x_1, x_2} dx_1 dx_2 \iint_{y_1, y_2} dy_1 dy_2 \int_{-d}^d dz_1 \int_{-d}^d dz_2 \times P(r_1, r_2) \times P(r_2, r_2) \quad (2)$$

The function $P(r', r'')$ for an ideal linear chain in a slit-like pore has the form [14]:

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

$$P(z', z'') = \frac{1}{d} \sum_{k=1}^{\infty} \frac{\cos[\alpha_k \xi - (k-1)\pi/2] \times \cos[\alpha_k \xi' - (k-1)\pi/2]}{1 + \lambda/(\alpha_k^2 + \lambda^2)} \times \exp[-(g\alpha_k)^2] \quad (4)$$

where $R = b\sqrt{N/6}$ is the radius of gyration of a free ideal linear chain of N units; $\xi' = (z' - d)/d$ 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 a dimensionless parameter of a polymer-wall interaction; and α_k are the roots (non-negative, real or imaginary) of the equation:

$$\alpha_k = \arctg\left(\frac{\lambda}{\alpha_k}\right) + (k-1)\frac{\pi}{2}, \quad k = 1, 2, \dots, \infty \quad (5)$$

The Green's function (3)–(5) has been used previously for developing analytical theories describing chromatography of linear [13], star-shaped [21], cyclic [16,22], and several types of multi-cyclic polymers [23,24].

For a manacle-shaped polymer RLR (Fig. 1C) the partition function is equal:

$$Z_{\text{RLR}} = \iint_{x_1, x_2} dx_1 dx_2 \iint_{y_1, y_2} dy_1 dy_2 \int_{-d}^d dz_1 \int_{-d}^d dz_2 P(r_1, r_1) P(r_1, r_2) P(r_2, r_2) \quad (6)$$

By substituting the function (3)–(5), into Eqs. (2), (6), and (1), and by integrating, we have obtained the exact equations for the distribution coefficients K_{LR} and K_{RLR} of tadpole- and manacle-shaped polymers. Analogous equations have been obtained also for other types of partially cyclic polymers (shown in Fig. 1B, D, and E). These new theoretical results are presented in Appendix A. The exact Eqs. (A1)–(A7) are quite complicated, but can be used for numerical calculation of the distribution coefficient at various adsorption interactions.

Additionally, a number of simpler asymptotic equations are derived, approximately describing situations of wide and narrow

Download English Version:

<https://daneshyari.com/en/article/7610251>

Download Persian Version:

<https://daneshyari.com/article/7610251>

[Daneshyari.com](https://daneshyari.com)