

Complexation of a Polyelectrolyte Brush with Oppositely Charged AB Diblock Copolymers: The Zipper Brushes

Christos Gioldasis, Leonidas N. Gergidis, and Costas Vlahos*

The internal stratification of a polyelectrolyte complex (zipper brush) formed by mixing of an anionic charged polyelectrolyte brush (PEB) with cationic-neutral diblock copolymers bearing a very long neutral block is studied by means of molecular dynamics simulations. The authors find that the fraction of the neutralized PEB units in the mixture increases as the fraction of the PEB charged units (α) increase for high grafting densities (d). Due to the charge neutralization condition, from the initial PEB through the complexation with the appropriate choice of a cationic-neutral copolymer, neutral brush having grafting density lower, equal, or much higher than that of the PEB are obtained. The addition of monovalent salt in the mixture with concentrations 0.1 and 1 M leads to a reduction in complexed diblock copolymer chains of up to 91% and practically the initial PEB is recovered. The findings are in full agreement with existing experimental predictions and provide new insights into the structure and the shape of the coacervate. The latter progressively changes from a dense film to perforated film, to lamella, to pinned micelles, to stacks as α , d , and the molecular weights of the PEB and diblock copolymer blocks are altered.

1. Introduction

Polymer brushes are assemblies of polymer chains with one of their ends grafted to a planar surface.^[1] Usually, this grafting is sufficiently dense to ensure that the polymer chains, instead of attaining a typical random-coil arrangement, are forced to stretch away from the adhering surface like a brush. The thickness of the brush results from the excluded volume interactions between polymer units and can be controlled either by changing molecular weight of the chains, the solvent quality, or the grafting density.^[2–8] All these factors can have a significant influence on properties like the friction coefficient, flow incitation, drug

release, and control of membrane permeability of a polymer brush-coated surface.^[9,10]

Also important in terms of applications are the polyelectrolyte brushes (PEBs), which are composed from partially or fully charged polymer chains.^[11–13] Earlier studies on PEB indicated that the conformational changes of tethered macromolecules are mainly governed by electrostatic interactions and the osmotic pressure exerted by the counterions, rather the osmotic pressure of the macromolecular segments.^[14] Upon the increase of grafting density, it was found that the counterions condense inside the brush volume.^[14–16] Thus, additional environmental parameters such as the pH and ionic strength can control surface properties such as the wettability, lubricity, and protein adsorption.^[10]

When a solution of polyelectrolyte chains (PE) comes in contact with an oppositely charged PEB, the PE chains are absorbed into the brush, forming a polyelectrolyte complex coacervate (PEC).^[17,18] At low ionic strengths, the driving force of the complexation, is the entropy gain from the release of a large number of small counterions in the solution, while at high ionic strengths the enthalpic effects (Coulombic interactions) drive the complexation.^[19] PECs have very interesting properties. For instance, it is shown that the dynamic friction coefficients of the PEB is drastically reduced in salt-free PE aqueous solutions, and the lubrication mode transition from the brush-lubrication regime to hydrodynamic lubrication is promoted with the complexation.^[20]

Recently, the zipper brush method (**Figure 1**) was proposed for producing very dense neutral brushes throw the complexation of an existing PEB with diblock copolymers composed from one charged and one very long neutral block.^[19,21,22] Due to the strong attraction between the oppositely charged polyelectrolytes and the large number of charges in the PEB a large number of diblock copolymer can be adsorbed, and thus, a very high grafting density can be reached. The number of complexed diblock copolymers can be determined by the full charge compensation condition between the charges in the brush and the charge of the adsorbed diblock copolymer.^[21] This means that, it is possible to control the grafting density of the neutral brush by tuning the density, the degree of polymerization of the PEB chains, and the degree of polymerization of the charged block of the copolymer. A great advantage of the zipper brush method is that the original

C. Gioldasis, C. Vlahos
 Department of Chemistry
 University of Ioannina
 Ioannina 45110, Greece
 E-mail: cvlahos@uoi.gr

L. N. Gergidis
 Department of Materials Science & Engineering
 University of Ioannina
 Ioannina 45110, Greece

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/mats.202200011>

DOI: 10.1002/mats.202200011

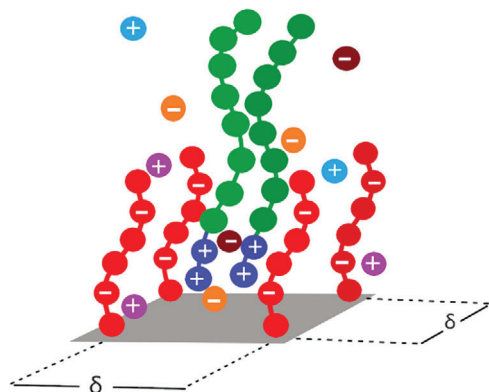


Figure 1. Cartoon representation of the mixture comprising: a) a negatively charged PEB formed from four linear PE chains with six S-type units and a charged units fraction $\alpha = 0.33$ denoted as $(-)$ S6a0.33. The surface area per grafted PE chain is $s = \delta^2$, b) positively charged AB diblock copolymers with two A-type charged units and eight neutral B-type units denoted as $(+)$ A2B8. Counterions are shown in blue and red color, while monovalent salt ions are shown in orange and purple color.

PEB can be recovered, by adding salt or changing the pH of the solution. Then the recovered PEB can be reused to produce another neutral brush with different density.^[22]

The suggested structure of the zipper brush consists of a collapsed complex coacervate layer on the top of the planar surface covered with a swollen brush formed by the neutral blocks of the copolymer. However, this structure is based on indirect evidence.^[22] Namely, the very good antifouling properties observed experimentally for the zipper brushes suggest the presence of a thick neutral brush.^[22] Moreover, the very low zeta potential measured in zipper brushes is evidence of an almost complete charge compensation and a collapsed coacervate layer.^[22] Micelles of oppositely charged diblock copolymers is well known to form neutral separate polyelectrolyte-rich coacervate cores surrounded by neutral blocks forming a corona.^[23,24] Similarly, the complex coacervate of the zipper brush is expected to be covered with the neutral copolymer blocks. However, the anchored PE in zipper brushes are not free to move in the solution as the respective chains (with the same charge) in the micelles. This may lead to a different structure of the coacervate of the zipper brush varying from a dense film to perforated film, to lamella, to pinned micelles.^[25]

To the best of our knowledge, there are no prior molecular simulations studies dealing with the structure of the zipper brushes. Here, we perform an exhaustive molecular simulation study of zipper brushes base on our previous work on the PEBs,^[16] the complexation of oppositely charged double hydrophilic diblock copolymers,^[26] the complexation of PEB with oppositely charges micelles,^[27] and the complexation on mixed PEB.^[25] We use molecular dynamics simulations using the Primitive model^[25] (spherical charged particles and implicit solvent), to elucidate the effects of the grafted chains fraction of charged units α , the brush grafting density, the molecular weights of both grafted and diblock copolymer chains, and the salt concentration on the height and the internal stratification of zipper brush. The properties of interest are the distributions of grafted and diblock chains center of mass, free-ends and units, counterions, the mean distance of

all type of units from the surface, and the mean square radii of gyration components and of the grafted and diblock chains. Our results are compared with the respective experiments reported in the literature.

2. Model

We used a coarse-grained model to study the complexation of negatively charged grafted PE chains with positively charged AB diblock copolymer chains. A group of atoms equivalent to the Kuhn segment were modeled as a unit with diameter σ . For the negatively charged grafted PE chains, a fraction of randomly assigned S-type units α , is charged with elementary quenched charge equal to $-1e$. In the positively charged A-type blocks all units are charged with elementary charge equal to $1e$. The units of the B-type block are always considered neutral. For chain charge neutralization, counterions with a diameter σ carrying an opposite charge are also added to the system. The monovalent (i.e., 1:1) salt ions are modeled in the same way as counterions.

The substrate surface for the PE brush is a piece of the xy -plane with dimensions $L \times L$. Periodic boundary conditions are applied in x - and y -directions. We consider 64 replicated PE chains grafted on the plane and the respective counterions. The separation distance between the grafted chains is set equal to δ in both x - and y -directions as shown in Figure 1. The surface area per grafted chain s is calculated as $s = \delta^2$ and, therefore, the grafting density is specified by $d = 1/s = 1/\delta^2$. The AB copolymer chains can freely move in the solution.

Electrostatic interactions between two charged particles q_i and q_j are determined by the Coulomb potential:^[28]

$$U(r_{ij}) = k_B T l_B \frac{q_i q_j}{r_{ij}} \quad (1)$$

where r_{ij} is the center-to-center distance between charged species. The Bjerrum length l_B which determines the strength of electrostatic interactions, is defined as $l_B = e^2 / (4\pi\epsilon_0\epsilon_r k_B T)$, where ϵ_0 and ϵ_r are the permittivity of the vacuum and the relative permittivity of the solvent, respectively.

In addition to the electrostatic interaction, bead-bead interactions were considered, to mimic the macroscopic solvent conditions. These interactions are calculated by means of a truncated Lennard-Jones potential:^[29]

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{cij}} \right)^{12} + \left(\frac{\sigma}{r_{cij}} \right)^6 \right], & r_{ij} \leq r_{cij} \\ 0, & r_{ij} > r_{cij} \end{cases} \quad (2)$$

where ϵ is the well-depth and r_{cij} is the cutoff radius. The surface is considered as a reflecting wall. Different units of PE or of the copolymer chain were connected with finitely extensible nonlinear elastic bonds expressed as:^[29]

$$U_{Bond}(r_{ij}) = \begin{cases} -0.5kR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], & r_{ij} \leq R_0 \\ \infty, & r_{ij} > R_0 \end{cases} \quad (3)$$

where r_{ij} is the distance between units i and j and R_0 is the maximum extension of the bond ($R_0 = 1.5\sigma$). These parameters prevent chain crossing by ensuring an average bond length of 0.97σ .^[30,31]

The solvent molecules are implicitly considered. The model allows the statistical treatment of the solvent, incorporating its influence on the polymer by a combination of random forces and frictional terms. The friction coefficient and the random force couple the simulated system to a heat bath and therefore the simulation has canonical ensemble (NVT) constraints. The equation of motion of each unit i of mass m in the simulation box follows the Langevin equation:^[29]

$$m_i \ddot{\mathbf{r}}_i(t) = -\nabla \left[U_{LJ}(r_{ij}) + U_{\text{Bond}}(r_{ij}) + U_{\text{Coulomb}}(r_{ij}) \right] - m_i \xi \dot{\mathbf{r}}_i(t) + \mathbf{F}_i(t) \quad (4)$$

where m_i , \mathbf{r}_i , and ξ are the mass, the position vector, and the friction coefficient of the i unit, respectively. The friction coefficient is equal to $\xi = 0.5\tau^{-1}$, with $\tau = \sigma\sqrt{m/\epsilon}$. The random force vector \mathbf{F}_i is assumed to be Gaussian, with a zero mean, and satisfies the equation

$$\langle \mathbf{F}_i(t) \cdot \mathbf{F}_j(t') \rangle = 6k_B T m \xi \delta_{ij} \delta(t - t') \quad (5)$$

where k_B is the Boltzmann constant and T is the temperature.

The individual constituents for the complexation are: 1) negatively grafted PE chains with spacer length $S = 160$ or $S = 80$ units with charged units fraction $\alpha_- = 0.2, 0.4, 0.8$, and 1 denoted as $(-)S160\alpha 0.2$, $(-)S160\alpha 0.4$, $(-)S160\alpha 0.8$, $(-)S160\alpha 1$ and $(-)S80\alpha 0.8$, 2) positively charged AB diblock copolymers, containing 30 or 60 fully charged A-type beads and 120 or 240 neutral B-type beads and denoted as $(+)A30B240$ and $(+)A60B120$. Some of the PE and copolymer chains are illustrated in Figure 1.

All simulations were performed using the open-source massive parallel simulator LAMMPS.^[32] Long range electrostatic interactions were taken with cutoff $r_{cij} = 5\sigma$ using the particle-particle mesh (PPPM) method^[28] for the slab geometry implemented in LAMMPS with a charge interpolation scheme. This method allows a PPPM solver to be used for systems that are periodic in x, y but nonperiodic in z . An estimated accuracy of 10^{-4} was used for calculations of the electrostatic interactions between any charges in the system. The Bjerrum length l_B , was set equal to 1σ , a value corresponding to water solvent in our model.

The reduced temperature of the simulation was set to $T^* = k_B T/\epsilon = 3$ corresponding to theta solvents conditions.^[25,30] Different cut-off distances in the Lennard-Jones potential were used^[33] to describe the interactions between all type of units in the mixture. The S-S and A-A interactions were considered attractive ($r_{cij} = 2.5\sigma$). The A-B, A-S, B-B, B-S, the interactions between counterions and those between counterions and polymer units were considered repulsive ($r_{cij} = 2^{1/6}\sigma$). For the sake of simplicity, the beads, the counterions, and the salt ions were considered to have the same mass ($m = 1$) and diameter ($\sigma = 1$). In all simulations we use $\epsilon = 1$.

Simulations with three different grafting densities with $d = 0.0494, 0.0247$, and $0.0123\sigma^{-2}$ were performed. The concentration of the monovalent salt solutions (both ions counted) was $c_s = 0.0036$ and $0.036\sigma^{-3}$ which is equivalent to $c_s = 0.1$ and

1 M . The L_z simulation box dimension along z -axis was set equal to 240σ and 270σ for mixtures consisting of $(+)A60B120$ and $(+)A30B240$ diblock copolymers, respectively. The integration time step was $\Delta t = 0.006\sqrt{\frac{m\sigma^2}{\epsilon}}$. The system was allowed to equilibrate for a million steps. For the production phase of the simulations at least 5 million steps were performed. The properties of interest were calculated from at least 1000 snapshots of the simulated system.

3. Results and Discussion

3.1. Complexation of PEBs with $(+)A60B120$ Diblock Copolymers

Three different binary mixtures containing a varying number n_+ of $(+)A60B120$ diblock copolymer chains with fully charged A units, and one oppositely charged PEB with varying a are simulated in order to elucidate the effects of the PEB charged unit fraction on the height and the internal stratification of the resulting zipper brush. n_+ in the mixture is chosen so the ratio of the total positive to total negative charges to be $Z_{+/-} = 1$. In particular, simulations were performed for mixtures with: 1) 34 $(+)A60B120$ chains and a $(-)S160\alpha 0.2$ PEB, 2) 68 $(+)A60B120$ chains and a $(-)S160\alpha 0.4$ PEB, and 3) 136 $(+)A60B120$ chains and $(-)S160\alpha 0.8$ PEB. The grafting density in all mixtures was $d = 0.049\sigma^{-2}$. In the initial configuration, both grafted and copolymer chains are placed perpendicular to the surface and all types of counterions are buried into the brush as illustrated in Figure 1. Initially, a short run of 50.000 timesteps is performed with all cutoff radii set equal to $r_{cij} = 2^{1/6}\sigma$, to eliminate biases introduced from the initial conformation and also to secure that the diblock copolymer chains are not moved completely out of the brush volume. This method leads to zipper brushes with high charge neutralization fraction in reasonable computational time. The mean distance $\langle z \rangle_{\text{zipper}}$ of each polymer and copolymer unit from the surface, proportional to the height of the zipper brush, is defined as the first moment of the probability density distribution $P(z)$ according to

$$\langle z \rangle = \frac{\int_0^\infty z P(z) dz}{\int_0^\infty P(z) dz} \quad (6)$$

The partial mean distances of units from the surface $\langle z_- \rangle$, $\langle z_+ \rangle$, and $\langle z_{\text{neutral}} \rangle$ of the grafted chains, the charged A block, and neutral block B of the copolymer chains, respectively, in the zipper brush are defined in similar way. For comparison, the mean distances $\langle z_{\text{PEB}} \rangle$ and $\langle z_{\text{ci}} \rangle_{\text{PEB}}$ of PEB units and the counterions from the surface before the complexation were also considered. Our results for these quantities are listed in Table S1, Supporting Information. The small differences of 0.6 and 0.3σ observed between the values of $\langle z_{\text{PEB}} \rangle$ and $\langle z_{\text{ci}} \rangle_{\text{PEB}}$ in the $(-)S160\alpha 0.2$, $(-)S160\alpha 0.4$, and $(-)S160\alpha 0.8$ PEBs at $d = 0.049\sigma^{-2}$ indicate that all counterions are integrated to the PEB volume, and thus, the brushes before the complexation are in the osmotic regime.^[16]

In the first mixture (containing the least charged $(-)S160\alpha 0.2$ brush), the calculated fraction of charges compensated by the complexation with $(+)A60B120$ copolymers is 0.79 (Table S2, Supporting Information). This indicates that the

zipper brush is almost fully neutralized. The height of the zipper brush proportional to $\langle z \rangle_{\text{zipper}}$ is 24% smaller compared to the respective $\langle z_{\text{PEB}} \rangle$ of the PEB before mixing. This shrinkage results from the collapse of PEB due to the charge neutralization of the grafted chains as shown from the mean values of distances of brush units before and after the mixing $\langle z_{\text{PEB}} \rangle = 26.8$ and $\langle z_- \rangle = 14.9\sigma$, respectively. As expected, the cationic and anionic units of the (+)A60B120 chains and PEB, forming the coacervate, equilibrate at almost the same mean distance from the surface ($\langle z_+ \rangle = 14\sigma$ and, $\langle z_- \rangle = 14.9\sigma$). The neutral units of the copolymer are found at larger distances above the coacervate ($\langle z_{\text{neutral}} \rangle = 41\sigma$). The internal stratification of the zipper brush is shown in more detail in Figure 2a, where the values of $P(z)$ for all types of units and counterions are illustrated. The density profiles of cationic, anionic, and all zipper brush units show a thick layer with high density for distances corresponding close to the surface due to the coacervate formation. A thicker layer with lower density above the coacervate was formed by the neutral units of the copolymer. The distribution of grafted chain free end units shows a maximum value at the outer part of the coacervate. This strongly indicates that the grafted chains remain perpendicular to the surface after the complexation occurs. Due to incomplete charge neutralization PEB free end units are found at higher distances above the coacervate throughout the layer formed by neutral copolymer units. Thus, the interface between the neutral units and the coacervate is not sharp. The shapes of the distribution functions of neutral block units, free ends, and their center of masses are typical for linear homopolymer brushes: A single fold density distribution function of the centers of mass with the peak placed at distance approximately equal to $\langle z_{\text{neutral}} \rangle$, and a single fold density distribution function of free end units with the peak located at z distance equal to the height of the brush. The vast majority of counterions are found in the supernatant solvent phase but counterions are also located into coacervate and in the neutral units phase on the top of the zipper brush as expected from the incomplete neutralization of PEB.

Fully neutralized zipper brush from the mixture of (–)S160a0.2 PEB with (+)A60B120 copolymers can be produced after a modification of the initial configuration which ensures that copolymer chains cannot escape from the brush volume. In the new configuration, the 34 wrapped diblock copolymer chains are placed horizontally at the bottom of the brush. Equilibration can be achieved due to the low fraction of charged units of the PEB resulting in the very good mobility of the oppositely charged chains thus avoiding kinetically freezing of structures. Indeed, performing the same simulation steps, we obtained fully equilibrated zipper brushes as shown from the autocorrelation function $C(t)$

$$C(t) = \frac{\langle r_k(t) \cdot r_k(0) \rangle}{\langle r_k^2 \rangle}, \quad k = x \text{ or } y \quad (7)$$

illustrated in Figure S1, Supporting Information. r_k stands for x or y component of the end-to-end vector of the grafted chains in the zipper brush.

The differences in the size of grafted and the diblock copolymer chains, between the partial and complete neutralized zipper brush, expressed by the radii of gyration, can be observed from values presented in Table S3, Supporting Information. In a

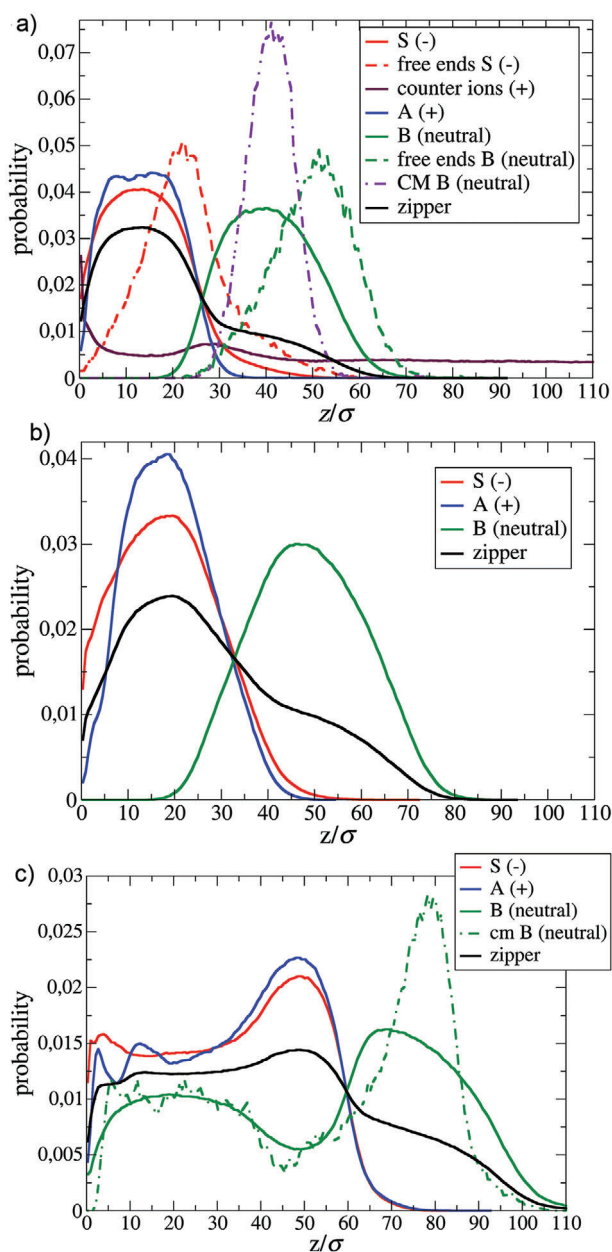


Figure 2. Probability density distributions of z for cationic A, neutral B, and anionic S-type units, free ends of anionic grafted and neutral chains, PEB counterions, centers of mass of neutral copolymer blocks, and all type zipper units a) for the mixture of (–)S160a0.2 PEB with (+)A60B120 copolymers, b) for the mixture of (–)S160a0.4 PEB with (+)A60B120 copolymers, and c) for the mixture of (–)S160a0.8 PEB with (+)A60B120 copolymers. In all cases the grafting density is $d = 0.049\sigma^{-2}$.

neutralized zipper brush, the mean square radius of gyration of the grafted chains $\langle R_g^2 \rangle_-$ is reduced by 20% in comparison with the former one due the reduction of the z component $\langle R_{gz}^2 \rangle_-$ while the $\langle R_{gxy}^2 \rangle_-$ remains unaffected. The size of the diblock copolymer chains also remains unaffected. The probability density distributions functions of the oppositely charged units, forming the coacervate in the complete neutralized brush, almost coincide (Figure S2, Supporting Information). This results

to identical $\langle z_- \rangle$ values (i.e., $\langle z_- \rangle = 13.1$ and $\langle z_+ \rangle = 13.3\sigma$ in Table S3, Supporting Information). The interface between the coacervate and the neutral phase is sharper, and the free ends of the grafted chains are removed from the top layer of the zipper brush. Simulation snapshots showing the zipper brush and the top neutral layer can be seen in **Figure 3a**. In summary, what we have succeeded with the zipper brush is to replace a charged brush consisting of 64 grafted chains with a neutral brush of 34 chains and half the grafting density. To increase the number of complexed copolymer chains, and consequently the density of the neutral brush, mixtures consisting of grafted chains with higher charged units fraction a are needed.

Simulation results for the mixtures of $(-)\text{S160a0.4}$ and $(-)\text{S160a0.8}$ PEB with $(+)\text{A60B120}$ diblock copolymers are illustrated in **Figures 2b,c, 4, and 5**. In the zipper brushes formed, the fraction of charge neutralization is equal to 0.76 and 0.86, respectively, and increases as the charged units fraction a of the PEB increases (Table S2, Supporting Information). The internal stratification of the zipper brush consisting of $(-)\text{S160a0.4}$ grafted chains is very similar to one obtained from $(-)\text{S160a0.2}$ brushes: a thick coacervate layer covered by a neutral brush of 52 copolymer B blocks with a nonsharp interface (**Figures 2b and 3b**). In the mixtures of $(-)\text{S160a0.8}$ PEB, the neutral blocks of the totally 117 complexed $(+)\text{A20B160}$ copolymer chains are unable to form a single layer and are distributed throughout the zipper brush (**Figure 2b**). The probability distribution function of the centers of mass of the neutral copolymer blocks indicates the existence of two distinct populations of neutral blocks. The first population resides close to the surface, and the other on the top of the zipper brush. **Figure S3**, Supporting Information, clearly shows clearly shows the existence of a perforated coacervate where the holes are filled with the diblock copolymer neutral units. The variation of $\langle z \rangle$ of the cationic, anionic, neutral, and the units forming the zipper brush as a function of a are illustrated in **Figure 4**. It can be observed that $\langle z \rangle_{\text{zipper}}$ increases linearly with a , and the height of the $(-)\text{S160a0.8}$ zipper brush becomes equal to the respective of the $(-)\text{S160a0.8}$ PEB before complexation. This linear dependence arises from the contribution of the two nonlinear variations of $\langle z_{\text{neutral}} \rangle$, and $\langle z_- \rangle$, and $\langle z_+ \rangle$ with a . $\langle z_{\text{neutral}} \rangle$ increases with a (from 0.2 to 0.4). This is due to the increase of the number of complexed copolymer chains. The increase becomes smaller at $a = 0.8$, where a significant number of neutral blocks perforate the coacervate and are placed at small distances from the surface. On the other hand, $\langle z_- \rangle$ increases significantly at $a = 0.8$ since $\langle R_g^2 \rangle_-^{1/2}$ of the grafted chains increases (**Figure 5**). The increase in $\langle R_g^2 \rangle_-^{1/2}$ comes from the excluded volume repulsions between the charged and neutral copolymer units which perforate the coacervate, and from the repulsions with the larger number of oppositely charged units that are complexed to form the coacervate. For the $(-)\text{S160a0.8}$ zipper brush, the number of neutral blocks lying above the coacervate can be calculated by integrating the respective probability distribution function of the centers of mass after the distance $z = 45\sigma$ (which is the beginning of the second population of neutral blocks residing on the top of zipper brush) (**Figure 2c**). We found that 61% of the total copolymer blocks, namely 71 chains, form the neutral layer on top of the zipper brush.

To study the effects of the grafting density of PEB on the internal stratification of the zipper brush, another three mixtures

of $(+)\text{A60B120}$ diblock copolymers with $(-)\text{S160a0.8}$ PEB were simulated at lower $d = 0.024, 0.012$, and $0.006\sigma^{-2}$. The radii of gyration of PEB chains before the complexation (Table S1, Supporting Information) remain unaffected by the increase of the distance between the successive grafted chains. This indicates that PEB at least in cases $d = 0.049, 0.024$, and 0.012 are in osmotic regime. This conclusion is also supported by the equality of mean distances of PEB units and counterions showing that the later are trapped into the brush volume. The larger space between the grafted chains facilitates the complexation with $(+)\text{A60B120}$ copolymers and thus the fraction of the charge neutralization increases rapidly from 0.86 in $d = 0.049\sigma^{-2}$ to 1 for the lower grafting densities (Table S2, Supporting Information). The complete neutralization of the zipper brush is also reflected in the probability distribution functions of A and S-type units for z shown in **Figure 6**, where the two curves fully overlap for any value of z . The root of the mean square radii of gyration of the neutral and charged blocks of the copolymer remain practically unaffected by the decrease of the PEB grafting density as clearly shown in **Figure 7**. This can be explained from the contributions of the $\langle R_{gz}^2 \rangle^{1/2}$ and $\langle R_{gxy}^2 \rangle^{1/2}$ components of the radii of gyration which cancel each other out: $\langle R_{gz}^2 \rangle^{1/2}$ decreases while $\langle R_{gxy}^2 \rangle^{1/2}$ increases (Table S3, Supporting Information). As expected, the square root of the mean square radius of gyration of the neutralized grafted chains decreases enormously with the decrease of grafting density. Since the size of the grafted chains determines the thickness of the coacervate, it also significantly decreases with the decrease of the PEB grafting density (**Figure 8**). At the lower PEB grafting densities $d = 0.012$ and $0.006\sigma^{-2}$, the mean distance of the grafted chain units from the surface $\langle z_- \rangle$ becomes equal to the diameter of the charged block of the diblock copolymer. As shown in **Figure 6**, the probability distribution function of the centers of mass of the neutral copolymer block is twofold with distinct populations of neutral blocks.

The first population consists of blocks residing at distances above the coacervate, while the other consists of blocks residing close to the grafted surface. As the grafting density decreases, the thickness of the coacervate decreases and the population of the neutral chains residing on the top of the zipper brush increases. The shape of the coacervate, of the neutral blocks phase, and the whole zipper brush is also of interest. The characteristic simulation snapshots shown in **Figures 3c and 9** clearly indicate the shape evolution of the zipper brush. As discussed in the previous section, at $d = 0.049\sigma^{-2}$ the shape of the coacervate is a perforated film (**Figure 3c and Figure S3**, Supporting Information). The coacervate becomes a lamella along the z axis at $d = 0.024\sigma^{-2}$, a perforated lamella at $d = 0.012\sigma^{-2}$, and finally consists of pinned micelles at $d = 0.006\sigma^{-2}$. For better clarity of the coacervate shape, replicated snapshots of the simulation boxes along x and y axes are illustrated in **Figure S3**, Supporting Information.

3.2. Complexation of PEB with $(+)\text{A30B240}$ Diblock Copolymers

As shown earlier, at moderate and low grafting densities the PEBs in the zipper brushes were almost completely neutralized due to the relative weak excluded volume interactions between units.

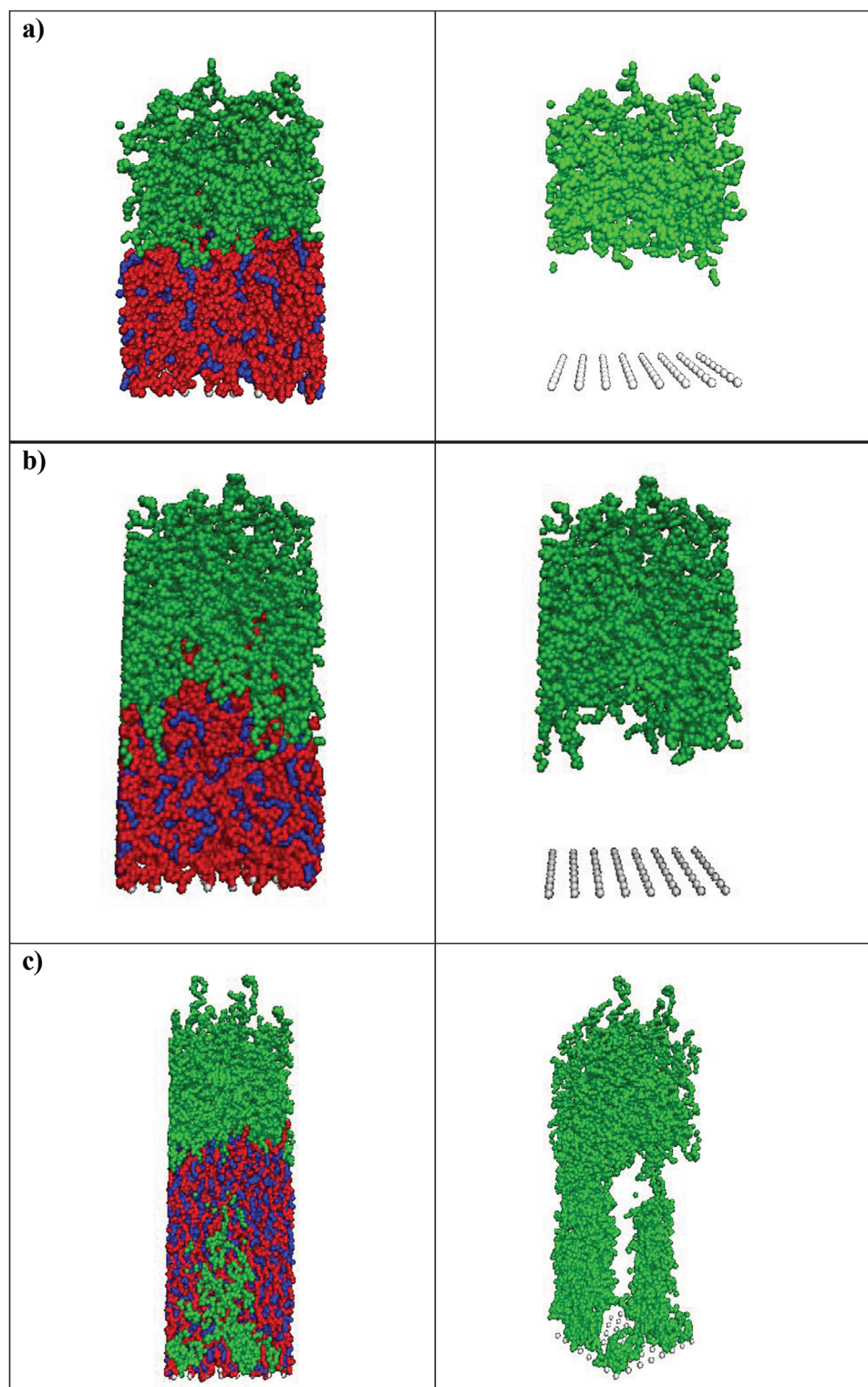


Figure 3. Simulation snapshots showing the coacervate and the neutral phase of zipper brushes formed by the mixtures of a) (–)S160a0.2 PEB with (+)A60B120 copolymers, b) (–)S160a0.4 PEB with (+)A60B120 copolymers, and c) (–)S160a0.8 PEB with (+)A60B120 copolymers. In all cases the grafting density is $d = 0.049\sigma^{-2}$.

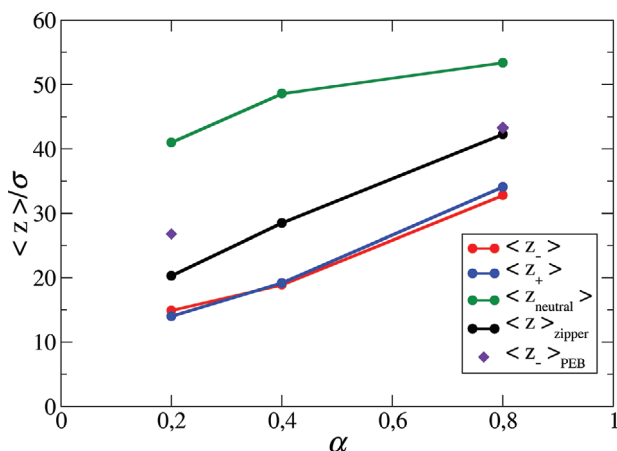


Figure 4. The mean distances from the surface of the anionic grafted units $\langle z_- \rangle$, of the cationic copolymer units $\langle z_+ \rangle$, of the neutral copolymer units $\langle z_{\text{neutral}} \rangle$, of the total zipper units $\langle z \rangle_{\text{zipper}}$, and of anionic units of PEB before the complexation $\langle z \rangle_{\text{PEB}}$ as function of the grafted chain charged units fraction α .

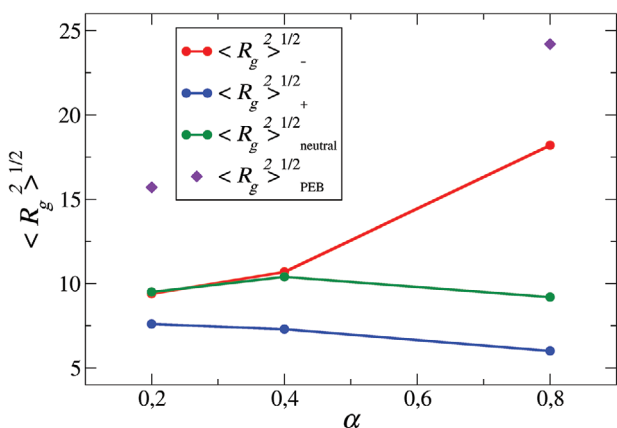


Figure 5. The square root of mean square radii of gyration anionic grafted chains $\langle R_g^2 \rangle_-^{1/2}$, of the cationic copolymer block $\langle R_g^2 \rangle_+^{1/2}$, of the neutral copolymer block $\langle R_g^2 \rangle_{\text{neutral}}^{1/2}$, and of grafted chains before complexation $\langle R_g^2 \rangle_{\text{PEB}}^{1/2}$ as a function of the grafted chain charged units fraction α .

Thus, another way to further increase the density of the resulting zipper brush is to replace the cationic-neutral (+)A60B120 diblock copolymers with chains having shorter charged block. This will result in more copolymer chains complexing in the zipper brush to accomplish the charge neutralization. To this purpose, we use the (+)A30B240 diblock copolymers which comprise half the charged units of (+)A60B120, and a much longer neutral block. Simulations of mixtures of (+)A30B240 copolymers with (−)S160a0.2, (−)S160a0.4, (−)S160a0.8, and (−)S160a1 PEBs were performed at the moderate grafting density $d = 0.012\sigma^{-2}$. The results are presented in Tables S2 and S3, Supporting Information, and in the Figures 10, 11, 12 and 13. The number of the complexed (+)A30B240 copolymer chains scales almost linearly with the increase in the PEB charged units fraction α (Table S2, Supporting Information) reaching a number of 312 chains in the zipper brush formed by (−)S160a1 PEBs. The fraction of the charged units neutralization of PEB increases

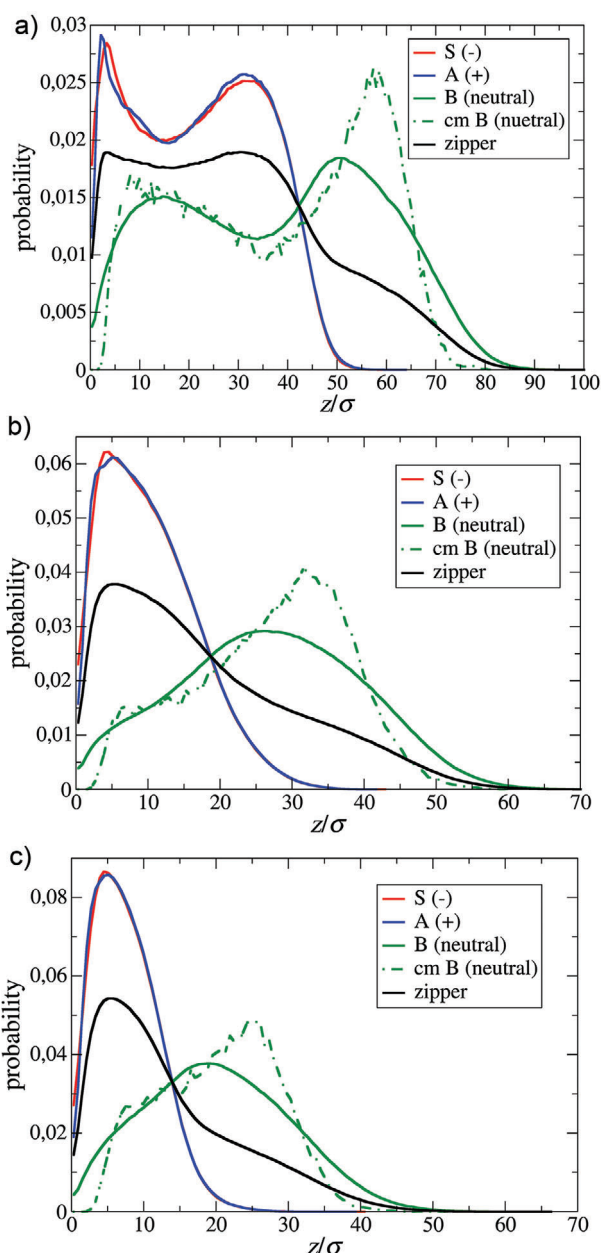


Figure 6. Probability density distributions of z for cationic A, neutral B, and anionic S-type units, centers of mass of neutral copolymer blocks, and all type zipper units for the mixture of (−)S160a0.2 PEB with (+)A60B120 copolymers a) at grafting density $d = 0.024\sigma^{-2}$, b) at $d = 0.012\sigma^{-2}$, and c) at $d = 0.006\sigma^{-2}$.

with α reaching a value of 0.91 for the fully charged grafted chains (−)S160a1. The linear increase in the number of neutral chains with α in the zipper brush also results to a linear increase of $\langle z_- \rangle$, $\langle z_+ \rangle$, $\langle z_{\text{neutral}} \rangle$, and $\langle z \rangle_{\text{zipper}}$ as can be clearly seen in Figure 10. This happens because the excluded volume interactions between units force them away from the surface. As can be observed in Figure 11, the radii of gyration of the charged and neutral blocks of the copolymer remain unaffected by the increase in α . This is because the copolymer

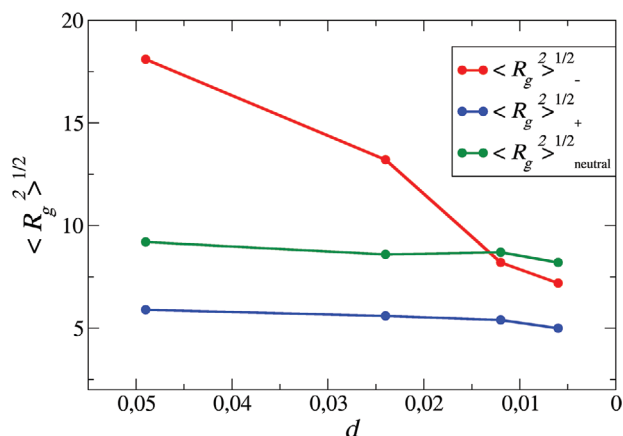


Figure 7. The square root of mean square radii of gyration of the anionic grafted chains $\langle R_g^2 \rangle_-^{1/2}$, of the cationic copolymer block $\langle R_g^2 \rangle_+^{1/2}$, and of the neutral copolymer block $\langle R_g^2 \rangle_{\text{neutral}}^{1/2}$, for the mixture of (–)S160a0.8 PEB with (+)A60B120 diblock copolymers at different grafting densities d .

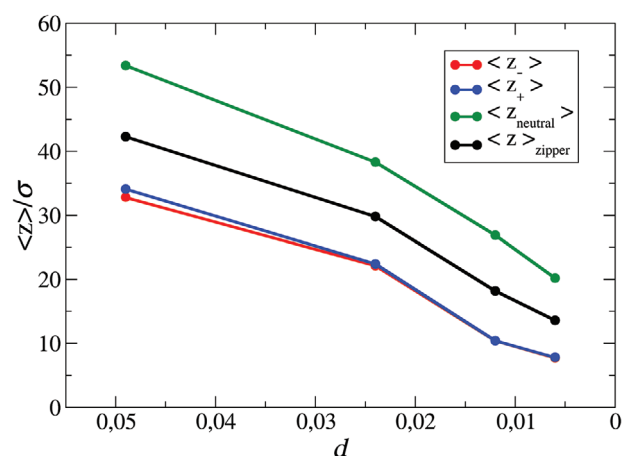


Figure 8. The mean distances from the surface of anionic grafted units $\langle z_- \rangle$, of cationic copolymer units $\langle z_+ \rangle$, of the neutral copolymer units $\langle z_{\text{neutral}} \rangle$, and of the total zipper units $\langle z \rangle_{\text{zipper}}$, for the mixture of (–)S160a0.8 PEB with (+)A60B120 diblock copolymers at different grafting densities d .

chains can move freely all over the zipper brush. In contrast, the radius of gyration of the PEB chains increases enormously with a because are grafted by the one end. This increase in $\langle R_g^2 \rangle_-^{1/2}$ is much higher compared to the respective one computed for the (–)S160a0.8/(+)A60B120 mixtures at the same grafting density. This explains why the value of $\langle z_- \rangle$ in the (–)S160a0.8/(+)A30B240 mixture is three times higher than the respective value of $\langle z_- \rangle$ for the (–)S160a0.8/(+)A60B120 mixture (Table S2, Supporting Information).

The height of the resulting zipper brush proportional to the $\langle z \rangle_{\text{zipper}}$ is almost the same with the height of the constituent PEB before the complexation for the low charged grafted chains (–)S160a0.2 and becomes higher as the fraction of the charged units of the grafted chains increases.

As can be seen in Figure 12a,b, the probability density distributions of the positive and negative charged units forming the coacervate in the zipper brushes consisting from (–)S160a0.2 and

(–)S160a0.4 grafted chains, are single fold with the maximum density being at the distance of half the height of the coacervate. For the highly charged (–)S160a0.8 and (–)S160a1 grafted chains the density distribution function becomes twofold (Figure 12c,d). The peaks are located at distances close to the surface and at the top of coacervate where the density is found to be the highest. Even in the case of (–)S160a0.2 zipper brushes which have the lowest number of complexed copolymer chains, neutral copolymer units penetrate the coacervate. The number of neutral copolymer units residing inside the coacervate volume increases as the charged fraction of grafted chains (–)S160a0.4, (–)S160a0.8, and (–)S160a1 increases. Therefore, the distribution function of the centers of mass of the neutral copolymer becomes multimode indicating different copolymer chain populations. Nevertheless, a significant part of neutral blocks and their end units can be found above the coacervate on the top of the zipper brush.

Figure 13 shows representative simulations snapshots that clearly demonstrate the structure of the coacervate and the whole zipper brush. It is clear that in zipper brushes formed by (–)S160a0.2 grafted chains, the structure of the coacervate is a perforated film with few neutral copolymer units penetrating the coacervate. This is in line with the probability distributions of the neutral units. The increase in the (–)S160a0.4 grafted chains charge fraction is proportional to the thickness of the coacervate, which adopts a pinned micelle structure due to the duplication of the number of neutral units incorporated in the zipper brush. Further increase in the number of the complexed copolymer chains—in the zipper brushes formed by (–)S160a0.8 chains—leads in a large increase in the radius of gyration of the grafted chains (Figure 11). In that case, the coacervate consists of tall stacks of oppositely charged units. Finally, in the case of zipper brushes formed from completely charged (–)S160a1 grafted chains, the increase in the number of complexed copolymer chains leads to even taller stacks of the charged units with some of them being interconnected at the top of the coacervate forming a reversed U tube structure.

To study the effect of the grafted chain length on the structure and the internal stratification of the zipper brush, a new type of mixture consisting of (–)S80a0.8 PEB with (+)A30B240 diblock copolymers was simulated at $d = 0.012\sigma^{-2}$. Compared to the (–)S160a0.4 PEB (used in the simulations presented earlier), the (–)S80a0.8 PEB has much shorter grafted chains but the same total number of negative charges. The number of the complexed (+)A30B240 copolymer chains with the (–)S80a0.8 PEB was found to be smaller, and the fraction of the charge neutralization was computed to be 0.59 instead of the value of 0.7 that it was found for the S160a0.4 PEB (Table S2, Supporting Information). The radii of gyration of the (+)A30B240 copolymer blocks were found to be equal in both mixtures (Table S4, Supporting Information). This is reflected to the almost equal $\langle z \rangle_{\text{zipper}}$ values of all units since most neutral copolymer units in both mixtures reside out of the coacervate (Figures 12b and 14).

The computed values of mean distances of the coacervate units $\langle z_- \rangle$ and $\langle z_+ \rangle$ were both smaller than the respective of (–)S160a0.4 PEB and little higher than those of (–)S160a0.2 PEB. The representative simulation snapshots in Figure 15 show that coacervate consists of short stacks of few oppositely charged chains along the z axis.

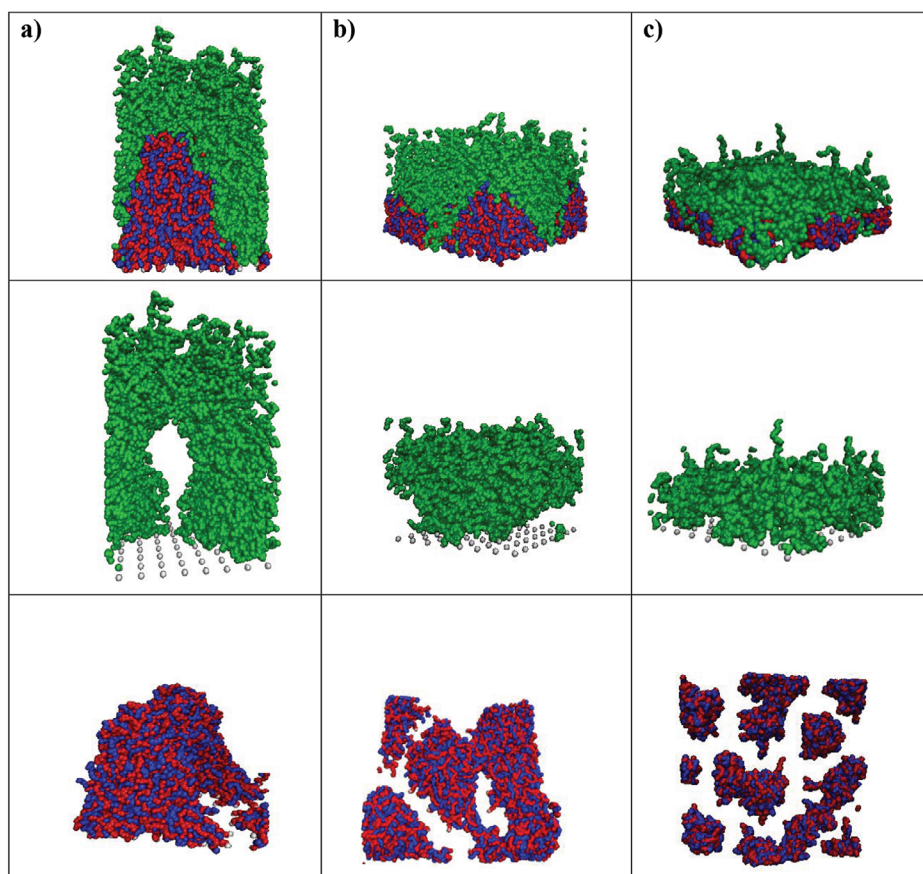


Figure 9. Simulation snapshots showing the zipper brush, the neutral phase, and the coacervate formed by the mixture of (–)S160a0.2 PEB with (+)A60B120 copolymers a) at $d = 0.049\sigma^{-2}$, b) $d = 0.024\sigma^{-2}$, and c) $d = 0.012\sigma^{-2}$.

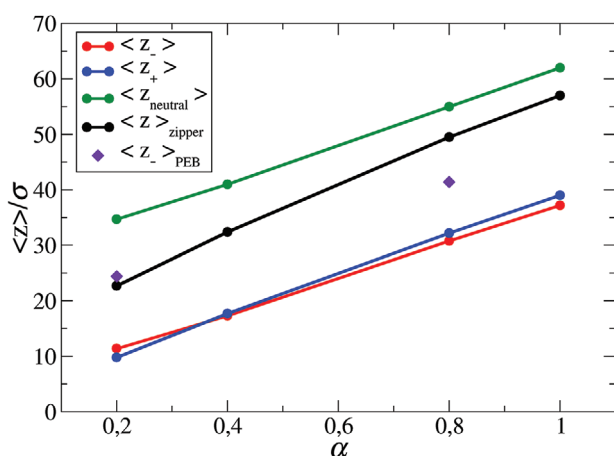


Figure 10. The mean distances from the surface of the anionic grafted units $\langle z_- \rangle$, of the cationic copolymer units $\langle z_+ \rangle$, of the neutral copolymer units $\langle z_{\text{neutral}} \rangle$, of the total zipper units $\langle z_{\text{zipper}} \rangle$, and of anionic units of PEB before the complexation $\langle z_{\text{PEB}} \rangle$ as function of the grafted chain charged units fraction α .

The effect of the monovalent salt on the formation of a zipper brush was studied for the mixture of (–)S160a0.2 PEB with cationic-neutral (+)A30B240 linear diblock copolymers contain-

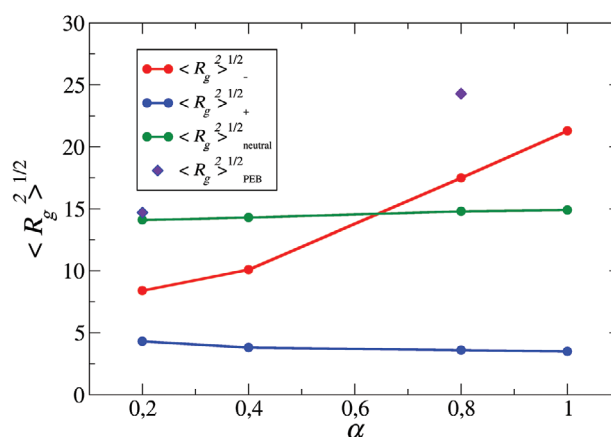


Figure 11. The square root of mean square radii of gyration anionic grafted chains $\langle R_g^2 \rangle_-^{1/2}$, of the cationic copolymer block $\langle R_g^2 \rangle_+^{1/2}$, of the neutral copolymer block $\langle R_g^2 \rangle_{\text{neutral}}^{1/2}$, and of grafted chains before the complexation $\langle R_g^2 \rangle_{\text{PEB}}^{1/2}$ as function of the grafted chain charged units fraction α .

ing the less charged PEB at $d = 0.012\sigma^{-2}$. The volume fractions Φ of the added salt were 0.0036 and 0.035. These salt concentrations correspond to $c_s = 0.1$ and 1 M, respectively. The system was considered to be in equilibrium if no change in the number

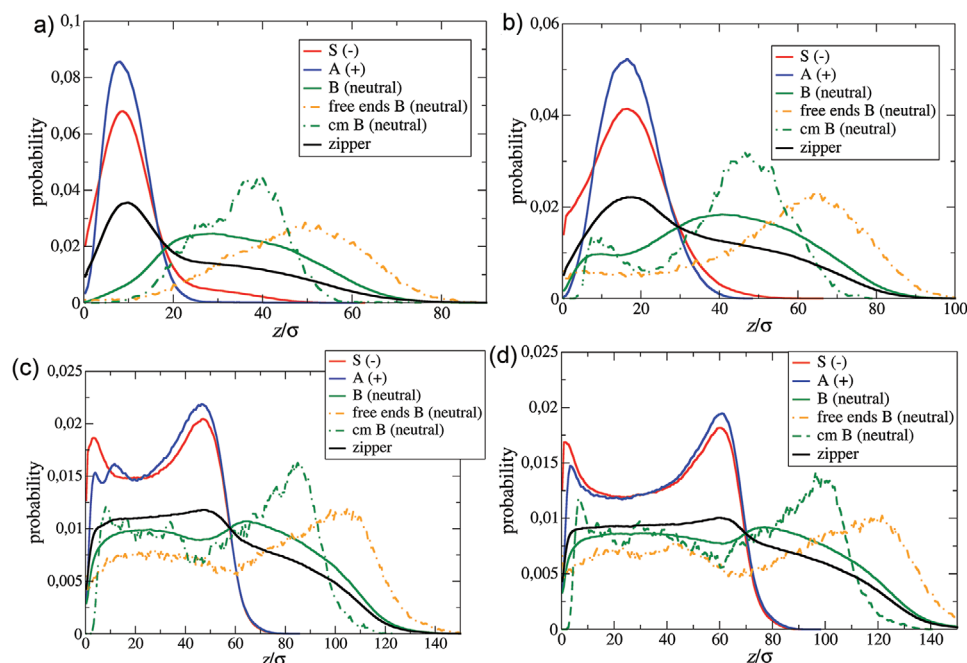


Figure 12. Probability density distributions of z for cationic A, neutral B, and anionic S-type units, free ends of anionic grafted and neutral chains, PEB counterions, centers of mass of neutral copolymer blocks, and all type zipper units for the mixture of (+)A30B240 copolymer with: a) (–)S160a0.2 PEB, b) (–)S160a0.4 PEB, c) (–)S160a0.8 PEB, and d) (–)S160a1 PEB. In all cases the grafting density is $d = 0.012\sigma^{-2}$.

of complexed copolymer chains with the PEB was evident after at least 2 million simulation timesteps. The zipper brush formed by the nonsalted mixture contained 46 out of the 68 diblock copolymer chains corresponding to the complete neutralization of PEB. In the mixture with $c_s = 0.1$ M, 63% of the copolymer chains remained complexed, (i.e., 29 chains). Further increase of the salt concentration up to $c_s = 1$ M led to a reduction in the percentage of the complexed chains of up to 13% (i.e., 6 chains) (Table S5, Supporting Information). It is expected that for higher salt concentrations, the initial PEB should be recovered. This is the great advantage of zipper brush technique as also mentioned in the introduction: From the initial PEB through the complexation with the appropriate choice of a cationic-neutral copolymer, a neutral brush having grafting density lower, equal, or much higher than that of the PEB can be obtained (e.g., for specific application), and finally with the addition of salt the initial PEB can be recovered. These results are in full agreement with experimental findings.^[19,21,22]

4. Fast versus Slow Complexation of PEB with Diblock Copolymers

In simulations discussed earlier, the units of the anionic PEB and the cationic-neutral diblock copolymers were initially placed very close to each other. Therefore, the complexation of the opposite charges was very fast. To investigate if this fast complexation has influence on the final structure of the coacervate of the zipper brush, simulations of the mixture of (–)S160a0.8 PEB with (+)A60B120 diblock copolymers at $d = 0.024\sigma^{-2}$ were performed starting from an initial configuration which mimics the experimental process as much as possible. This mixture was chosen be-

cause it previously (fast complexation method) led to a coacervate shaped as a well-defined lamella (Figure S3b, Supporting Information). We started from fully equilibrated (–)S160a0.8 PEB (Table S1, Supporting Information) and (+)A60B120 diblock copolymer solutions obtained from separate simulations. To facilitate the complexation in the mixture, an excess of diblock copolymer chains were placed above the equilibrated brush. The ratio of total positive to total negative charges of the mixture was set to $Z_{+/-} = 1.5$, corresponding to 200 diblock copolymer chains. The length of the simulation box along the z direction was set to $L_z = 214\sigma$. In this way, the total volume fraction of all type of units and counterions in the mixture is the same with the one we used in the micellization through complexation of opposite charged diblock copolymer chains and equal to $\Phi = 0.12$.^[26] The number of the complexed diblock copolymer chains in the zipper brush as a function of time τ is shown in Figure 16. As can be seen, the number of the complexed chains increases gradually with τ , reaching a plateau corresponding to 112 chains after $\approx 3.6 \times 10^4$ tau. Thus, with this slow complexation method, the charge neutralization fraction of PEB is equal to 0.82, while with the fast method the resulting zipper brush is completely neutralized.

As expected, the partial neutralization of the charges in the zipper brush formed by using the slow complexation method leads up to 18% higher values for all distances $\langle z_- \rangle$, $\langle z_+ \rangle$, $\langle z_{\text{neutral}} \rangle$, and $\langle z \rangle_{\text{zipper}}$ compared to the respective distances computed using the fast method (Table S3, Supporting Information). The probability density distribution function of the PEB units produced by using both methods is twofold (Figures 6a and 17). However, by using the fast method, the density close to the surface is higher. In contrast, the slow method yields a higher

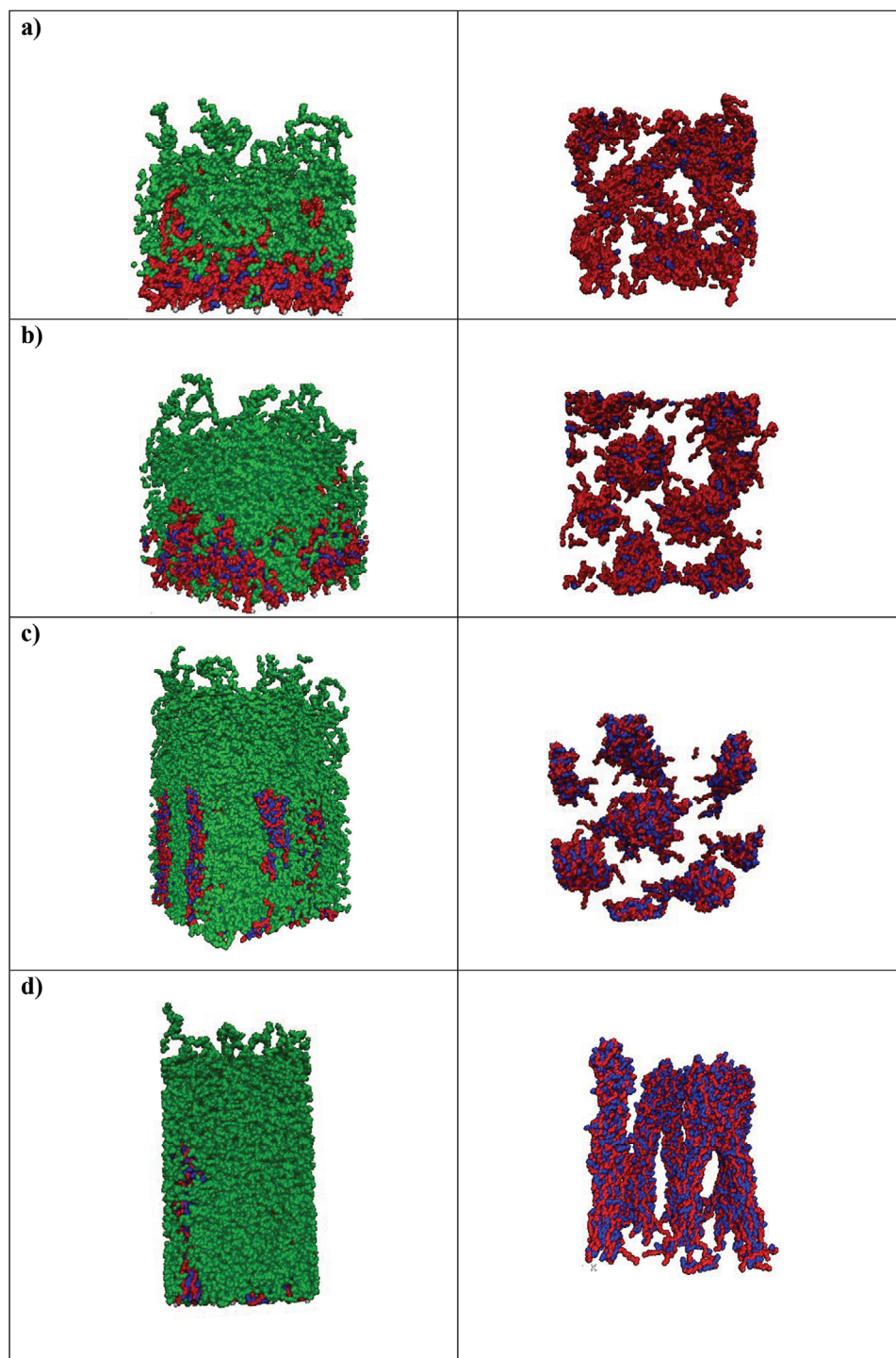


Figure 13. Simulation snapshots showing the zipper brush and the coacervate formed by the mixtures of (+)A30B240 diblock copolymer with: a) (–)S160a0.2 PEB, b) (–)S160a0.4 PEB, c) (–)S160a0.8 PEB, and d) (–)S160a1 PEB. In all cases the grafting density is $d = 0.012\sigma^{-2}$.

density at the top of the coacervate. The probability density distribution function of the centers of mass of the copolymer chains is almost identical in both methods. Again the shape of the coacervate as shown from the snapshot analysis is also lamella but along the diagonal of the simulation box. The autocorrelation

function $C(t)$ illustrated in Figure S4, Supporting Information, showcases the difficulty of the PEB units to move along the x and y axes, and thus, to “jump” between different lamellas. In conclusion, both fast and slow complexation methods predict the same results for the structure of the coacervate of the whole zipper

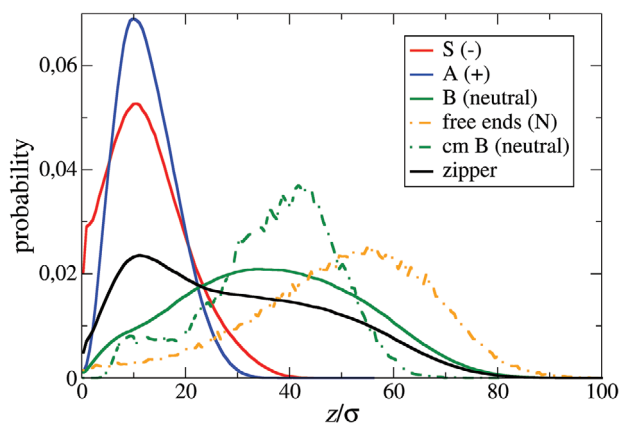


Figure 14. Probability density distributions of z for cationic A, neutral B, and anionic S-type units, free ends of neutral chains, centers of mass of neutral copolymer blocks, and all type zipper units for the mixture of (+)A30B240 diblock copolymer with (–)S80a0.8 PEB at the grafting density is $d = 0.012\sigma^{-2}$.

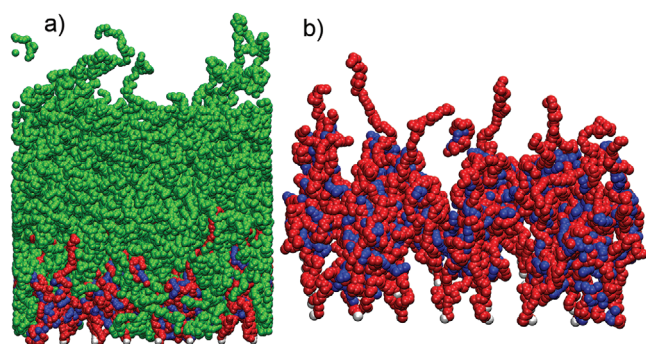


Figure 15. Simulation snapshots showing the zipper brush and the coacervate formed by the mixtures of (+)A30B240 diblock copolymer with (–)S80a0.2 PEB at the grafting density is $d = 0.012\sigma^{-2}$.

brush. However, the slow complexation method requires simulation times that are computationally nonfeasible in a realistic timeframe to obtain completely neutralized zipper brushes.

5. Comparison with Experiments

Neutral zipper brushes with high grafting density have been produced experimentally^[19,21,22] through the complexation of cationic-neutral P2MVP₄₁-PEO₂₀₅, P2MVP₄₂-PEO₄₅₀, P2MVP₇₂-PEO₄₅₀, PDMAEMA₃₅-PEO₁₂₀, and PDMAEMA₇₇-PEO₁₂₀ diblock copolymers with anionic PAA₂₇₀ or PAA₁₂₀ PEBs at different pH and $d = 0.05, 0.1, 0.2$, and 0.3 nm^{-2} . The subscripts denote the number of Kuhn segments in the cationic-neutral blocks of the copolymer or in the grafted PAA chains, and are equivalent to the number of A, B, or S type units used in our simulations. It was found that the charge neutralization fraction in the resulting zipper brush increases as the grafting density of PAA₂₇₀ brush decreases, approaching unity at the lowest grafting density.^[21] This is in full agreement with our simulation results presented in Table S2, Supporting Information. In addition, experimental results predicted that the increase of the grafted PAA chain length from 120 to 270 segments at $d = 0.1 \text{ nm}^{-2}$ led in an increased number of complexed P2MVP₄₁-PEO₂₀₅ copolymer

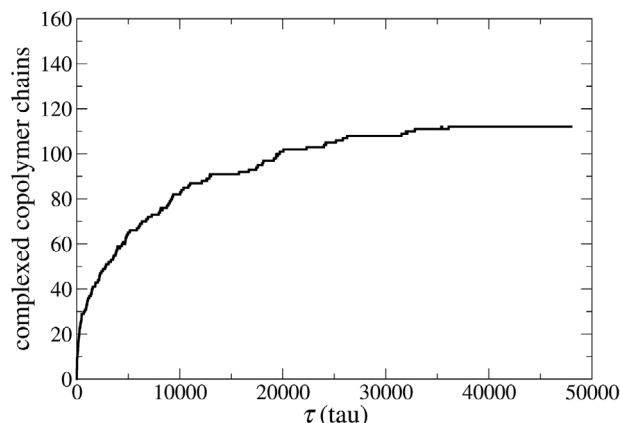


Figure 16. The number of (+)A60B120 diblock copolymer chains complexed with (–)S160a0.8 PEB as a function of the simulation time. $d = 0.024\sigma^{-2}$.

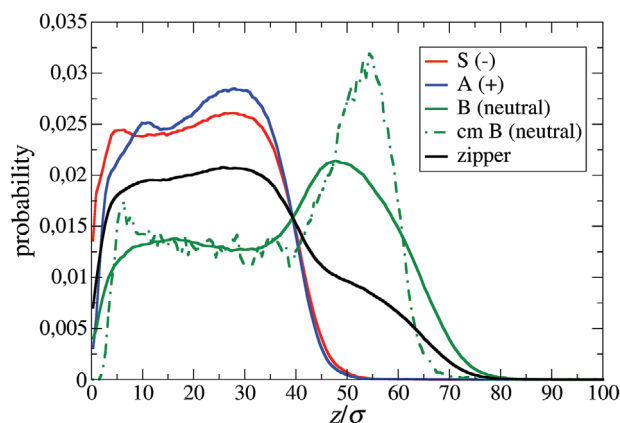


Figure 17. Probability density distributions of z for cationic A, neutral B, and anionic S-type units, centers of mass of neutral copolymer blocks, and all type zipper units for the mixture of (+)A60B120 diblock copolymer with (–)S160a0.8 PEB at the grafting density is $d = 0.012\sigma^{-2}$.

chains.^[22] Again, this is fully in line with the simulation results obtained from the mixtures of (–)S80a0.8 and (–)S160a0.8 PEB with (–)A30B240 copolymer chains (Table S2, Supporting Information). Regarding the effect of the charged PAA segments fraction (proportional to the pH of the solution) on the adsorbed amount of the P2MVP₄₁-PEO₂₀₅ copolymers it was found that the later increases with the increase of pH.^[21,22] These findings are also in full agreement with our results obtained from mixtures of (–)S160a0.2, (–)S160a0.4 (–)S160a0.8, and (–)S160a1 brushes with (+)A60B120 or (+)A30B240 copolymers (Table S2, Supporting Information). Finally, it was predicted experimentally^[22] that the adsorbed amount per m^2 of P2MVP-PEO diblock copolymers on a PAA₂₇₀ brush increases linearly with the increase of grafting density in full agreement with our simulation results illustrated in Figure S5, Supporting Information.

Due to the good antifouling properties of the zipper brushes against various proteins and other indirect evidences it was concluded that their internal stratification consists of one dense collapsed layer of complex coacervate covered with a swollen neutral brush.^[22] The grafting density of the swollen neutral brush resulted from the charge neutralization condition given by the

grafting density of the PEB enhanced by a factor equal to the ratio between the charged segments of PEB and the respective of the copolymer chain.^[21,22] The simulation results presented here show that the structure of the coacervate depends on various parameters such as the lengths of both copolymer blocks and the grafted chain, the grafting density, the PEB units charged fraction, and varies from a dense film, to perforated film, to lamella, to pinned micelles, and to stacks. Thus, some neutral blocks of the copolymers lie separately inside the coacervate volume, and consequently, the density of the neutral chains on the top of the zipper brush is equal or smaller than the one suggested by the experiments.^[19,21,22]

An interesting extension of the concept of zipper brushes is to examine the effects of sequence of charged and neutral monomers along the grafted and free copolymer chains especially for antifouling applications. Recent articles show the importance of sequence of monomers on the complex coacervate structure.^[17,34–36]

6. Conclusions

The internal stratification of the polyelectrolyte complex (zipper brush) formed by mixing of anionic charged PEBs with cationic-neutral diblock copolymers (with a very long neutral block) is studied by means of molecular dynamics simulations at Bjerrum length $l_B = 1\sigma$, which correspond to an aqueous solvent. In particular, mixtures of (+)A60B120 diblock copolymers consisting of 60 cationic charged and 120 neutral units with PEBs comprising 64 grafted (–)S160a0.2, (–)S160a0.4, and (–)S160a0.8 chains, each one consisting of 160 anionic units with different charged units fraction a were studied. It is found that for the high grafting density $d = 0.049\sigma^{-2}$ the fraction of the neutralized PEB units in the mixture increases as the fraction of the PEB charged units a increase. The internal stratification of the zipper brush formed by the (–)S160a0.2 and (–)S160a0.4 PEBs is consisted of a thick coacervate layer covered by a neutral brush of copolymer B blocks with a nonsharp interface. In the mixtures of (–)S160a0.8 PEB the neutral blocks of the complexed (+)A20B160 copolymer chains were found to be unable to form a single layer, and were distributed throughout the zipper brush. The simulation snapshot analysis revealed the existence of a perforated coacervate, where the holes are filled with the diblock copolymer neutral units. The decrease of the grafting density to $d = 0.025, 0.012$, and $0.006\sigma^{-2}$ for the mixture of (–)S160a0.8 PEB led to the shape evolution of the coacervate which became a lamella, a perforated lamella, and pinned micelles, respectively.

Simulations for the mixtures of (+)A30B240 copolymers with (–)S160a0.2, (–)S160a0.4, (–)S160a0.8, and (–)S160a1 PEBs were performed at the moderate grafting density $d = 0.012\sigma^{-2}$. It was found that in zipper brushes formed by (–)S160a0.2 grafted chains the structure of the coacervate is a perforated film. It adopts a pinned micelle structure for the mixture containing (–)S160a0.4 PEB, while in the zipper brushes formed by (–)S160a0.8 grafted chains, it consisted of tall stacks of oppositely charged units. Finally, in the mixture containing (–)S160a1 PEB even taller stacks of the charged units were formed with some of those interconnected at the top of coacervate forming a reversed “U” tube structure.

The addition of monovalent salt with molarities of 0.1 and 1 M in the mixture of (–)S160a0.2 PEB with (+)A30B240 copolymers at $d = 0.012\sigma^{-2}$ led to a reduction in the number of complexed diblock copolymer chains of up to 91% and practically the initial PEB is recovered. This is the great advantage of zipper brush technique. From the initial PEB through the complexation with the appropriate choice of a cationic-neutral copolymer, neutral brush having grafting density lower, equal, or much higher than that of the PEB can be obtained for applications, and finally with salt addition the initial PEB is recovered. Our findings agree with the existing experimental predictions and provide new insights into the structure and shape of the coacervate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Prof. O. Moulton for the critical reading of the manuscript. This work was supported 1) by computational time granted from the Greek Research & Technology Network (GRNET) in the National HPC facility ARIS under project ID pr010042– Zipper_Brushes, and 2) by project “Dioni: Computing Infrastructure for Big-Data Processing and Analysis” (MIS No. 5047222) cofunded by European Union (ERDF) and Greece through Operational Program “Competitiveness, Entrepreneurship and Innovation,” NSRF 2014–2020.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

brushes, complexation, molecular dynamics, polyelectrolytes, simulation

Received: February 9, 2022

Revised: March 17, 2022

Published online:

- [1] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY **1979**.
- [2] A. Halperin, *J. Phys. (Paris)* **1988**, 49, 547.
- [3] S. T. Milner, T. A. Witten, M. E. Cates, *Macromolecules* **1988**, 21, 2610.
- [4] G. Rossi, I. G. Elliott, T. Ala-Nissila, R. Faller, *Macromolecules* **2012**, 45, 563.
- [5] E. B. Zhulina, F. A. M. Leermakers, O. V. Borisov, *Langmuir* **2015**, 31, 6514.
- [6] M. Kröger, O. Peleg, A. Halperin, *Macromolecules* **2010**, 43, 6213.
- [7] H. Merlitz, W. Cui, C.-X. Wu, J.-U. Sommer, *Macromolecules* **2013**, 46, 1248.

- [8] L. N. Gergidis, A. Kalogirou, A. Charalambopoulos, C. Vlahos, *J. Chem. Phys.* **2013**, 139, 044913.
- [9] S. Ma, X. Zhang, B. Yu, F. Zhou, *NPG Asia Mater.* **2019**, 11, 24.
- [10] R. C. Advincula, W. J. Brittain, K. C. Caster, J. Ruhe, *Polymer Brushes: Synthesis, Characterization, Applications*, Wiley-VCH, Weinheim **2004**.
- [11] R. S. Ross, P. Pincus, *Macromolecules* **1992**, 25, 2177.
- [12] L. Chen, H. Merlitz, S.-Z. He, C.-X. Wu, J.-U. Sommer, *Macromolecules* **2011**, 44, 3109.
- [13] F. A. M. Leermakers, M. Ballauff, O. V. Borisov, *Langmuir* **2008**, 24, 10026.
- [14] O. V. Borisov, E. B. Zhulina, *Macromolecules* **2015**, 48, 1499.
- [15] N. P. Shusharina, P. Linse, *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2001**, 4, 399.
- [16] K. Miliou, L. N. Gergidis, C. Vlahos, *J. Polym. Sci., Part B: Polym. Phys.* **2017**, 55, 1110.
- [17] V. Sethuraman, M. McGovern, D. C. Morse, K. D. Dorfman, *Soft Matter* **2019**, 15, 5431.
- [18] C. V. Synatschke, T. I. Löblich, M. Förtsch, A. Hanisch, F. H. Schacher, A. H. E. Müller, *Macromolecules* **2013**, 46, 6466.
- [19] J. V. D. Gucht, E. Spruijt, M. Lemmers, M. A. C. Stuart, *J. Colloid Interface Sci.* **2011**, 361, 407.
- [20] K. Igata, T. Sakamaki, Y. Inutsuka, Y. Higaki, M. K. Okajima, N. L. Yamada, T. Kaneko, A. Takahara, *Langmuir* **2020**, 36, 6494.
- [21] W. M. De Vos, J. M. Kleijn, A. De Keizer, M. A. C. Stuart, *Angew. Chem., Int. Ed.* **2009**, 48, 5369.
- [22] W. M. De Vos, G. Meijer, A. De Keizer, M. A. C. Stuart, J. M. Kleijn, *Soft Matter* **2010**, 6, 2499.
- [23] S. Van Der Burgh, A. De Keizer, M. A. C. Stuart, *Langmuir* **2004**, 20, 1073.
- [24] I. K. Voets, W. M. De Vos, B. Hofs, A. De Keizer, M. A. C. Stuart, R. Steitz, D. Lott, *J. Phys. Chem. B* **2008**, 112, 6937.
- [25] K. Miliou, L. N. Gergidis, C. Vlahos, *J. Polym. Sci.* **2020**, 58, 1757.
- [26] C. Gioldasis, L. N. Gergidis, C. Vlahos, *J. Polym. Sci.* **2021**, 59, 191.
- [27] K. Miliou, L. N. Gergidis, C. Vlahos, *J. Polym. Sci., Part B: Polym. Phys.* **2019**, 57, 621.
- [28] R. Ni, D. Cao, W. Wang, A. Jusufi, *Macromolecules* **2008**, 41, 5477.
- [29] A. Kalogirou, L. N. Gergidis, K. Miliou, C. Vlahos, *J. Phys. Chem. B* **2017**, 121, 1982.
- [30] M. Murat, G. S. Grest, *Macromolecules* **1996**, 29, 1278.
- [31] O. Moulτος, L. N. Gergidis, C. Vlahos, *Macromolecules* **2012**, 45, 2570.
- [32] S. Plimpton, *J. Comput. Phys.* **1995**, 117, 1.
- [33] K. Miliou, L. N. Gergidis, C. Vlahos, *J. Polym. Sci., Part B: Polym. Phys.* **2018**, 56, 924.
- [34] L.-W. Chang, T. K. Lytle, M. Radhakrishna, J. J. Madinya, J. Vélez, C. E. Sing, S. L. Perry, *Nat. Commun.* **2017**, 8, 1273.
- [35] C. E. Sing, *J. Chem. Phys.* **2020**, 152, 024902.
- [36] A. M. Rumyantsev, N. E. Jackson, B. Yu, J. M. Ting, W. Chen, M. V. Tirrell, J. J. De Pablo, *ACS Macro Lett.* **2019**, 8, 1296.