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# Liquid Chromatography of Theta-Shaped and Three-Armed Star Poly(tetrahydrofuran)s: Theory and Experimental Evidence of Topological Separation

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**A theoretical background is provided for the methods of the analysis and topological separation of complex macrocyclic polymers by means of size exclusion chromatography (SEC), liquid adsorption chromatography, and liquid chromatography at the critical condition. We focus on a particular problem of the separation of *θ*-shaped polymers from its three-armed star analogues. Based on the theory, we simulate chromatograms for model mixtures of polydisperse *θ*- and star-polymers and analyze conditions for good separation of these polymers by topology. A theory is compared with the behavior of star- and *θ*-shaped poly(THF)s in size exclusion and interactive chromatography, and a good qualitative agreement between theory and experiment is observed. In particular, it is shown that in both SEC and interactive chromatography *θ*-polymers elute after the corresponding stars of the same molar mass. According to theory and experiment, chromatography under the critical and near-critical interaction conditions is especially promising for the separation of polydisperse macrocyclic polymers from their linear or branched analogues.**

Complex macrocyclic polymers have gained increasing attention, since these will realize unprecedented properties and functions because of their unique topologies, which are distinct from linear or branched counterparts. Considerable progress has been achieved in the synthesis of complex polymers,[1,2] having either semicyclic,[3−5] eight-shaped,[4,6] *θ*-shaped,[7,8] manacle-shaped,[8,9] macrotricyclic,[10] or multicyclic[11] topologies. In particular, an electrostatic self-assembly and covalent fixation process has now been introduced for the efficient synthesis of these unconventional polymer topologies, as well as topological isomers, and topological block copolymers.[2,12]

Chromatographic methods have proven to be very efficient in separations of polymers not only by molar mass and by composition,[13−19] but also by their topology.[2,15,20] In particular, it has been shown that ring-shaped polymers can be fully separated from linear analogues by liquid chromatography at the

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critical condition of adsorption (LCCC).[20] Tezuka et al.[7,8] have reported chromatographic results showing the possibility of separation of topologically different macrocyclic polymers. In order to achieve good results in separation of polymers by topology, the experimental conditions (i.e., the combination of stationary and mobile phases as well as the operating temperature) must be selected very carefully to provide the optimal chromatographic mode. Experimental work on finding good separation conditions could be facilitated by applying theoretical approaches. Development of a molecular theory and simulation of the chromatographic behavior of macromolecules seems to be the most straightforward way to the goals of optimization.

A theory of chromatography of linear polymers based on the model of an ideal macromolecule in a slitlike pore has been developed by Gorbunov and Skvortsov.[21,22] The same model as in the Casassa theory of size exclusion chromatography[23] was used in the theory,[21,22] but adsorption interactions were additionally taken into account. Analogous theories have been developed also for star-shaped polymers,[24,25] for polymer rings,[22,26] and for eight-shaped macromolecules and for a family of daisylike polymers.[27]

The theory[21,22,26] has proven reasonably good to describe chromatography of real linear and ring-shaped polymers.[20,28,29] This theory has been already used to predict the possibility of very efficient separation of linear and ring polymers at the point of critical adsorption interaction, and now the method of LCCC has become a recognized technique in separation and characterization of macrocycles.[20]

Despite many efforts, the necessity for further theoretical treatment and understanding of the subject is large because of the increasing use of macromolecules with special architecture. In this paper, we present a theory of chromatography for a family of macrocyclic polymers, which will be referred to as bunch-shaped polymers.

Since the primary practical goal of the present work is separation of $\theta$-shaped polymer from three-arm star-polymer that is a precursor for the $\theta$-polymer, we shall focus on the analysis of the chromatographic behavior of a $\theta$-shaped polymer, which is the simplest member of the considered family. Experimental data on both size exclusion (SEC) and interactive chromatography of $\theta$-shaped poly(THF)s, prepared from corresponding three-armed, star-shaped precursors will be discussed and compared with the theory.

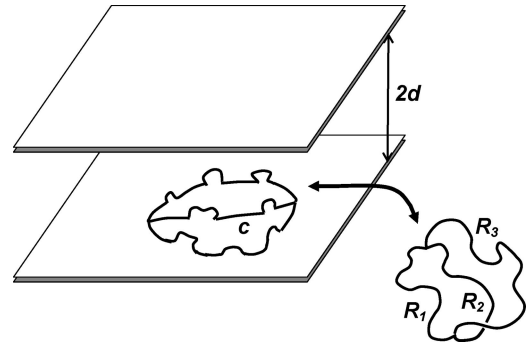


**Figure 1.** $\theta$-Shaped polymer chain in a slitlike pore with adsorptive walls and in an unrestricted space. Model parameters are indicated: pore width $2d$; radii of gyration of subchains $R_1$, $R_2$, $R_3$; adsorption interaction parameter $c$.

## THEORETICAL CONSIDERATION

**Model and Mathematical Solution.** To develop a theory of chromatography of a $\theta$-shaped polymer, we consider an equilibrium partitioning of this macromolecule between an unrestricted space and a slitlike pore of a width $2d$ (Figure 1). To account for statistical properties of subchains, we use as previously[27] a continuum ideal-chain approach,[22] which is analogous to describing the motion of a Brownian particle under spatial constraints. Each chain fragment $i$ ($i = 1, 2, 3$) connecting two branch points in a $\theta$-polymer is modeled as an ideal polymer chain of contour length $n_i b$, where $b$ is the segment length. The size of every subchain is characterized by the radius of gyration $R_i$ of this individual chain in an unrestricted space (for an ideal-chain $R_i = b(n_i/6)^{1/2}$).

As in the theories,[21,24−27] the interaction of polymer chain units with pore walls is accounted for by an interaction parameter $c$.[22] Negative values of $c$ correspond to effective repulsive forces. The point $c = 0$, at which an adsorption of an infinitely long chain starts, is referred to as a critical point of adsorption. Positive values of $c$ correspond to the adsorption, and therefore, $c$ may be considered as the adsorption interaction parameter. Its inverse $1/c$ has the meaning of an average thickness of the layer formed by an adsorbed macromolecule on the surface. The parameter $c$ has the dimension of inverse length. The formal definition of $c$ is given in the Appendix; its physical meaning and its relevance to the lattice model adsorption energy parameter has been discussed previously.[22,30]

By using this approach, we have derived equations describing chromatography of a family of polymers, which will be referred to as bunch-shaped polymers. An $f$-bunch polymer is composed of $f$ subchains connecting two branch points; the bunch family includes a $\theta$-polymer ($f = 3$); $f = 4, 5,...$, etc., correspond to more complex macrocyclic polymers. The obtained general exact equations and a number of simpler approximate formulas, which

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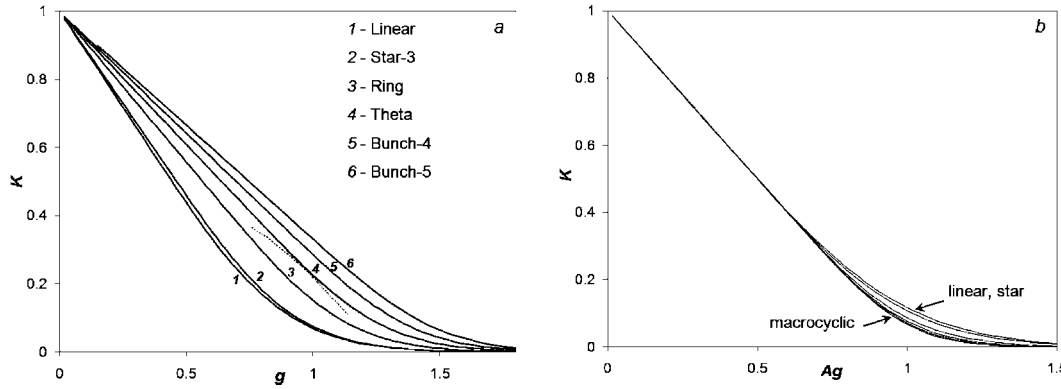


**Figure 2.** Distribution coefficient $K$ of polymers of different topology in size exclusion chromatography (a) as a function of the parameter $g = R/d$ and (b) as a function of $Ag$ (the coefficients $A$ are listed in Table 1). Dotted lines correspond to eqs 1.

**Table 1. Topologically Conditioned Size Factor *A* for Different Polymers**

| polymer | linear | three-armed star, symmetric | ring | eight, symmetric | $\theta$ ($f = 3$), symmetric | $\delta$-graph ($f = 4$), symmetric | bunch $f = 5$, symmetric |
|---|---|---|---|---|---|---|---|
| A | 1.1284 | 1.0830 | 0.8862 | 0.8102 | 0.7829 | 0.7173 | 0.6695 |

correspond to narrow- and wide-pore situations and to the interaction conditions of special interest (SEC and critical adsorption point), are given in Appendix.

According to the theory, the distribution coefficient of an $f$-bunch polymer $K_f = \varphi(\lambda,g_1,g_2,...,g_f)$ depends on $f+1$ dimensionless parameters: on a scaled interaction parameter $\lambda = -cd$ and $f$ subchain to pore size ratios $g_i = R_i/d$; $i = 1, 2,...,f$. This dependence is represented by the exact equation A6−A7 of the Appendix. At $f = 3$, the general equation A6−A7 results in the simpler equation A11 for a $\theta$-polymer.

For symmetric polymers (with all subchains of equal length), the general solution simplifies to $K_f = \varphi_f(\lambda,g)$, where $g = (g_1^2 + g_2^2 + ... + g_f^2)^{1/2} = R/d$. Here $R$ is the radius of gyration of a reference linear macromolecule of the same molar mass, while $d$ characterizes the pore size ($2d$ is the distance between pore walls). Evidently, the parameters $\lambda = -cd$ and $g = R/d$ do not depend on the chain topology.

The equations A11 and A6−A7 can be used to calculate the distribution coefficient of $\theta$- and bunch-shaped polymers and to analyze the chromatographic behavior of these polymers in all modes of chromatography. These new theoretical results will be compared with those obtained previously for linear, star-, and ring-shaped polymers in order to understand both general and specific features of the behavior of topologically complex polymers in various modes of liquid chromatography.

We focus on the behavior of the considered polymers in three special modes of chromatography, namely, in SEC, LCCC, and liquid adsorption chromatography (LAC). A particular problem of separation of polydisperse star- and $\theta$-polymers will be discussed in some detail.

**Size Exclusion Chromatography.** SEC corresponds to the special case of absence of adsorption interactions $\lambda = -cd \gg 1$. A theory of SEC is developed in much detail for many types of polymers,[23,24,26,27,31] and it is interesting to compare the SEC behavior of polymers of different topology.

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In our theory, the SEC behavior of a $\theta$-polymer is described by eq A11 at $\lambda \to \infty$, while the wide- and narrow-pore asymptotes for a symmetric $\theta$-polymer are the following:

$$K_{\theta,\mathrm{SEC}} \approx \begin{cases} 1 - \dfrac{g}{\sqrt{\pi}}\left[\dfrac{2}{3} + \dfrac{3\arcsin(1/3)}{\sqrt{2}}\right] & g \ll 1 \\ \dfrac{128}{9\sqrt{3}\pi} g^2 \exp\left(-\dfrac{\pi^2}{4} g^2\right) & g \gg 1 \end{cases} \quad (1)$$

Figure 2 shows the theoretical results on the distribution coefficient of various symmetric polymers at the condition of SEC. The data for $\theta$- and bunch-shaped polymers are calculated by using the exact equations A11 and A6−A7 at $\lambda \to \infty$; for other polymers, we have used the previously reported equations.[22−27] The simplified formulas of eq 1 are shown by dotted lines in Figure 2a, and one can see that the set of these asymptotes is a very reasonable approximation. Figure 2a shows the dependences of the distribution coefficient $K$ of different polymers on the ratio $g = R/d$. As was explained above, the parameter $g$ does not depend on chain topology.

As can be seen in Figure 2a, at the SEC condition $K$ decreases with $g$ for all bunch-shaped polymers, and this behavior is qualitatively similar to that of the other types of polymers. In particular, this is the well-known fact[23,22] that for linear, star, and ring polymers in wide pores $K$ linearly decreases with $g$. A linear decrease of $K$ with $g$ at $g < 1$ also takes place for $\theta$- and bunch-shaped polymers (eqs 1 and A9; Figure 2a).

Thus, the general result of the SEC theory for all considered polymers in wide pores can be formulated as $K \approx 1 - Ag$. The theoretical values of the topologically specific factor $A$ for various types of polymers are listed in Table 1 (for a $\theta$-polymer, $A$ is calculated from eq 1; for bunch-shaped polymers with $f = 4$ and $f = 5$, eq A10 is used; for linear, star-, ring-, and eight-shaped polymers, the coefficients $A$ have been obtained previously[22,23,27]).

Figure 2b shows the data of Figure 2a replotted as $K$ ($A \cdot R/d$). As can be seen in Figure 2b, the theoretical SEC data for all types of macrocyclic polymers practically form a single depen-

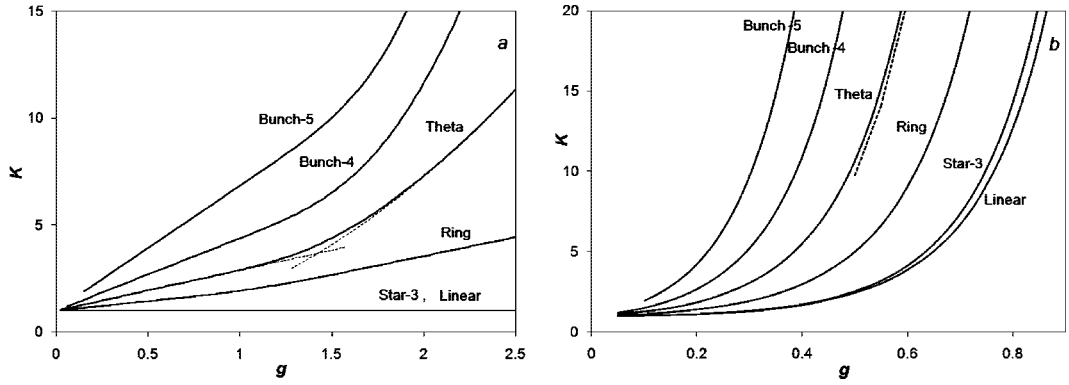


**Figure 3.** Theoretical dependences of $K$ on $g$ (a) in LCCC (at $\lambda = 0$) and (b) in LAC (at $\lambda = -2$) for symmetric polymers of different topology. The asymptotes of eqs 2 and 3 are shown by dotted lines.

dence in coordinates $K$ versus $Ag$. The values of $K$ for linear and three-star polymers, although being somewhat higher in narrow pores, also fit the master curve in wide pores (at $R/d < 0.7$). Since the wide-pore situation is the most common one in the SEC practice, one can conclude on the existence of the master curve $K(A \cdot R/d)$, which describes SEC of linear, star, and macrocyclic polymers. This means that the parameter $s = AR$ (which is a product of topology and molar mass-conditioned factors) can be considered as an effective size of a macromolecule, which determines its behavior in size exclusion chromatography.

By using the results of the SEC theory, one can estimate expected positions of the peaks of $\theta$-shaped and bunch-shaped polymers in size exclusion chromatography, if the peak positions of the corresponding simpler polymers (linear or star-shaped ones) are known.

**Interactive Chromatography.** In interactive chromatography ($c > 0$), the chromatographic behavior becomes quite different from that of SEC mode. At $c > 0$, macromolecules form adsorption layers on the pore walls, which results in the LAC behavior with $K > 1$ and in the increase of $K$ with $M$. Of special interest is the LCCC mode, which corresponds to the critical interaction point $c = 0$, where the chromatographic behavior of linear polymers changes from SEC to LAC type.

Theoretical dependences of $K$ on $R/d$ for various symmetric polymers in LCCC (at $c = 0$) and in LAC (at $c > 0$) are shown in Figur 3a and b, respectively.

According to the theory, unlike linear and star-polymers for which $K = 1$ (and does not depend on $M$) at the critical point $\lambda = 0$, for macrocyclic polymers at $\lambda = 0$, $K$ increases with $g = R/d$ (and, therefore, with $M$). As has been discussed previously,[26,27] the reason of this behavior is in the specific entropic attraction of macrocycles to pore walls, which results in the increase of the concentration of cyclic chain units near the walls.

In particular, the distribution coefficient of a symmetric $\theta$-shaped polymer in wide and narrow pores at $\lambda = 0$ scales as

$$K_{\theta,\mathrm{cr}} \approx \begin{cases} 1 + \dfrac{3\sqrt{\pi}}{2\sqrt{2}} g \sim 1 + B\sqrt{M} & g \ll 1 \\ \dfrac{\pi}{\sqrt{3}} g^2 \sim M & g \gg 1 \end{cases} \qquad (2)$$

Similar dependences $K_{\mathrm{cr}} \sim 1 + B\sqrt{M}$ are predicted by the theory for all macrocyclic polymers in wide pores; the coefficients $B$ are different (for the considered family of bunch-shaped polymers, these coefficients can be calculated from eq A10).

In LAC, the order of retention stays as in LCCC, but the retention of all polymers (including linear and star-shaped ones) increases with $M$ (Figure 3b). The molar mass dependences in the adsorption mode are stronger than at the critical point. According to the theory, at high values of $cR$, all these dependences are of the exponential type. In particular, the distribution coefficient of a $\theta$-shaped polymer scales as

$$K_{\theta,\mathrm{ads}} \approx \frac{32\pi}{9\sqrt{3}} \frac{cR^2}{d} \exp(c^2R^2) \qquad cR \gg 1 \qquad (3)$$

It follows from the theory (Figure 3a and b) that the interactive chromatography can be used to separate $\theta$-polymers and other macrocyclic polymers by molar mass.

According to the theory, in LCCC, retention of linear and star polymers is the same; in LAC, stars are retained stronger, but the retention behavior of linear and star-polymers is very similar (Figure 3b). The differences in $K$ between all other polymers (at equal values of $g$) are quite pronounced; moreover, as it follows from Figure 3 and from eqs 2 and 3, these differences increase with $M$. Therefore, in principle, both LCCC and LAC can be used to separate $\theta$- and bunch-polymers from linear, star- and ring-shaped analogues of the same molar mass. It should be noted, however, that topological separation may become difficult if polymers are heterogeneous in molar mass; in such cases, the optimal chromatographic mode must be applied to achieve good results. This will be demonstrated in the next section, where a problem of separation of polydisperse $\theta$- and star-polymers is considered in a more detail.

**Separation of Polydisperse $\theta$- and Star-Shaped Polymers.** Since a $\theta$-polymer can be produced from a relevant three-armed star precursor, of practical importance is a problem of separation of $\theta$-polymers and corresponding star-polymers.

Figure 4 shows the calculated dependences of $K$ of star- and $\theta$-polymers on the interaction parameter $\lambda = -cd$ at some fixed value of $g$. It follows from Figure 4 that a $\theta$-shaped polymer always retains stronger than a star of the same molar mass; therefore, such polymers, in principle, can be separated in all modes of chromatography.

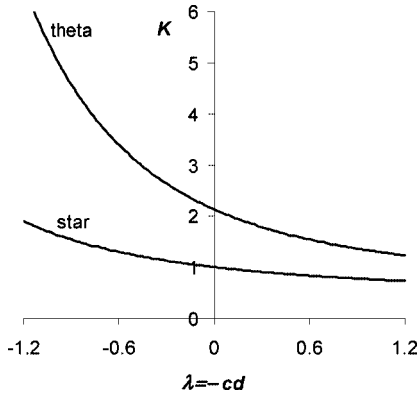


**Figure 4.** Theoretical dependences of the distribution coefficient $K$ on the interaction parameter $\lambda = -cd$ at $g = R/d = 0.6$ for a symmetric three-armed star and a $\theta$-shaped polymer. Negative $\lambda$ correspond to LAC; $\lambda = 0$ is the critical adsorption point; large positive $\lambda$ represents the pure SEC mode.

In order to study the effect of molar mass heterogeneity on the separation by topology we apply a "virtual chromatograph"[29] —a special software for the simulation of chromatograms of polymers, which is based on the theory of the distribution coefficient. This technique has been already used to predict separations of other polymers by their architecture, composition, and number of adsorption active functional groups;[25,27,32] chromatograms simulated for polydisperse linear polymers have proven to be very similar to the real ones.[29,33] We have incorporated eq A11 into the virtual chromatography software and have performed simulations for model mixtures of polydisperse star- and $\theta$-shaped polymers. As was expected, the virtual separation of star- and $\theta$- polymers with narrow molar mass distributions, $M_w/M_n < 1.05$, has been possible in all chromatographic modes; however, the problem has turned out more difficult for polydisperse polymers.

Figure 5 shows chromatograms simulated for a model mixture of equal amounts of symmetric three-star and $\theta$-shaped poly(THF)s (in simulations we used an equation $R = 0.0367M^{0.5}$ for the radius of gyration of an unperturbed linear poly(THF) chain[34]). It was assumed that arms in a star-polymer are of equal average molar mass $M_w = 2000$ and have quite broad logarithmically normal molar mass distribution with $M_w/M_n = 1.25$. The second component in the mixture was a corresponding $\theta$-shaped polyTHF with the subchains of $M_w = 2000$, $M_w/M_n = 1.25$.

As can be seen, if polymers are polydisperse, rather poor virtual separations are obtained in SEC and in LAC at strong adsorption interaction (Figures 5a,b), while a perfect separation takes place at the critical point of adsorption (Figure 5c). An excellent separation in Figure 5c is conditioned by the considerable difference in $K_{star}$ and $K_\theta$, and by the absence of the molar mass dependence of $K_{star}$ at the critical interaction point (Figure 3a). Quite good virtual separations were obtained also at near-critical conditions, which are slightly shifted from the critical point to either SEC or adsorption side.

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## EXPERIMENTAL SECTION

**Synthesis of $\theta$- and Star-Shaped Poly(THF)s.** A series of $\theta$-shaped poly(THF)s and their star-shaped analogues having the corresponding molecular weights and having the relevant linking/chain end structures were prepared according to the procedure detailed before.[7] Thus, as shown in Scheme 1, a series of size-controlled trifunctional star-shaped poly(THF)s having an *N*-phenylpyrrolidinium salt end group[35] were prepared and subjected to the ion-exchange reaction with benzoate, and subsequent covalent conversion provided a series of three-armed star-shaped poly(THF)s (molecular weights of 7300, 9600, and 11 900 by $^1$H NMR).[36]

The corresponding $\theta$-shaped poly(THF)s were also prepared from identical star telechelic precursors having *N*-phenylpyrrolidinium salt end groups. The subsequent ion-exchange reaction with trimesate was conducted typically as follows. A THF solution (1.0 mL) of 0.200 g (0.026 mmol) of trifunctional star-shaped poly(THF)s having *N*-phenylpyrrolidinium salt end groups was added dropwise to an ice-cooled (<5 °C) aqueous solution (120 mL) containing an excess amount of a sodium trimesate (0.083 g, 10 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo for up to 1.5 h. This precipitation treatment was repeated three times to give a trifunctional star-shaped poly(THF)/trimesate, 0.173 g (containing a trace amount of residual water to avoid uncontrolled ring-opening reaction), with 94% ion-exchange yield.

The covalently linked $\theta$-shaped polymers were subsequently prepared as in the following example.[7] The ionic polymer precursor, i.e., star-shaped poly(THF)/trimesate, (0.025 g) was dissolved in 250 mL of acetone (0.1 g/L) and was heated to reflux (bath temperature of 90 °C) for 18 h. The reaction solvent was removed, and the recovered product (0.023 g) was subjected to preparative thin-layer chromatography ($SiO_2$, hexane/acetone = 2/1) in order to remove unreacted ionic polymer precursors and side products. The final yield of a $\theta$-shaped poly(THF) was 0.011 g (49%).

The obtained $\theta$-shaped polymers as well as the star-shaped polymer precursor analogues were subjected to $^1$H NMR and to MALDI-TOF mass spectroscopic analyses to confirm their topologies. The details were reported in the preceding papers.[7,9]

**Chromatographic Measurements.** Safety note: THF and acetonitrile are suspected toxic. All procedures were done while wearing a goggle, gloves, and under closed hoods.

SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of TSK G4000HXL (300 mm long, 7.8 mm i.d., 5-$\mu$m average particle size) was employed with THF as an eluent at a flow rate of 1.0 mL/min at 40 °C. In a typical procedure, 40 $\mu$L of sample solution (sample concentration of 0.5 wt %) was injected. Interactive chromatography measurements were conducted by an isocratic mode using a Tosoh model CCPS equipped with a UV detector model UV 8020 at 254 nm. A C18 bonded silica column of TSK ODS-80TS (80 Å pore, 250 mm long, 4.6 mm, i.d., 5-$\mu$m average particle size) was employed with a mixed THF/$CH_3CN$ mobile phase at a flow rate of 0.75 mL/min at 25 °C.

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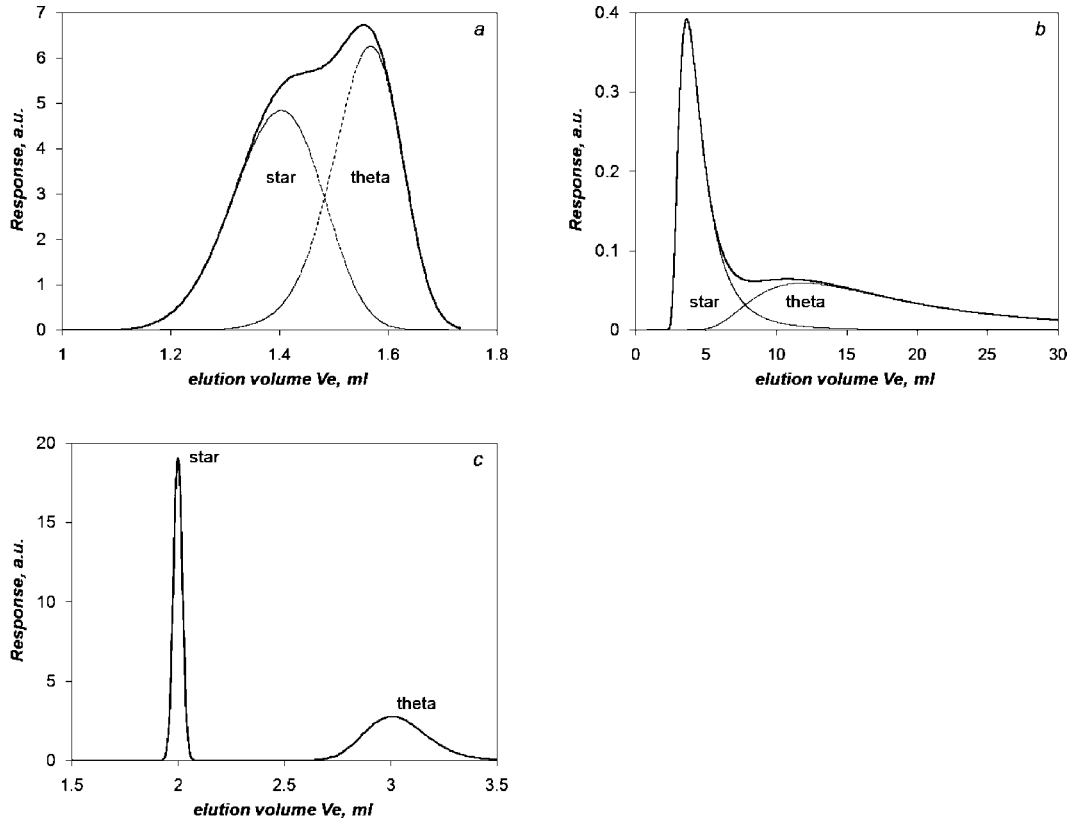
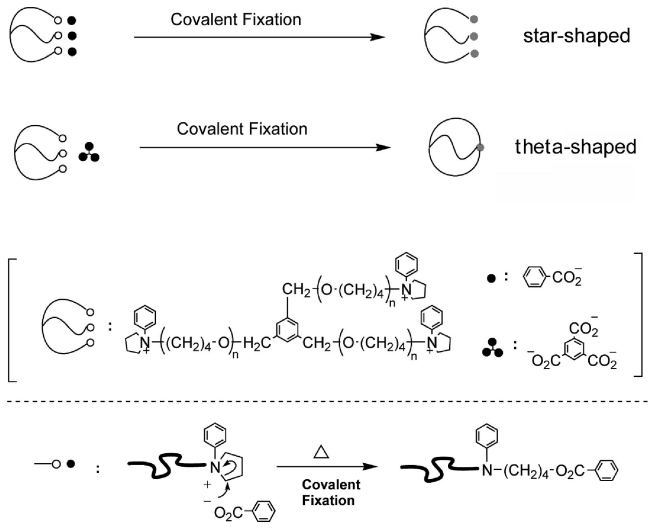



**Figure 5.** Theoretical chromatograms for a mixture of star- and $\theta$-shaped polyTHFs under the condition of (a) SEC, (b) strong adsorption, and (c) critical interaction. Simulation parameters: arms in a star-polymer and subchains in a $\theta$-polymer are of equal $M_w = 2000$ and of equal $M_w/M_n = 1.25$; values of the interaction parameter, $\lambda$ (a) 50 000, (b) $-2$ and (c) 0; pore width $2d = 10$ nm, pore volume $V_p = 1.0$ mL, and interstitial volume $V_i = 1.0$ mL. Dotted lines represent chromatograms for the individual components of the mixture.

**Scheme 1. Synthesis of Star- and $\theta$-Shaped Poly(THF)s by Electrostatic Self-Assembly and Covalent Fixation**




## CHROMATOGRAPHIC BEHAVIOR OF STAR- AND Θ-SHAPED POLY(THF)S

The elution volume $V_e = V_i + V_pK$, which characterizes retention in chromatography, is linearly related to the distribution coefficient $K$. In a given chromatographic system, $V_i$ (which is the volume between the particles of the packing) and the pore volume $V_p$ are constants; therefore, one may qualitatively compare experimental data obtained in terms of the elution volume with the theoretical results for the distribution coefficient $K$.

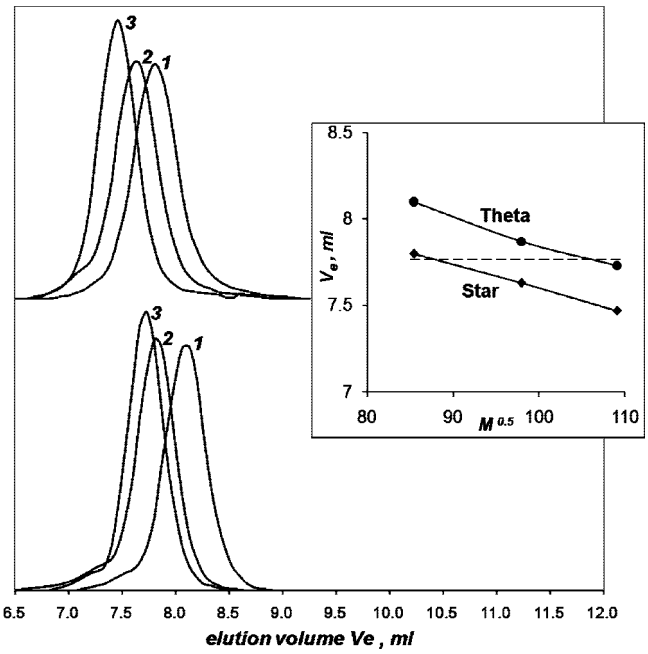



**Figure 6.** SEC chromatagrams (RI) of three-armed star (top) and $\theta$ (bottom) polymers of $M_w$ of 7300 (1), 9600 (2), and 11 900 (3), respectively. (column, TSK G4000 HXL; eluent, THF, 1.0 mL/min). An inset shows a plot of the elution volume $V_e$ of these polymers versus $\sqrt{M}$.

**$\theta$-Shaped and Star-Shaped Poly(THF)s in SEC.** Figure 6 shows the experimental SEC chromatograms of $\theta$- and star-shaped

poly(THF)s; an inset shows dependences of the elution volume, $V_e$, on the square root of molar mass, $M^{0.5}$. These dependences can be qualitatively compared with the corresponding theoretical plots $K$ versus $g$ (Figure 2a).

The experimental results of Figure 6 are in a qualitative agreement with the theoretical ones (Figure 5a, and Figure 2a). In particular, both theory and experiment shows that $\theta$-shaped polymers are eluted later than star-shaped ones of the same molar mass. This effect is due to the fact that $\theta$-polymers are more compact than stars.

To compare the SEC theory and experiment quantitatively, we make use of the fact that $K_\theta = K_{star}$ at $s_\theta = s_{star}$ (where $s = AR \sim AM^{0.5}$), and consequently, $(V_e)_\theta = (V_e)_{star}$ at $A_\theta M_\theta^{0.5} = A_{star} M_{star}^{0.5}$). By taking $M_\theta^{0.5}$ and $M_{star}^{0.5}$ as intersection points of the corresponding curves with the line $V_e = Const$ (dashed line in the inset of Figure 6), we thus obtain $(A_\theta/A_{star})_{exp} = M_{star}^{0.5}/M_\theta^{0.5} \approx 0.83$. The theoretical value of this ratio, calculated by using the data of Table 1, is $(A_\theta/A_{star})_{theor} \approx 0.72$.

More data on the SEC behavior of complex polymers are available.[5,8,36] Although these data are not of high enough precision, it seems that generally macrocyclic polymers are more expanded than can be expected from the theory. This is not surprising, because the swelling of real macrocyclic polymers due to the excluded-volume effects is not described by the ideal-chain model.

A $\delta$-graph polymer (which here is referred to as bunch $f = 4$) has been synthesized as well, and its SEC behavior in comparison with that of its eight-shaped precursor was investigated.[37] According to the data of ref 37, both polymers again are more expanded than can be expected from the theory. It is interesting, however, that the experimental value of the ratio, which characterizes a comparative expansion of two macrocyclic polymers, $(A_{\delta-graph}/A_{eight})_{exp} \approx 0.88$ is quite close to the theoretical value $(A_{\delta-graph}/A_{eight})_{theor} \approx 0.89$.

**Behavior of $\theta$- and Star-Shaped Poly(THF)s in the Interactive Chromatography.** In the interactive chromatography, polymer adsorption depends on the mixed mobile-phase composition and temperature. In our experiments on the TSK ODS-80TS column, the temperature 25 °C was fixed, and the interaction was varied by varying the composition of the mixed solvent THF/$CH_3CN$.

The overplayed chromatograms of star- and $\theta$-poly(THF)s of the same $M = 9600$ at various mobile-phase compositions, and the dependences of the elution volume of these polymers on the eluent composition, are shown in Figure 7. These chromatograms can be qualitatively compared with the theoretical ones of Figure 5. The chromatograms of Figure 7a, obtained in pure THF, are very similar to those of Figure 5a, simulated at the SEC condition: both figures show very poor separation by topology. The mobile-phase compositions of 52−50% THF in the THF/$CH_3CN$ mixed solvent correspond to the interaction conditions that are close to the critical interaction point, and therefore, Figures 7b and 7c can be compared with Figure 5c. Although not as perfect as in the theory, quite good separations are really seen in Figure 7b,c. Figure 7d corresponds to stronger adsorption interaction and, thus, can be compared with Figure 5b. The separation in Figure 7d is obviously poorer than in Figure 7b,c; this fact also well agrees with the theory.

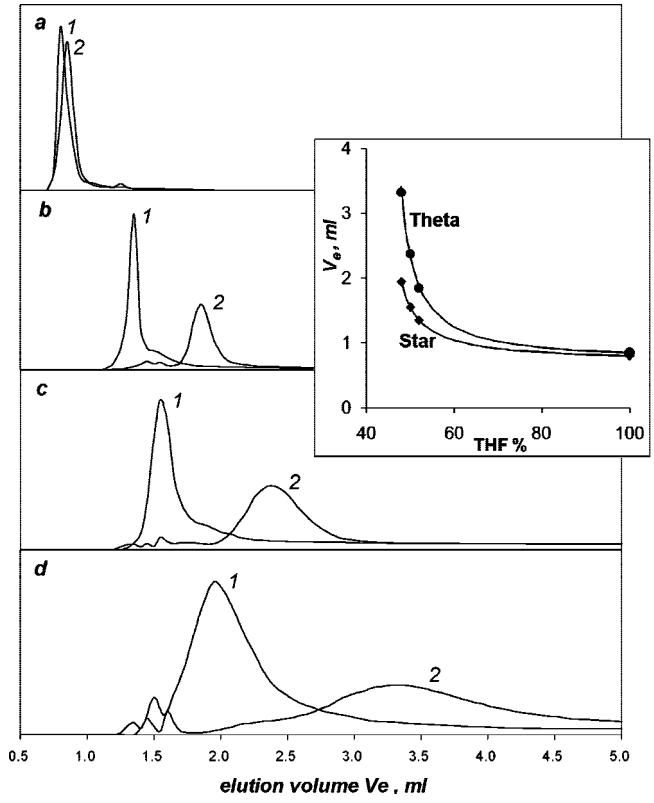



**Figure 7.** Overlaid chromatograms of star (1) and $\theta$ (2) polymers of $M_w = 9600$ at different eluent compositions of THF/acetonitrile of 100/0 (a), 52/48 (b), 50/50 (c), and 48/52 (d).[38] Column, TSK ODS-80TS; flow rate, 0.75 mL/min. Inset: dependences of the elution volume of these $\theta$- and star-shaped poly(THF)s on the THF content in mixed eluent.

Since a variation of the mobile-phase composition corresponds to a variation of an adsorption interaction, the dependences shown in the inset of Figure 7 can be qualitatively compared with the analogous theoretical ones (Figure 4). As seen in Figure 7, the retention of both polymers changes with mobile-phase composition, but the retention order stays the same, as predicted by the theory.

In Figure 8, chromatograms of star- and $\theta$-poly(THF)s of different molar mass in the 50/50 THF/$CH_3CN$ mixed eluent are shown, and the elution volumes of these polymers are plotted against $\sqrt{M}$. Evidently, the experimental behavior at this mobile-phase composition is quite close to that at the critical point (in fact, since the retention of star-shaped poly(THF) weakly increases with molar mass, it seems that the selected condition is slightly shifted from the critical point to the adsorption side). Anyway, the molar mass dependences of the elution volume, which are shown in the inset of Figure 8, can be qualitatively compared with those of Figure 3, where the theoretical plots of $K$ on $g = R/d \sim \sqrt{M}/d$ at the critical point and in the adsorption interaction are presented. Figure 8 clearly shows that $\theta$-shaped polymers elute after their star-shaped precursors and that the difference in the

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(38) The modest base-line shift in RPC measurements was noticeable under the present condition without rigorous temperature control. The apparent negative baseline shift in the $\theta$-3 in Figure 8 was anomaly accompanied with the peak height normalization procedure.

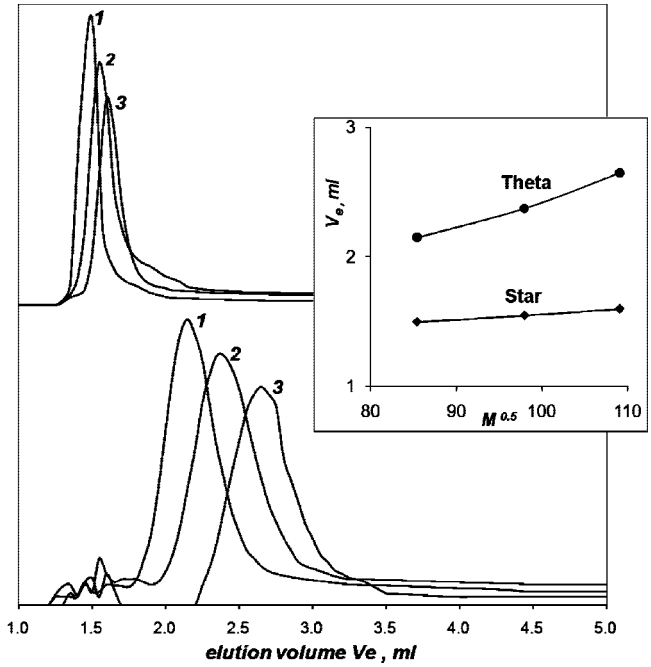


**Figure 8.** Chromatograms of star (top) and $\theta$ (bottom) polymers of $M_w$ of 7300 (1), 9600 (2), and 11 900 (3), respectively.[38] Column, TSK ODS-80TS; eluent, THF/acetonitrile (50/50), 0.75 mL/min. Inset: dependences of the elution volume of star- and $\theta$-shaped poly(THF)s on $\sqrt{M}$.

elution volumes increases with $M$. These observations are in a good agreement with the theory.

Although the interaction condition of 50/50 THF/$CH_3CN$ is not exactly the critical one, Figure 8 shows that the separation by topology at this condition is less influenced by molar mass than at the condition of SEC (Figure 6), and therefore, the critical or near-critical interaction conditions really can be used to optimize topological separation of polymers.

## CONCLUDING REMARKS

The theory of chromatography of $\theta$- and bunch-shaped polymers, like the analogous theories for polymers of simpler topologies, is based on the ideal-chain model of a macromolecule. An ideal-chain model permits intersections of chain units, which of course cannot happen in real macromolecules, and therefore, this model does not account for the excluded-volume effects. The argument for the use of such theory is that it should be reasonably close to the $\theta$-temperature, when excluded-volume effects are weak, and that it allows exact analytical results to be obtained for polymers of quite complex architectures. Nowadays the ideal-chain-based theory is the only one available to describe analytically chromatography of complex polymers. When applied to macrocyclic polymers, the ideal-chain model allows accounting for a given way of connection of the chain units, but not for the exact topological status of a macromolecule. For example, when such a model is applied to a ring-shaped polymer, it describes both unknotted and knotted rings, but not any one of these topologically different individual forms. Of course, the same is also true for more complex macrocyclic polymers, where knotting of each loop may result in a variety of topologically different forms: the ideal chain theory describes none of these individual forms, but rather an ensemble composed of them all. Since the ideal chain model has obvious physical limitations, it is very important to verify theoretical results by the experiment.

The present study demonstrates that the theory can qualitatively describe chromatographic behavior of real star-shaped and $\theta$-shaped polymers. Some quantitative differences between the theory and experiment, such as those observed in the size exclusion mode of chromatography, can be conditioned by the excluded-volume effects and topological constraints, which are not taken into the account in the theory.

We think that further theoretical efforts are still necessary to clarify the chromatographic behavior of complex polymers. We believe that analogous theories can be developed for other important types of complex polymers, in particular, for semicyclic polymers. It is also possible to extend the theory in order to describe chemically heterogeneous polymers having two or several different types of the chain units. Polymers often include specific groups (such as terminal and branch-point groups), which may be different from the other chain units in the aspect of their adsorption interaction; the presence of such groups may considerably influence the chromatographic behavior of polymers. The theory of chromatography of linear polymers with functional groups is developed in much detail;[39] recently, similar theories have appeared for several types of more complex polymers.[32,40] Further extensions of the theory are possible to describe chromatography of macrocyclic polymers in the systems where the effect of specific groups is expected to be important. The theoretical description of the chromatographic behavior of two- and multicomponent cyclic block copolymers would also be of interest. We hope to proceed with these extensions in forthcoming papers.

On the other hand, we think that the Monte-Carlo numerical modeling of the behavior of complex polymers in pores with a proper account of excluded-volume effects and topological constraints, extending the previous studies on linear[41,42] and more complicated polymers,[43] would be of high interest. The results of analytical theory based on the ideal-chain model may serve as a useful reference case for more sophisticated theoretical studies that employ more realistic physical assumptions.

A method of electrostatic self-assembly and covalent fixation, which is applied in the present study to obtain $\theta$-shaped polymers, has also proven to be a very prospective one for the synthesis of other types of topologically unique polymers, such as, for example, those having topological shapes such as “tadpole”, “manacle”, and “ring with branches”; work on designing of even more exotic topological structures is in the progress. It would be interesting to study the chromatographic behavior of these polymers and to compare the experimental results with the theory. Of special interest would be an experimental study of the behavior of complex macrocyclic polymers near the critical interaction point, where the theory predicts an especially good separation of polydisperse polymers by their topology.

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## APPENDIX

**Distribution Coefficient of Bunch-Shaped Polymers.** The distribution coefficient $K$ 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:

$$K = \frac{Z^{(\text{pore})}}{Z^{(0)}} \tag{A1}$$

The partition functions $Z_f^{(\text{pore})}$ and $Z_f^{(0)}$ for an $f$-bunch polymer are expressible in terms of subfunctions $P_i(r',r'')$ for subchains having ends at fixed points $x',y',z'$ and $x'',y'',z''$:

$$Z_f = \int_{x',x''}\int \mathrm{d}x' \cdot \mathrm{d}x'' \int_{y',y''}\int \cdot \mathrm{d}y' \cdot \mathrm{d}y'' \int_{-d}^{d} \mathrm{d}z' \int_{-d}^{d} \mathrm{d}z'' \cdot P_1(r',r'') \cdot P_2(r',r'') \cdot \ldots \cdot P_f(r',r'') \tag{A2}$$

The subpartition function $P(r',r'')$ for an ideal linear chain of $n$ units in a slitlike pore is a solution of the diffusion equation with the de Gennes' boundary condition,[44] $P^{-1}(\partial P/\partial z)|_{\text{on pore walls}} = -c$, where $c$ serves as a parameter of adsorption interaction. A mathematical solution of this boundary problem for a slitlike pore is well-known; it has a form[22]

$$P(r',r'') = \frac{1}{4\pi R^2} \exp\left[-\frac{(x'-x'')^2 + (y'-y'')^2}{4R^2}\right] \cdot P(z',z''), \tag{A3}$$

$$P(z',z'') = \frac{1}{d}\sum_{k=1}^{\infty} \frac{\cos[\alpha_k \xi' - (k-1)\pi/2]\,\cos[\alpha_k \xi'' - (k-1)\pi/2]}{1 + \lambda/(\alpha_k^2 + \lambda^2)} \times \exp[-(g\alpha_k)^2] \tag{A4}$$

where $R = b(n/6)^{1/2}$ is the radius of gyration 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 the molecule-to-pore size ratio; $\lambda = -cd$ is a dimensionless parameter of a polymer−wall interaction; and $\alpha_k$ are the roots of the equation

$$\alpha_k = arctg\left(\frac{\lambda}{\alpha_k}\right) + (k-1)\frac{\pi}{2}, \qquad k = 1, 2, \ldots, \infty \tag{A5}$$

The chain propagator $P(r',r'')$ as given by eqs A3; A4 has been used previously to develop an analytical theory of chromatography for linear, star-shaped, ring-shaped, and daisy-like polymers.[21−27]

By substituting this function into eqs A1 and A2, and by integration, we have obtained the following exact formula for the distribution coefficient of a bunch-shaped polymer:

$$K_f = \pi^{(f-1)/2}\left(\prod_{i=1}^{f} g_i\right) \cdot \left(\sum_{i=1}^{f} g_i^{-2}\right)^{1/2} \times \sum_{\substack{k_1,k_2,\ldots,k_f=1 \\ f+\sum_{i=1}^{f} k_i \text{ even}}}^{\infty} C_{k_1,k_2,\ldots,k_f} \exp\left(-\sum_{i=1}^{f} \alpha_{k_i}^2 g_i^2\right) \tag{A6}$$

where

$$C_{k_1,k_2,\ldots,k_f} = 2^{-f}\prod_{i=1}^{f} \frac{\lambda^2 + \alpha_{k_i}^2}{\lambda + \lambda^2 + \alpha_{k_i}^2} \times \left[\sum_{\sigma_1,\ldots,\sigma_f=\pm 1}\left((-1)^{0.5\sum_{i=1}^{f}\sigma_i(k_i-1)} \frac{\sin(\sum_{i=1}^{f}\sigma_i\alpha_{k_i})}{\sum_{i=1}^{f}\sigma_i\alpha_{k_i}}\right)\right]^2 \tag{A7}$$

and the eigenvalues $\alpha_{k_i}$ are the roots of eq A5. At negative values of $\lambda$ some of these eigenvalues are imaginary values,[21] however the coefficients C are always real. At some special values of $\lambda$ and at some eigenvalues the denominator of eq A7 turns zero; however the numerator turns zero as well. Such uncertainties always can be resolved by means of taking corresponding limits.

In addition to the general exact equation it is useful also to have approximate asymptotic formulas describing chromatographic behavior in narrow and in wide pores. In a narrow-pore situation where all $g_i \gg 1$ the first term with $k_1 = k_2 = \ldots = k_f = 1$ dominates in the series of eq A6. By keeping only this term we obtain the following narrow-pore asymptote:

$$K_f = \pi^{(f-1)/2}\left(\prod_{i=1}^{f} g_i\right)\left(\sum_{i=1}^{f} g_i^{-2}\right)^{1/2} C_{1,1,\ldots,1} \exp(-\alpha^2 g^2) \tag{A8}$$

wherein the main eigenvalue $\alpha \equiv \alpha_1$ is the first root of eq A5, and $g^2 = g_1^2 + g_2^2 + \ldots + g_f^2$. As was explained previously,[27] the strong adsorption asymptotes at $-\lambda \gg 1$ are obtainable by keeping the terms with $k_1 = k_2 = \ldots = k_f = 1, 2$.

By using the solution for a chain propagator of an ideal macromolecule near one adsorbing wall,[45] we have obtained other useful approximations describing chromatographic behavior of an $f$-bunch polymer in wide pores under the condition of SEC $\lambda \to \infty$ and at the critical interaction point $\lambda = 0$. These equations can be presented in a form

$$K_f \approx 1 + \frac{1}{\sqrt{\pi}}\left(\frac{\sigma^f - 1}{\sqrt{\sum_{j=1}^{f} g_j^{-2}}} + \sqrt{\sum_{j=1}^{f} g_j^{-2}} \sum_{j=1}^{f-1} \sigma^j \sum_{1}^{C_f^j} \times \frac{\operatorname{arctg}\sqrt{(g_{i_{j+1}}^{-2} + \ldots + g_{i_f}^{-2})/(g_{i_1}^{-2} + \ldots + g_{i_j}^{-2})}}{\sqrt{(g_{i_1}^{-2} + \ldots + g_{i_j}^{-2})(g_{i_{j+1}}^{-2} + \ldots + g_{i_f}^{-2})}}\right) \tag{A9}$$

where $\sigma = -1$ corresponds to the condition of SEC, while $\sigma = 1$ gives a result for the critical point of adsorption. The operation $\sum_1^{C_f^j}$ means the summation over all combinations of $j$ elements (taken from total $f$ elements); a set of indices $i_1,\ldots,i_j$ designates one particular combination, while $i_{j+1},\ldots,i_f$ is a corresponding complementary combination.

For a symmetric $f$-bunch (with all subchains of equal length) eq A9 reduces to

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$$K_f \approx 1 + \frac{g}{\sqrt{\pi}}\left[\frac{\sigma^f - 1}{f} + \sum_{j=1}^{f-1} \sigma^j C_f^j \frac{\operatorname{arctg}\sqrt{(f-j)/j}}{\sqrt{(f-j)\cdot j}}\right] \quad \text{(A10)}$$

At $f = 1$ and at $f = 2$, eqs A6−A10 recover the well-known formulas for linear and ring polymers.[21,22,26] If the length of one subchain tends to zero, the bunch-shaped series transforms into the daisy-like family.[27] Of course, the theoretical results for an $f$-bunch at one $g_i \to 0$ converge to those for a corresponding $(f-1)$ daisy.[27]

For a $\theta$-shaped polymer ($f = 3$) the general eq A6−A7 reduces to the following exact formula:

$$K_\theta = \pi G^2 \sum_{\substack{k,l,m=1 \\ (k+l+m)\text{odd}}}^{\infty} A_k A_l A_m \lambda^2 \left(\frac{2\lambda^2 + E}{2F - E^2}\right)^2 \exp(-\alpha_k^2 g_1^2 - \alpha_l^2 g_2^2 - \alpha_m^2 g_3^2) \quad \text{(A11)}$$

where $G^2 = (g_1^2 g_2^2 + g_1^2 g_3^2 + g_2^2 g_3^2)^{1/2}$; $A_j = 2\alpha_j^2/(\alpha_j^2 + \lambda^2 + \lambda)$, $(j = k,l,m)$; $E = \alpha_k^2 + \alpha_l^2 + \alpha_m^2$; $F = \alpha_k^4 + \alpha_l^4 + \alpha_m^4$; while depending on $\lambda$ eigenvalues $\alpha_k$, $\alpha_l$, $\alpha_m$ are the roots of eq A5. At $f = 3$, the approximate formulas A8 and A10 reduce to the asymptotes of eq 1 (at the condition of SEC) or to eqs 2 (at the critical adsorption point). At strong adsorption (at $-\lambda \gg 1$ and $-\lambda g = cR \gg 1$), eq A11 results in eq 3.

## ACKNOWLEDGMENT

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