Chromatography under critical conditions: An analogy between functionalized and partially cyclic polymers

Alexei A. Gorbunov[*], Andrey V. Vakhrushev

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

ABSTRACT

An analogy is established between functionalized polymers and partially cyclic macromolecules (PCMs) in the liquid chromatography at critical conditions (LCCC). Application of the functionalized chain analogy (FCA) for prediction of the behavior of complex multi-cyclic PCMs in the LCCC mode is demonstrated. By using FCA, we discuss possibilities of LCCC to separate multi-cyclic PCMs by the number of cycles, and with respect to molecular topology. FCA is also extended to describe PCMs with specifically adsorbing groups; this results in a simplified theory of LCCC of functionalized PCMs. By simulating chromatograms of heterogeneous functionalized PCMs at the conditions of LCCC, we show possible dramatic effects of functional groups on the topological separation of PCMs: even the retention order of components may change to opposite.

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1. Introduction

Liquid chromatography at critical conditions (LCCC) is a special mode of interactive chromatography of polymers. It is realized at week adsorption interactions corresponding to the critical interaction point (CIP), where the entropy losses of a linear macromolecule in a pore are compensated by an energy gain due to the adsorption. LCCC takes its origin from the studies, where the critical adsorption conditions were discovered [1,2], and the chromatographic behavior of homopolymers at these conditions was explained theoretically [3,4]. A basic feature of the LCCC mode is that at the CIP, the chromatographic retention is not affected by molar mass distribution, but stays sensitive to other types of chain heterogeneity [5].

In particular, a possibility to separate by LCCC polydisperse polymers according to the number of functional groups was predicted [6], and verified [7]. LCCC mode also turned out useful in studies of topologically different polymers. The separation of linear and ring macromolecules by LCCC, predicted by the theory [8], was really achieved experimentally [9]. In subsequent years, critical conditions of adsorption were found for many of experimental systems; excellent LCCC separations and analyses of functionalized and macrocyclic polymers were reported. Nowadays LCCC has become a recognized method for analysis and separation of functionalized and cyclic macromolecules [10–14].

In recent years, great progress has been achieved in the synthesis of complex macrocyclic polymers with predetermined molecular topology [15–18], which resulted in making eight-shaped, theta-shaped and manacle-shaped polymers [16], as well as even more complex structures, such as double-eight and double-trefoil macromolecules [19].

Method development for chromatographic separation of such complex polymers can be facilitated by using approaches based on the molecular theory. In addition to the theory of chromatography of linear and ring polymers [20], extensions describing several types of more complex cyclic polymers, such as eight-shaped and theta-shaped macromolecules [21,22], have been reported. Some results of these theories found the experimental confirmation [22,23]. Recently we have developed a theory of chromatography for partially cyclic macromolecules (PCMs), having tadpole- and manacle-type topological structures [24].[1] In principle, it seems possible to construct similar theories for topologically more complex macromolecules. However, with increasing topological complexity, theories will become increasingly complicated, and it will be difficult to use these theories.

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

[1] Unfortunately, some references in [24] have not been properly updated. We apologize to readers for a number of misleading references in [24].
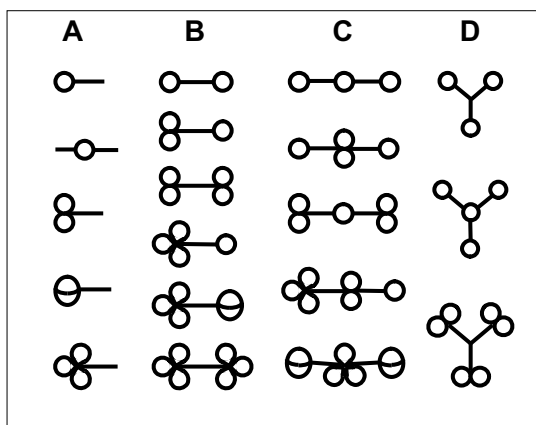
Fig. 1. Examples of complex partially cyclic macromolecules of different topology. (A) tadpole-type structures; (B–D) bridged multi-cyclic structures (B) PCMs with one bridge, (C) linearly-bridged PCMs with two bridges, (D) star-bridged PCMs.

In the present paper, we therefore propose another theoretical approach, which is based on the similarity of the LCCC behavior of functionalized macromolecules and PCMs. By comparing theoretical results for tadpole- and manacle-type polymers at the CIP [24] with the well-known results of the LCCC theories of functionalized polymers [5,25–28], we establish an analogy between functionalized macromolecules and PCMs at the CIP.

We will demonstrate how the approach, based on the functionalized chain analogy (FCA), can be applied to predict LCCC behavior of complex multi-cyclic PCMs, e.g. having topological structures shown in Fig. 1.

FCA will be also extended for describing PCMs with specifically adsorbing groups. This will result in a simplified theory of LCCC of functionalized PCMs.

2. An analogy in the behavior of functionalized macromolecules and simple PCMs at the CIP

The theories of LCCC [5,8,20–28] operate with a distribution coefficient K, which characterizes the chromatographic retention at the CIP, and use a model of an ideal-chain polymer in a slit-like pore. A macromolecule is modeled by a chain of N segments, having the contour length Ns, where s is the segment length. There are two length-dimensional parameters in this problem. One parameter is the radius of gyration of the chain $R = s\sqrt{N/6} \sim \sqrt{M}$. The second parameter is the pore width, which will be denoted as $2d$. In fact, a dimensionless macromolecule-to-pore size ratio $g = R/d$ appears in the theory.

The theoretical result for a linear chain is very simple – at the CIP, the distribution coefficient of a linear polymer K_L does not depend on g:

$$K_L = 1 \tag{2.1}$$

The LCCC theory for a ring polymer [5,20] results in different equations. Here and in the rest of the paper we consider situations of $g_R < 1$, where rings are small compared with the pore width. According to [5,20], at $g_R < 1$, the distribution coefficient of a ring equals:

$$K_R = 1 + \frac{\sqrt{\pi}}{2} g_R \tag{2.2}$$

where $g_R = R_{Ring}/d$. Note that $R_{Ring} = s\sqrt{N/6}$ is not the radius of gyration of a ring, it equals to the radius of gyration of a linear chain having the same contour length (and therefore the same molar mass M) as the ring.

Theories describing LCCC of functionalized macromolecules and PCMs use similar models (see Fig. 2). It was mentioned in Ref. [24], that at the CIP, features of the chromatographic behavior of manacles and di-functional macromolecules with adsorptive terminal groups are rather alike.

Really, there is an analogy in the behavior of PCMs and functionalized polymers. This analogy is based on the fact, that at the CIP, there is an effective attraction of rings to pore walls, attraction of entropic (topological) nature [20]. Attractive pseudo-potentials for an adsorptive functional group and for a ring at the CIP are depicted in the inserts to Fig. 2a, b. Due to this fact, chain conformations, determining the behavior of mono- and di-functional macromolecules (such as chains with one and two ends at the pore walls) have corresponding analogues in tadpole and manacle structures – Fig. 2.

In the Sections 2.1–2.4 we discuss this analogy in more detail. FCA will be justified by comparing exact equations describing LCCC of functionalized polymers and PCMs.

Let us start with the comparison of mono- and di-functional chains with simple PCMs (tadpoles and manacles).

2.1. LCCC of functionalized macromolecules: main theoretical results

A model used in the theories [5,25–27] of LCCC of functionalized polymers (Fig. 2a) is a modification of the basic model, described above. Apart from R and d, there is one more parameter $W = \delta\left(e^{-\Delta\varepsilon} - 1\right)$ accounting for additional adsorption interaction of a functional group. A small length-dimensional δ is an effective radius of interaction (assumed as being of order s), while $\Delta\varepsilon$ (expressed in units of kT) accounts for the difference in the interaction free energy of a terminal chain fragment and the repeating unit. Parameter W is positive if the functionalized unit is more adsorptive than the other ones. It is convenient to introduce a dimensionless interaction parameter q [25,27]:

$$q = \frac{W}{d} = \frac{\delta}{d}\left(e^{-\Delta\varepsilon} - 1\right) \tag{2.3}$$

According to the theories [5,25–27], at the CIP, the distribution coefficient K_{La} of a mono-functional linear chain La (with a terminal functional group, a) equals:

$$K_{La} \equiv K_1(q_a) = 1 + q_a \tag{2.4}$$

An equation for K_{aLb} of a linear di-functional, aLb, having two terminal functional groups (with the interaction parameters q_a and q_b), is somewhat more complicated [27]:

$$K_{aLb} = K_2(q_a, q_b, g) = 1 + q_a + q_b + q_aq_b \times \phi(g) \tag{2.5}$$

The function $\phi(g)$ appearing in Eq. (2.5) is defined by Eq. (2.6); this function is plotted in Fig. 3.

$$\phi(g) = \sum_{k=-\infty}^{\infty} e^{-(k\pi g)^2} \approx \begin{cases} \left(\sqrt{\pi}g\right)^{-1} & , g < g_0 \\ 1 & , g > g_0 \end{cases} \tag{2.6}$$

where $g_0 \approx \pi^{-0.5} \approx 0.564$.

The first term in both Eqs. (2.4) and (2.5) corresponds to chains with no ends at pore walls. The second term in Eq. (2.4), as well as two similar terms in Eq. (2.5), are due to mono- and di-functional chains having one functional group near a wall; the last term in Eq. (2.5) is relevant to di-functionals with both functional groups contacting the walls simultaneously (these types of chain conformations are depicted in Fig. 2a).