

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

Analysis of the Longitudinal Structure of a Collapsed Molecular Bottle Brush Using a Self-Consistent Field Approach

A. Polotsky^a; M. Daoud^a; O. Borisov^a; M. Charlaganov^b; F. A. M. Leermakers^b

^a CEA DSM-DRECAM-SPEC, Orme des Merisiers, Gif-sur-Yvette, France ^b Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, The Netherlands

To cite this Article Polotsky, A. , Daoud, M. , Borisov, O. , Charlaganov, M. and Leermakers, F. A. M.(2007) 'Analysis of the Longitudinal Structure of a Collapsed Molecular Bottle Brush Using a Self-Consistent Field Approach', *International Journal of Polymer Analysis and Characterization*, 12: 1, 47 – 55

To link to this Article: DOI: 10.1080/10236660601060151

URL: <http://dx.doi.org/10.1080/10236660601060151>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Analysis of the Longitudinal Structure of a Collapsed Molecular Bottle Brush Using a Self-Consistent Field Approach

A. Polotsky, M. Daoud, and O. Borisov

CEA DSM-DRECAM-SPEC, Orme des Merisiers, Gif-sur-Yvette, France

M. Charlaganov and F. A. M. Leermakers

Laboratory of Physical Chemistry and Colloid Science, Wageningen University,
Wageningen, The Netherlands

Abstract: The two-gradient self-consistent field Scheutjens-Fleer (SCF-SF) approach is employed for study of conformational transition occurring in molecular bottle brushes upon decrease in the solvent strength for grafted chains. In particular, the solvent strength was varied from theta to poor solvent conditions. It was found that at moderately poor solvent strength the bottle brush collapses, keeping cylindrically uniform shape. Further decrease in the solvent strength leads to appearance of longitudinal undulations in the collapsed cylindrical structure. This result of our SCF modeling is in agreement with earlier predictions of scaling theory concerning longitudinal instability of uniform cylindrical structure of the collapsed brush. In particular, predicted by scaling theory dependence for the period of the structure on the degree of polymerization of grafted chains ($\sim n^{1/2}$) and independence of the transition temperature of the molecular weight are in good agreement with results of our SCF modeling.

Received 10 August 2006; accepted 29 September 2006.

This work, part of the European Science Foundation EUROCORES Programme SONS-AMPHI, has also been supported by funds from the EC Sixth Framework Programme.

Address correspondence to Dr. Oleg Borisov, Laboratory of Physical Chemistry and Colloid Science, UMR 5067, CNRS/UPPA, 2 Avenue President Angot, 64053 Pau, France. E-mail: oleg.borisov@univ-pau.fr

INTRODUCTION

Recent advances in synthetic polymer chemistry have made it possible to produce macromolecules of complex and well-defined topology with precise control of molecular architecture parameters (molecular weight of building blocks) and low polydispersity. In particular, graft copolymers comprising a long main chain with multiple side chains terminally attached at intervals have recently attracted considerable interest.^[1] Modification of the (main) polymer chain by grafted side chains of different chemical natures enables modifying significantly properties of molecules in solution, to enhance solubility and to improve processibility of intrinsically stiff or poorly soluble polymers.

If the chemical distance between the grafting points along the contour of the main chain is small, then the graft copolymers are classified as molecular bottle brushes. High grafting density or/and bulkiness of grafted chains induce significant conformational changes in the main chain, i.e., leads to induced rigidity, which is responsible for ability to undergo nematic ordering and also the ability of the copolymers to self-organize into ordered mesophases.

Conformations of graft copolymers with nonionic side chains in good or theta solvents are well understood on the basis of scaling theories.^[2-4] It has been established that their local and large-scale conformational properties are governed by excluded volume repulsive interactions of crowded side chains. These repulsions lead to extension of the grafted chains and induce axial stress in the main chain (the backbone).^[3]

When the strength of interaction between grafted chains and their solubility can be tuned by varying environmental conditions (temperature, solvent composition, etc.), the graft copolymers exhibit stimuli-responsive properties. Conformational transition related to collapse of the grafted chains in the bottle brush has been analyzed on the basis of scaling approach.^[5-7] One of the most intriguing predictions of the scaling theory, also supported by experimental observations,^[7] concerns instability of the cylindrically uniform structure of a collapsed brush with respect to longitudinal undulations below a certain solvent strength threshold. However, the scaling approach applies in asymptotic limits far from the transition range from cylindrically uniform to axially inhomogeneous structures.

The aim of the present study is to apply the numerical self-consistent field Scheutjens-Fleer (SCF-SF) method in its two-gradient version for the analysis of conformational transition occurring in molecular bottle brushes upon a decrease in the solvent strength for grafted chains below the theta point. The advantage of the SCF-SF method over analytical theoretical approaches is the ability to avoid most approximations except of the mean-field approximation. In particular, it enables exploring

carefully both the transition range and asymptotic limits corresponding to uniform cylindrical and axially inhomogeneous structures of the brush.

The rest of the article is organized as follows: in the next section we outline predictions of analytical scaling theory on the collapse transition in molecular bottle brushes. In the following section we introduce our computational model. The results are then summarized and followed by conclusions.

OUTLINE OF SCALING THEORY

We start with a brief review of predictions of analytical scaling theory concerning conformations of polymer chains in a cylindrical (bottle) brush, that is, an array of flexible polymer chains of degree of polymerization $n \gg 1$ end-grafted onto a thin long cylinder (mimicking the main chain) and immersed in a solvent. The grafting density (number of chains per unit length of the cylinder, $h^{-1} \geq n^{-1/2}a^{-1}$) ensures crowding of neighboring chains along the cylinder (Figure 1). The grafted chains are assumed to be intrinsically flexible, i.e., the Kuhn segment length is of the order of the monomer size, a . The solvent strength is characterized by monomer-monomer excluded volume parameter (second virial coefficient) $a^3v \cong a^3(0.5 - \chi)$. The values of the Flory-Huggins interaction parameter $\chi <, > 0.5$ correspond to good or poor solvent conditions for the monomers of grafted chains, respectively.

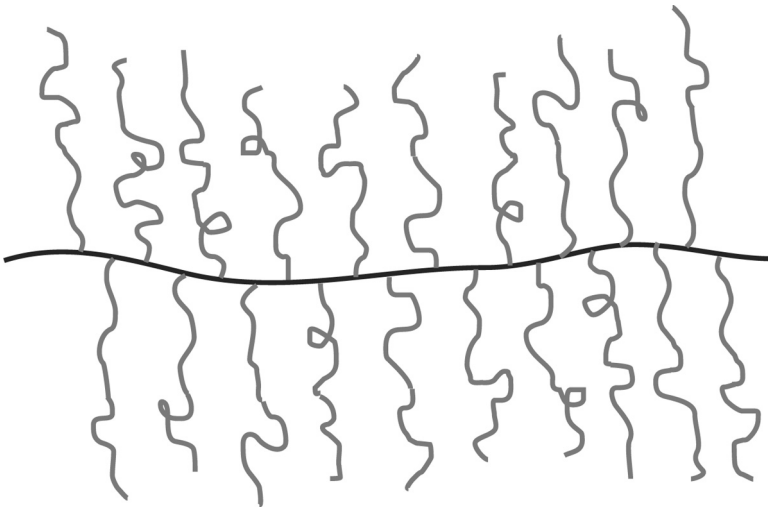


Figure 1. Schematic presentation of a molecular bottle brush: n is the number of monomers in a grafted chain; h is axial separation between grafting points.

Conformations of chains in a polymer brush are determined by the balance between conformational entropy and repulsive interactions between monomers of overlapping grafted chains. In order to minimize unfavorable (under good or theta solvent conditions) monomer-monomer contacts, the chains get extended in the direction perpendicular to the axis of a cylinder. As discussed by Birshtein and coworkers,^[2,3] repulsions between crowded chains in the bottle brush lead to their radial extension with respect to the Gaussian coil dimensions under good ($\chi < 0.5$) and theta-solvent ($\chi = 0.5$) conditions. This extension partially remains even under poor solvent conditions ($\chi > 0.5$).

It has been discussed by Borisov et al.^[5] and Zhulina et al.^[6] that the onset of collapse transition in cylindrical polymer brushes occurs below the theta point, at $|v_c| \sim n^{-1/3}(h/a)^{-1/3}$, due to strong ternary repulsive interactions between monomers in the brush. (Compare to the onset of coil-to-globule transition in a single polymer chain at $|v_c| \sim n^{-1/2}$).^[8] The collapse begins from the sparser periphery and propagates upon decrease in the solvent strength (increase in χ) towards more dense central regions of the brush and is accompanied by progressive decrease in the chain extension in the radial direction. At $|v| \gg |v_c|$ the collapsed bottle brush acquires the shape of a uniform cylindrical globule with a uniform polymer concentration $\sim |v|$ and radius $R \cong n^{1/2}a \cdot (h/a)^{-1/2}|v|^{-1/2}$.

The scenario of the uniform collapse holds as long as chains in the brush remain extended with respect to their Gaussian dimensions, i.e., $R \geq n^{1/2}a$, that is, the case in the range of $|v_c| < |v| < (h/a)^{-1}$. Further decrease in the solvent strength down to $|v| \approx (h/a)^{-1}$ leads to the appearance of longitudinal undulations along the cylindrical globule. Remarkably, within the accuracy of a scaling approach the solvent strength threshold corresponding to the instability of a uniform cylindrical shape of a collapsed brush is predicted to be independent of the degree of polymerization of grafted chains. In the transition range, $|v| \approx (h/a)^{-1}$, both the characteristic wavelength and magnitude of undulations are $\sim n^{1/2}a$.

In the range of limiting poor solvent strength conditions, $(h/a)^{-1} < |v| \leq 1$, the brush loses its axial continuity and splits into spherical globular clusters comprising several chains and pinned to the axis of the brush by extended segments of the chains. The size of the collapsed core of a cluster scales as $R \cong n^{1/2}a \cdot v^{-1/4}(h/a)^{-1/4}$, whereas the average distance between clusters scales as $L \cong n^{1/2}a \cdot v^{1/4}(h/a)^{1/4}$.

CALCULATION METHOD (SCF APPROACH)

At the basis of the SCF approach is a mean-field free energy, which is expressed as a functional of the volume fraction profiles (normalized

concentrations) and the self-consistent field potentials. The optimization of this free energy leads for Gaussian polymer chains to the Edwards diffusion (ED) (differential) Equation (8), which for any coordinate system may be expressed as

$$\frac{\partial G(n, \mathbf{r})}{\partial n} = \frac{1}{6} \nabla^2 G(n, \mathbf{r}) - u(\mathbf{r})G(n, \mathbf{r}) \quad (1)$$

The self-consistent potential $u(\mathbf{r})$ represents the surroundings of a probe chain and serves as an external field used in the Boltzmann equation to find the statistical weight for each chain conformation. Consequently, the end-point distribution $G(n, \mathbf{r})$ that obeys Equation (1) is related to the volume fraction profile of the polymer chains. In our case all first segments of the grafted chains are pinned to the backbone by the initial condition, and the boundary conditions provide constraints on the spatial solutions, i.e., they influences the period of the undulations.

Approximate analytical solutions of the ED equations are possible (for various geometries) for polymer brushes where the chains are strongly stretched. To solve these equations rigorously, it is necessary to introduce a numerical algorithm. Such numerical scheme unavoidably involves space discretization (i.e., the use of a lattice). Here we follow the method of Scheutjens and Fleer (SF-SCF)^[9] who used the segment size a as the cell size. A mean-field approximation is applied to a set of lattice sites. This set (often called a lattice layer) is referred to with a single coordinate \mathbf{r} . The way the sites are organized in layers depends on the symmetry in the system and must be pre-assumed. The approach allows for, for example, volume fraction gradients between these layers. For example, polymer adsorption onto a flat solid-liquid interface requires planar lattice layers with just one concentration gradient in the normal direction (1-gradient approach). The method can be used for various solvent conditions. As mentioned above, the interactions are parameterized by the Flory-Huggins parameter χ . It is relevant to mention that in the SF-SCF method these volume interactions, accounted for by the self-consistent potential, have local as well as nonlocal (molecules sitting on different coordinates \mathbf{r}) nearest neighbors contributions. These nonlocal contributions are typically neglected in the ED approaches. Typically, the numerical accuracy of the SCF solutions is sufficient to evaluate the (mean-field) free energy with an accuracy of at least five significant digits. If in a particular system there are several independent SCF solutions, one can use the free energy to select the most favorable one.

In order to consider a molecular bottle brush with longitudinal undulations, it is necessary to use a two-gradient version of the SCF algorithm.^[10] The natural geometry for this is a cylindrical coordinate system for which $\mathbf{r} = (r, z)$. In this case, all volume fraction profiles as

well as other thermodynamical values depend only on the radial coordinate r and the axial coordinate z , while the mean-field approximation is used along the angular coordinate.

More specifically, within our model the (rigid) main chain of a bottle brush coincides with the axis of the cylinder (i.e., at $r = 0$). An array of polymer chains originates from this line and is homogeneously distributed along the z -direction with an inter-chain distance h between the grafting points. All chains have their first segment at a fixed z -coordinate, i.e., the chains cannot slide along the line.

The boundary conditions are chosen such that there is sufficient space in the radial direction to avoid system size effects. This implies that the results are obtained for the limit of a very dilute solution of bottle brushes in excess of solvent. The boundary condition in the z -direction is more complicated. In principle we would like to avoid end effects and, therefore, to consider an infinitely long main chain. However, we are limited to only finite box sizes in the z -direction. We use periodic boundary conditions in the z -direction to mimic an infinitely long main chain. In the limit of poor solvent conditions it is anticipated that significant gradients occur in the z -direction (undulations). These undulations have a particular wavelength associated to them. The boundary conditions impose a restriction to the system such that an integer number of wavelengths must fit the box size. Typically, the system size in the z -direction coincides with the wavelength. The system size in the z -direction was varied in order to find the optimal wavelength of the undulations.

For convenience, we normalize all linear lengths by the cell size a and normalize all energy units by the thermal energy kT . There are just three parameters in our model. The first one is the dimensionless grafting density, which is given by l/h instead of a/h . The second parameter is the number of segments of the side chains n . Unoccupied lattice sites are taken by a monomeric solvent (incompressible system), and thus the third remaining parameter is the Flory-Huggins interaction parameter (χ) for polymer-solvent interactions.

RESULTS

Scenario of the Transition

In Figure 2 side chain monomer density profiles in coordinates (r, z) are presented, for several values of χ corresponding to θ - and poor solvent for fixed values of $n = 100$ and grafting density $l/h = 0.5$. One can see that in the θ -solvent ($\chi = 0.5$) the bottle brush has a cylindrically uniform shape. An increase in χ from 0.5 to 0.9 leads to the progressive collapse of the cylinder. Upon further increase in χ from 0.9 to 1, the homogeneous in

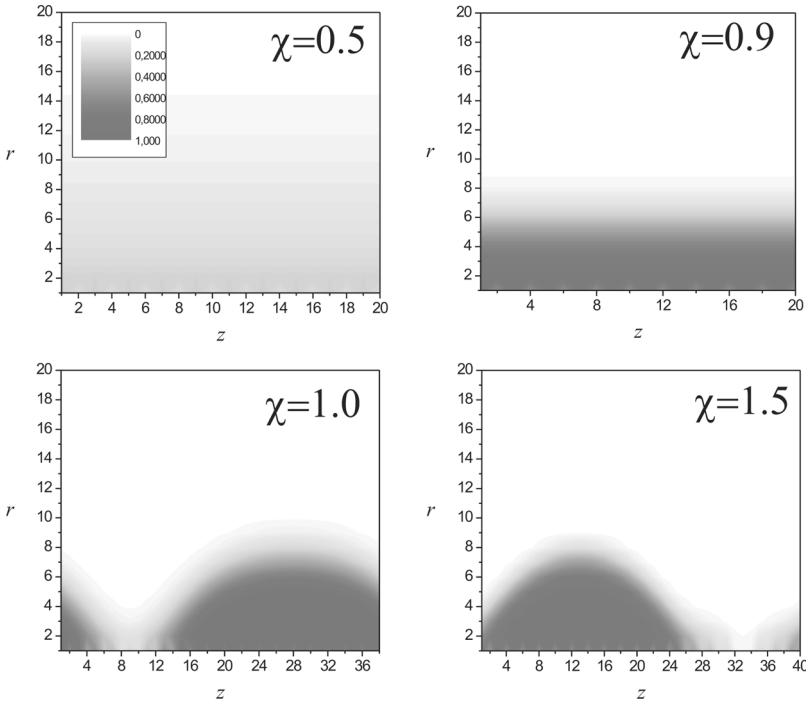


Figure 2. Density of side chain monomers in (r, z) -coordinates for different values of χ . The bottle brush parameters are: $n = 100, h = 2$. Box sizes for undulated structures are optimal.

z -directions cylindrical structure splits into dense clusters with well-defined size and shape, i.e., a structure with longitudinal undulations develops. More detailed analysis in the interval $0.9 < \chi < 1$ allowed us to localize the transition point $\chi_{tr} \approx 0.97$. Moreover, our analysis indicates that an increase in the number of monomers in a grafted chain up to $n = 150$ leads to very weak increase in χ_{tr} (up to 1.06). This finding is in a good agreement with results predicted by the scaling approach concerning the absence of power law dependence of χ_{tr} on the number of monomers in a grafted chain.

Note that the use of periodic boundary conditions in the z -direction leads to two following consequences for the undulated structures: (1) an integer number of clusters are always obtained for any (sufficiently large) box size, and (2) the placement of the structure in the box is not necessarily symmetric in the z -direction with respect to the center of the box. Notice also that in Figure 2, the z -scale (equal to the structure period) is different for $\chi = 1$ and 1.5 and equal to 38 and 40 respectively.

Since the box size remains unchanged in each run of the SCF method, for each set of parameters a series of calculations for different box sizes in z -direction was done to determine the optimal box size and, hence, the structure's period corresponding to the minimum of the free energy per side chain as a function of the box size.

Structure Period as a Function of Side Chain Length

To check the scaling dependence $H = R + L \propto n^{1/2}$, a series of calculations for different side chain lengths ($n = 50, 100, 150, 250$) and grafting densities ($h = 2, 4, \text{ and } 5$) has been performed. The results are presented in Figure 3 in double logarithmic coordinates and can be fitted using a power law dependence of the $H(n)$. The exponent determined by the least-square fitting method is slightly different from the value 0.5 predicted by scaling and equal to 0.58, 0.56, and 0.54 for $h = 2, 4, \text{ and } 5$, respectively. Hence, upon an increase in h , the (effective) exponent of the $H(n)$ dependence progressively decreases, approaching the value of 0.5 predicted by scaling theory.

One of the sources of this discrepancy can lie in the fact that the period of the undulated structure should not necessarily be equal to the integer number of h . To catch this effect, one should make calculations in quite large (in z -direction) boxes corresponding to several periods of

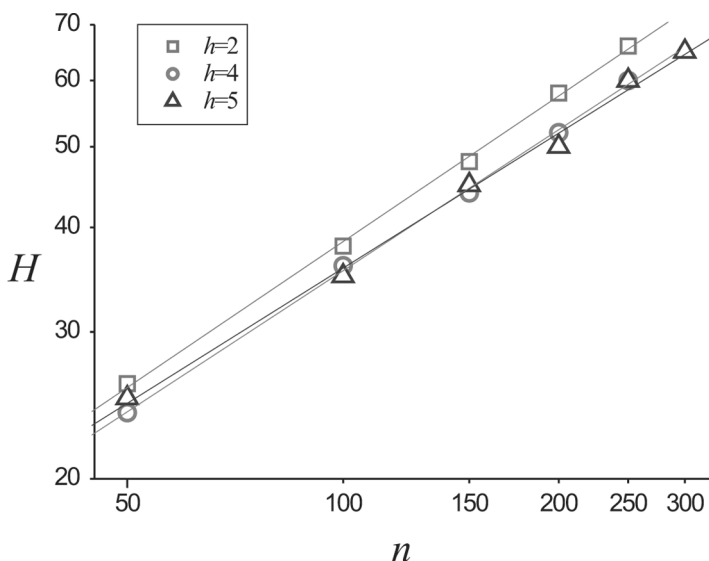


Figure 3. Period of undulated structure as function of the number of monomer units in a side chain n for $\chi = 1.2$ and different grafting densities (indicated in figure).

the structure. Of course, this would increase considerably the time needed to converge to the solution, therefore, calculations reported in the present article were made for the boxes corresponding to one, two, and a maximum of three periods.

CONCLUSION

The results of our SCF modeling prove unambiguously and quantitatively the prediction of the scaling theory concerning the structure of a polymer bottle brush collapsed under poor solvent conditions. We have demonstrated that the cylindrically uniform structure remains stable in a limited range of solvent strengths below the theta point where chains in the brush retain their radial extension with respect to Gaussian dimensions. Further decrease in the solvent strength leads to developing longitudinal instability of the cylindrically uniform structure and appearance of undulations with a characteristic wavelength proportional to Gaussian chain dimensions. Remarkably, the transition point (critical solvent strength) corresponding to instability of the cylindrical structure is fairly independent of the molecular weight of grafted chains.

REFERENCES

- [1] Zhang, M. and A. H. E. Müller. (2005). Cylindrical polymer brushes. *J. Polym. Sci. Part A Polym. Chem.* **43**, 3461–3481.
- [2] Birshtein, T. M. and E. B. Zhulina. (1985). *Polym. Sci. USSR* **27**, 570.
- [3] Birshtein, T. M., O. V. Borisov, E. B. Zhulina, A. R. Khokhlov, and T. A. Yurasova. (1987). Conformations of comb-like macromolecules. *Polym. Sci. USSR* **29**, 1293–1300.
- [4] Fredrickson, G. (1993). Surfactant-induced lyotropic behavior of flexible polymer solutions. *Macromolecules* **26**, 2825–2831.
- [5] Borisov, O. V., E. B. Zhulina, and T. M. Birshtein. (1988). Diagram of the state and collapse of grafted chains layer. *Polym. Sci. USSR* **30**, 772–779.
- [6] Zhulina, E. B., O. V. Borisov, V. A. Pryamitsyn, and Birshtein, T. M. (1991). Coil-globule type transitions in polymers. I: Collapse of layers of grafted polymer chains. *Macromolecules* **24**, 140–149.
- [7] Sheiko, S. S., O. V. Borisov, S. A. Prokhorova, and M. Möller. (2004). Cylindrical molecular brushes under poor solvent conditions: Microscopic observation and scaling analysis. *Europ. Phys. J. E* **13**, 125–131.
- [8] de Gennes, P. G. (1979). *Scaling Concepts in Polymer Physics*. Ithaca: Cornell University Press.
- [9] Fleer, G. J., M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent. (1993). *Polymers at Interfaces*. London: Chapman and Hall.
- [10] Feuz, L., F. A. M. Leermakers, M. Textor, and O. V. Borisov. (2005). Bending rigidity and induced persistence length of molecular bottle brushes: A self-consistent-field theory. *Macromolecules* **38**, 8891–8901.