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Designed AB Copolymers as Efficient Stabilizers of Colloidal Particles

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ABSTRACT: We propose a model of amphiphilic AB copolymer which possesses low tendency toward intermolecular aggregation in selective solvent and high adsorption ability on solventphobic surfaces. The primary structure of the copolymer has elements of linear triblock copolymer. It contains solventphobic (A) and solventphilic (B) end-blocks and regularly alternating AB multiblock copolymer as a middle block which is surface-active. This block is localized at the core−corona interface of the micelle reducing the aggregation number. Kinetics of adsorption of the designed copolymer on planar solventphobic surface is compared with that of equivalent diblock copolymer. It is shown that even strong attraction of the molecules to the surface cannot destroy diblock copolymer micelles (at least during simulation time), whereas designed macromolecules form dense planar brush on the surface for a short enough time.

1. Introduction

Sequence design of monomer units in copolymers is known to be very efficient way to obtain new polymers for sophisticated functions.[1−5] There are practically infinite possibilities to vary sequences in copolymers: from the variation of some simple characteristics like composition of monomer units, average length of blocks[6,7] (for the chains with blocky structure), availability of branching,[8,9] etc., to more sophisticated features like long-range correlations[10,11] or gradient structure.[12−15] For example, long-range (Levy flight[11]) correlations of monomer units in random linear AB copolymer were shown to be responsible for stability of globular conformation of the copolymer toward aggregation in selective solvent that mimics solubility of globular proteins in water.[5] Specially designed linear multiblock copolymers containing blocks of different lengths,[16] comb−coil diblock copolymers,[17,18] and double-grafted copolymers[19,20] are the examples of macromolecules revealing hierarchical (multiscale) spatial order as a result of self-organization (microphase segregation). Gradient structure of the sequence of monomer units makes macromolecules more compatible.[15] Therefore, in the sequence design approach a wide variety of new functional copolymers can be tailored.

Diblock copolymers in selective solvents are known to form micelles whose size and shape are primarily controlled by chemical composition of the copolymers.[6,21] The typical value of the aggregation number of the spherical micelles is much larger than unity: the longer the insoluble block, the larger the aggregation number. However, in some applications aggregation of the diblocks in selective solvents is undesirable. The example is the use of block copolymers as stabilizers of colloidal particles.[22,23] In this case the solventphobic blocks of the copolymer adsorb on the surfaces of the solventphobic particles, and the soluble blocks protect particles from aggregation (Figure 1). Enhancement of stability of colloidal dispersions is a key problem in many modern technological processes. For instance, optical properties of coatings strongly depend on that how much a pigment disperse in a solvent. Taking into account a cost of block copolymers, economic are conditions when most of the macromolecules "work", i.e., adsorb on the surface of the particles. However, when polymer is mixed with the colloidal particles, a competing process of micelle formation makes very expensive the use of conventional block copolymers (Figure 1). In this case, one has to add a higher amount of polymer to saturate particles surface or wait for a long time to achieve decomposition of the micelles (if attraction to the surface is stronger than the intermolecular one): kinetics of molecular exchange in micellar solutions is very slow.

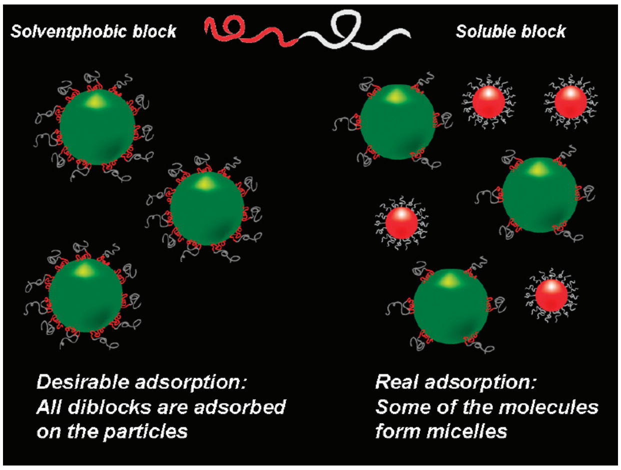

Figure 1. Sketch of diblock copolymer adsorption on colloidal particles. Ideal adsorption (left) involves all macromolecules, whereas some of them form micelles (right).

For acceleration of the adsorption process, we propose to optimize a primary structure of copolymer. In this paper, we will analyze micelle formation and adsorption of "triblock" copolymers containing solventphobic (A) and solventphilic (B) end-blocks and regularly alternating AB multiblock copolymer as a middle block which is surface-active (it is localized at the core−corona interface of the micelle). The designed AB copolymer provides low aggregation ability of the macromolecules in

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selective solvents and, under certain conditions, stability of single molecules. On the other hand, adsorption ability of such copolymer is high enough. The designed copolymer can be used not only as efficient stabilizer of colloidal particles but also for fast preparation of planar brushes on solid surfaces.

To the best of our knowledge, synthesis and micelle formation of similar designed "triblock" copolymers were studied only in two groups.[13,14,24] Hadjichristidis et al. studied micellization of copolymers consisting of styrene and isoprene with various sequences of the monomer units in the middle block (random, gradient, and inverse gradient) in *n*-decane, which is a selective solvent for the isoprene part of the macromolecules.[14] Aqueous solutions of triblock copolymers based on methyl methacrylate and methacrylic acid and on butyl methacrylate and methacrylic acid with random sequence of monomer units in the middle block were investigated in ref 24. In all cases a decrease of the aggregation number of the spherical micelles of the triblock copolymers in comparison with equivalent diblock copolymers (the same fraction of A and B units) was observed. However, adsorption of the triblock copolymers was not studied yet.

In the next section we propose simple scaling estimations explaining the decrease of the aggregation number of the micelles formed by triblock copolymers. Then, we describe results of computer simulations on micellization of the designed copolymers and on their ability to adsorb on flat solventphobic surfaces.

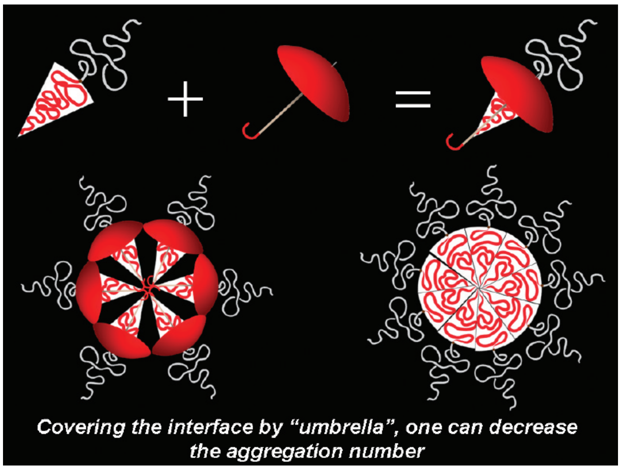

Figure 2. "Covered" micelles (left) can have smaller aggregation number than equivalent diblock copolymer micelles (right).

2. Theoretical Background

2.1. Diblocks. Formation of spherical micelles by diblock copolymers in a selective solvent, which is good for one of the blocks and poor for another one, is mainly controlled by a balance between (i) stretching of the blocks in the corona of the micelle and (ii) unfavorable contacts of insoluble blocks with the solvent. The core of the micelle is densely packed by A segments (each A block consists of $N_A \gg 1$ segments), and the elastic free energy of the blocks is the same as for the melt case,[25] $F_A/k_BT \sim QR^2/(a^2N_A)$, where Q and R are the aggregation number of the micelle and the radius of the core, respectively. They are related by the dense packing condition, $R^3 \sim vQN_A$, where for flexible blocks the excluded volume of the segment v is proportional to the cube of its linear size a, $v \sim a^3$ (here and afterward all numerical coefficients are omitted). The stretching of the B blocks in the corona with respect to their swollen state in a good solvent can be described using the concept of blobs of variable sizes[21,26,27] (scaling concept), the free energy of the corona being proportional to the total number of blobs. The size ξ of a blob at a distance r from the center can be obtained from the geometrical packing condition, $Q\xi(r)^2 \sim r^2$, i.e., $\xi(r) \sim r/Q^{1/2}$. Within the blob, the segments do not "feel" presence of neighbor blocks and statistics of each subchain of g segments within the blob corresponds to that of a coil in a good solvent, $\xi \sim ag^{3/5}$. Keeping in mind that each B block is represented as a completely aligned (along the micelle's radius) sequence of blobs, the free energy of the B blocks is estimated as

$$\frac{F_B}{k_BT} \sim Q\int_R^{R_0}\frac{dr}{\xi(r)} \sim Q^{3/2}\ln\left(\frac{R_0}{R}\right) \sim Q^{3/2} \qquad (1)$$

where R_0 is the outer radius of the corona and the logarithmic multiplier can be omitted. Comparing F_A and F_B, we find that the core contribution is negligible, $F_A \ll F_B$. Unfavorable contacts of solventphobic blocks with the solvent contribute to the free energy of the micelle as $F_{int} \sim \gamma R^2$, where $\gamma \approx \gamma_{AS}$ is core–solvent surface tension coefficient if the A and B blocks are incompatible and A–B surface tension coefficient $\gamma_{AB} \geq \gamma_{AS}$ (the fraction of the B monomer units in the vicinity of the core is small enough). In the opposite case, $\gamma_{AB} \ll \gamma_{AS}$, the core is wrapped by thin layer of polymer B to shield A–S contacts and $\gamma \approx \gamma_{AB}$. The equilibrium aggregation number of the micelle is calculated by minimization of the total free energy per chain over Q:

$$\frac{F}{k_BTQ} \sim \frac{\gamma R^2}{Qk_BT} + Q^{1/2} \sim \frac{\bar{\gamma}{N_A}^{2/3}}{Q^{1/3}} + Q^{1/2} \sim \bar{\gamma}^{3/5}{N_A}^{2/5},$$
$$Q \sim \bar{\gamma}^{6/5}{N_A}^{4/5} \gg 1 \qquad (2)$$

where $\bar{\gamma} = \gamma a^2/k_BT \sim 1$ is dimensionless surface tension coefficient. The aggregation number is mainly controlled by the length of the insoluble block: the longer the block, the larger the aggregation number. The interfacial area of the micelle per one molecule

$$A_0 \sim \frac{R^2}{Q} \sim a^2\left(\frac{N_A}{\bar{\gamma}}\right)^{2/5} \qquad (3)$$

is not a fixed parameter; it also grows with N_A.

Equation 2 clearly states that the aggregation number can be decreased only via decrease of N_A. On the other hand, the decrease of the length of the insoluble block weakens adsorption ability of the diblock copolymer on solventphobic surfaces, and this way cannot improve applicability of the copolymer as stabilizer. Another way is schematically illustrated in Figure 2. Let us imagine that we are able to increase the area of the interface per one diblock via introduction of some "umbrella" into the molecule whose area is fixed and independent of N_A. Then the aggregation number of the "covered" micelle will be smaller than that of equivalent diblock copolymer micelle if the area of the umbrella is higher than A_0 (Figure 2). In the latter case, dense packing of the umbrellas at the interface rather than free energy minimum determines the aggregation number: the higher the area, the smaller the aggregation number.

2.2. "Triblocks". In order to get the umbrella at the interface, we propose to use "triblock" copolymers where the middle block (umbrella) is surface-active (Figure 3). The end-blocks are conventional homopolymers of A (solventphobic) and B (solventphilic) types; each consists of $N_A \gg 1$ and $N_B \gg 1$ segments, respectively. The middle block is regularly alternating AB copolymer containing $n \gg 1$ segments. The blockiness of A and B units of the middle block is

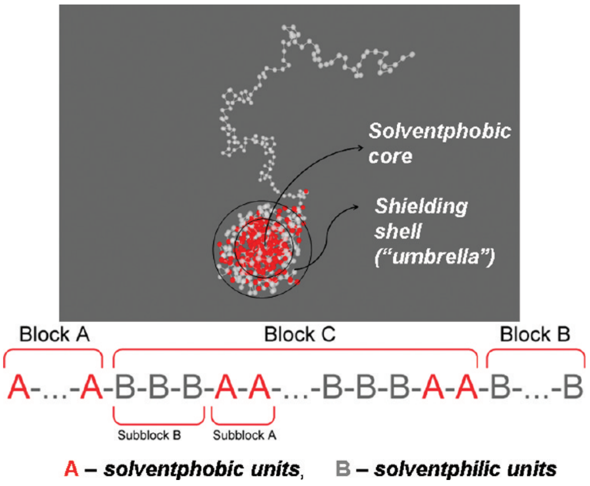

Figure 3. The designed AB "triblock" copolymer consists of solventphobic (A) and solventphilic (B) end-blocks. The middle block (C) is regularly alternating AB copolymer. The typical conformation of the single macromolecule in the selective solvent is tadpole-like. The solventphobic block forms dense core which is wrapped by the middle block. The soluble groups of the middle block form shielding shell preventing intermolecular aggregation. The soluble end-block forms the tail.

on the order of unity, $m_A \sim m_B \sim 1$ ($m_A = 2$ and $m_B = 3$ in Figure 3), so that the numbers of A and B units are $n_A \sim n_B \sim n$. We will analyze a regime of strong incompatibility of insoluble A units with the solvent and with the B units.[28] In this case the middle block is strongly adsorbed on the core–corona interface[29] (the A units dip into the core and B units float on the interface) (Figure 3), and conformation corresponds to that of a two-dimensional chain. One can expect that the middle block adopts Gaussian conformation corresponding to the dense packing in 2D; i.e., area of the interface covered by the block is $A \sim a^2 n$. Such expectation is valid if repulsion between solventphilic B units is weaker than incompatibility between the solvent and A units. Otherwise, the 2D block should have a swollen conformation. It is evident that the presence of the middle (surface-active) block becomes essentially detectable if the area covered by it, A, is larger than the area of the interface per one molecule in the case of diblock copolymer, $A > A_0$, i.e., $n > (N_A/\bar{\gamma})^{2/5}$. In this case, the aggregation number of the micelle is determined from the steric conditions rather than the free energy minimum. Surface activity of the middle block means fulfillment of the condition for the covering of total surface area of the core, $R^2 \sim Qna^2$, and together with dense filling of the core, $R^3 \sim a^3 Q N_A$, one gets

$$Q \sim \frac{N_A{}^2}{n^3} \tag{4}$$

This aggregation number is smaller than the aggregation number of equivalent diblock copolymer micelles, $N_A{}^2/n^3 < \bar{\gamma}^{6/5} N_A{}^{4/5}$, which corresponds to the inequality $A_0 < A$. Furthermore, if $n \sim N_A{}^{2/3}$ then $Q \sim 1$; i.e., the surface of the collapsed block of the single molecule is fully covered by the middle block, and the diblocks are protected from aggregation.

Variation of the length of the surface-active block can control the critical micelle concentration (cmc), Φ_{cmc}. In the case of diblock copolymers, Φ_{cmc} can be estimated as

$$\begin{aligned}\Phi_{cmc}^{db} &\approx \Phi_0 \exp\left\{\frac{F-F_0}{k_B TQ}\right\}\\ &\approx \frac{1}{N_A}\exp\{\bar{\gamma}^{3/5} N_A{}^{2/5} - \bar{\gamma} N_A{}^{2/3}\}, \quad \bar{\gamma} N_A{}^{2/3} \gg 1\end{aligned} \tag{5}$$

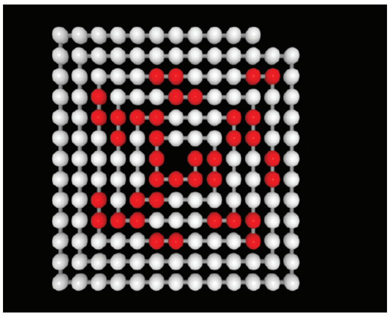

Figure 4. Initial 2D conformation of the designed copolymer.

where Φ_0 is dimensionless concentration of chains in the micelle, $\Phi_0 \sim Qa^3/R^3 \sim 1/N_A$; F and F_0 are the free energies of the micelle, eq 2, and of Q nonaggregated chains, respectively. The main contribution to F_0 comes from the surface energy of the collapsed block, $F_0 \sim Q\gamma R^2 \sim Qk_B T\gamma \bar{N}_A{}^{2/3}$. Taking into account that $\bar{\gamma} N_A{}^{2/3} \gg 1$, the negative term in the exponent is dominant and the cmc is exponentially small, $\Phi_{cmc}^{db} \approx \exp\{-\bar{\gamma} N_A{}^{2/3}\}$.

The free energy of the micelle formed by the designed triblock copolymer also includes the surface energy and the free energy of stretched B blocks:

$$\frac{F_{tb}}{k_B TQ} \sim \bar{\gamma}_{AB} n + Q^{1/2} \sim \bar{\gamma}_{AB} n + \frac{N_A}{n^{3/2}} \tag{6}$$

The second term is important only for the case when the aggregation number is high enough. Otherwise, it is negligible. It has to be noticed that F_{tb}/Q is an increasing function of n: it has a minimum at $n \sim (N_A/\bar{\gamma}_{AB})^{2/5}$, whereas eq 6 is only valid at $(N_A/\bar{\gamma}_{AB})^{2/5} < n < N_A{}^{2/3}$ where the free energy increases with n. For calculation of Φ_{cmc}^{tb}, let us derive the free energy of the single triblock, F_0/Qk_BT, in strongly selective solvent. Conformation of each nonaggregated triblock can be imagined as a tadpole one: the A block forms dense spherical core of the radius $R \sim aN_A{}^{1/3}$; part of the core surface is covered by the surface-active block, and the soluble B block is not stretched (in comparison with the micelle). Therefore, the main contribution to the free energy comes from the surface energy, $F_0/Qk_BT \approx \bar{\gamma}_{AB} n + \bar{\gamma}(N_A{}^{2/3} - n)$, and

$$\begin{aligned}\Phi_{cmc}^{tb} &\approx \Phi_0 \exp\left\{\frac{F_{tb}-F_0}{k_B TQ}\right\}\\ &\approx \frac{1}{N_A}\exp\left\{\bar{\gamma} n + \frac{N_A}{n^{3/2}} - \bar{\gamma} N_A{}^{2/3}\right\}\\ &\approx \Phi_{cmc}^{db}\exp\left\{\bar{\gamma} n + \frac{N_A}{n^{3/2}} - \bar{\gamma}^{3/5} N_A{}^{2/5}\right\}\end{aligned} \tag{7}$$

If the length of the middle block $n \sim (N_A/\bar{\gamma})^{2/5}$, the area, covered by it, is approximately equal to the interfacial area per molecule of the diblock copolymer micelles and $\Phi_{cmc}^{tb} \sim \Phi_{cmc}^{db}$. On the other hand, if $(N_A/\bar{\gamma})^{2/5} \ll n < N_A{}^{2/3}$, the term $\bar{\gamma} n \gg 1$ in the exponent of last expression of eq 7 is dominant and the critical micelle concentration of the designed copolymer is much (exponentially) higher than that of the conventional diblock copolymer: the longer the middle block the higher the concentration, $\Phi_{cmc}^{tb} \sim \Phi_{cmc}^{db} \exp\{\bar{\gamma} n\}$. Furthermore, the single chains of the designed copolymer can be stable even in the concentrated solution, $\Phi_{cmc}^{tb} \sim 1/N_A$, if $n \sim N_A{}^{2/3}$.

3. Computer Simulations

The primary structure of the designed copolymer in computer simulations is chosen as that depicted in Figure 3. The middle

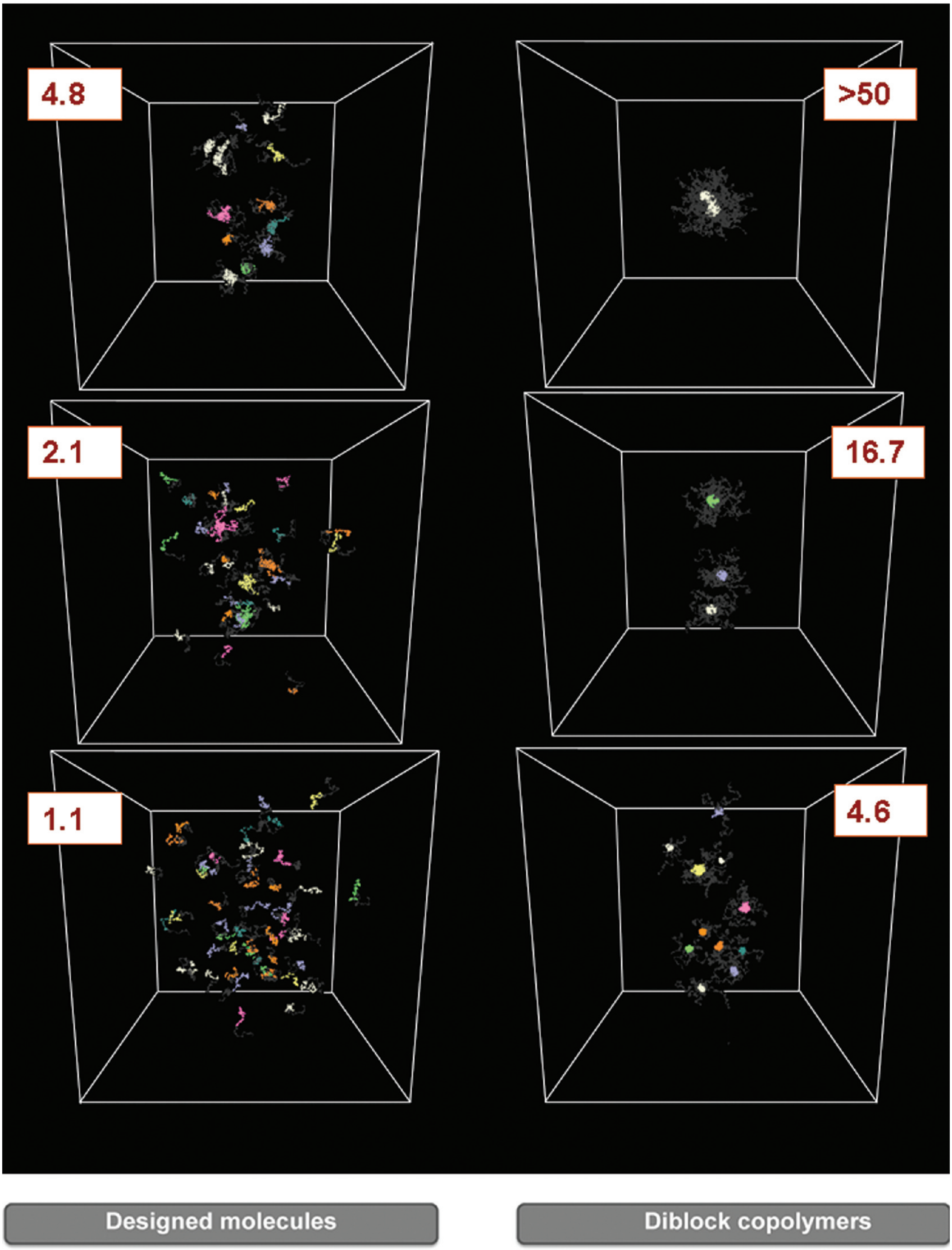

Figure 5. Snapshots of the micelles formed by the designed (left column) and diblock (right column) copolymers. The upper, middle, and bottom rows correspond to different values of the interaction parameter: $\varepsilon_{AA} = 1, 0.8$, and 0.6, respectively. The numbers in the frames are the average aggregation number. Dark gray segments are soluble, and the cores of the micelles are depicted as multicolor.

block is a regularly alternating copolymer containing $m_A = 2$ units in each solventphobic subblock and $m_B = 3$ units in the solventphilic subblock, so that the total number of the subblocks of each type is $n/(m_A + m_B)$. The length of the A block is fixed,

$N_A = 6$, whereas computer simulations of aggregation and adsorption of the copolymer are done for various lengths of the middle and the soluble blocks, $n = 80 \rightarrow 110$, $N_B = 40 \rightarrow 100$. Aggregation and adsorption properties of the designed copolymers are compared with those of equivalent diblock copolymers. Here, the equivalency means that the diblock contains the same number of solventphobic and solventphilic units as the designed copolymers; i.e., the numbers of the segments in A and B blocks of the diblock copolymer are $\bar{N}_A = N_A + m_A n/(m_A + m_B)$ and $\bar{N}_B = N_B + m_B n/(m_A + m_B)$, respectively.

The number of macromolecules in both systems is equal to 50. Initial conformation of each chain corresponds to a two-dimensional helical one placed in the *xy*-plane of the Cartesian coordinates (Figure 4). The chains are arranged into a stack along *z*-axis with the distance between them $\Delta z = 1$. The stack is placed into the middle of the box having dimensions $L_x = L_y = L_z = 200$ and periodic boundary conditions. The chemical bonding between monomer units is simulated using the sum of FENE potential and Lennard-Jones potential:

$$E = -\frac{1}{2} K R_0^2 \ln\left(1 - \left(\frac{r}{R_0}\right)^2\right) + 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right) + \varepsilon \tag{8}$$

where $K = 10$, $R_0 = 1.3$, $\varepsilon = 1$, and $\sigma = 1$. Pairwise attraction between the solventphobic units is modeled by Lennard-Jones potential with the interaction parameter ε_{AA} and cutoff radius $r_{cut} = 2.5$, while the purely repulsive "soft spheres" potential U is used for B−B and A−B interactions:

$$U = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right) + \varepsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases} \tag{9}$$

Dynamics of the systems is simulated using Brownian dynamics (BD) algorithms implemented in LAMMPS[30] package with damping parameter set to 10 timesteps. The time step is equal to $\Delta t = 0.0001$. To study aggregation properties of the systems, we use the clustering algorithm given in ref 31. This algorithm allows calculating the average size and the size distribution function of the clusters (micelles).

4. Results and Discussion

The effect of the decrease of the aggregation number of the designed copolymer in comparison with equivalent diblock copolymer is demonstrated in Figure 5. These results are obtained for the chains with $N_A = 6$, $n = 80$, $N_B = 80$, $\bar{N}_A = 38$, and $\bar{N}_B = 128$. After equilibration of the system, the initial stack of macromolecules transforms into the spherical micelles for both diblock and designed copolymers. In the case of diblock copolymer with high enough attraction energy between the solventphobic units, $\varepsilon_{AA} = 1$, all molecules form one micelle (Figure 5). Therefore, one can expect that the equilibrium aggregation number of the micelle $Q \geq 50$. On the contrary, the designed copolymer forms micelles which have much smaller aggregation number, $Q \approx 5$. This result supports our assumption that long, surface-active middle block plays a role of "umbrella" reducing aggregation of the molecules (Figure 2). The aggregation number of both di- and triblock copolymer micelles decreases with the decrease of the attraction energy, and single molecules of the designed copolymer are stable toward aggregation at $\varepsilon_{AA} = 0.6$ (Figure 5).

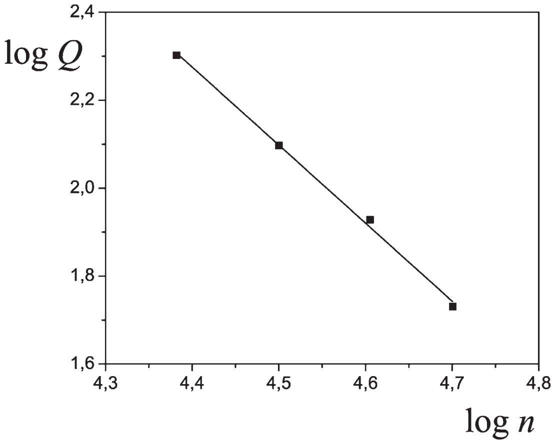

Figure 6. Log−log plot of the aggregation number of the micelles, Q, formed by the designed copolymers versus the length of the middle block, n. $N_A = 6$, $n = 80 \rightarrow 110$, $N_B = 80$, and $\varepsilon_{AA} = 0.8$.

The effect of the length of the middle block of the triblock copolymer on aggregation number of the micelles is demonstrated in Figure 6. The log−log plot is obtained for the following values of the parameters: $N_A = 6$, $n = 80 \rightarrow 110$, $N_B = 80$, and $\varepsilon_{AA} = 0.8$. The aggregation number decreases with the growth of n as $Q \sim n^{-\alpha}$ in accordance with simple theoretical estimations. However, the exponent $\alpha \approx 1.77$ is smaller than the predicted one, $\alpha = 3$. Such discrepancy is related to incomplete adsorption of the middle block on the core−solvent interface at particular choice of moderate value of the attraction energy ε_{AA}. Higher values of ε_{AA}, which should provide 2D adsorption, significantly slow equilibration of the system, and we do not consider them. Another reason for lower α is that the middle block is too short to correspond to the scaling regime and that the range of n values is limited: n cannot exceed some certain value to remain within the concept of umbrella.

Summarizing aggregation properties of the amphiphilic polymers, one can say that the proper design of the sequence of monomer units along the chain (retaining the number of solventphobic and solventphilic units) is an efficient tool to reduce the aggregation number. The proposed sequence of monomer units in the middle block is not an unique one: many others like random, direct, and inverse gradient[13,14] sequences are acceptable for this purpose. The most important feature of the middle block is its surface activity.

To demonstrate fast adsorption of the designed copolymers on solventphobic surface, we perform the following simulations. Two stacks of the tri- and diblock copolymers are placed into the boxes having two strongly attractive (solventphobic) surfaces (chessboard-like surfaces in Figure 7). They attract insoluble units of the copolymers with the energy $\varepsilon = 5$, which is much higher than the energy of intermonomer attraction, $\varepsilon_{AA} = 0.8$. Therefore, one can expect that both kinds of the copolymers will form stable layers (planar brushes) in the vicinity of the surfaces. However, only designed macromolecules are adsorbed on the surfaces during simulation time (3000 timesteps), whereas spherical micelles of the diblock copolymer remain stable during this time (Figure 7). Only those diblocks of the stacks, which were in the vicinity of the attractive surfaces before annealing, are adsorbed. Stability of the diblock copolymer micelles can be explained as follows. There are two ways for adsorption of the diblocks. In true equilibrium, the micelles can exchange the molecules, and the released molecule is adsorbed when meets the surface (colloidal particle). However, this process is too slow, and in many real systems the true equilibrium is not achievable. The second way for adsorption is a collision of the whole micelle with the surface. In this case adsorption is possible if the micelle is able to overcome a high entropic barrier to deform dense corona and to have a contact of the core with the surface (Figure 8). However,

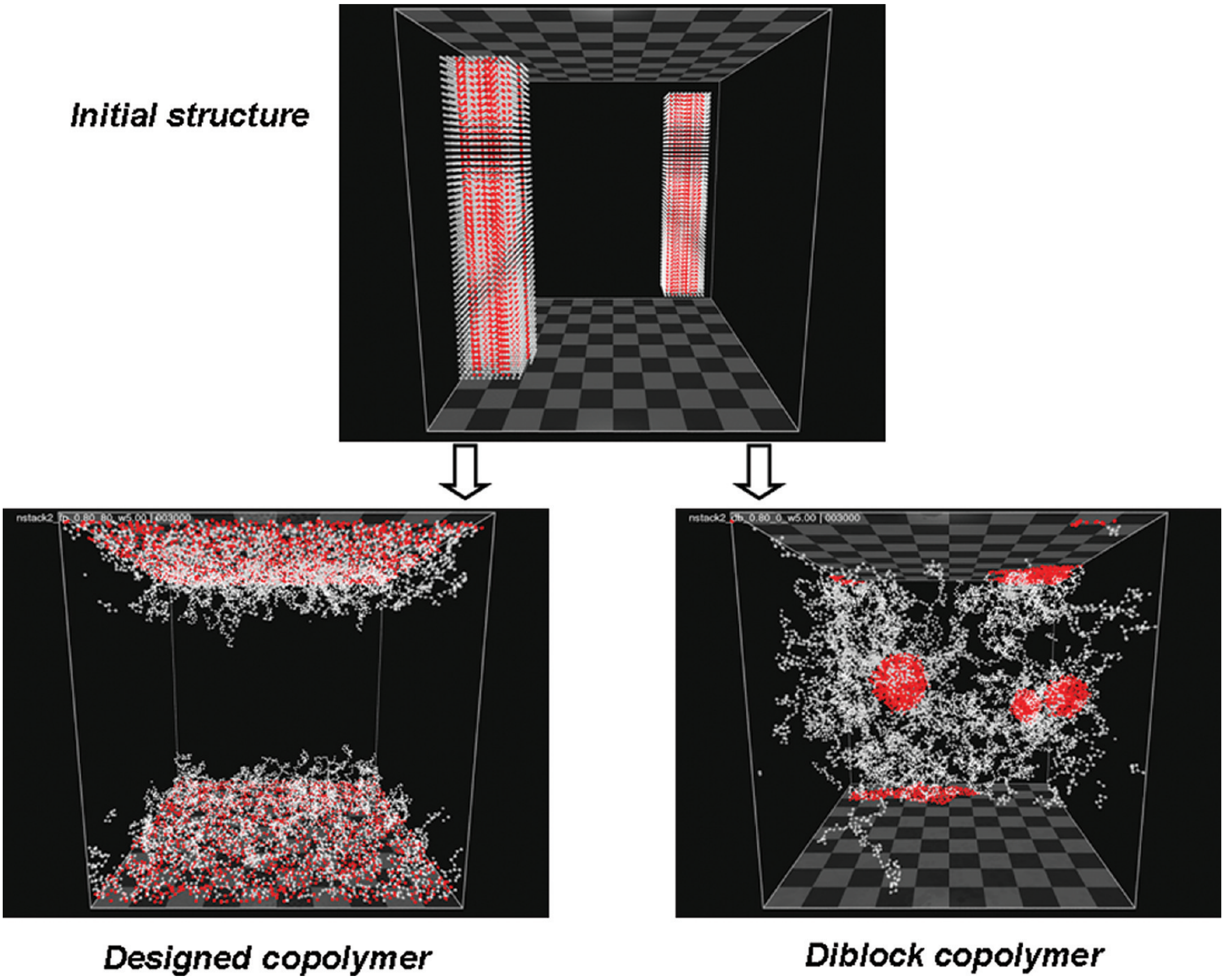

Figure 7. Snapshots of the designed and diblock copolymers between two attractive walls (chessboard-like surfaces) after 3000 timesteps. The number of macromolecules in two stacks is 100. The attraction energy of the insoluble group to the surface is $\varepsilon = 5$. $N_A = 6$, $n = 80$, $N_B = 40$, $\bar{N}_A = 38$, $\bar{N}_B = 88$, and $\varepsilon_{AA} = 0.8$.

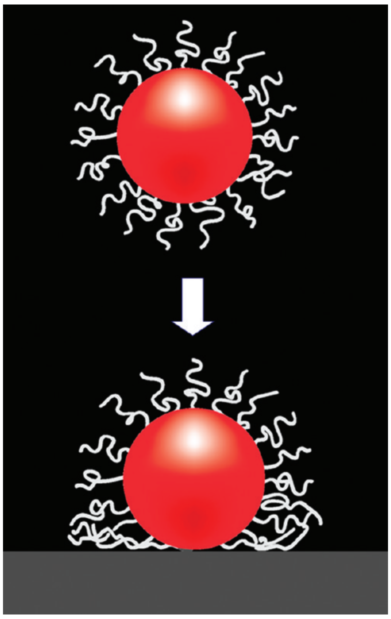

Figure 8. Deformation of micellar corona caused by collision with surface.

this way is also hardly realizable especially for long corona-forming blocks. Therefore, the micelles can be stable for a very long time. In contrast, the designed copolymers have much smaller aggregation number and collisions with the surface result in faster adsorption.

The designed copolymer forms well-defined brushlike structure. The A block and most of soluble and insoluble groups of the middle block are localized in thin surface layers of the thickness 3 (Figure 9), whereas the B block is brush forming. Kinetics of adsorption of the designed copolymer from two stacks structure is presented in Figure 10 for different lengths of the B block. The fastest kinetics corresponds to the shortest B block, $N_B = 40$ (black curve). Shortly after 600 timesteps, all insoluble units are adsorbed on the surfaces (100 molecules, each contains 38 insoluble units). Increasing of the length of the soluble block, $N_B = 60$ (red curve), slows adsorption, and relatively long brush forming tails, $N_B = 100$, prevent complete adsorption of the macromolecules (blue curve). All curves in Figure 10 are steplike in the shape. The length of each subsequent plateau, corresponding to constant value of the number of adsorbed insoluble units, increases with time. This effect has a clear physical meaning. Adsorbed macromolecules make entropic barrier for adsorption of free ones: the larger the number of adsorbed molecules, the higher the barrier and the more time is needed to overcome the barrier.

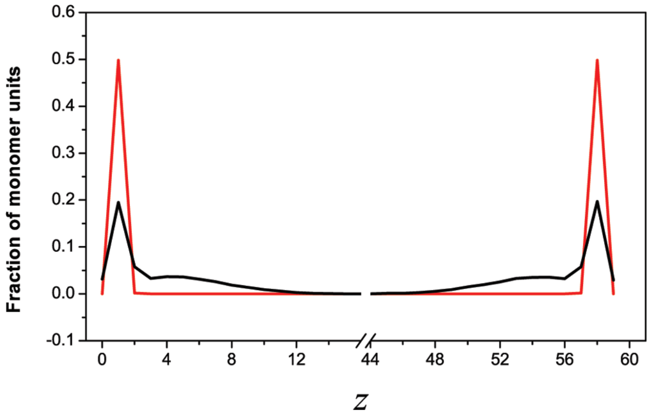

Figure 9. Fraction of insoluble (red) and soluble (black) units of the designed copolymer as a function of the coordinate z perpendicular to the attractive surfaces. The fraction is defined as a ratio of the number of units of certain kind in the layer z = constant to the total number of units of this kind. $N_A = 6$, $n = 80$, $N_B = 40$, $\varepsilon = 5$, and $\varepsilon_{AA} = 0.8$.

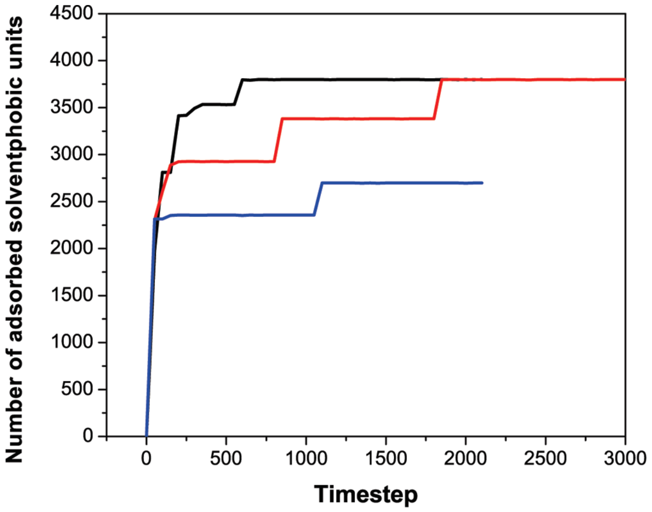

Figure 10. Dependence of the number of adsorbed insoluble units on time. Simulations are performed with 100 macromolecules, each of $N_A = 6$ and $n = 80$, so that the total number of insoluble units in the system is 3800. The length of the brush forming B block is different: $N_B = 40$ (black), 60 (red), and 100 (blue). $\varepsilon = 5$ and $\varepsilon_{AA} = 0.8$.

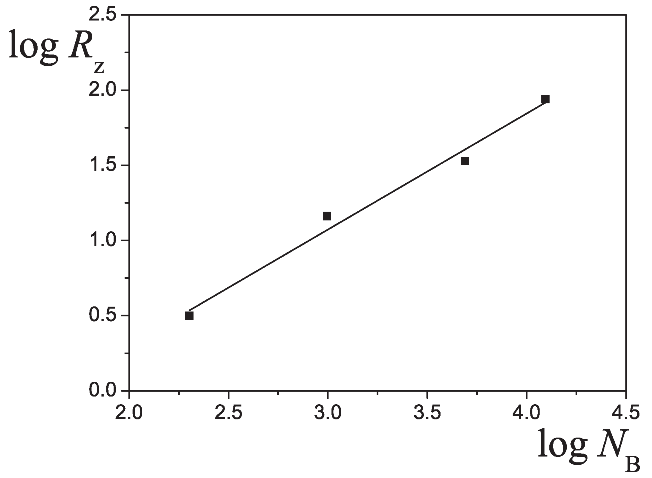

Figure 11. Log−log plot of average z-component of the end-to-end vector of the B block, R_z, versus $N_B = 10$, 20, 40, and 60 (squares). All other parameters are the same as in Figure 9.

The designed copolymer adsorbed on strongly attractive surface forms planar brush with relatively high "grafting" density. The B blocks in the brush "feel" (interact with) each other which results in their stretching perpendicular to the surface. The log−log plot of the average z-component of the end-to-end vector of the B block, R_z, versus N_B is presented in Figure 11. The slope of the straight corresponds to the exponent $\nu \approx 0.77$, $R_z \sim N_B^{\nu}$, which is larger than the exponent $\nu \approx 0.6$ for the single swollen block. On the other hand, $\nu \approx 0.77$ is smaller than the theoretical one obtained for densely grafted brushes, $R_z \sim N_B/s^{1/3}$, where s is the area per one block. This discrepancy is related to simulations with short enough B blocks. The overlap of the blocks of the length $N_B = 10$, 20 and their stretching in the brush is less probable.

5. Conclusion

We propose a primary structure of AB copolymer which diminishes aggregation of macromolecules in selective solvent and accelerates adsorption of the macromolecules on solventphobic surfaces in comparison with equivalent diblock copolymer. The decrease of the aggregation number of the micelles is achieved due to the presence of surface-active middle block (Figure 3), and fast adsorption of the copolymer micelles or single chains is a result of a loose corona of soluble blocks which can easily bare the insoluble core because of thermal fluctuations and collisions with the surface. The proposed copolymer can be used as efficient stabilizer of colloidal particles in colloidal suspensions and for fast preparation of planar brushes.

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