



ELSEVIER

Journal of Chromatography A, 959 (2002) 37–47

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Molecular modelling of chain end effects in separating oligomers by reversed-phase gradient polymer elution chromatography; adsorption transition as revealed by a self-consistent-field theory for polymer adsorption

F.A.M. Leermakers^{a,*}, H.J.A. Philipssen^b, B. Klumperman^c

^aLaboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, Netherlands

^bResearch and Development Department, Océ Technologies, P.O. Box 101, 5900 MA Venlo, Netherlands

^cLaboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

Received 25 October 2001; received in revised form 11 January 2002; accepted 7 March 2002

Abstract

HPLC experiments to separate butyl-terminated polystyrene (B-PS) oligomers have been mimicked by equilibrium self-consistent-field calculations based upon the Scheutjens Fler formalism for polymers at interfaces. The adsorption–desorption transition as a function of the fraction of good solvent in a non-solvent (water)–solvent (tetrahydrofuran) mixture has been analysed and correlated to corresponding experiments. Much attention is paid to keeping the modelling as realistic as possible; for example, the effects of the solvent mixture on the C₁₈-alkyl tails that are grafted on the silica surface are retained in the calculations. It is shown that the butyl end groups affect the elution properties up to chains with approximately 30 styrene units. Excellent semi-quantitative comparison is found with experiments for a realistic set of interaction parameters. Molecular-level information is available for the adsorption layer as a function of the solvent quality. Going from poor to good solvent, it is typical to find that the B-PS is fully absorbed inside the alkyl brush, then adsorbed on top of it, and finally depleted from it. The depletion effect in good solvents increases with increasing molecular mass. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molecular modelling; Chain end effects; Adsorption transition; Gradient elution; Oligomers; Polystyrene, butyl-terminated

1. Introduction

HPLC experiments are suitable to analyse the chain length distribution of a mixture of oligomers. Invariably in such an experiment, many parameters

play a role. For this reason it is often rather difficult to reconstruct from successful HPLC experiments the molecular details of the adsorption mechanism that played a central role in the overall separation process. This is a problem in the rational design of experiments to determine the molecular details of a polymer sample. There is thus a need to have a modelling strategy that can be used to point to some of the underlying molecular features.

*Corresponding author. Tel.: +31-7-482-268; fax: +31-7-483-777.

E-mail address: frans@fenk.wau.nl (F.A.M. Leermakers).

Recent HPLC experiments on butyl-terminated polystyrene (B-PS) and several other polymeric samples have been performed and are discussed in the literature. From this strong evidence it was found that the molar mass dependence of the retention of oligomers is largely influenced by the relative contributions to the adsorption process of end groups, on the one hand, and monomeric repeat units, on the other. For instance, for butyl-polystyrene with a relatively small repeat unit, under certain conditions, pronouncedly curved functions for (% solvent) at the point of the elution of an oligomer versus $(1/\sqrt{M})$ were found. A typical example is given in Fig. 1. Increasing the molar volume of the repeat unit, which decreases (relatively) the influence of the end group, causes the shape of the curve to become more linear [1].

In recent years many theoretical developments have taken place in the field of polymers at interfaces [2]. By using the numerical model of Scheutjens and Fleer [3,4] it is now possible to model quite complex interfacial systems in great detail [5,6]. It is important to realise, however, that the Scheutjens Fleer (SF) formalism is a theory based upon a self-consistent-field (SCF) framework [2]. This means that, in this formalism, a mean-field approximation is

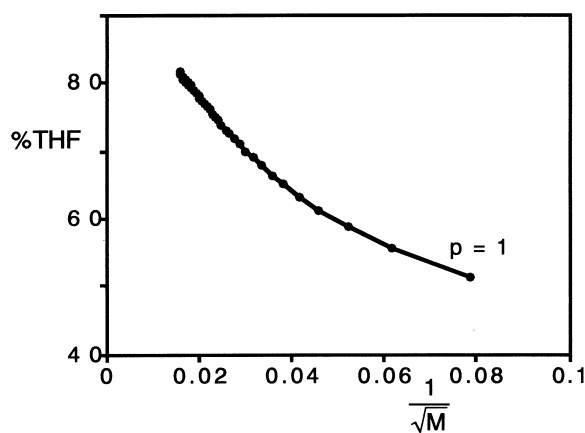


Fig. 1. Typical example of an atypical GPEC experiment on a polystyrene sample. The percent THF versus $1/\sqrt{M}$ for PS is plotted. GPEC conditions: sample concentrations, 10 mg/mL in THF; column, Novapak C_{18} (150×3.9 mm); temperature, 25 °C; eluent, water–THF (+200 μ L acetic acid per litre) (75:25, v/v) to (0:100) (0 to 75 min); flow, 1.0 mL/min; injection, 10 μ L; detection, UV at 254 nm.

introduced. A consequence of this approximation is that predictions are expected to follow the experiments only semi-quantitatively. The best way to use this type of modelling is thus to vary some system parameters systematically and interpret the observed trends. With this in mind, HPLC experiments were analysed that were performed to separate oligomers of a polystyrene sample. In particular, the SF SCF model was used to analyse the adsorption behaviour of oligomers on a silica surface that was modified hydrophobically by C_{18} alkyl chains in a non-solvent (water)–solvent (tetrahydrofuran, THF) mixture. The interest is in predicting the influence of the degree of polymerisation (p) on the adsorption–desorption transition induced by gradually increasing the solvent quality in the system. Special attention was paid to how a butyl end group attached to each of the polystyrene oligomers modified the adsorption–desorption transition. These adsorption predictions are then compared with the HPLC experiments.

The paper is organised as follows. First, the main features of the SF SCF model are outlined, concentrating on the assumptions behind the modelling. For most of the mathematical details we refer to the original literature [2]. Next, the parameters in the model that are needed to mimic the B-PS hydrophobically modified silica–mixed solvent system are discussed. Finally, the results are presented and discussed with special attention given to how the SCF results can be correlated with the HPLC data.

2. Theory

In a model for polymers and oligomers at interfaces, one should not only pay attention to the phenomena that occur at the interface, but also to the behaviour of the molecules in solution. The equilibration between the chain molecules at the surface and the molecules in solution is particularly relevant in the context of an HPLC experiment. In this system, adsorption is used to retard the molecules, whereas the molecules that are not adsorbed are transported rather quickly through the column. Thus the adsorption process is used to separate the molecular components of a mixture. In principle, there are several modelling options to study these interfacial phenomena. From a theoretical perspec-

tive it is attractive to use Monte Carlo (MC) or molecular dynamics (MD) simulations [7]. In these simulations, one can, in principle, include many molecular details and account for all relevant correlations in the system. However, the length and time-scale of the adsorption of oligomers at interfaces are orders of magnitude out of reach for these molecular simulations. For this reason it is reasonable to use an approximation scheme.

A less computer intensive, but still very flexible, approximate scheme that can be used for polymers at interfaces was formulated by Scheutjens and Fler some 20 years ago [3,4]. The theory makes use of a numerical procedure to solve a set of equations [5]. Modern implementations of this theory allow for quite complex systems where a polydisperse mixture of (co)polymers in mixed solvents can easily be handled. Also, it is possible to end-graft molecules onto surfaces [6]. Thus all ingredients needed for the present system are readily available in this model.

The main idea behind the model of Scheutjens and Fler is that the complex inhomogeneous system of many interacting molecules is reduced to the problem of determining the statistical weight of chain conformations in an external and inhomogeneous (self-consistent) potential field. Therefore, there are two conjugated functions in the system, the density profiles and the potential profiles. In the SCF approach there are rules governing how to obtain the density profiles from the potentials and how to obtain the potential profiles from the densities. When these two conjugated profiles are consistent with each other, one speaks of a self-consistent-field solution. Such a solution is found with appropriate boundary conditions. In the case of adsorption, an absorbing boundary condition is used. This means that there is a solid surface positioned on one side of the system. In addition, there is an incompressibility constraint imposed to ensure that there is only a single SCF solution. For many liquids, such an incompressibility constraint is an excellent approximation. Having mentioned the general strategy, it is illustrative to introduce more details of the theory that are necessary to understand the results obtained with it.

Consider a system composed of a flat solid–liquid interface, where the liquid spans a fixed volume next to a homogeneous solid material A (silica). It is natural to assume that there are no important density

gradients parallel to the interface and that the main interest is in the density gradient perpendicular to it. Therefore, it is customary to reduce the SCF equations such that only information in the perpendicular direction is kept. This implies a mean-field approximation parallel to the interface and, consequently, all quantities are expressed per unit area. The next step is to introduce a system of coordinates regularly spaced as a lattice. All molecules are restricted such that they can only take positions on these lattice sites. The lattice sites are organised in layers parallel to the surface and numbered $z = 0, 1, 2, \dots, M$. Layer $z = 0$ is reserved for the surface sites, which implies that the volume fraction of surface sites in layer $z = 0$ is unity: $\rho_A(0) = 1$. In all other layers $z > 0$ there are no segments of type A and these coordinates are exclusively occupied by polymer units or solvent molecules. A simple cubic symmetry is assumed in the lattice. The coordination number in this lattice is $Z = 6$. A fraction of $4/6$ of neighbouring sites is in the same layer ($\lambda_0 = 4/6$), and a fraction of $1/6$ is in each of the adjoining layers ($\lambda_1 = 1/6$). Layer $z = M$ is sufficiently far from the interface that its value has a minor influence on the adsorption process near the solid boundary. In this paper it is assumed that there is a reflecting boundary condition between layers $z = M$ and $z = M + 1$, which implies that, at $z = 2M + 1$, a second wall is situated. Thus the value of M fixes the volume-to-surface ratio in the system.

Various molecules are introduced into this lattice. Molecule types are indicated with the index i . Molecules can be composed of one or more segments. Segment types are indicated by the indices x and y . Each segment is assumed to fit exactly on a lattice site. The errors introduced by this pragmatic approximation may be compensated, in part, by the values of the interaction parameters in the system. The interactions will be discussed below. The water molecule is given the segment type $x = W$, it is referred to as $i = 1$, and the molecular structure is W_1 . The THF molecule is indicated by $x = T$, it is referred to as $i = 2$ and the structure is T_1 . The hydrocarbon chains in the system have segments of type $x = C$, are referred to as $i = 3$ and have the structure C_{18} . B-PS has segment types $x = C$ and $x = S$ and the molecule structure is C_4S_p , where p is the degree of polymerisation of the polystyrene part.

The numbers of the molecules are $i = 4, 5, \dots, p + 3$. Segments in polymer chains obtain ranking numbers $s = 1, 2, \dots, N_i$, where N_i is the total number of segments in the chain of type i . In the B-PS case, $s = 1, \dots, 4$ are of type $x = C$, and $s = 5, \dots, N$ are of type S, where $N = p + 4$.

An advantage of using a lattice is that the number of possible conformations of the chain molecules is countable. Already for relatively small N , however, the total number of possible configurations grows astronomically high. Therefore, it is necessary to introduce an approximation to compute the statistical weight of the full set of chain conformations. A first-order Markov approximation is used. This approach guarantees that two segments along the chain occupy neighbouring lattice sites, but the scheme does not prevent chain backfolding such that segments further than one segment apart can sit on the same site. The excluded volume problem is corrected for partly by forcing that all sites within a layer are, on average, filled exactly once, either by a polymer segment or by a solvent molecule. The Markov approximation allows for a very efficient way to compute the statistical weight of the whole set of conformations. This cannot be illustrated before the statistical weights of individual segments with ranking number s of molecule i , $G_i(z, s)$, are introduced. As mentioned above, for a segment of type x , there is a potential at coordinate z given by $u_x(z)$ (this quantity is specified below). For this segment the so-called free segment distribution function, $G_x(z)$, is defined as the Boltzmann weight:

$$G_x(z) = e^{-u_x(z)/kT} \quad (1)$$

where kT is the thermal energy. It is convenient to introduce a chain architecture operator $\delta_{i,s}^x$. This quantity assumes the value unity when segment s of molecule i is of type x and zero otherwise. Using $\delta_{i,s}^x$ allows the generalisation of Eq. (1) such that the free segment distribution function can be applied to a chain segment:

$$G_i(z, s) = \sum_x G_x(z) \delta_{i,s}^x \quad (2)$$

An essential step to obtain statistical weights for chains in various conformations is to account for the chain connectivity. To this end the so-called chain end distribution function $G_i(z, s|1)$ is defined, which

expresses the statistical weight to find the s th segment of the chain fragment $s' = 1, \dots, s$ of molecule i at coordinate z where $s' = 1$ is allowed to be in all possible coordinates. Likewise, the function $G_i(z, s|N)$ is introduced to find the statistical weight of segment $s' = s$ from the fragment $s' = N_i, \dots, s$. In the Markov approximation it can be shown [2] that these end point distributions are connected to each other by a propagator scheme:

$$G_i(z, s|1) = G_i(z, s) [\lambda_1 G_i(z - 1, s - 1|1) + \lambda_0 G_i(z, s - 1|1) + \lambda_1 G_i(z + 1, s - 1|1)] \quad (3a)$$

$$G_i(z, s|N) = G_i(z, s) [\lambda_1 G_i(z - 1, s + 1|N) + \lambda_0 G_i(z, s + 1|N) + \lambda_1 G_i(z + 1, s + 1|N)] \quad (3b)$$

The starting conditions for this scheme can be expressed as $G_i(z, 0|1) = G_i(z, N + 1|N) = 1$, which implies that a chain containing no segments does not feel any potential field. Combining the two complementary chain end distribution functions results directly in the observable volume fraction or (dimensionless) segment densities, ρ :

$$\rho_i(z, s) = C_i \frac{G_i(z, s|1) G_i(z, s|N)}{G_i(z, s)} \quad (4)$$

Here, C_i is a normalisation which can easily be found if the number of molecules per unit area, $n_i = \theta_i/N_i$, is known. In this formula, $\theta_i = \sum_{z=1}^M \rho_i(z)$ is the amount (number) of segments per unit area of molecule i . Two useful expressions for C_i are

$$C_i = \frac{\rho_i^b}{N_i} = \frac{\theta_i}{N_i \sum_{z=1}^M G_i(z, N|1)} \quad (5)$$

This equation shows that when θ_i is known it is possible to calculate the volume fraction of chain molecules of type i in the bulk, ρ_i^b , and the other way around. Obviously, when the distributions of all segments of all molecules are available, it is trivial to collect the volume fraction profiles for a given segment type x :

$$\rho_x(z) = \sum_i \sum_s \rho_i(z, s) \delta_{i,s}^x \quad (6)$$

These dimensionless densities are subsequently used to compute the segment potentials. In the segment potentials, one accounts for the excluded volume and for the various short-range interactions in the system:

$$u_x(z) = u'(z) + kT \sum_y \chi_{xy} \{ [\lambda_1 \rho_y(z-1) + \lambda_0 \rho_y(z) + \lambda_1 \rho_y(z+1)] - \rho_y^b \} \quad (7)$$

In this potential, $u'(z)$ is a Lagrange field coupled to the space filling (incompressibility) constraint in the system:

$$\sum_x \rho_x(z) = 1, \quad \forall z \quad (8)$$

In words, this equation states that the volume fractions add up to unity. The value of $u'(z)$ is adjusted until Eq. (8) is satisfied. In the second term of Eq. (7) the Flory–Huggins interaction parameters χ_{xy} were used. The χ_{xy} parameter is a short-range dimensionless exchange energy parameter which is positive for repulsion between segments of type x and y and negative for attraction between the two. Both terms in Eq. (7) are normalised such that, in the bulk, the potential $u_x(z)$ is zero, where the segment density of segment type x is given by ρ_x^b .

The set of equations (1)–(8) is closed and is routinely solved by a computer. In these calculations the density of the surface component remains fixed as discussed above. The amount of polymeric components is fixed by specifying θ_i for all $i > 3$. Normalisation for THF is controlled by fixing the bulk density $\rho_2^b = \rho_T^b$. The normalisation of the water component is chosen such that the density in the bulk sums exactly to unity.

At this point, most of the essentials of the SF SCF theory have been reviewed. The method is easily applied to evaluate the conformational properties of end-grafted chain molecules. In the calculations discussed below, the C_{18} tails are grafted with $s = 1$ onto the silica surface. This means that it is forced that $\rho_3(z,1) = 0$ for all $z > 1$. This is realised by initialising the propagator scheme as given in Eq. (3a) with $G_3(0,0|1) = 1$ and $G_3(z,0|1) = 0$ for all $z > 0$. It is easily shown that segment $s' = N_3$ will always be in the region $0 < z < N_3$.

It is illustrative to mention that the above equa-

tions reduce to the Flory–Huggins equations in the bulk [8]. From the Flory–Huggins theory it is known that, for a two-component polymer–solvent system, there is a critical interaction parameter χ^{cr} , which is a function of the degree of polymerisation N , that gives the onset of phase separation between the two components:

$$\chi^{cr} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{N}} \right)^2 = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N} \quad (9)$$

This equation shows that, with increasing molecular mass of the polymer, there is a decrease in χ^{cr} : $\chi^{cr}(N=1) = 2$ and $\chi^{cr}(N=\infty) = 1/2$. The same critical interaction parameters thus also apply to the SF SCF approach. The strategy used in the HPLC experiments discussed below is based on the fact that χ^{cr} can be reached by adjusting the ratio between non-solvent (poor) and (good) solvent.

3. Parameters

The aim is to mimic a HPLC experiment that consists of a hydrophobically modified silica surface and a polydisperse mixture of B-PS or PS in a mixture of good and poor solvents. Unfortunately, this system is characterised by many parameters. It is not possible to present a full analysis of all of them. This is left for future work. Instead, most of the parameters are fixed as discussed below. Some parameters have been varied and typical results are reported. Without specifying otherwise, the following parameters were used.

In the current system there are five segment types: A, W, T, C and S. Consequently, there are 10 unlike contacts in the system and, therefore, there are 10 short-range FH χ interaction parameters (Table 1). It

Table 1
Set of interaction parameters used in this study. By definition $\chi_{xy} = \chi_{yx}$ and $\chi_{xx} = 0$

χ_{xy}	W (water)	T (THF)	C (alkyl)	S (styrene)	A (silica)
W (water)	0	1	1.6	2	0
T (THF)	1	0	0.5	0.3	1
C (alkyl)	1.6	0.5	0	0.5	2
S (styrene)	2	0.3	0.5	0	1.5
A (silica)	0	1	2	1.5	0

is important to discuss each of these parameters in some detail as the results depend on these choices. It should be noted that the value of these parameters should be in accordance with the level of detail retained in the SCF analysis. This is the main reason why it is not straightforward to borrow such parameters from the literature; for some information on these parameters in relation to interfacial systems we refer to the book by Flerer and coworkers [2].

It is assumed that surface A is hydrophilic (silica). As the density of the surface sites is fixed, and as the lattice sites next to the surface are always occupied by either W, T, C, or S, it suffices to specify relative interactions with the surface [2]. For this reason it is allowed to take $\chi_{AW} = 0$. It is further assumed that the affinity for silica decreases on going from water, to THF, to styrene and to hydrocarbon. This is reflected in an increasing repulsive interaction with the surface in this order. Styrene is made more surface active than hydrocarbon as it is known that styrene adsorbs onto silica from an alkane solution [9].

The interaction parameter of water with styrene, hydrocarbon and THF is chosen to be decreasingly repulsive in this order. The C–water interaction is set to 1.6. This value is taken from surfactant studies [10,11]. A repulsion is introduced between THF and water, but this value is low enough to ensure complete mutual compatibility (cf. Eq. (9)).

The interaction parameter for the hydrocarbon–styrene contacts is estimated to be 0.5, and the same value was used for the hydrocarbon–THF contacts. These values are consistent with the mutual solubility of these components [9].

The remaining parameter is the interaction of styrene in THF. It is known that THF is a very good solvent for polystyrene [9]. This is reflected in the setting $\chi_{TS} = 0.3$.

The C_{18} alkyl chains are grafted onto the silica surface in such a way that the total amount of C_{18} is three equivalent monolayers: $\theta_3 = 3$. This value is well above the overlap condition, but only one-sixth of the maximum coverage. In the experiments the coverage was in the same order of magnitude [12]. This coverage allows significant incorporation of (B-)PS in the layer. Evidence for such behaviour was obtained from a recent study [13]. It also allows significant variation of the swelling of the grafted

layer with THF when the solvency condition for the alkyl chains is good.

The total amount of polymer in the system was fixed independent of the solvent ratio in the low coverage regime. This means that the adsorption is in the Henry region: $\sum_{i>3} \theta_i = 0.1$. Each component in the polydisperse mixture contributes equally to this total (thus, $\theta_4 = \theta_5 = \theta_6 = \text{etc.}$). Typically, a polydisperse mixture with chain lengths in the range $p = 1–100$ has been used.

Finally, the system size was set to $M = 50$ layers. This value is small enough to expect effects of the volume-to-surface ratio, but large enough to allow the density gradients at the surface to relax to the constant density in the bulk.

4. Results

Clearly, there are two physical properties manipulated in the HPLC experiments. The first is that the solubility of the polymer is changed from poor (non-solvent) to good (solvent). Under non-solvent conditions the chains are insoluble and they demix according to the relevant phase diagram to form a polymer-rich phase (precipitate). The second is to make the S–L interface compatible (adsorptive) with the demixed polymer phase, so that the formation of the polymer phase occurs there. In terms of wetting, the strategy is to modify the surface such that the condensed polymer phase wets the surface completely [14].

We have chosen to follow the HPLC experiment by introducing a binary liquid. The effective interaction of the mixed solvent with styrene, χ_{MS} , can be approximated by

$$\begin{aligned}\chi_{MS} &= \rho_T^b \chi_{TS} + \rho_W^b \chi_{WS} \\ &= \rho_T^b \chi_{TS} + (1 - \rho_T^b) \chi_{WS}\end{aligned}\quad (10)$$

Thus with increasing volume fraction of THF the effective solvent strength increases. It is illustrative to first discuss how B-PS interacts with the brush and the effect of solvent strength on brush conformation.

It is expected that the alkyl layer on silica is collapsed in pure water [15]. This means that, to first order, the density profile should be a step function, being nearly unity for about three layers ($\theta_3 = 3$) and

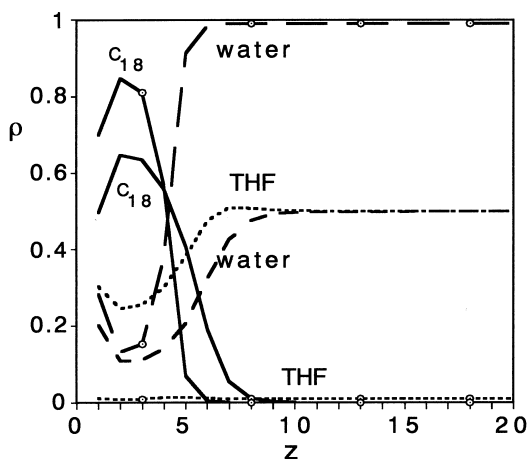


Fig. 2. Density profiles of water (— — —), THF (· · ·) and the C_{18} brush (——) for a volume fraction of water in the bulk of 0.99 (○) and 0.5. Other parameters are given in the text.

then dropping quickly to zero. However, there are two additional effects. (i) The alkyl chains are repelled by the silica somewhat, and thus some water and (if present) THF is expected to be near the surface. (ii) There is a finite width of the interface between the alkyl phase and water which is expected to be such that the water density remains relatively large inside the hydrocarbon phase. Both effects can be seen in Fig. 2. In this figure it is shown that the brush profile has a maximum in layer $z = 2$ and that,

at this point, the water density goes through a minimum. The influence of the addition of THF is also presented in Fig. 2. As an example a solvent composition of 50% water–50% THF is selected. Clearly, the alkyl layer is swollen by THF. There is a significantly higher concentration of THF than water in the brush. The absolute density of C segments drops significantly and thus the height of the brush layer increases with increasing THF fraction. Increasing the THF fraction further (not shown) only gives a modest further increase in the brush height. This is because, at this high grafting density, an extra decrease in density can only be realised if the chains are more stretched. This stretching is unfavourable entropically.

Fig. 3 gives a small selection of the adsorption profiles for the B-PS system. For this system, both the shortest molecule in the series, C_4S_1 , where the end group dominates the adsorption behaviour, and a longer molecule, C_4S_{64} , where the end group effect is vanishingly small, were selected. There are many details worth discussing in these figures. For both molecules the C (of the butyl) and S segment density profiles are plotted for several solvent strength conditions. In the poor (non) solvent (solid lines) both the low- and the high-molecular-mass B-PS molecules are completely absorbed inside the brush. They do not adsorb strongly onto the silica. Clearly, water displaces them from the silica surface. In-

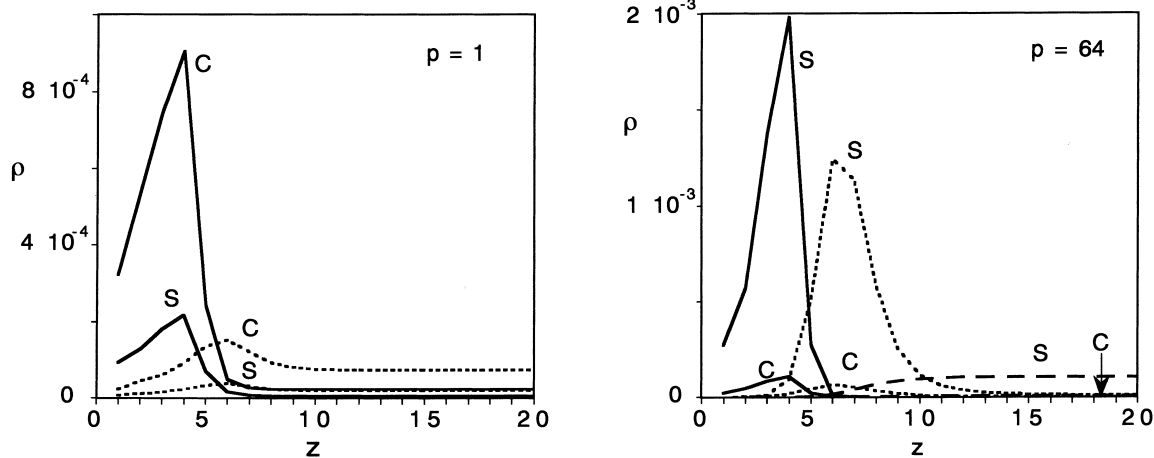


Fig. 3. Density profiles of the C and S segment types of B-PS with $p = 1$ (left) and $p = 64$ (right). For $p = 1$ and 64, solvent strengths $\rho_T^b = 0.01$ (——) and $\rho_T^b = 0.5$ (· · ·) are used. In addition, for $p = 64$ the $\rho_T^b = 0.7$ case (— — —) is given. The data presented correspond to the systems indicated by (○) in Fig. 4.

ing the solvent strength to an equal water–THF volume ratio causes C_4S_1 to desorb from the brush. This results in a significant concentration of this component in the continuous bulk phase. Note, however, that there is still adsorption of the molecules at the surface. The C_4 tail can still hold a few B-PS molecules near the surface. The small number of weakly adsorbed chains are not strongly oriented. The C units are only marginally closer to the surface than the S segments. A small level of adsorption remains present in this case even for $\rho_T^b \approx 0.9$ (not shown). For $\rho_T^b = 0.5$ solvency conditions, C_4S_{64} is not yet displaced from the brush. Interestingly, the molecules are no longer placed inside the brush, but they tend to accumulate on the outside of the brush. Note that the C and S segments have only slightly shifted profiles, which indicates that the molecules are not strongly oriented. Apparently, the C_4 tail only weakly influences the adsorption behaviour. The molecules remain on top of the brush, primarily because of the poor solvency conditions, which is of course a function of both the C and S solubilities. The dashed curve in Fig. 3 corresponds to the case where the solvent strength was increased to $\rho_T^b = 0.7$. As expected, now virtually all the C_4S_{64} chains have left the interface. Clearly, a depletion layer is seen near the brush, i.e. a density drop is found near the interface. This depletion layer has the effect that the bulk density at high solvent strength is higher for C_4S_{64} than for C_4S_1 (Fig. 4). This effect, of course, diminishes with increasing volume-to-surface ratio in the system.

It is relatively straightforward to obtain a measure of the degree of adsorption from the results shown in Fig. 3. As the total amount of polymer of each of the components is fixed in the region $0 < z < M + 1$, it is possible to either determine the excess amount at the interface, or to calculate the concentration of the polymer in the bulk (near layer M). Obviously, when the bulk concentration is very low, most of the chains are adsorbed, and when the bulk concentration is high, only a few of them can be at the interface. As in chromatography the concentration of polymers in the bulk determines the mobility of the product, it was decided to monitor the density in the bulk as a measure of the adsorbed amount.

Fig. 4 shows how the bulk density of B-PS is a function of the bulk density of THF for a selection of

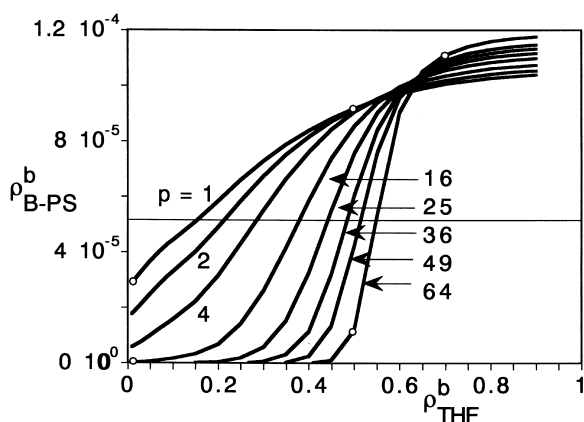


Fig. 4. Bulk volume fraction of the B-PS chains as a function of the fraction of THF in the bulk. The degree of polymerisation of the B-PS is indicated. The five points (○) refer to the conditions from which the density profiles of Fig. 3 were taken. The use of the horizontal line in this graph is discussed in the text.

chains in the system. Remember that the total amount of polymer (for each chain length) in the system and the surface-to-volume ratio was fixed. As anticipated, for all molecules a transition from the adsorbed to the desorbed state is observed: the bulk density for B-PS goes from a low to a high value in a relatively small region of increase of solvent strength. It can be seen from Fig. 4 that the adsorption–desorption transition is sharper with increasing molecular mass. Another interesting feature already anticipated from the results discussed in Fig. 3 is that the displacement isotherms cross each other. This crossing is a manifestation of the fact that the larger chains have a stronger depletion effect near the alkyl-brush than the shorter chains. Under practical chromatographic conditions, such a crossing, e.g. (near) molar mass independent elution, is a well-known phenomenon known as “critical conditions”. It is noteworthy that, in Fig. 4, the lines do not intersect exactly at one point. This contradicts existing theories on critical conditions [16]. However, it was demonstrated recently that, for butyl-polystyrene in various solvent–non-solvent systems, in none of the investigated cases could an exact molar mass independence be found as shown in Fig. 4 [17]. In a later study this was ascribed to entropic effects [13]. Obviously, the model used in this study can provide a description of the retention behaviour of polymers

which is in better agreement with practical observations than conventional theories. The SCF technique was recently applied to the similar problem of critical chromatography by Van de Gucht and co-workers [18].

It is of interest to correlate the displacement isotherms with the chromatography experiment. Clearly, as soon as the bulk concentration of B-PS becomes significant, it is expected that the chain becomes mobile and is transported through the column. On the other hand, when the bulk concentration is extremely low, the chains are fully immobile. To make a connection to the HPLC experiment it was decided to cut through the curves as indicated in Fig. 4. Now, the Ansatz is that, below the horizontal line, the chains are not mobile, and above the line they are mobile. In other words, it is assumed that the transition from mobile to immobile is sudden. The line is positioned near the steepest parts of the adsorption isotherm. By measuring the volume fraction of THF in the bulk where each displacement isotherm crosses the horizontal line, one arrives at the SF SCF equivalent of the HPLC experiment.

Fig. 5 shows the results of such an exercise for two types of polymers, the homopolymer PS and butyl-terminated b-PS. Here the fraction of THF in the bulk at which the individual polymers desorb from the surface, as found by the crossing with the horizontal line in Fig. 4, is plotted as a function of the inverse square root of the molecular mass of the component. With (B)-PS in mind we used the molecular mass of a monomeric styrene unit and the molecular mass of the butyl end group to convert the number of segments in the chain into its molecular mass. The motivation to use the inverse square root of the molecular mass is that this is expected to result in linear plots in the limit of large N as can be concluded from Eq. (9). The other motivation to plot the results in this way is that the experimental data are treated similarly [9].

Fig. 5 clearly illustrates that, with the present set of parameters, there is a strong influence of the butyl end group. Especially at low p values it is seen that the PS chains can be bound to the hydrophobised silica by the butyl group. If this group is absent, it is found that up to the tri-mer of PS elution is possible even with pure water as solvent. This last result is in

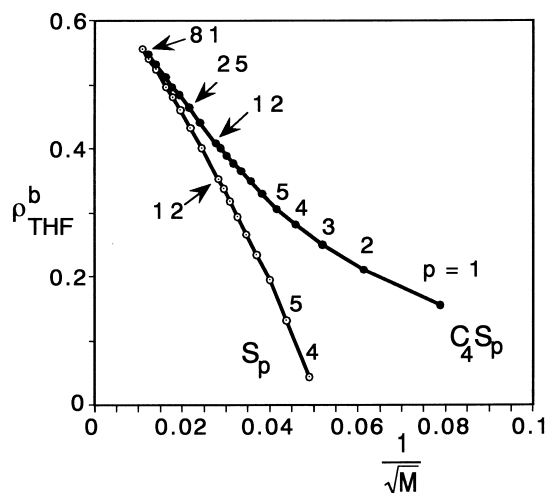


Fig. 5. Bulk volume fraction of THF at which the polymers desorb from the surface plotted as a function of the inverse square of the molecular mass for homopolymers of polystyrene and co-oligomers of butyl-polystyrene. The molecular mass was calculated from $M = 104p$ and $M = 104p + 58$ in the case of PS and B-PS, respectively. (●) B-PS, (○) PS. Some of the p values are indicated.

conflict with experiments from which it is known that water is too poor a solvent to displace single styrene units from an apolar column. The failure of the Flory–Huggins-type theory to predict the phase diagram of small molecules is well known and for this reason we did not attempt to fine-tune parameters to obtain full overlap with experimental data for the present system. As the main interest is a qualitative interpretation of the influence of end groups, this minor error is accepted. It is noteworthy that deviations between B-PS and the corresponding points on the PS curve are significant up to p values of approximately 30. This is a surprisingly large value considering the fact that the end group is only a butyl group. Note, however, that a similarly large effect is seen in the result presented in Fig. 1. Apparently, a small end group can have a significant effect on the retention of even relatively large polymer chains. These results confirm the findings of Fig. 7 of Ref. [1], where the influence of the butyl end group was tested by using conventional models for reversed-phase chromatography. The homopolymer PS curve of Fig. 5 is qualitatively a typical result for a successful oligomer separation experi-

ment: almost a straight line is found, although a critical inspection of the curve reveals a slight sigmoidality. This sigmoidality is also commonly observed experimentally [1]. The extent of deviation from linearity is also commonly observed experimentally and should also be expected (cf. Eq. (9)). The B-PS curve deviates in the *other* direction. This is a rather atypical result, and in line with experimental findings for this system [1]. It should be noted, however, that, in other experimental systems, it was not possible to obtain results for the lowest molecular mass. As the atypical upward deviation is most pronounced for the low-molecular-mass species, the atypical effect might also potentially be present in other systems. Note the strong correlation between the experimental results shown in Fig. 1 and the theoretical prediction presented in Fig. 5.

In the model calculations it is possible to investigate how the atypical upward curvature can be realised. By scanning a large part of the parameter space (not shown) it was concluded that it is not possible to obtain this type of elution behaviour for *homopolymer* systems. Only when an end group with solubility characteristics that differ from those of the monomeric repeat units was introduced was it possible to generate this behaviour. A detailed investigation of the influence of several parameters (not shown) indicated that it is possible to suppress the upward curvature in several ways. One way to do this is to make the polymer units much more hydrophobic. Then the effect of the butyl group is simply too small to affect the elution properties even for very small p values. It was also found that replacing the grafted C_{18} by grafted C_4 , while keeping the amount of hydrocarbon at the surface constant, transformed the curve to a large extent to a “normal” one. Experimentally, it was found that the effect of reducing the length of the grafted chains was not very pronounced for C_2 , and for C_8 a similar upward curvature was found for B-PS [1]. It should be noted, however, that, in the calculations, the amount of hydrocarbon at the surface was kept constant, which means that the spacing between grafted chains decreased dramatically going from C_{18} to C_4 . In the C_4 case the chains were packed to up to 75% of the theoretical grafting density limit (remember that $\theta_3 = 3$), leaving little space for the

B-PS to partition inside the brush. Then, obviously, the silica surface cannot easily be reached. Experimentally, this control on the grafting density was not realised. This suggests that a full systematic investigation of the influence of the grafting density and the chain length of the grafted molecules is useful. The selectivity of the (underlying) silica surface for the various components, especially at low grafting densities, also needs further attention. In such a study, one may hope to obtain more insight that can be used to further optimise the conditions for reversed-phase gradient polymer elution chromatography of oligomers.

In general, it may be concluded that the SF SCF technique is an interesting tool to investigate chromatography problems. The use of the SF SCF theory to evaluate chromatography experiments was investigated in the context of alkane and alcohol separations some years ago [19,20]. Much progress in our understanding can still be made, however, especially if the numerical SCF technique can be coupled to analytical models. In the domain of polymer chromatography and critical chromatography this route is currently being considered [21,22].

5. Conclusions

An equilibrium self-consistent-field theory for polymer adsorption was used to model HPLC experiments of butyl-terminated polystyrene. It was found that it is possible to bring the calculations in semi-quantitative agreement with experiment. Even the highly specific effect of an end group on the elution properties of a mixture of polystyrene molecules can be reproduced. Detailed information on the adsorption mechanism that controls the elution process was extracted from the calculations. Having established the potential use of the SF SCF theory for this purpose it is likely that the theory can be used for similar problems in related systems.

Acknowledgements

Part of this work was made possible by INTAS project 200-0031.

References

- [1] H.J.A. Philipsen, B. Klumperman, F.A.M. Leermakers, F.P.C. Wubbe, A.L. German, *Chromatographia* (submitted for publication).
- [2] G.J. Fleer, J.M.H.M. Scheutjens, M.A. Cohen Stuart, T. Cosgrove, B. Vincent, *Polymers at Interfaces*, Chapman & Hall, London, 1993.
- [3] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* 83 (1979) 1619.
- [4] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* 84 (1980) 178.
- [5] O.A. Evers, J.M.H.M. Scheutjens, G.J. Fleer, *Macromolecules* 23 (1990) 5221.
- [6] C.M. Wijmans, J.M.H.M. Scheutjens, E.B. Zhulina, *Macromolecules* 25 (1992) 2657.
- [7] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, Academic Press, New York, 1996.
- [8] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [9] W.J. Staal, Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, Netherlands, 1996.
- [10] F.A.M. Leermakers, J.M.H.M. Scheutjens, *J. Chem. Phys.* 89 (1988) 3264.
- [11] F.A.M. Leermakers, J.M.H.M. Scheutjens, *J. Colloid Interface Sci.* 136 (1990) 231.
- [12] A.B. Scholten, Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, Netherlands, 1997.
- [13] H.J.A. Philipsen, H.A. Claessens, H. Lind, B. Klumperman, A.L. German, *J. Chromatogr.* 790 (1997) 101.
- [14] M. Schick, in: J. Charvolin Joanny, J.F. Zinn-Justin (Eds.), *Liquids at Interfaces*, Les Houches Session 48 NATO ASI, Elsevier, Amsterdam, 1990.
- [15] S.M. Staverov, A.Yu. Fadeev, *J. Chromatogr.* 544 (1991) 77.
- [16] S.G. Entelis, V.V. Evreinov, A.V. Gorshkov, *Adv. Polym. Sci.* (1986) 129.
- [17] H.J.A. Philipsen, B. Klumperman, A.M. Herk van, A.L. German, *J. Chromatogr.* 727 (1996) 13.
- [18] J. van der Gucht, N.A.M. Besseling, G.J. Fleer, *Macromolecules* (submitted for publication).
- [19] M.R. Böhmer, L.K. Koopal, R. Tijssen, *J. Phys. Chem.* 95 (1991) 6285.
- [20] R. Tijssen, P.J. Schoenmakers, M.R. Böhmer, L.K. Koopal, H.A.H. Billiet, *J. Chromatogr. A* 656 (1993) 135.
- [21] A.A. Gorbunov, L.Y. Solovyova, A.M. Skvortsov, *Polymer* 9 (1998) 697.
- [22] A.A. Gorbunov, A.M. Skvortsov, B. Trathnigg, M. Kolroser, M. Parth, *J. Chromatogr. A* 789 (1998) 187.