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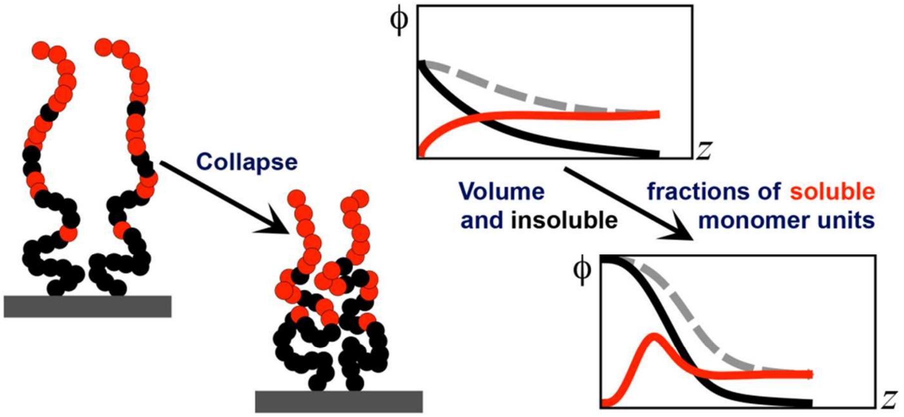

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PAPER

# Swelling of Chemical and Physical Planar Brushes of Gradient Copolymers in a Selective Solvent

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We propose a mean-field theory of chemical and physical planar brushes of linear gradient copolymers swollen in a selective solvent. The polymer chains are grafted to the substrate by ends with the excess of insoluble monomer units, and majority of the soluble units is located near the free ends of the chains. The grafting points are considered to be immobile (chemical brush) and mobile in-plane (physical brush). In the latter case the grafting density is determined from the equilibrium conditions (minimum of the free energy). A common peculiarity of the brushes of both types is that the polymer concentration gradually changes from relatively high value near the substrate (collapsed region of the brush) to a small value near the free surface (swollen region of the brush). In the case of the chemical brush, a polymer depletion zone can appear in the middle of the brush if incompatibility between insoluble and soluble (A and B) units is high enough. Here the polymer density is even lower than near the free surface of the brush. The grafting density of the physical brush is inversely proportional to the chain length and increases with the decrease of the solvent quality for the insoluble (A) units. The latter can be accompanied by shrinkage of the brush thickness due to broad distribution of the insoluble units through the chain: a minor fraction of insoluble units near the free ends can aggregate with a major fraction of them near the substrate. As a result, the concentration of the soluble (B) units can have a maximum in the middle of the brush rather than near the free surface.

## Introduction

Conventional AB gradient copolymers exhibit a gradual change in monomer composition from predominantly one specie (A) in an one end of the chain to predominantly the other (B) in the opposite end, unlike with block copolymers, which have an abrupt change in composition, Figure 1. Although the first publication about the preparation of gradient copolymers appeared already 30 years ago,[1] their controlled synthesis became possible only recently due to the new developments in the methods of polymerization.[2–8] Control over the sequence of segments made it possible to conduct reproducible and thorough experimental investigation of their properties. Pioneering studies suggested gradient copolymers as an alternative to block copolymers in the preparation of compatibilizers of immiscible polymer blends, for the stabilization of emulsions and dispersions,[6,9] shock adsorbing materials (because these molecules form broad interfaces and have a broad range of glass transition temperatures[10]), adhesives, coatings, etc. [6] Most of the experimental contributions published to the date dealt with micelle formation,[11–13] microphase separation[4] and interfacial activity[14,15] of the gradient copolymers. On the one hand, these studies have shown that gradient copolymers and block copolymers have some common properties. For example, the phase diagram of microphase separation is similar to the one of diblock copolymers.[16] It has been shown[16] that stable morphologies in melts of gradient copolymers correspond to conventional lamellar, hexagonal and body-centered cubic structures. Furthermore, lamellar thickness of linear gradient copolymer in the strong segregation regime has the same scaling dependence like in the case of diblock copolymers.[17] On the other hand, other properties exhibit substantial differences and effects which are uncommon for other copolymer architectures. For instance, gradient copolymer micelles are able to increase the radius of the core with simultaneous decrease of the corona radius under temperature variation (“reel-in” effect [12,18]). This tendency is opposite to the one in diblock copolymer micelles. Aggregation of the gradient copolymers leads to formation of very wide interfaces in contrast to relatively sharp ones in conventional copolymers.[6] The viscosity of copolymers with gradient distribution of monomer units in melts is significantly different from the viscosity of random and block copolymers.[19]

The first theoretical work dealing with gradient copolymers appeared just fourteen years ago.[16] It describes microphase separation in melts of such molecules. There were only few theoretical publications since then.[14, 15,17, 20–24] They dealt with interfacial activity,[20] melt copolymer brush properties[21] and microphase separation.[17,22] To the best of our knowledge, there are no theoretical papers dealing with planar brushes of gradient copolymers swollen in a selective solvent. On the other hands, homopolymer[25-27] and block copolymer[28-38] brushes are very perspective systems for a number of applications.[39,40] Furthermore, one can expect that the gradual variation of hydrophobic/hydrophilic monomer units along the chains in the gradient copolymers can be more efficient for some functions of the brushes like uptake and release of guest-molecules, etc.

In the present paper we will develop a theory of densely grafted planar brushes of gradient copolymers swollen in a selective solvent. Both chemical and physical brushes will be considered. It will be explored how the incompatibility between different monomer units of the copolymer and solvent quality influences the polymer density profile. In particular, we will demonstrate that strong incompatibility of A and B monomer units is responsible for a non-monotonous density profile: collapsed and swollen layers of the brush are separated by a depletion zone whose polymer concentration is lower that the concentration of the swollen layer. In the case of the physical brush (polymer chains are in-plane mobile), concentration of the soluble units can have maximum value inside the brush rather than near the free surface.

## Model

Let us consider a dense planar brush obtained by end-grafting of gradient AB copolymers to a surface, Figure 2. The segments of both sorts are characterized by equal lengths $a$ and excluded volumes $v \approx a^3$. The numbers of A and B segments per chain are $N_A$ and $N_B$, respectively, so that the total number of the segments per chain is $N=N_A+N_B$. Let us assume that A-rich ends of the chains are grafted to the substrate, Figure 2. Gradual variation of a sort of the segments along the chain is described by a function $g(n)$, which is defined as a local fraction of B species. Here, the argument $n$ is the segment number counted from the grafting point, which is considered to be continuous variable, $0 < n < N$. For the gradient copolymer, it has the following boundary values: $g(0) = 0,\ g(N) = 1$. If we consider a narrow "window" of the segments on the chain of the width $dn$, it will contain $g(n)dn$ B segments, and

$$\int_0^N g(n)dn = N_B \cdot \qquad (1)$$

For the sake of simplicity, we postulate a power law for the function $g$, $g(n) = Cn^{\alpha}$, where constants $C$ and α are calculated from the condition $g(N) = 1$ and normalization done by Eq. (1):

$$g(n) = \left(\frac{n}{N}\right)^{\frac{1-f}{f}}, \qquad (2)$$

Here $f$ is the average fraction of B segments in the chain, $f = N_B/N$. The dependence of $g$ on $n$ at different values of the composition $f$ is presented in Figure 3. The linear form of the function is obtained for the symmetric copolymer, $f$=1/2.

Let us assume that distribution of free (non-grafted) ends of the chains corresponds to the Alexander- de Gennes model,[41,42] i.e., they are equidistantly located with respect to the substrate. Such assumption is supported by calculation of the distribution in the case of melt brushes of the gradient copolymer.[21] It has been demonstrated that the free ends are expulsed from inner region of the brush to the upper layer.[21] One can expect that swelling of one of the components and strong incompatibility between the monomer units will not change the distribution significantly.

In the present paper, we will confine ourselves by consideration of polymer segregation only in the direction perpendicular to the substrate plane ($z$-direction, sandwich-like structure, Figure 2). In the case of the diblock copolymer brushes, such structure is stable in very wide range of grafting densities and composition of the copolymer if the solvent is poor for the grafted blocks and good for the upper ones.[34] One can expect that the sandwich-like structure of the gradient copolymers is stable in much wider region of the parameter values due to weaker segregation of monomer units. The case of low grafting density (below of the overlap concentration of the chains or slightly above), when the lateral segregation is possible, is excluded from consideration. Thus, the polymer volume fraction of the brush, $\phi$, as well as the fractions of the components (A, B monomer units and solvent S), $\phi_i$, $i = A, B, S$ are one-dimensional functions:

$$\phi(z) = \phi_A(z) + \phi_B(z) = 1 - \phi_S(z) \qquad (3)$$

where the last equality corresponds to the incompressibility of the whole (polymer+solvent) system. Within the Alexander-de Gennes model, the space filling condition for a narrow layer of the thickness $dz$ located at a distance $z$ from the substrate, which is occupied by $dn$ segments from each chain, takes the form:

$$\Sigma dz \phi_A(z) = Q(1 - g(n))dnv, \qquad \Sigma dz \phi_B(z) = Qg(n)dnv,$$
$$\Sigma dz \phi(z) = Qdnv, \qquad (4)$$

where $\Sigma$ and $Q$ are the area of the brush and the total number of grafted chains, respectively. Let us introduce a dimensionless grafting density $\sigma = Qa^2/\Sigma$, which takes values $0 < \sigma < 1$. In the case of high grafting density, when the neighbor chains "feel" each other, i.e., there are interchain interactions, the chains are strongly stretched in the z-direction. For homopolymer brushes in good and poor solvents, the thickness of the brush $H$ (end-to-end distance of the chains) is proportional to the number of the segments $N$, $H$~$N$. In the case of the gradient brush in a selective solvent, one can expect that the chain stretching will be inhomogeneous: the parts of the copolymer with excess of the soluble units will be more stretched. The local stretching of the copolymer in the $z$-direction can be calculated from the space filling conditions, Eq. 4, as a derivative of the coordinate with respect to the number of the segments:[43,44]

$$\frac{dz}{dn} = \frac{\sigma a}{\phi(z)}, \qquad (5)$$

This differential equation also determines a "trajectory" of the chains, $z(n)$. Considering the overall polymer volume fraction as a complex function of the number of the segments $n$, $\tilde{\phi}(n) = \phi(z(n))$, one can calculate $z$(n) via integration of Eq. 5:

$$z(n) = \int_0^n dn' \frac{\sigma a}{\tilde{\phi}(n')} \qquad (6)$$

Eqs 4 also give a connection between concentrations of different species:

$$\phi_A(z(n)) = \tilde{\phi}_A(n) = \frac{1 - g(n)}{g(n)} \tilde{\phi}_B(n) \qquad (7)$$

Equilibrium characteristics of the brush of gradient copolymers are determined by a balance between elastic stretching of the chains and interactions of the monomer units with the solvent and each other. The soluble monomer units of the brush promote swelling of the chain fragments where their fraction is in excess, and vice versa. Incompatibility of A and B monomer units prevents their mixing. Therefore, the polymer density profile in the brush is inhomogeneous. The presence of the density inhomogeneities is responsible for entropic penalties. Thus, the total free energy of the brush can be split into three terms:

$$F_{brush} = F_{elast} + F_{FH} + F_{in\hom} \qquad (8)$$

The elastic free energy of the brush per chain takes a conventional form:[43,44]

$$\frac{F_{elast}}{k_BT}=\frac{3}{2a^2}\int_0^N dn\left(\frac{dz}{dn}\right)^2=\frac{3\sigma^2}{2}\int_0^N\frac{dn}{\tilde{\phi}^2}\,. \tag{9}$$

The Flory-Huggins free energy per chain allows describing interactions between various species of the system:[45]

$$\begin{aligned}\frac{F_{FH}}{k_BT}&=\int_0^H\frac{dz}{a\sigma}\left(\phi_s\ln\phi_s+\chi_{AS}\phi_A\phi_s+\chi_{BS}\phi_B\phi_s+\chi_{AB}\phi_A\phi_B\right)\\&=\int_0^N\frac{dn}{\tilde{\phi}}\left(\left(1-\tilde{\phi}\right)\ln\left(1-\tilde{\phi}\right)-\chi_{eff}(n)\tilde{\phi}^2\right)+const\end{aligned} \tag{10}$$

Here $\chi_{AS}$, $\chi_{BS}$, and $\chi_{AB}$ are the Flory-Huggins parameters describing interactions of A monomer units with the solvent, B monomer units with the solvent, and A with B monomer units, respectively. The effective Flory-Huggins parameter $\chi_{eff}$ is a function of the current number of monomer units $n$ , i.e., it varies along the chain:

$$\chi_{eff}(n)=\chi_{AS}\left(1-g(n)\right)+\chi_{BS}g(n)-\chi_{AB}g(n)\left(1-g(n)\right) \tag{11}$$

In the vicinity of the substrate ($n=0$) enriched by A monomer units, $\chi_{eff}(0)=\chi_{AS}$, and this parameter describes interactions of A monomer units with the solvent. In the upper side of the brush, where free ends of the sort B are located ($n=N$), $\chi_{eff}(N)=\chi_{BS}$. Interactions between A and B monomer units become detectable in the middle of the brush ($g(n)\approx 1/2$). This parameter clearly demonstrates that variation of the interactions along the chain is responsible for inhomogeneous distributions of the polymer in the brush. It has to be noticed that introduction of the effective Flory-Huggins parameter is valid only in the case of the Alexander-de Gennes model. Also, the mean-field expression of Eq 10 is applicable for poor and $\theta$ -solvent.[45] Therefore, in our calculations the values of the parameter $\chi_{AS}$ will correspond to the poor solvent conditions ($\chi_{AS}$>1/2) and $\chi_{BS}$ will be slightly below ½ to approach a regime of the marginal solvent.

Finally, the entropic penalties because of inhomogeneous density of the brush can be calculated using the following arguments. First of all, Eq. 10 states that the gradient copolymer in the brush is equivalent to a homopolymer with variable interaction parameter. In polymer brushes, there are two kinds of entropic contributions coming from “long-range” stretching of the chains (Eq. 9) and from “short-range” density inhomogeneities. The later one quantifies the entropic penalties at the length scales on the order of the blob size (the length scales where the chains do not “feel” each other). For densely grafted brushes, the number of blobs per chain is high enough. Therefore, in the case of the gradient copolymer brushes, variation of local composition of the chain at the length scale of the blob is negligible, and each chain fragment of the blob size behaves as a homopolymer with certain effective interaction parameter. Thus, we can approximate the entropic contribution by a conventional gradient term:[46]

$$\frac{F_{in\hom}}{k_BT}=\int_0^H\frac{dz}{a\sigma}\frac{\left(a\nabla\phi(z)\right)^2}{24\phi(z)}=\int_0^N dn\,\frac{\dot{\tilde{\phi}}^2}{24\sigma^2} \tag{12}$$

where $\dot{\tilde{\phi}}\equiv\partial\tilde{\phi}/\partial n$. In fact, this term introduces a “surface tension coefficient” which is responsible for the description of attraction of polymer chains in the physical brushes. The equilibrium polymer volume fraction is calculated by minimization of the functional

$$\frac{F_{brush}}{k_BT}=\int_0^N dn\left(\frac{\dot{\tilde{\phi}}^2}{24\sigma^2}+\frac{3\sigma^2}{2\tilde{\phi}^2}+\frac{h\left(\tilde{\phi}\right)}{\tilde{\phi}}\right) \tag{13}$$

$$h\left(\tilde{\phi}\right)=\left(1-\tilde{\phi}\right)\ln\left(1-\tilde{\phi}\right)-\chi_{eff}(n)\tilde{\phi}^2$$

with respect to $\tilde{\phi}(n)$ resulted in the following equation

$$\begin{cases}-\dfrac{\ddot{\tilde{\phi}}}{12\sigma^2}-\dfrac{3\sigma^2}{\tilde{\phi}^3}+\dfrac{\tilde{\phi}\,\partial h/\partial\tilde{\phi}-h}{\tilde{\phi}^2}=0\\ \dot{\tilde{\phi}}(0)=\dot{\tilde{\phi}}(N)=0\end{cases} \tag{14}$$

The boundary conditions ensure constant values of the polymer volume fraction near the substrate and the free surface. Calculation of the polymer volume fraction as a function of normal coordinate $z$, $\phi(z)$, can be done with Eq 6. Numerical solution of Eq 14 is obtained using the Numerov method developed to solve ordinary differential equations of second order in which the first-order term does not appear.[47] It is based on fourth order accuracy finite difference scheme.

## Results and discussion

### A. Chemical brush

In this subsection, we will analyze behavior of chemical brushes obtained by chemical grafting of gradient copolymers to a plane substrate. The grafting density $\sigma$ is a constant parameter for such brushes, which is controlled by synthesis conditions.

Before studying the gradient copolymers, let us reproduce conventional results for the homopolymer brush using Eq. 14. For the sake of definiteness, let A monomer units compose the brush, so that $\chi_{eff}(n)=\chi_{AS}=const$. In this case Eq. 14 has a trivial solution which is independent on $n$, $\tilde{\phi}(n)=\phi_0$:

$$-\frac{3\sigma^2}{\phi_0^3}+\frac{\phi_0\,\partial h/\partial\phi_0-h}{\phi_0^2}=0 \tag{15}$$

For the good solvent (the second virial coefficient is positive, $B=1/2-\chi_{AS}>0$) and θ-solvent ($\chi_{AS}=1/2$), the polymer volume fraction $\varphi_0$ is small and the function $h$ can be expanded into the series in powers of $\varphi_0$:

$$-\frac{3\sigma^2}{\phi_0^3}+\begin{cases}B & \text{good solvent}\\ \phi_0/3 & \theta\text{-solvent}\end{cases}=0 \tag{16}$$

This equation enables calculating the brush density in each of the regimes. The solution of Eq. 15 tends to unity, $\phi_0\to 1$, in the regime of the poor solvent far from the θ-point ($\chi_{AS}>>1$). Thus, the equilibrium thickness of the homopolymer brush, $H$=$z$($N$), is calculated with Eq. 6:

$$H = aN\begin{cases}(\sigma B/3)^{1/3} & \text{good solvent}\\ (\sigma/3)^{1/2} & \theta\text{-solvent}\\ \sigma & \text{poor solvent}\end{cases} \qquad (17)$$

and reproduces the conventional results. The linear dependence of the brush thickness on the number of the segments, $H$~$N$, should also be valid for the gradient brushes, where the solvent quality is variable along the chain. This assumption is justified by coefficients independent of the absolute value of $N$ in the differential equation 14. The parameter $N$ comes into $g(n)$ only, Eq. 2, i.e., into the effective Flory-Huggins parameter $\chi_{eff}(n)$, Eq. 11. Keeping in mind that $0<g(n)<1$, the absolute value of $\chi_{eff}(n)$ is primarily controlled by the parameters $\chi_{ij}$, *i,j=A,B,S.*

The characteristic dependences of the polymer volume fraction in the brush of the gradient copolymer on the vertical distance $z$ are presented in Figure 4. These curves were obtained by solving Eq. 14 and using Eq. 6 to convert dependence $\tilde{\phi}(n)$ into $\phi(z)$. They are plotted for two different values of the grafting density: $\sigma=10^{-2}$ (upper row), $10^{-1}$ (bottom row), and two values of the Flory-Huggins parameter of incompatible A and B monomer units: $\chi_{AB}=0.1$ (left column), 1 (right column). Different curves correspond to the different values of the copolymer composition $f$ which are depicted on the right of Figure 4. All other parameters are fixed and provide poor solvent quality for A monomer units, $\chi_{AS}=0.6$, and good solvent quality for B monomer units $\chi_{BS}=0.4$; $N=10^3$. All profiles reveal monotonous decay with $z$ (left column), if A and B monomer units are weakly incompatible, $\chi_{AB}=0.1$. Insoluble A units are in excess near the substrate while the upper part of the brush is swollen. The difference in the concentration at the boundaries is dependent of the fraction $f$: the higher the fraction of insoluble units (lower $f$), the bigger the difference. It also depends on the grafting density of the chains. Lower grafting density provides more inhomogeneous polymer density profile in z-direction and smaller stretching of the chains. The increase in the grafting density makes the brush more homogeneous of higher density and thickness (stretching of the chains) independently on composition and selectivity of the solvent. Indeed, in the limiting case of a maximum grafting density $\sigma\to 1$, one deals with a molten brush with constant polymer density.

It is possible to observe a non-monotonous behavior of the density profile if incompatibility between A and B monomer units becomes high, $\chi_{AB}=1$, Figure 4 (b,d). The polymer depletion layer is formed in the middle of the brush. The physical reason for the layer formation is the strong repulsion between A and B monomer units which is stronger than repulsion of soluble B units and the solvent molecules, $\chi_{AB}>\chi_{BS}$. The latter are concentrated in the middle of the brush (a maximum number of A-B contacts) to shield interactions between A and B units and decrease the free energy. As a result, the middle part of the brush can be more swollen than the upper region enriched by soluble units. In contrast to the diblock copolymer systems,[38,48] the width of the depletion zone in the gradient copolymer brush is very broad and can be comparable with the brush thickness. Despite the non-monotonous behavior of the total polymer volume fraction, the fractions of solvophobic (A) and solvophilic (B) species reveal monotonous decay and growth, respectively (inserts in Figure 4).

The presence of the depletion zone results in higher stretching of the chains in the brush as compared to equivalent homopolymer brush in a good solvent, Figure 5. The latter corresponds to the point $f$=1 at the $H$-$f$ graph. If the parameter $\chi_{AB}$ is small enough, gradual substitution of insoluble A by soluble B units (the increase of $f$) leads to monotonous increase in the chain stretching. On the contrary, strong incompatibility of A and B monomer units, $0.4<\chi_{AB}<1$, makes the gradient copolymer chains more stretched.

Collapse of initially swollen gradient copolymer brush via decrease of the solvent quality for grafted (A) monomer units proceeds in a more gradual way as compared to equivalent homopolymer brush ($f$=0), Figure 6. This effect is due to the stimuli response of the part of each of the chain: "bottom" part of the chain is able to collapse, whereas the soluble "upper" segments do not feel variation of the solvent quality.

## B. Physical brush

If polymer chains are physically attached to a substrate, one deals with so-called physical brushes. Examples are amphiphilic copolymers adsorbed on solvophobic surface and semi-layer of lamellae (vesicles) formed by amphiphilic copolymers in a selective solvent. In contrast to the chemical brush, the chains in the physical brush are mobile and their "grafting" density is not a fixed parameter. It is determined by a competition between stretching of the chains and gain in energy of aggregating insoluble units. In other words, the parameter $\sigma$ is determined via minimization of the total free energy, Eq. 13, with respect to $\sigma$:

$$36\sigma^4 = \int_0^N dn\,\tilde{\phi}^2 \Big/ \int_0^N \frac{dn}{\tilde{\phi}^2} \qquad (18)$$

Equilibrium characteristics of the physical brush are calculated with Eqs. 14 and 18. One of the consequences of these two equations is that the integral of the osmotic pressure $p$ of equivalent semidilute solution (described by the free energy $h$) is equal to zero:

$$\int_0^N dn\left(\frac{\partial h}{\partial\tilde{\phi}}-\frac{h}{\tilde{\phi}}\right)=\int_0^H\frac{dz}{\sigma a}\left(\phi\frac{\partial h}{\partial\phi}-h\right)=\int_0^H\frac{dz}{\sigma a}\,p(\phi(z))=0 \qquad (19)$$

This equation is obtained via multiplying Eq. 14 by the function $\tilde{\phi}$ and via integrating with respect to $n$. The latter is done using the boundary conditions of Eq. 14 and the equilibrium value of $\sigma$, Eq. 18. If we imagine each chain of the physical brush as a sequence of blobs, inside which the chains are not stretched, Eq 18 means that the osmotic pressure of each blob is equal to zero, i.e., the blob size is determined from the equilibrium condition.

Before studying the brush of the gradient copolymer, let us address to a homopolymer physical brush in a poor solvent slightly below the θ-temperature. The polymer volume fraction $\varphi$ in such a brush is small enough and determined by the dimensionless temperature $\tau=(\Theta-T)/T$, $\phi\sim\tau\sim\chi-1/2<<1$, like in the case of the single globule.[45] The equilibrium thickness and grafting density of the brush is calculated by minimization of the sum of the elastic free energy and the interfacial energy per chain:

$$\frac{F}{k_B T} = \frac{3}{2}\frac{H^2}{a^2 N} + \frac{\gamma\Sigma}{k_B T Q} = \frac{3}{2}\frac{H^2}{a^2 N} + \frac{\gamma a^3 N}{k_B T \phi H} \qquad (20)$$

where we use the space filling condition, $\Sigma H\phi \approx a^3 NQ$. The dimensionless surface tension coefficient at the boundary brush-solvent has square dependence on the reduced temperature (second virial coefficient[45]), $\gamma a^2 / k_B T \approx \tau^2$. Minimization of Eq. 20 with respect to $H$ leads to the following values (all numerical factors are omitted):

$$\begin{aligned} H &\approx aN^{2/3}\tau^{1/3} \\ \sigma &= \frac{Qa^2}{\Sigma} \approx \frac{\tau^{4/3}}{N^{1/3}} \end{aligned} \qquad (21)$$

Therefore, the chains in the physical brush are less stretched than in the chemical one ($H \approx aN\sigma/\tau$) because of very small, $N$-dependent grafting density of the chains. The decrease of the solvent quality (increase of $\tau$) makes the brush denser which is accompanied by the increase in the grafting density ($\sim\tau^{4/3}$) and stretching of the chains ($\sim\tau^{1/3}$).

In the case of the brush of gradient copolymers, the grafting density reveals similar behavior. It decreases with the increase of $N$ and the brush becomes denser as soon as the solvent quality becomes poorer for the A units (with the increase of the parameter $\chi_{AS}$), Figure 7. However, in contrast to the homopolymer brush, the thickness of the gradient brush decreases with the increase of $\chi_{AS}$, Figure 8. Such behavior is related to a broad distribution of the soluble and insoluble units. The soluble units diminish attraction of the insoluble ones in the bottom part of the brush. As a result, the grafting density of the gradient brush is lower than that of equivalent homopolymer brush. A minor fraction of the insoluble groups of the upper part of the brush can participate in the formation of denser "core" in the bottom part. That is why the thickness of the gradient copolymer brush can decrease. The latter is directly related to the so-called "reel-in" effect[12,18]: the gradient copolymer micelles are able to increase the radius of the core with simultaneous decrease of the corona radius (brush thickness) under decrease of the solvent quality. If incompatibility between A and B monomer units is increased, the shrinkage of the chains in the brush becomes more pronounced, Figure 8 a,b. For example, variation of $\chi_{AS}$ from 0.7 to 1.0 leads to the thinning of the brush from 34 to 30 at $\chi_{AB} = 0.1$ ($N$=3000) and from 61 to 48 at $\chi_{AB} = 1$, Figure 8. This effect is due to higher swelling of the brush at $\chi_{AB} = 1$ caused by repulsion of A and B monomer units. In this case the minor fraction of the insoluble groups in the upper part of the brush is responsible for higher conformational changes caused by their aggregation with major fraction of the insoluble groups in the bottom part.

It has to be noticed that the developed approach is applicable if the chains in the brush are stretched. In other words, the end-to-end distance in z-direction must be higher than the size of a single (non-grafted) gradient copolymer chain whose size is intermediate between a globular $\sim aN^{1/3}$ and swollen coil $\sim aN^{3/5}$. Otherwise, the stretching of the chains cannot be described by Eq. 9. Our analysis demonstrated that the chain stretching exceeds the size of the single chain for all sets of parameters. If we approximate the dependence of $H$ on $N$ by a power function $aN^{\nu}$, the values of $\nu$ belong to the interval $0.6<\nu<1$ which justifies the stretching of the chains along z-axis.

In contrast to the chemical brush, the physical brush reveals monotonous decay of total polymer volume fraction even in the case of strong incompatibility between A and B monomer units, Figure 9 b,d. However, the fraction of the soluble B monomer units has a maximum in the middle part of the brush as the solvent becomes very poor for the insoluble A units, Figure 9 c,d. This fact is a consequence of the broad distribution of A and B monomer units in the chains. When a minor fraction of insoluble units from the "upper" regions of the chains aggregates with the major fraction of the insoluble units, they bring high enough amount of soluble units which provide the local maximum.

The grafting density of the physical brush decreases with the increase of the fraction of soluble groups, Figure 7, wherein the swelling degree increases, Figure 10. This effect has a clear physical meaning: interchain attraction of the insoluble units diminishes due to increasing number of the soluble groups which also provide higher swelling in normal direction. It should be noted that solution of Eqs. 14 and 18 for $f$=0.6 and $\chi_{AS}$=0.7, 0.8 exists not in the whole range of $N$ values: the lower the $\chi_{AS}$, the higher the $N$ at which the solution exists, Figures 7b, 10. This peculiarity is related to conformations of the chains and stability of the physical brush. It is well known[45] that a single homopolymer chain of the length $N$ collapses (or semidilute solution precipitates) at temperatures which are slightly below the θ-temperature, i.e., at $\chi > 1/2 + 1/\sqrt{N}$. Therefore, very long polymer chain will be in collapsed state as soon as $\chi > 1/2$ (for example at $\chi = 0.7$), whereas a short polymer chain can have a coil conformation at the same value of the Flory-Huggins parameter. It is also valid for the gradient copolymer which can partially be collapsed (A-rich end) only at high value of $N$ or $\chi_{AS}$. Otherwise, the physical brush is unstable. Therefore, the lower the $N$, the more homogeneous density profile of the brush, Figure 11. Keeping in mind that $\sigma^4 \sim \int_0^N dn \dot{\tilde{\phi}}^2$, Eq. 18, the grafting density vanishes at constant polymer volume fraction. Figures 7b and 10 also demonstrate that despite an increase in the grafting density with $\chi_{AS}$, contraction of the brush ("reel-in" effect) is possible only at high values of $N$, if the solvent is not so poor for the insoluble units.

## Conclusion

In conclusion, we have studied swelling of chemical and physical planar brushes of gradient copolymers in a selective solvent. The chain ends, enriched by insoluble monomer units, were considered to be grafted to the substrate and soluble ends are considered to be free. In the case of the chemical brush (the grafting density of the chains is fixed), the polymer volume fraction profile can reveal non-monotonous behavior. We have demonstrated that there is a polymer depletion zone inside the brush if incompatibility of A and B monomer units is high enough, Figure 4. Variation of the solvent quality is analyzed. In the case of the physical brush (the chains are mobile in-plane and their grafting density is determined from equilibrium conditions), the grafting density is primarily controlled by selectivity of the solvent and by the length of the chains. The grafting density increases as soon as the solvent becomes poorer for the insoluble units, Figure 7. Furthermore, it can be accompanied by the decrease of the brush thickness, Figure 8, which is opposite to the behavior of a homopolymer brush in the poor solvent. The ability of the contraction of the physical brush explains so-called “reel-in” effect known for micelles[12,18]: the gradient copolymer micelles are able to increase the radius of the core with simultaneous decrease of the corona radius (brush thickness) under decrease of the solvent quality. The density profile of the physical brush reveals monotonous decay, whereas distribution of the soluble units can also be non-monotonous. They can concentrate in the middle of the brush.

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## References

1 T. Hashimoto, Y. Tsukahara, K. Tachi and H. Kawai, *Macromolecules,* 1983, **16** (4), 648-651.
2 K. Matyjaszewski, M. J. Ziegler, S. V. Arehart, D. Greszta and T. J Pakula, *Phys. Org. Chem.,* 2000, **13** (12), 775-786.
3 K. Matyjaszewski and J. Xia, *Chem. Rev.,* 2001, **101** (9), 2921-2990.
4 P. Hodrokoukes, G. Floudas, S. Pispas and N. Hadjicristidis, *Macromolecules*, 2001, **34** (3), 650-657.
5 P. Hodrokoukes, S. Pispas and N. Hadjichristidis, *Macromolecules*, 2002, **35** (3), 834-840.
6 U. Beginn, *Colloid Polym. Sci.,* 2008, **286,** 1465-1474.
7 M. Yu. Zaremski, D. I. Kalugin and V. B. Golubev, *Polym. Sci., Ser. A*, 2009, **51**(1), 103-122.
8 K. Matyjaszewski and N. V. Tsarevsky, *Nat. Chem.*, 2009, **1**, 276-288.
9 O. E. Perelstein, V. A. Ivanov, M. Möller and I. I. Potemkin, *Macromolecules*, 2010, **43** (12), 5442-5449.
10 M. Mok, J. Kim and J. M. Torkenson, *J. Polym. Sci., Part B : Polym. Phys.*, 2008, **46** (1), 48-58.
11 S. Okabe, C. Fuse, S. Sugihara, S. Aoshima and M. Shibayama, *Phys. B (Amsterdam, Neth.)*, 2006, *385-386*, 756-758.
12 S. Okabe, K. Seno, S. Kanaoka, S. Aoshima and M. Shibayama, *Macromolecules*, 2006, **39** (4), 1592-1597.
13 T. Bonne, K. Lüdtke, R. Jordan and C. Papadakis, *Macromol. Chem. Phys.*, 2007, **208** (13), 1402-1408.
14 M. D. Lefebvre, C. M. Dettmer, R. L. McSwain, C. Xu, J.R. Davila, R. J. Composto, S. T. Nguyen and K. R. Shull, *Macromolecules*, 2005, **38** (25), 10494-10502.
15 W. Yuan, M. M. Mok, J. Kim, C. L. H. Wong, C. M. Dettmer, S. T. Nguyen, J. M. Torkelson and K. R. Shull, *Langmuir*, 2010, **26** (5), 3261-3267.
16 A. Aksimentiev and R. Holyst, *J. Chem. Phys.*, 1999, **111**, 2329-2339.
17 N. B. Tito, S. T. Milner and J. E. G.Lipson, *Macromolecules*, 2010, **43** (24), 10612-10620.
18 N. Merlet-Lacroix, E. Di Cola and M. Cloitre, *Soft Matter*, 2010, **6**, 984-993.
19 G. Kraus, K. W. Rollmann, *Angew. Makromol. Chem.*, 1971, ***16–17***, 271-296.
20 K. R. Shull, *Macromolecules*, 2002, **35** (22), 8631-8639.
21 G. Picket, *J. Chem. Phys.*, 2003, **118** (8), 3898-3903.
22 M. D. Lefebvre, M. Olvera de la Cruz and K. R. Shull, *Macromolecules*, 2004, **37** (3), 1118-1123.
23 R. Jiang, Q. Jin, B. Li, D. Ding, R. A. Wickham and A.-C. Shi, *Macromolecules*, 2008, **41** (14), 5457-5465.
24 R. Wang, W. Li, Y. Luo, B.-G. Li, A.-C. Shi and S. Zhu, *Macromolecules*, 2009, **42** (6), 2275-2285.
25 S. T. Milner, T. A. Witten and M. E. Cates, *Europhys. Lett,* 1988, **5** (5), 413-418.
26 S. T. Milner. *Science*, 1991, **251**, 905-914.
27 A. Halperin, M. Tirrell and T. Lodge, *Adv. Polym. Sci.*, 1992, **100** (1), 31-71.
28 P. G. Ferreira and L. Leibler, *J. Chem. Phys.*, 1996, **105** (20), 9362-9370.
29 D. Meng, Q. Wang, *J. Chem. Phys.*, 2009, **130**, 134904.
30 B. Akgun, G. Uğur, W. J. Brittain, C. F. Majkrzak, X. Li, J. Wang, H. Li, D. T. Wu, Q. Wang and M. D. Foster, *Macromolecules*, 2009, **42**(21), 8411-8422.
31 E. B. Zhulina, C. Singh and A. C. Balazs, *Macromolecules*, 1996, **29** (25), 8254-8259.
32 Y. Yin, P. Sun, B. Li, T. Chen, Q. Jin, D. Ding and A.-C. Shi, *Macromolecules*, 2007, **40** (14), 5161-5170.
33 M. R. Tomlinson and J. Genzer, *Polymer*, 2008, **49**, 4837-4845.
34 J. Wang and M. Müller, *Macromolecules*, 2009, **42** (6), 2251-2264.
35 M. W. Matsen and G. H. Griffiths, *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2009, **29** (2), 219-227.
36 B. M. D. O’Driscoll, G. H. Griffiths, M. W. Matsen and I. W. Hamley, *Macromolecules*, 2011, **44** (21), 8527−8536.
37 O. A. Guskova and C. Seidel, *Macromolecules*, 2011, **44** (3), 671-682.
38 A. A. Rudov, P. G. Khalatur and I. I. Potemkin, *Macromolecules*, 2012, **45** (11), 4870-4875.
39 I. Luzinov, S. Minko and V. V. Tsukruk, *Prog. Polym. Sci.* 2004, **29**, 635-698.
40 S. A. Prokhorova, A. Kopyshev, A. Ramakrishnan, H. Zhang and J. Rühe, *Nanotechnology*, 2003, **14**, 1098-1108.
41 S. Alexander, *J. Phys. (Paris)*,1977, **38** (8), 983-987.
42 P. G. de Gennes, *Macromolecules*, 1980, **13** (5), 1069-1075.
43 I.I. Potemkin, *Eur. Phys. J. E: Soft Matter Biol. Phys.*, 2003, **12**, 207-210.
44 I. I. Potemkin and K. I. Popov, *J. Chem. Phys.*, 2008, **129**, 124901.
45 A. Yu. Grosberg, A. R. Khokhlov, *Statistical Physics of Macromolecules*, AIP Press: New York, 1994.
46 I. M. Lifshitz, *J. Exp. Theor. Phys*, 1968, **55**, 2408.
47 B. V. Numerov, *Astron. Nachr.*, 1927, **230**, 359-364.
48 A. A. Rudov, E. S. Patyukova, I. V. Neratova, P. G. Khalatur, D. Posselt, C. M. Papadakis and I. I. Potemkin, *Macromolecules*, 2013, **46**, 5786-5795.

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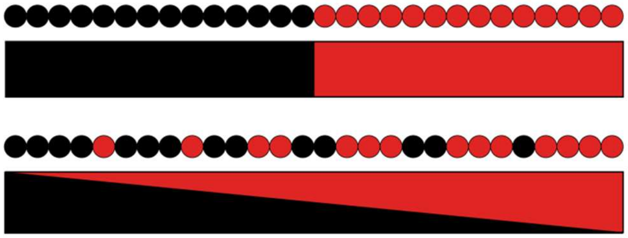

**Fig. 1.** Schematic representation of primary structures of a diblock copolymer (upper sketch) and a gradient copolymer (bottom sketch).

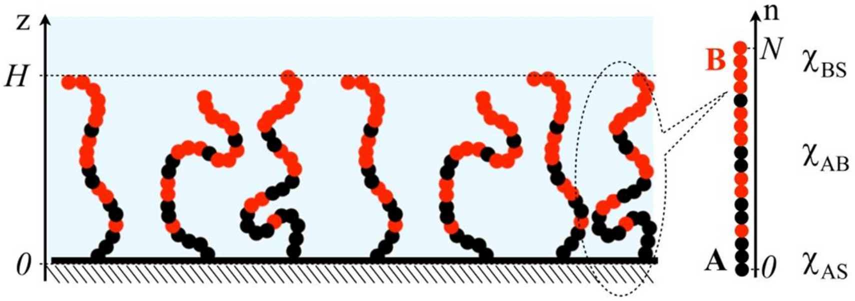

**Fig. 2.** Schematic picture of a planar brush of gradient copolymers swollen in a selective solvent. A-rich ends of the chains are grafted to the substrate. Insoluble A monomer units (black) and soluble B monomer units (red) are incompatible with each other. The solvent quality and incompatibility between A and B units are quantified by the Flory-Huggins interaction parameters $\chi_{ij}$, i,j=A,B,S.

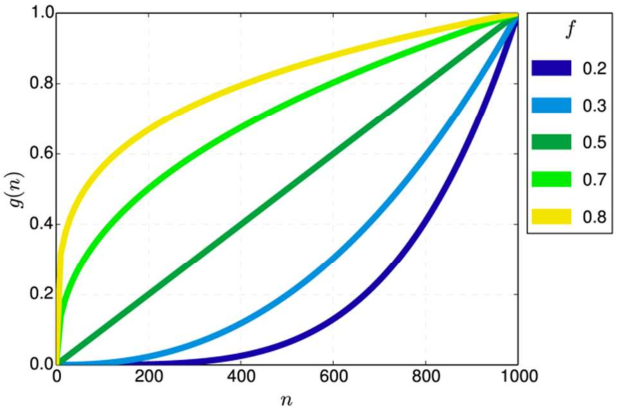

**Fig. 3.** Local composition of B (soluble) segments as a function of $n$-th segment at different values of the overall composition $f = N_B / N$; $N$=$10^3$. The bar on the right hand side depicts the values of the composition $f$. The colors of the bar and the curves correspond to each other.

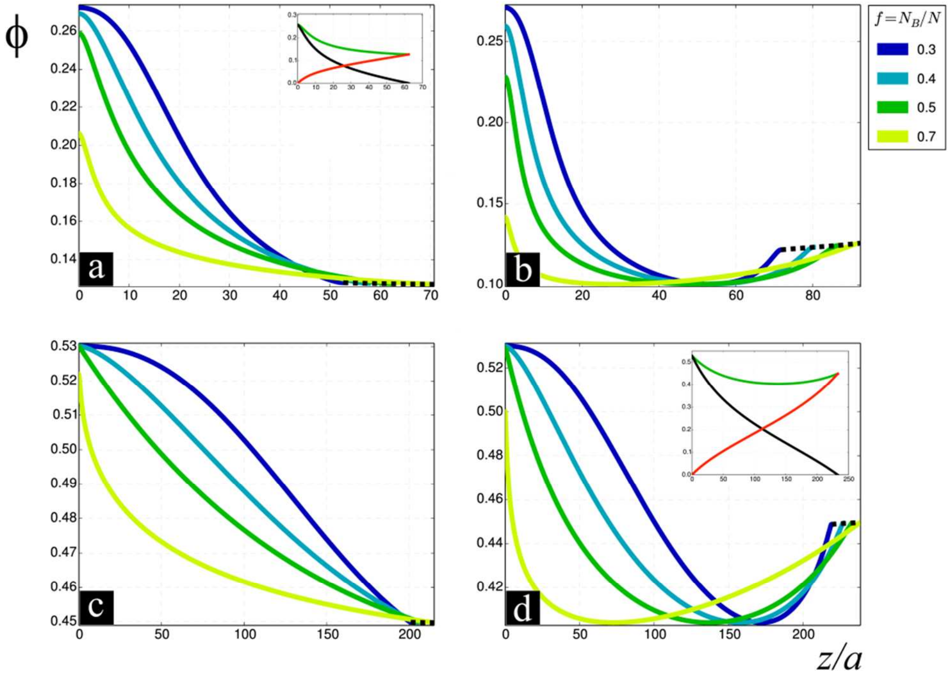

**Fig. 4.** The polymer volume fraction $\varphi$ as a function of normal coordinate $z$ at different values of the grafting density $\sigma$ and Flory-Huggins parameter $\chi_{AB}$ describing incompatibility of A and B monomer units: (a) $\sigma=10^{-2}$, $\chi_{AB}=0.1$, (b) $\sigma=10^{-2}$, $\chi_{AB}=1$, (c) $\sigma=10^{-1}$, $\chi_{AB}=0.1$, (d) $\sigma=10^{-1}$, $\chi_{AB}=1$. Each curve ends at the dashed line which corresponds to the thickness of the brush and polymer volume fraction at the free surface. The overall fraction of soluble groups $f$ is depicted by the bar on the right. Inserts: volume fractions of insoluble A monomer units (black), soluble B monomer units (red) and total polymer volume fraction (green) at $f$=0.5; all other parameters are the same as in figures (a) and (d).

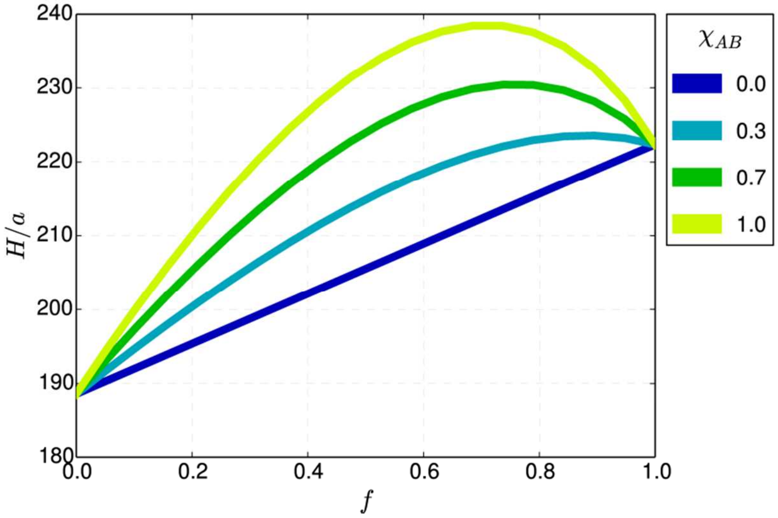

**Fig. 5.** Thickness of the brush $H$ as a function of the overall fraction of soluble groups $f$ at different values of the Flory-Huggins parameter $\chi_{AB}$ (bar on the right); $\sigma=10^{-1}$, $\chi_{AS}=0.6$, $\chi_{BS}=0.4$, $N=10^3$.

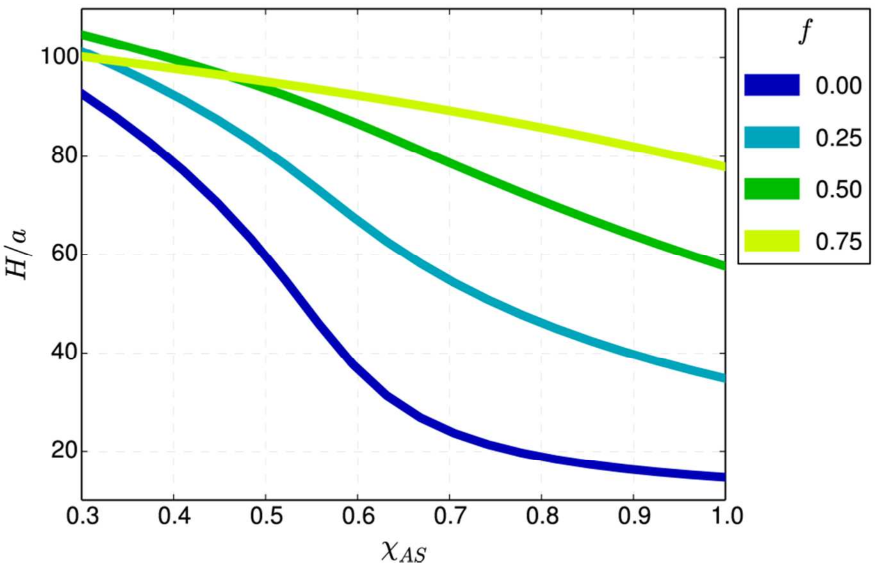

**Fig. 6.** Swelling and collapse of the gradient copolymer brush under variation of the solvent quality (parameter $\chi_{AS}$) for grafted (A) monomer units. Different curves correspond to different values of the overall fraction of B monomer units $f$ (bar on the right) ; $\sigma=10^{-2}$, $\chi_{AB}=1$, $\chi_{BS}=0.4$ , $N=10^3$.

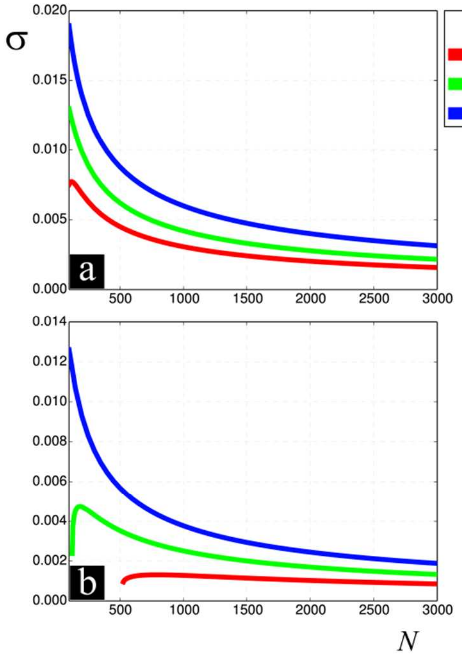

**Fig. 7.** Grafting density of the physical brush $\sigma$ as a function of the number of monomer units in the chain N at different values of the Flory-Huggins parameter $\chi_{AS}$ : 0.7 (red), 0.8 (green), 1 (blue). The overall fraction of soluble B units $f$=0.3 (a), 0.6 (b); $\chi_{AB}=0.1$, $\chi_{BS}=0.4$.

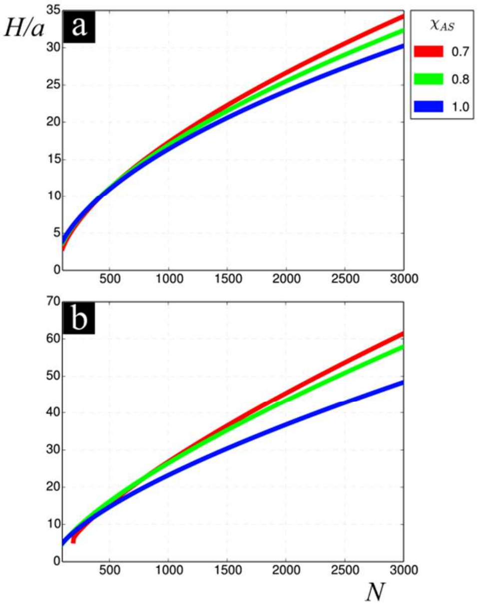

**Fig. 8.** The physical brush thickness *H* as a function of the number of the segments in polymer chain *N* under variation of selectivity of the solvent (parameter $\chi_{AS}$) and incompatibility of A and B monomer units (parameter $\chi_{AB}$): $\chi_{AS}$=0.7 (red), 0.8 (green), and 1.0 (blue) in both plots. $\chi_{AB}$ =0.1 (a), 1.0 (b); *f*=0.3, $\chi_{BS} = 0.4$ .

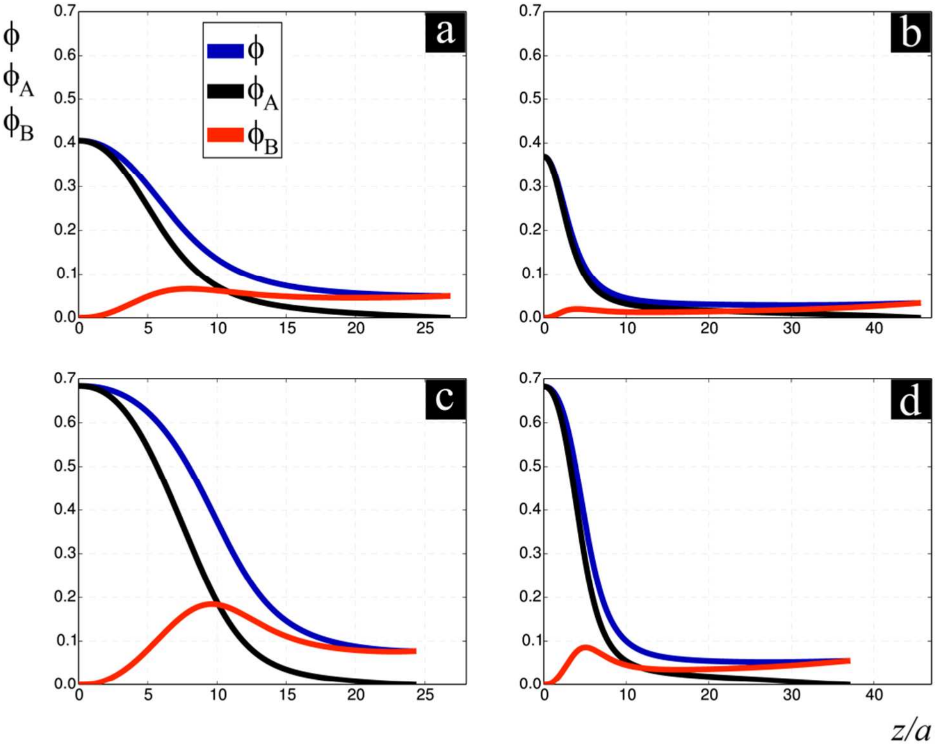

**Fig. 9.** Total polymer volume fraction (blue), and volume fractions of insoluble A monomer units (black) and soluble B monomer units (red) of the physical brush as functions of normal coordinate *z*. Different plots correspond to different selectivity of the solvent (parameter $\chi_{AS}$) and incompatibility between A and B monomer units (parameter $\chi_{AB}$): $\chi_{AS}$=0.7 $\chi_{AB}$ =0.1 (a), $\chi_{AS}$=0.7 $\chi_{AB}$ =1.0 (b), $\chi_{AS}$=1.0 $\chi_{AB}$ =0.1 (c), $\chi_{AS}$=1.0 $\chi_{AB}$ =1.0 (d); *f*=0.3, $\chi_{BS} = 0.4$ , $N$=$2\cdot10^3$.

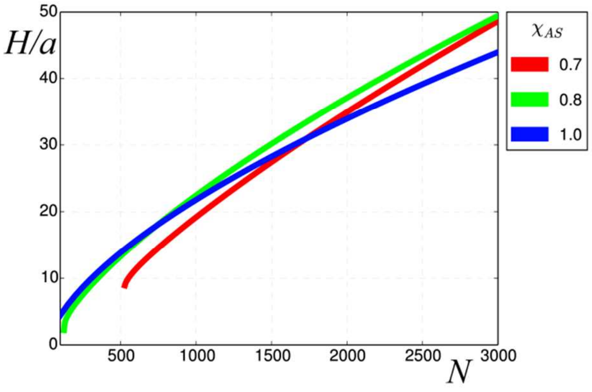

**Figure 10.** The physical brush thickness *H* as a function of the number of the segments in polymer chain *N* under variation of selectivity of the solvent (parameter $\chi_{AS}$): $\chi_{AS}$=0.7 (red), 0.8 (green), and 1.0 (blue). $\chi_{AB}$=0.1, $\chi_{BS} = 0.4$ , *f*=0.6.

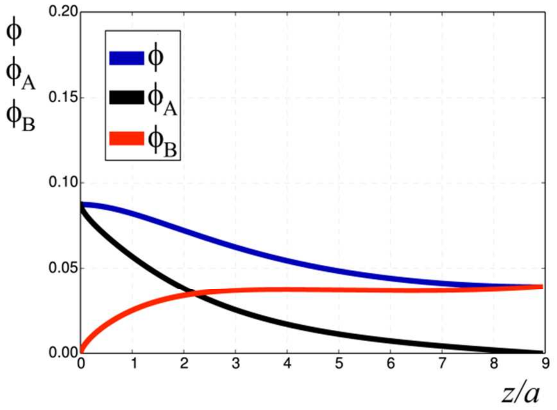

**Fig. 11.** Total polymer volume fraction (blue), and volume fractions of insoluble A monomer units (black) and soluble B monomer units (red) of the physical brush as functions of normal coordinate *z*. $\chi_{AS}$=0.7 $\chi_{AB}$ =0.1, $\chi_{BS} = 0.4$ ,*f*=0.6, *N*=524.