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Chromatographic behavior of functionalized star-shaped poly(lactide)s under critical conditions of adsorption. Comparison of theory and experiment

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Abstract

Star-shaped poly(lactide)s (PLAs) with various numbers of secondary OH-groups at the PLA's arm ends and primary OH-groups attached directly to the core of the star were analyzed under critical conditions determined for linear PLAs. The same set of PLAs was then analyzed after blocking the core OH-groups with benzyl moieties. Depending on the number and the placement of the OH-groups in the star polymer different elution behavior was observed. As expected, on a 'normal' phase column, increasing the number of functional OH-groups results in a stronger interaction with the stationary phase and therefore in a larger retention volume. Keeping the number of functional groups constant, but varying the number of arms leads to a minimum in retention volume for the four arm star-shaped PLAs. The elution behavior could be discussed quantitatively on the basis of theories for polymer chromatography for large and small pores. It was possible to derive the parameters necessary to quantitatively fit the experimental results. The model for large pores and the model for small pores result in equally good descriptions of the experimental data.

Keywords: Star-shaped polylactide; Star-shaped polymers; LCCC

1. Introduction

Tailoring the properties of polymers for the desired application is one of the major tasks for polymer scientists. Beside the proper selection of the monomers and the molar mass distribution of the resulting polymers and/or copolymers, the introduction of appropriate functional groups and selection of various architectures are useful tools to target the desired properties. While a large diversity of polymerization techniques and synthetic procedures exist which allow to synthesize the desired products, there is still a lack of analytical techniques to prove the structural agreement of the polymer obtained with the target macromolecule and to check its purity. NMR, FTIR and other spectroscopic methods can only give information on average properties, while often the functionality type distribution (FTD) and chemical composition distribution (CCD) are highly important. Quantification of MALDI-TOF-MS is complicated by the possibility of differences in ionization depending on end group and molar mass, which without prior fractionation leads to erroneous average molecular weights. While size exclusion chromatography (SEC, GPC) is widely used for the determination of the molar mass distribution (MMD) and the average molar masses, methods of adsorption chromatography are less used. Chromatography under critical conditions (LCCC) has been proven to be extremely useful for FTD characterization [1–5]. Furthermore, its application to the analysis of polymer blends [6–9], block [10–16], graft [17] and miktoarm starpolymers [18] has been described.

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Experimental elution behavior has been compared with theoretical predictions for linear homo- and block copolymers and good agreement was found between a simple Gaussian model of chain adsorption and real practice [14, 19,20]. While the elution behavior is well understood for linear polymers only limited information is available on the elution behavior of more complex architectures. Using critical conditions for the linear polymer, the corresponding ring polymers are slightly stronger adsorbed, giving the possibility to separate linear polymers and rings having the same size [20–25]. According to Gutmann and Di Marzio star-shaped polymers are also expected to be slightly more adsorbed than their linear counterparts [26]. However, the differences are negligible for practical application. Kosmas et al. derived equations for the elution behavior of star polymers and predicted identical critical behavior of linear and star polymers [27]. Recently, Gorshkov extended the theory of polymer chromatography for Gaussian chains to branched species including functionalized star-shaped polymers [28].

Previously, the ability of separation of star-shaped polymers according to the number of arms by LCCC has been demonstrated [29–32]. The present paper considers this problem in a more systematic way. The main attention is paid to the comparison of experimental results for functionalized star-polymers with theoretical predictions in order to check the ability of separation theory based on the Gaussian chain model to predict the elution behavior of complex polymers.

2. Experimental part

2.1. Synthesis of star-shaped poly(lactide)s (star-shaped PLAs)

Star-shaped, hydroxyl group terminated PLAs were prepared as described for the linear and other star-shaped PLA's synthesis[31–34]. Namely, L,L-dilactide was polymerized with $Sn(Oct)_2$ and the corresponding polyol (bearing 1–6 primary OH-groups) as components of the catalytic initiating system. The synthesis of appropriated multi-hydroxyl cores was based on partially blocked OH-group of dipentaerythritol, that were used as coinitiators and transfer agent in polymerization of the L,L-dilactide.

Polymerizations were carried out in bulk at 120 °C in sealed glass ampoules, prepared using standard high vacuum technique. Conversion of LA monomer was followed by ^{1}H NMR of the reacting mixture/chloroform-d solutions.

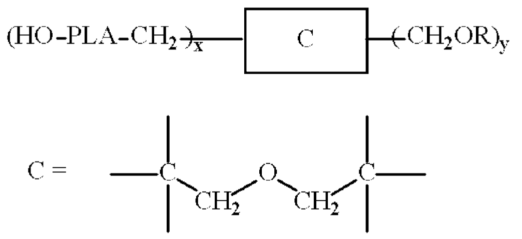
Hydrogenation with palladium catalyst in THF solvent was employed to remove the protecting benzyl groups in the star-shaped PLAs. Details on the synthesis and characterization of the products will be given in a separate paper [35].

Four different series of star-shaped PLAs with arm number, *f*, ranging from 1 to 6 were prepared and investigated under critical conditions for the linear PLAs. The schematic structures of the star-shaped PLAs with different number of arms and core protected and deprotected OH-groups are given in Scheme 1. Series A of the synthesized stars consisted of star-shaped PLAs having nearly constant molar mass of the arms. The OH-functionalities at the core were blocked by benzyl moieties (Bn). In series B the molar masses of the star-shaped PLAs are nearly identical and the primary OH-groups of the core are still protected. Series C results from series A by deprotection of the core OH-groups. Series D was obtained by deprotection of the core OH-groups of series B. For the polymers of series A and B the number of functional OH-groups is identical to the number of arms, while in series C and D all polymers have six functional groups (primary and/or secondary). Here the number of primary OH-groups decreases with the number of arms. The characterization data of the star-polymers and their elution volumes under critical conditions are given in Table 1.

2.2. Characterization

Molar masses (M_n) of the star-shaped PLA were determined by size exclusion chromatography (SEC) equipped with RI and MALLS detector.

HPLC-experiments were performed on an Agilent 1100 HPLC system consisting of degasser G1311A, quaternary gradient pump G 1322A, auto sampler G 1313A, column oven G 1316A and UV-detector G 1314A. In addition an evaporative light scattering detector ELS 1000 (Polymer Labs, Shropshire, Great Britain) has been added. Data acquisition was performed using PSS-WINGPC software version 4 (Polymer Standards Service, Mainz, Germany). Samples were dissolved at concentrations of 4 g/l in the mobile phase. The injection volume was 10 µl. Separations



R = H or Bn

1 = : x = 1; y = 5;
2 = : x = 2; y = 4;
3 = : x = 3; y = 3
4 = : x = 4; y = 2
5 = : x = 5; y = 1
6 = : x = 6; y = 0

Scheme 1. Structures of analyzed star-shaped PLAs with protected (R = Bn) and deprotected (R = H) core OH-groups.

Table 1
Characterization data and elution volumes of linear and star-shaped PLAs

Sample no.	Number of arms	M_n (theor.)	M_n (SEC-MALLS)	M_w/M_n (SEC-MALLS)	Elution volume (ELSD) in ml
A1	1	3700	3750	1.02	4.69
A2	2	6400	5600	1.02	5.07
A3	3	9500	7800	1.03	5.49
A4	4	12400	10300	1.03	6.01
A5	5	14850	13200	1.25	6.82
A6	6	18000	15800	1.05	7.42
B1	1	12700	11600	1.07	4.60
B2	2	12600	10000	1.04	4.98
B3	3	12500	9800	1.04	5.43
B4	4	12400	10400	1.03	6.00
B5	5	12350	8300	1.03	6.86
B6	6	12250	13100	1.09	7.49
C1	1	3250	4300	1.15	–[a]
C2	2	6050	5500	1.03	13.03
C3	3	9250	7700	1.04	8.67
C4	4	12250	9800	1.03	6.88
C5	5	14750	9000	1.25	7.20
C6	6	18000	15800	1.05	7.42
D1	1	12250	10100	1.08	–[a]
D2	2	12250	11100	1.03	12.53
D3	3	12250	11800	1.04	8.29
D4	4	12250	9800	1.03	6.88
D5	5	12250	9200	1.02	7.22
D6	6	12250	13100	1.09	7.49
W1	Linear	5900	4800	1.38	4.740
W2	Linear	12000	9700	1.42	4.680
W3	Linear	18000	15300	1.42	4.670
W4	Linear	30000	26000	1.75	4.673

Data partially extracted from Ref. [35].

[a] Polymer does not appear in chromatogram because of strong interaction with stationary phase.

were performed at a flow rate of 0.5 ml/min. using 2 bare silica Nucleosil columns (100 Å, 0.46×20 cm, 300 Å, 0.46×25 cm, Macherey and Nagel, Düren, Germany) connected in series at 50 °C in dioxane/*n*-hexane mixtures. Mixing was performed from the pure solvents using the gradient pump.

3. Results and discussion

The critical conditions for linear PLAs with molar masses ranging from 4800 to 26000 g/mol were determined at 50 °C at a composition of 57.1/42.9 (1,4-dioxane/*n*-hexane). Despite the different molar masses, all samples elute at the same elution volume (Fig. 1). Small variations of the solvent composition result in strong changes of the elution volume. Increasing the amount of the good solvent 1,4-dioxane results in a decreasing elution volume with increasing molar mass, while for an increase of the weak solvent (*n*-hexane) the retention volume increases strongly with molar mass.

Figs. 2 and 3 show the chromatograms of star-shaped PLAs with protected and deprotected primary OH-groups attached to the core. Figs. 4 and 5 compare the elution behavior of the functionalized PLAs. The comparison of Figs. 1 and 2 shows that end-functionalized PLA-stars exhibit an increasing retention volume with increasing number of arms. In series A the number of functional OH-groups increases with the number of arms. However, since the molecular weight of the arm is kept constant within this series, the molecular weight of the star-polymer increases with the number of arms as well. Thus, the increase in retention volume could be due either to an increase in the

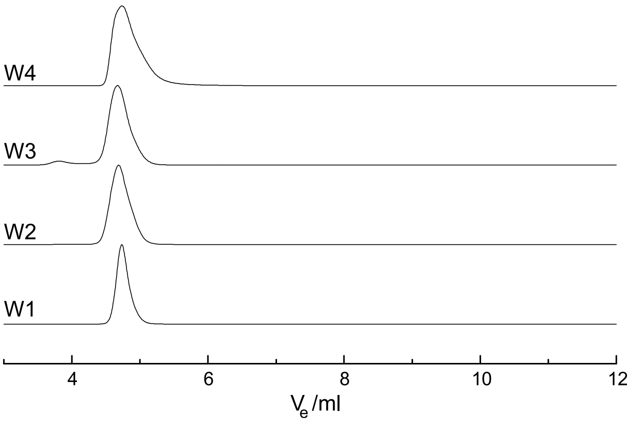


Fig. 1. Elution behavior of linear poly(lactide)s under critical conditions (series W).

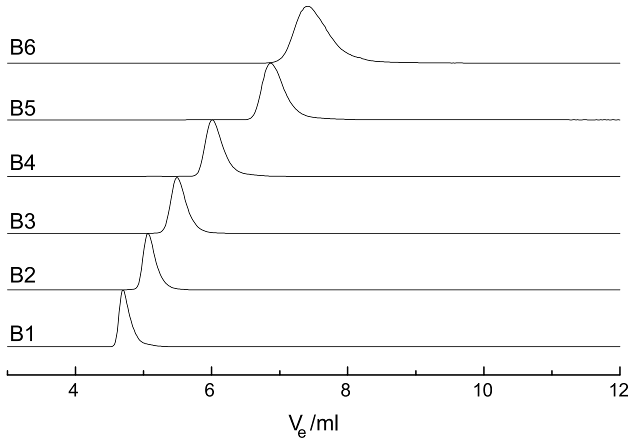


Fig. 2. Elution behavior of star-shaped PLAs having protected core functionalities (series B).

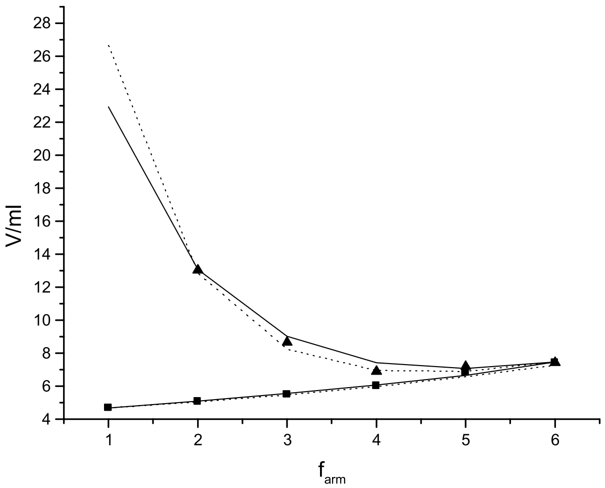


Fig. 4. Experimental and calculated retention behavior of star-shaped PLAs having constant molar mass of arms (■: series A, ▲: series C, solid line: calculated data $R \gg D$; dotted line: calculated data $R < D$).

number of functional groups or to the increase in molecular weight.

However, comparing the data for series A and C and for the series B and D, respectively, shows that the effect of different molar mass on the elution behavior of a given structure is negligible since the elution volumes for stars of the same arm number but different molar masses are nearly identical (Table 1, Figs. 4 and 5). This is in agreement with the naïve picture that in critical chromatography (LCCC) the repeating units become chromatographically invisible. We therefore, can conclude that the number of functional groups, thus, the number of arms, dominates the retention behavior of end-functionalized star-polymers under critical conditions. However, keeping the number of functional groups constant, but replace core OH-groups by OH-groups attached to the arms the elution behavior changes completely (Figs. 3–5). At first glimpse one would expect the elution volume to be constant, since the number of interacting functional groups is constant. However, starting from the 6-arm star we observe decreasing elution volumes with decreasing number of arms. If the number of arms is decreased below four a strong increase in the elution volume is observed, which finally leads to irreversible adsorption on the column for the 'one arm star' (Figs. 4 and 5). This behavior shows that separation under critical conditions may reflect not only the number of functional groups but also the way these groups are arranged within the macromolecule.

Despite the rather simple homopolymer structures, the samples show a relative complex elution pattern under critical conditions. This leads to problems in establishing methods for determining the purity of such samples. It would be helpful if separation capabilities could be estimated based on theoretical considerations.

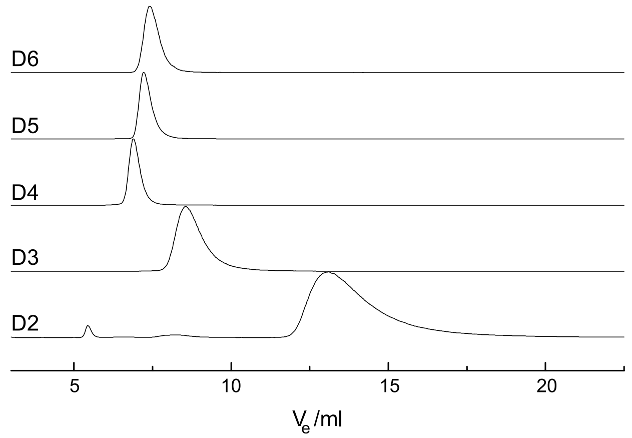


Fig. 3. Elution behavior of star-shaped PLAs having deprotected core functionalities (series D).

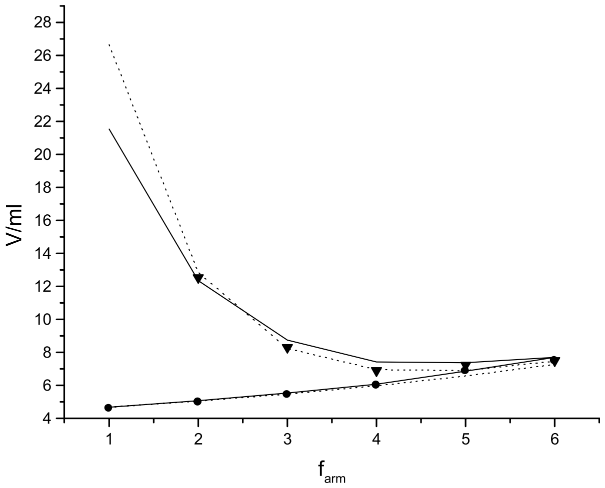


Fig. 5. Experimental and calculated retention behavior of star-shaped PLAs having constant total molar mass (●: series B, ▼: series D, solid line: calculated data $R \gg D$; dotted line: calculated data $R < D$).

4. Theoretical considerations

The elution volume, V_e, of any compound can be described using the chromatographic standard equation.

$$V_e = V_0 + KV_P \tag{1}$$

Here V_0 and V_P are the interparticle and pore volumes, respectively, while K is the distribution coefficient of the polymer molecule. It should be mentioned that the definition of V_0 used in the present is different from the common definition in HPLC of low molar mass compound, where V_0 is taken as the void volume, which is the sum of the interparticle and pore volume.

For Gaussian chains adsorbed in a slit—like pore of size D the distribution coefficient, K_f, of star with f arms is expressed as:

$$K_f = \frac{1}{D}\int_0^D [Z(z,z_i)]^f \mathrm{d}z\,\mathrm{d}z_i \tag{2}$$

in Eq. (2) $Z(z,z_i)$ is the partition function of a linear chain starting at point z_i and ending at point z, the junction point (core) of all arms. The partition function depends on the interaction energy ε (expressed in kT) of the repeating units (monomers). It is assumed that all arms in Eq. (2) have one and the same length and identical chemical structure. To obtain exact results one has to consider two limiting cases when the radius of gyration of an arm, R, is either smaller or much larger than the pore diameter ($R<D$ and $R>D$). The radius of gyration used in the subsequent calculations is a hypothetical quantity defined as the radius of an isolated arm if it would be isolated from the star center.

If $R<D$ the Eq. (2) can be simplified as:

$$K_f = \frac{2}{D}\int_0^{D/2} \mathrm{d}z \int_0^\infty [Z(z,z_i)]^f \mathrm{d}z_i \quad R<D \tag{3}$$

For a chain at the adsorption critical point the interaction energy of a repeating unit takes the value ε_c (the general case is considered in [36]) and the partition function $Z(z,z_i)$ is the superposition of a chain starting at point z_i and its 'positive mirror image':

$$Z(z,z_i) = \sqrt{\frac{1}{4\pi R^2}}\left(\mathrm{e}^{-(z-z_i)^2/4R^2} + \mathrm{e}^{-(z+z_i)^2/4R^2}\right) \tag{4}$$

For homogenous stars integration of Eq. (3) for critical conditions results in:

$$K_f = 1 \tag{5}$$

Thus, at critical conditions there is no difference in adsorption between homogeneous stars and linear chains. They feel neither attraction nor repulsion and elute at one and the same elution volume independent on their molar mass.

If the chain has functional groups one has to account for the difference $\Delta\varepsilon$ in the interaction energy of the terminal repeating unit containing that group, ε_f, and the repeating units, ε_c.

$$\begin{aligned} K_f &= \frac{2}{D}\int_0^{D/2} \mathrm{d}z \prod_{i=1}^{f} \int_0^\infty [Z(z,z_i)]\mathrm{e}^{\Delta\varepsilon(z_i)}\mathrm{d}z_i \\ &= \frac{2}{D}\int_0^{D/2} \mathrm{d}z \prod_{i=1}^{f} \int_0^\infty [Z(z,z_i)][1+q\delta(z_i)]\mathrm{d}z_i \quad R<D \end{aligned} \tag{6}$$

where for short-range interactions we have used the common approximation [37]:

$$\mathrm{e}^{\Delta\varepsilon(z_i)} \approx 1 + q\delta(z_i) \tag{7}$$

$$q = \int_0^\infty (\mathrm{e}^{\Delta\varepsilon(z_i)} - 1)\mathrm{d}z_i = \xi(\mathrm{e}^{\Delta\varepsilon} - 1)$$

here ξ is the distance (of order of repeating unit size a) over which the units can interact with the pore surface. The parameter q can take positive or negative values. Positive values correspond to a stronger adsorption of the terminal group at the pore wall as compared to the repeating unit. Negative values indicate less adsorption (repulsion) of the terminal group. Combining Eqs. (3)–(6) one obtains for star molecules with functional end groups the exact expression:

$$K_f(q) = 1 + \frac{2}{D}\sum_{i=1}^{f}\binom{f}{i}\left(\frac{q}{\sqrt{\pi R^2}}\right)^i \sqrt{\frac{\pi R^2}{i}} \quad R<D \tag{8}$$

here $\binom{f}{i}$ are binomial coefficients. In particular for the cases of $f=1$ and 2 (which correspond to a linear chain with one end group and a linear chain of size $\sqrt{2}R$ having two end groups, respectively) Eq. (8) results in:

$$K_1(q) = 1 + \frac{2q}{D} \tag{9}$$

$$K_2(q) = 1 + \frac{4q}{D} + \frac{2q^2}{\sqrt{\pi}D}\frac{1}{\sqrt{2}R} \quad R<D$$

These are well known expressions for linear chains with end groups [38–40] under critical conditions. If in addition to end groups there are also functional group at the chain core one has to account for the difference in interaction energy $\Delta\varepsilon'(z)$ between the core and the repeating unit. Doing so one obtains in analogy to Eq. (6) for the distribution coefficient:

$$\begin{aligned} K_f(q,q') &= \frac{2}{D}\int_0^{D/2} \mathrm{e}^{\Delta\varepsilon(z)}\mathrm{d}z \prod_{i=1}^{f} \int_0^\infty [Z(z,z_i)]\mathrm{e}^{\Delta\varepsilon(z_i)}\mathrm{d}z_i \\ &= \frac{2}{D}\int_0^{D/2} (1+q'\delta(z))\mathrm{d}z \int_0^\infty [Z(z,z_i)]^f \\ &\quad \times \Pi_{i=1}^{f}(1+q\delta(z_i))\mathrm{d}z_i \end{aligned} \tag{10}$$

where

$$q' = \int_0^\infty (e^{\Delta\varepsilon'(z_i)} - 1)\mathrm{d}z_i = \xi(\mathrm{e}^{\Delta\varepsilon'} - 1)$$

Integration of Eq. (10) results in another exact expression for stars with a functional core and functional end groups:

$$K_f(q,q') = 1 + \frac{2q'}{R}\frac{R}{D} + \frac{2R}{D}\sum_{i=1}^{f}\binom{f}{i}\left(\frac{q}{(R\sqrt{\pi})}\right)^{i}\left(\frac{q}{R}+\sqrt{\frac{\pi}{i}}\right) \quad R<D \tag{11}$$

In case of $R>D$ the chain ends become statistically independent and the distribution coefficient $K_f(q,q')$ is given by:

$$K_f(q,q') = \left(1+\frac{2q}{D}\right)^{f}\left(1+\frac{2q'}{D}\right) \quad R>D \tag{12}$$

Eqs. (11) and (12) provide the complete picture of separations under critical conditions for star chains having functionalized core or end groups. One can generalize these equations for the chains with different arm lengths or functionalities. It is important to mention that in wide pores ($R<D$) the elution volume depends not only on the number of arms with adsorbing end groups but also on the particular arm lengths (Eqs. (8) and (11)). In case of narrow pores, however, the elution volume is determined by the number of functional groups (number of arms) only and does not depend on molar mass (Eq. (12)).

If Eqs. (11) and (12) are useful to describe the elution behavior of the functionalized star-shaped polymers, it should be possible to adjust the parameters q/R, q'/R, R/D, etc. to fit the complete set of experimental data points.

5. Comparison of theory with experimental data

Before comparing theory with experimental data let's estimate the validity of assumptions made above in deriving Eqs. (11) and (12). In the chromatographic experiments a set of 100 and 300 Å columns has been used. While for the 300 Å column the condition $R \ll D$ is well applicable for all samples under investigation, this is not the case for the 100 Å column. A rough estimation of coil size $R \sim a\sqrt{N/6}$ (taking molar mass and size, a, of a repeating unit equal to 100 and 10 Å correspondingly) results for the 'two arms stars' of Table 1 (samples A2, B2, C2 and D2) in $R \sim 33$–45 Å which is comparable with the pore size. If $R \sim D$ the assumption on statistically independence of end groups seems to be more feasible and Eq. (12) should apply. It has to be mentioned also that the distribution coefficient is inversely proportional to the pore size D, thus the column with the smaller pore size has more influence on the overall separation. Finally the independence of elution volume on the molar mass of the star-shaped poly(lactide)s (see Table 1) also correspond to Eq. (12). Thus, to treat the experimental data both Eqs. (11) and (12) might be applicable in case of $R \sim D$ and will be used in the following discussion.

For series A $q'=0$ and it follows from Eq. (8) or Eq. (11):

$$V_{A,f} - V_{A,1} = V_P(K_f(q,0) - K_1(q,0)) = \frac{2V_P R}{D}\sum_{i=2}^{f}\binom{f}{i}\left(\frac{q}{(R\sqrt{\pi})}\right)^{i}\sqrt{\frac{\pi}{i}} \quad R<D \tag{13}$$

here $V_{A,f}$ is the elution volume of the f-arm star of series A and the distribution coefficients $K_f(q,0)$ are given by Eq. (8) or Eq. (11) ($q'=0$). In order to correct for small variations in the molar mass of the different arm-molar masses we assume

$$\frac{R_f}{R_1} = \left(\frac{M_f}{M_1}\right)^{1/2} \tag{14}$$

This assumption is consistent with the Gaussian chain approximation which is also involved in deriving the equations above. By replacing R in Eq. (13) by R_f derived in that way we have a dependence on R_1 and the known ratio of the molar masses of the arms. The parameters q/R and $V_P \times (R/D)$ derived from the above equation have then to be interpreted as q/R and R/D for the stars with arm molar masses of the one arm star of series A (3700 g/mol).

For $R>D$ Eq. (12) becomes:

$$V_{A,f} - V_{A,1} = V_P(K_f(q,0) - K_1(q,0)) = V_P\left(1+\frac{2q}{D}\right)\left(\left(1+\frac{2q}{D}\right)^{f-1} - 1\right) \quad R>D \tag{15}$$

By plotting $V_{A,f} - V_{A,1}$ versus the number of arms, f, the parameters q/R and $V_P R/D$ have been determined from Eq. (13) by non-linear least squares fitting to be $q/R = 0.351$ and $V_P R/D = 0.497$ for $R \ll D$ (Fig. 6). Using the assumption $R>D$ we obtain from a fit to Eq. (15) $V_P = 1.7$ ml and $q/D = 0.09$ for (Fig. 6).

Using these parameters it is possible to calculate the

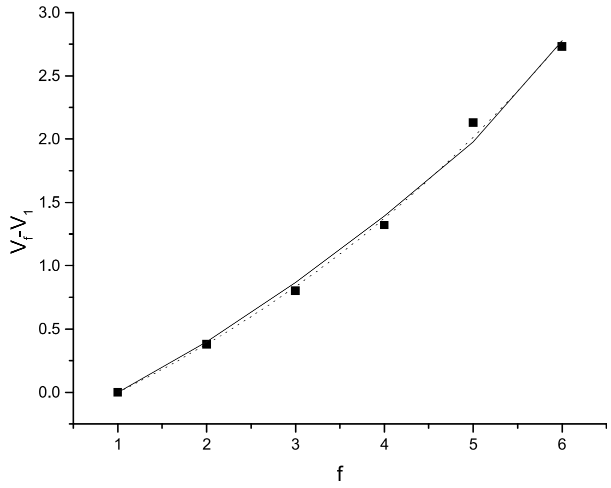


Fig. 6. Dependence of elution volume difference $V_{A,f} - V_{A,1}$ on functionality for series A star-shaped PLAs and fit to determine the parameters q/R and $V_P R/D$ for $R \ll D$ (solid line, Eq. (13)) and the parameters q/D and V_P (dotted line, Eq. (15)) for $R>D$.

elution volumes for the stars without functional cores having different molar masses (series B of Table 1). A good agreement is observed for both cases $R \ll D$ and $R > D$ as can be seen in Figs. 4, 5 and 8. Thus we can conclude that under the experimental conditions both limiting cases are equally applicable.

To derive the parameter q'/R in Eqs. (11) and (12) we calculated $V_{C,f} - V_{A,f}$ and $V_{D,f} - V_{B,f}$ for each of the samples of series C and D, respectively. According to Eq. (11) the following equation should be valid in case of $R \ll D$:

$$V_{C,f} - V_{A,f} = V_P \frac{2q'}{R} \frac{R}{D} \left[1 + \sum_{i=1}^{f} \binom{f}{i} \left(\frac{q}{(R\sqrt{\pi})} \right)^{i} \right] \qquad (16)$$

For the case of $R > D$ we derive from Eq. (12) the more simple equation

$$V_{C,f} - V_{A,f} = V_P \frac{2q'}{D} \left(1 + \frac{2q}{D} \right)^{f} \qquad (17)$$

Since the parameters q/R, q/D and $V_P R/D$ are known we just have to determine the parameters q'/R for $R \ll D$ and q'/D for $R > D$, which fit the experimental differences in elution volumes for every sample.

The values obtained by this procedure are given in Table 2. Fig. 7 shows the results graphically as q'/q'_1. Here q'_1 denotes the value of q' for just one functional group attached to the core. It becomes clear that q' increases strongly with increasing core functionality. To a first approximation each core OH-group contributes the same interaction energy if the functional groups interact simultaneously with the pore surface. Thus, the total interaction energy will be $\Delta\varepsilon_{\text{core}} = f_{\text{core}} \Delta\varepsilon'_1$, where $\Delta\varepsilon'_1$ is the difference in interaction energy of one OH-group attached to the core and a repeating unit. From the definition of the parameter q' we derive

$$\frac{q'}{q'(f_{\text{core}} = 1)} = \frac{q'}{q'_1} = \frac{\exp\{f_{\text{core}} \Delta\varepsilon'_1\} - 1}{\exp\{\Delta\varepsilon'_1\} - 1} \qquad (18)$$

Thus, a plot of q'/q'_1 can be used to estimate a value of $\Delta\varepsilon'_1$. Good agreement of the fits are shown in Fig. 7. The differences of the interaction energy are found to be $\Delta\varepsilon'_1 = 1.05$ ($R \ll D$) and 1.03 ($R > D$). Thus, the interaction energies obtained by the two procedures are in excellent agreement. Since the critical energy of the repeating unit for Gaussian chain is small (e.g. $\varepsilon_c = 0.18$ for random walk on a cubic lattice [41]), the functional groups are only slightly more adsorbed than a repeating unit.

Table 2
q'/R ($R \ll D$) and q'/D ($R > D$) parameter for core deprotected star-shaped PLAs

Series	f_{core}	q'/R, $R \ll D$	q'/D, $R > D$
C	5	Irrev. adsorption	Irrev. adsorption
C	4	5.465	34.6
C	3	1.73	11.4
C	2	0.375	2.8
C	1	0.217	1
C	0	0	0
D	5	Irrev. adsorption	Irrev. adsorption
D	4	5.62	33.6
D	3	1.65	10.8
D	2	0.377	2.8
D	1	0.12	0.97
D	0	0	0

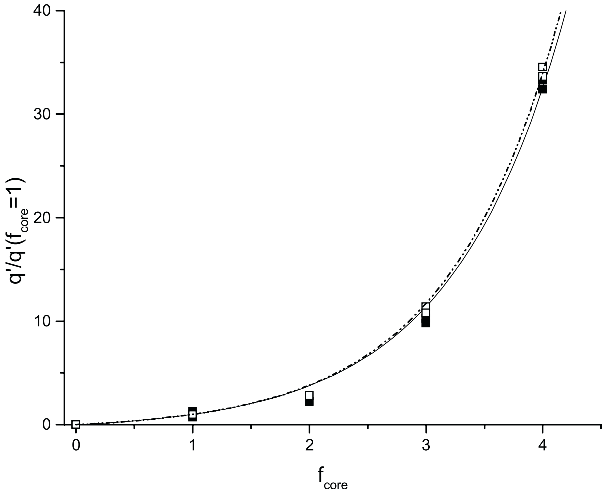


Fig. 7. Dependence of q'/q'_1 on core functionality, f_{core}, for the determination of interaction energy. The solid curve corresponds to $\Delta\varepsilon_1 = 1.05$ for $R \ll D$ (■), the broken line corresponds to 1.03 for $R > D$ (□).

Since we have estimated the parameters needed we can calculate the elution volumes for the samples and compare those with the experimental data. This is done in Figs. 4, 5 and 8.

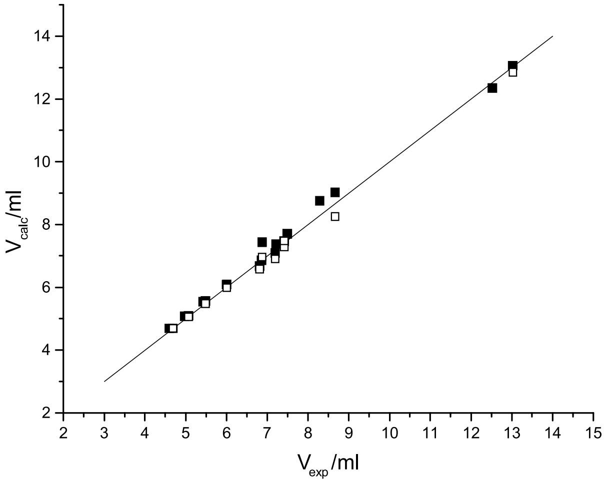


Fig. 8. Plot of calculated versus experimentally determined elution volumes ■: $R \ll D$; □: $R > D$. The solid line corresponds to $V_{\text{cal}} = V_{\text{exp}}$.

A good quantitative agreement is found from those graphs indicating that the theory based on Gaussian chain model is useful to predict the elution volume of star polymers even quantitatively. The parameters estimated enable us to calculate the elution volumes of all possible star structures, in order to clarify which structural defects might be present that could not be separated chromatographically and to identify unknown structures. Such an assignment plot is given in Fig. 9. As an example we have found non-consistent elution behavior for a core functionalized 4-arm star-sample, which is expected to elute around 6.8 ml. However, one sample of this polymer elutes at 6.26 ml. According to Fig. 9 there exist a variety of different structures which can be eluted at this volume (e.g. 3-arm star $f_{\text{core}}=2$ (6.25 ml), 4-arm star $f_{\text{core}}=0$ and 1 (6.1 and 6.4 ml, respectively)). Since from the protected sample we know that we are dealing with a 4-arm star, the elution volume seems to indicate incomplete cleavage of the benzylic blocking function. MALDI-TOF analysis confirmed this result. This sample was removed from the regular analysis of the series of star-shaped PLAs because of this defect but it was very useful to confirm our calculations. However, although MALDI-TOF-MS is an extremely powerful tool for the characterization of polymers up to several ten thousands molar mass (medium molar mass polymers) but does not allow analysis for higher molar mass samples. In addition for mixtures of different species and/or for polymers with broad molar mass distributions MALDI-TOF analysis becomes more and more complicated. In these cases analysis using assignment plots should be very useful.

Some further information can be obtained from the parameters derived, which might be useful from a more fundamental point of view. From the ratio $q_1/q_1' = 2.08$ (where q_1 is the energy of adsorption for arm end group) we obtain the difference between interaction energy as $\Delta\varepsilon = 1.58$. Thus, the difference of the interaction energy of the OH-group attached to the arm is approximately 60% higher that of an OH-group attached to the core. Since the OH-groups attached to the end of the arms are secondary ones, in contrast to the primary OH-groups at the core, this is in contradiction to the expected behavior of primary and secondary alcohols interacting with the stationary phase of silica columns. Apparently it is not enough to consider only the interaction of the OH-groups, but a larger region of the core has to be taken into account. This may reflect an effect, which is known in chromatography of low molecular substances as de-localization phenomenon [42]. In addition, due to steric requirements the simultaneous interaction of all OH-groups attached to the core might not be feasible, reducing the net interaction energy per OH-group of the core. Thus the additivity of the interaction energies for the core OH-groups might not be adequate.

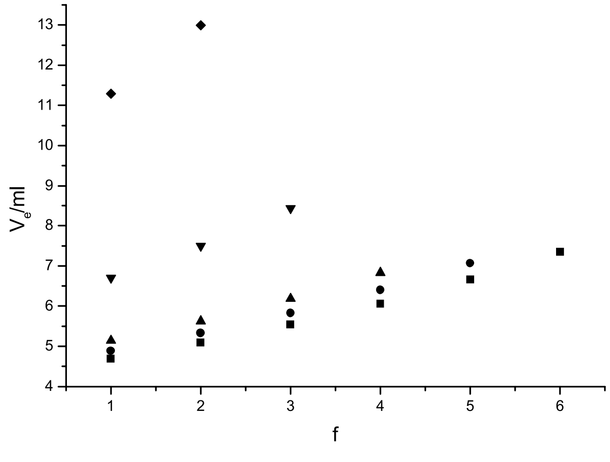


Fig. 9. Calculated dependence of elution volume versus number of arms, *f*, for various numbers of OH-groups attached to the core. ■: $f_{\text{core}}=0$; ●: $f_{\text{core}}=1$; ▲: $f_{\text{core}}=2$; ▼: $f_{\text{core}}=3$; ◆: $f_{\text{core}}=4$, $\Delta\varepsilon''=1.05$, $q_1'/R=0.165$ $q/D=0.351$ and $V_PR/D=0.497$.

Finally we can estimate the distance over which the OH-groups can interact with the stationary phase.

From the definition of q/R we can get an estimate of the interaction distance ξ.

For $q_1=0.351$ and $\Delta\varepsilon=1.58$ we end up with $\xi/R=0.09$. Since $R=l(N/6)^{0.5}$ we obtain, taking for $N=51$ the number of repeating units of the molar mass 3700 g/mol, $\zeta=0.03$ l. I.e. the OH-group can only interact over a distance much shorter than a monomer length, as is assumed in deriving Eqs. (11) and (12).

6. Conclusions

It has been shown that the Gaussian chain model of polymer adsorption can describe quantitatively the complex elution behavior of star-shaped PLAs with different number of arms terminated with secondary OH-groups and additional with primary OH-groups attached directly to the core at critical conditions of adsorption realized for linear polymers. Multiple OH-groups attached to the core behave differently to the same number of functional OH-groups at the chain ends. This is due to the simultaneous interaction of the OH-groups in close proximity to each other, which limits their interaction with the stationary phase.

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Appendix A. Appendix 1

In this appendix the interrelation between the partition function $Z_N(z,z')$ in wide and narrow pores under critical conditions is briefly discussed. In wide pores the solution gives the exact expression (Eq. (4)). If the coil size, *R*, becomes larger than the pore size, *D*, one has to take into consideration all mirror images of the starting point *z* in both surfaces. Thus the result is an infinite sum of Gaussian functions describing the chains starting at all mirror points $\pm z$, $D \pm z$, $2D \pm z \ldots$ and ending at point z'. The result is:

$$aZ_N(z,z') = \sqrt{\frac{1}{4\pi R^2}} \times \sum_{k=-\infty}^{\infty} \left(\mathrm{e}^{-(z-z'-2Dk)^2/4R^2} + \mathrm{e}^{-(z+z'-2Dk)^2/4R^2} \right) \tag{A1}$$

The approach above is common for many problems in physics. In particular, for the problem of heat conductivity it is discussed in details [21]. Applying Poisson summation formula [43]

$$\sum_{k=-\infty}^{\infty} f(k) = \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} f(x) \mathrm{e}^{2\pi\ \mathrm{i}n\ x} \mathrm{d}x \tag{A2}$$

to Eq. (A1) results in, after straightforward calculation in:

$$Z_N(z,z') = \frac{1}{2D} \times \sum_{n=-\infty}^{\infty} \left(\mathrm{e}^{\mathrm{i}\pi n(z+z')/D} + \mathrm{e}^{\mathrm{i}\pi n(z-z')/D} \right) \mathrm{e}^{-\pi^2 n^2 R^2/D^2} \tag{A3}$$

Using trigonometric representation of exponential and notice that the imaginary part identically equal to zero due to symmetry one can obtain finally:

$$Z_N(z,z') = \frac{1}{D} \times \sum_{n=-\infty}^{\infty} \mathrm{e}^{-\pi^2 n^2 R^2/D^2} \cos\left(\frac{\pi n z}{D}\right) \cos\left(\frac{\pi n z'}{D}\right) = \frac{1}{D} \left(1 + 2 \sum_{n=1}^{\infty} \mathrm{e}^{-\pi^2 n^2 R^2/D^2} \cos\left(\frac{\pi n z}{D}\right) \cos\left(\frac{\pi n z'}{D}\right) \right) \tag{A4}$$

Obviously the result (A4) is the solution in terms of the eigen functions of Schrödinger type equation describing a Gaussian chain in a slit like pore with boundary condition specific to the critical energy [44]:

$$\frac{\mathrm{d}Z_N}{\mathrm{d}z} = \frac{a^2}{6} \frac{\mathrm{d}^2 Z_N}{\mathrm{d}z^2} \tag{A5}$$

$$\frac{\mathrm{d}Z_N}{\mathrm{d}z}\Big|_{z=0,D} = 0 \tag{A6}$$

In case $R > D$ all terms of the Eq. (A4) are small compare with unity, so in narrow pores:

$$Z_N(z,z') \approx \frac{1}{D} \tag{A7}$$

If the linear chain has one functional group at the end interacting with the surfaces by a short range potential one can rewrite Eq. (7) in the form:

$$\mathrm{e}^{\Delta\varepsilon(z)} = 1 + q\delta(z) + q\delta(z-D) \tag{A8}$$

Integration over all pore volume gives well known result [2] for the distribution coefficient of monofunctional macromolecules:

$$K_\mathrm{d} = \frac{1}{D} \int_0^D Z(z,z') \mathrm{e}^{\Delta\varepsilon(z)} \mathrm{d}z \mathrm{d}z' = 1 + \frac{2q}{D} \tag{A9}$$

The generalization of the approach for star like macromolecules in case $R_\mathrm{arm} > D$ is obvious and results in Eq. (12).

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