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¹ Theory of Mesophases of Triblock Comb-Shaped Copolymers: ² Effects of Dead Zones and Bridging

3 Ekaterina B. Zhulina, Ivan V. Mikhailov, and Oleg V. Borisov*

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ABSTRACT: A the solvent-free mesoph developed using a st architecture-depend	eory describing the equilibriu bases of <i>ABA</i> triblock copo trong-stretching self-consisten ent parameters of the mo	m morphology and structural properties of olymers comprised of comblike blocks is nt field (SS-SCF) analytical approach with olecular potential. Morphological phase	A VIII BOOM

8 diagrams are constructed by implementing a two-layer model of convex solvent-free brushes 9 which enables us to account for the effect of "dead zones" on binodals separating regions of 10 thermodynamic stability of spherical, cylindrical, and lamellar mesophases. Fractions of the 11 middle comblike *B* blocks forming bridges and loops between neighboring *A* domains are 12 calculated for all of the morphologies as a function of the architectural parameters of the 13 blocks. These analytical calculations are supplemented by numerical Scheutjens—Fleer self-14 consistent field (SF-SCF) simulations of convex solvent-free brushes of comblike polymers 15 that mimic the matrix in the *ABA* triblock copolymer mesophases. The predicted domain 16 sizes and interdomain distances are compared to experimental data.

A Spherical (cylindrical) A Lamellae Spherical (cylindrical)

1. INTRODUCTION

17 Self-assembling block copolymers give rise to brushlike 18 structures in melts and solutions. Solvated and dry brushes 19 emerge, e.g., upon self-assembly of block copolymers with 20 linear and branched blocks in selective solvents¹⁻⁵ or in the 21 melt state.^{6–15} Microphase-segregated bulk morphologies of 22 block copolymers comprising branched blocks exhibit 23 mechanical properties resembling biological tissues.^{16–19} 24 Incorporation of comblike or bottlebrush blocks enables 25 adjusting the properties of nanostructured materials through 26 controlled variation of the grafting density or/and the 27 polymerization degree of the grafts without changing their 28 chemical nature. This control is assured by well-elaborated and 29 robust techniques developed for the synthesis of comblike 30 polymers and molecular brushes. Due to potential applications 31 in (bio)engineering and nanomedicine,^{5,20-22} brushes of 32 branched polymers with diverse topologies have become a 33 subject of intense theoretical investigation during the past 34 decade.²³⁻³⁰

The structural properties of brushes formed by end-tethered 36 macromolecules with various branched architectures (e.g., 37 regular dendrons, arm-tethered stars, macrocycle-containing 38 polymers, etc.) can be described via analytical theories 39 invoking architecture-dependent molecular potential. The 40 pioneering study of Pickett²³ demonstrated the parabolic 41 nature of the self-consistent molecular potential acting in 42 brushes formed by root-tethered regular dendrons and paved 43 the way to extension of this approach to other molecular 44 architectures.^{31–35}

45 Application of the parabolic potential framework to brushes 46 of branched polymers has a number of evident advantages. It

allows for closed analytical expressions for polymer density 47 distributions in both undeformed and compressed brushes 48 under various solvent conditions³⁴ and formulation of their 49 elastic response to deformation.³⁵ It also specifies the free 50 energy for both solvated and solvent-free brushes that 51 facilitates the analysis of micellization in solutions³³ and 52 microphase segregation in melts.³⁶ On the other hand, the 53 parabolic potential framework has its drawbacks as it specifies 54 only the most probable state of the system and, importantly, 55 ignores the possible presence of dead zones (regions depleted 56 of chain free ends). The latter could arise for certain 57 architectures of the tethered chains in both planar and 58 nonplanar geometries and perturb the parabolic shape of the 59 molecular potential. In this case, the parabolic self-consistent 60 field (SCF) potential should be considered as an approx- 61 imation whose accuracy could be evaluated via alternative 62 methods, e.g., numerical SCF modeling accounting for dead 63 zones.

In our recent study,³⁶ we applied the parabolic potential 6s framework (SS-SCF) to study microphase-segregated melts of 66 *AB* diblock copolymers with comblike and bottlebrush blocks. 67 Comblike and bottlebrush polymers were distinguished based 68 on the conformational state of their backbones in melts. While 69

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Figure 1. Schematic of the ABA block copolymer with a central comb-shaped block, and microphase-segregated structures in melts. Lamellar (a) and nonplanar (spherical, cylindrical) morphologies (b). Wigner–Seitz cell with half bridges attached to its boundary (c). Side chains of comb-shaped block are not shown.

70 comblike polymers with relatively loose grafts exhibit Gaussian 71 statistics on all length scales in melts, the densely grafted side 72 chains in bottlebrush polymers cause local stretching of the 73 backbones. Using the asymptotic expressions for elasticity of 74 branched polymers with long backbones, we examined three 75 basic morphologies (spherical, cylindrical, and lamellar) of 76 microphase-segregated melts in the strong segregation limit. 77 Although the parabolic potential framework invokes the development of dead zones in convex brushes with nonplanar 78 79 morphologies, 37-41 their presence was ignored in our previous study³⁶ due to conjecture that branching leads to a shrinkage 80 of the dead zones^{24,43} and thus that their effect on the 81 82 equilibrium parameters of superstructures is minor.

In this paper, we quantitatively evaluate the effect of dead to be a structural properties of microphase-segregated melts by implementing the two-layer model that was originally formulated for solvated cylindrical and spherical brushes of plinear polymers.⁴¹ We supplement the analytical model with the numerical Scheutjens—Fleer self-consistent field (SF-SCF) simulations of convex solvent-free brushes of comblike polymers with systematically varied lengths of side chains and spacers.

Using the two-layer model of dry brushes, we demonstrate 93 that the effect of a dead zone could be noticeable in a spherical 94 morphology, leading to smaller sizes of the domains and a mild 95 shift in the binodal separating spherical and cylindrical 96 superstructures to larger contents of a matrix-forming 97 component.

Similarly to *AB* diblocks, triblock copolymers *ABA* with branched blocks give rise to spherical, cylindrical, and lamellar superstructures. More complex structures, e.g., a double gyroid,⁴² are also possible. The major difference between microphase-segregated melts of *AB* and *ABA* block copolymers arises due to formation of *B* bridges by central blocks of *ABA* opolymers. In contrast to *B* loops returning to the same so domains, *B* bridges connect neighboring domains giving rise to domains, *B* bridges connect neighboring domains giving rise to while the presence of *B* bridges mildly affects the equilibrium dimensions of the domains and interdomain distances, the network elasticity is governed by both the fraction of bridges and the architecture of *B* blocks.

In our previous papers, 45,47 we analyzed how the grafting line density and length of the side chains affect the equilibrium line fraction of *B* bridges in lamellar mesophases of *ABA* block copolymers with a comb-shaped B block. We demonstrated 114 that the equilibrium fraction of bridging chains in lamellae can 115 be estimated from the equilibrium parameters of brushes 116 formed by B subchains (i.e., loops cut in two equal parts) with 117 the middle points of bridges pinched at the symmetry plain 118 between grafting surfaces. This theoretical approach was 119 checked and supported by the numerical Scheutjens-Fleer 120 self-consistent field (SF-SCF) modeling. Note that while the 121 analytical strong-stretching self-consistent field (SS-SCF) 122 theory presumes a Gaussian elasticity of tethered macro- 123 molecules on all length scales and describes the set of chain 124 conformations via "trajectories" (that is, the most probable 125 positions of monomer units), numerical SF-SCF modeling 126 accounts properly for conformational degrees of freedom 127 irrespective of the extent of stretching of the brush-forming 128 macromolecules, including the nonlinear elasticity regime. 129 Using the SS-SCF and SF-SCF approaches, we demonstrated 130 that comblike branching of B blocks leads to the structural 131 organization of *B* layers resembling that of linear chains, that is, 132 loops occupy the presurface regions in the apposing brushes, 133 while the central part of the gap is filled with segments of 134 bridges with associated side chains. However, the equilibrium 135 fraction of bridges formed by comblike polymers noticeably 136 decreases compared to linear chains with the same DP. 137

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The goal of this study is 2-fold: (i) we first investigate how 138 the fraction of bridging *B* chains connecting neighboring *A* 139 domains depends on the morphology of the microphase- 140 segregated state of the melt and on the architectural 141 parameters of the *ABA* triblock copolymer, and (ii) we 142 examine how the presence of dead zones affects the 143 equilibrium parameters of microphase-segregated superstruc- 144 tures and the binodals separating ranges of thermodynamic 145 stability of different morphologies. 146

The rest of the paper is organized as follows. In section 2, we 147 consider solvent-free brushes formed by comblike macro- 148 molecules, introduce a two-layer model of dry convex brushes, 149 and compare the analytical predictions to the results of 150 numerical SF-SCF simulations. In section 3, the two-layer 151 model was applied to describe the matrix in the microphase- 152 segregated melt of the *ABA* copolymer. In section 4, we 153 estimate the equilibrium fraction of the *B* bridges in 154 microphase-segregated melts of *ABA* triblock copolymers 155 versus the morphology of the *A* domains. In section 5, we 156 examine the effect of dead zones on the equilibrium parameters 157

В

158 of the superstructures and the binodals separating the 159 spherical, cylindrical, and lamellar morphologies of copolymers 160 with comb-shaped blocks. In section 6, we compare the 161 theoretical predictions to experiments. In section 7 we 162 formulate the conclusions.

2. BRUSH OF COMB-SHAPED MACROMOLECULES: 163 MODEL AND SS-SCF FORMALISM

164 Consider a comb-shaped homopolymer comprised of $P \gg 1$ 165 repeats each composed of the backbone spacer with a degree of 166 polymerization (DP) *m* and $q \ge 1$ side chains with *n* monomer 167 units each, linked to each junction on the backbone, see Figure 168 1. The backbone and side chains are assumed to be chemically 169 identical and have monomer units with length *l*, volume *v*, and 170 Kuhn segment b > l. If q > 1, the macromolecules are termed 171 "barbwire" polymers. The backbone has DP M = Pm, while the 172 total DP of the macromolecule is

$$N = P(m + qn) = M(1 + qn/m)$$
(1)

174 The macromolecules are tethered to an impermeable planar 175 surface (*AB* interface) with area *s* per chain. The grafting 176 density $\sigma = 1/s$ ensures strong overlap of individual 177 macromolecules so that the backbones are extended in the 178 direction normal to the grafting surface with a cutoff of 179 polymer density profile (brush thickness) at distance D = Nv/s180 from the surface.

Following the strong stretching self-consistent field (SS-SCF) approach formulated earlier,³⁶ the molecular potential U(z) in a solvent-free brush exhibits a parabolic dependence on distance z from the grafting surface

$$\frac{U(z)}{k_{\rm B}T} = \frac{3}{2lb}\kappa^2 (D^2 - z^2)$$
(2)

186 with architecture-dependent topological coefficient κ . Equation 187 2 presumes the Gaussian (linear) elasticity of the tethered 188 chains on all length scales. Crowding of the side chains near 189 the branching points is not taken into account, which restricts 190 the branching activity $q \simeq 1$. Other restrictions on the 191 applicability of eq 2 are the possible appearance of dead zones 192 depleted of the free ends of the backbones and vertical 193 stratification for certain architectures of comb-shaped poly-194 mers. In these cases, eq 2 serves as an approximation to be 195 checked by alternative scf methods, e.g., SF-SCF modeling.⁴⁶ 196 The basic elements of the SF-SCF method are described in our 197 preceding publication.⁴⁷

The topological coefficient κ in eq 2 depends on the 199 architectural parameters of the polymers with $q \ge 1$: DPs of 200 the side chain (n), spacer (m), and backbone, M = mP. We 201 demonstrated earlier⁴⁵ that κ exhibits different asymptotic 202 dependences for polymers with short, $M \ll (mn/q)^{1/2}$, and 203 long, $M \gg (mn/q)^{1/2}$, backbones. In this paper, we focus on 204 comblike polymers with long backbones, $M \gg (mn/q)^{1/2}$, and 205 use the corresponding asymptotic power law dependence for 206 the topological coefficient κ

$$\kappa = \frac{\pi}{2N} \left(1 + \frac{qn}{m} \right)^{1/2} = \frac{\pi}{2M} \left(1 + \frac{nq}{m} \right)^{-1/2},$$

$$M \gg (nm/q)^{1/2}$$
(3)

208 For linear chains with q = 0 and N = M, the topological 209 coefficient $\kappa = \kappa_{\text{lin}} = \pi/2N$. To eliminate the molecular weight 210 dependence of κ , we introduce the topological ratio

207

$$\eta = \frac{\kappa}{\kappa_{\rm lin}} = \frac{2\kappa N}{\pi} \tag{4}_{211}$$

which is approximated as

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$$\eta_{\text{comblike}} = \left(1 + \frac{qn}{m}\right)^{1/2} = (N/M)^{1/2}$$
(5) 213

for comblike polymers with $M \gg (mn/q)^{1/2}$ (locally un- 214 extended backbones). In conventional comblike polymers, q = 215 1.

The topological ratio η for bottlebrush (bb) polymers with ²¹⁷ locally extended backbones was also discussed earlier.³⁶ The ²¹⁸ onset of local backbone extension (i.e., the onset of the ²¹⁹ bottlebrush regime for comb-shaped polymer) is governed by ²²⁰ dense packing of the backbone segment with associated side ²²¹ chains in volume V with radius $r_0 = (lbn)^{1/2}$ equal to the ²²² Gaussian size of side chain, that is

$$V = \frac{4\pi}{3}r_0^3 = \frac{4\pi}{3}(lbn)^{3/2} = vn\left(\frac{qn}{m_*} + 1\right) \approx v\frac{qn^2}{m_*}$$
(6) 224

to specify the threshold value m_* of spacer length as 225

$$m_* \approx \frac{3}{4\pi} \frac{v}{(lb)^{3/2}} q n^{1/2} \tag{7}_{226}$$

For comb-shaped polymers with $m \ll m_*$, the backbone is 227 locally stretched and the topological ratio for such macro- 228 molecules is given by 229

$$\eta_{\text{bottlebrush}} = \alpha \frac{(lb)^{3/4}}{v^{1/2}} n^{1/4}$$
(8) 230

with the numerical coefficient $\alpha \simeq 1$. In this scenario, the 231 topological coefficient $\kappa = \pi \eta_{\text{bottlebrush}}/(2N)$ in eq 2 should be 232 renormalized according to eq 8.

Equations 8 and 5 indicate that the elastic free energy of 234 comb-shaped polymers in a brush is dominated by stretching 235 of their backbones while the side chains are weakly stretched 236 and retain almost unperturbed Gaussian conformations. 237

2.1. Dead Zone in Dry Convex Brush: Two-Layer ²³⁸ **Model.** In convex brushes of linear chains, the parabolic ²³⁹ molecular potential leads to a negative number density of the ²⁴⁰ free ends near the grafting surface, indicating the development ²⁴¹ of dead zones.³⁷ Dead zones emerge also for certain ²⁴² architectures of branched chains in a planar geometry.⁴⁸ ²⁴³ Importantly, dead zones of any origin modify the parabolic ²⁴⁴ shape of the molecular potential,^{38,39} making its precise ²⁴⁵ calculation challenging. ²⁴⁶

A simplified two-layer model accounting for dead zones in 247 solvated convex brushes of linear chains⁴¹ combined the power 248 law decay in polymer density inside the dead zone with the 249 planar-like distribution of chain segments in the brush 250 peripheral region. Matching the polymer density profiles in 251 the spherical (or cylindrical) dead zone and the planar-like 252 peripheral layer, supplemented with length conservation of 253 chain segments in both layers, relates the dead zone width, z_0 , 254 to the curvature of the grafting surface. It was demonstrated⁴ 255 and confirmed by more accurate calculations³⁹ that an inferior 256 solvent strength leads to the increased relative extension of the 257 dead zone, suggesting that dead zones could occupy a 258 significant part of strongly curved solvent-free brushes of 259 comb-shaped polymers. 260

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To evaluate the effect of dead zones on the properties of microphase-segregated melts of copolymers with comb-shaped blocks, we extend the original two-layer model⁴¹ to dry, solvent-free brushes. In contrast to brushes swollen in solvent, matching of polymer volume fractions $\varphi(z)$ at $z = z_0$ occurs in a solvent-free brush automatically because $\varphi(z) = 1$ everywhere in both layers. In this case, z_0 is specified by matching the average elastic tensions at the boundary between the two layers. A detailed description of the two-layer model of dry the provide the results solvent. The provide the results relevant to further discussion.

In a convex solvent-free brush of comb-shaped polymers with DP N and volume vN, end tethered to a cylinder (i = 2) or sphere (i = 3) with radius R_i and area s_i per molecule (see Figure S1, SI), the brush thickness D_i is related to N and R_i as

$$\frac{iNv}{s_iR_i} = \left(1 + \frac{D_i}{R_i}\right)^i - 1 \tag{9}$$

. .

277 The brush is divided into 2 layers: a dead zone with thickness 278 z_0 near the surface and a peripheral layer with thickness (D_i – 279 z_0). The dead zone contains equally stretched segments of 280 backbones, while the remaining backbone segments distribute 281 free ends all over the planar-like peripheral layer. Introduction 282 of the reduced variables

$$\omega_i = \frac{D_i}{R_i}; \quad y_i = \frac{z_0}{D_i} \tag{10}$$

284 and balance of the average elastic tensions at the boundary 285 between the two layers ($z = z_0$) allow for equations for reduced 286 width y_i of the dead zone in spherical (i = 3) and cylindrical (i287 = 2) geometries

$$y_{3} = \frac{z_{0}}{D_{3}}$$

$$= \left[\frac{1}{2}\left(\frac{\omega_{3}}{3} + 1 - \frac{\pi^{2}}{4}\right) + \sqrt{\frac{1}{4}\left(\frac{\omega_{3}}{3} + 1 - \frac{\pi^{2}}{4}\right)^{2} + \left(\frac{\pi^{2}}{8} - \frac{1}{3}\right)\left(\frac{\omega_{3}^{2}}{3} + \omega_{3} + 1 - \frac{\pi^{2}}{8}\right)}\right]$$

$$\div \left[\omega_{3}\left(\frac{\pi^{2}}{8} - \frac{1}{3}\right)\right]$$
(11)

289 and

288

2.90

292

283

$$y_{2} = \frac{z_{0}}{D_{2}} = \frac{2 + \omega_{2} - \frac{\pi^{2}}{4}}{\omega_{2} \left(\frac{\pi^{2}}{4} - 1\right)}$$
(12)

291 The dead zone disappears (i.e., $y_i = 0$) if

$$\omega_{i} < \omega_{i,0} = \left(\frac{D_{i}}{R_{i}}\right)_{0}$$

$$= \begin{cases} -\frac{3}{2} + \sqrt{\frac{3\pi^{2}}{8} - \frac{3}{4}} \approx 0.218 \quad i = 3 \\ \frac{\pi^{2}}{4} - 2 \approx 0.467 \qquad i = 2 \end{cases}$$
(13)

293 while its maximal relative width $y_i(\omega_i \rightarrow \infty)$ is given by

$$y_{i,\max} = \begin{cases} \frac{1}{\pi^2/4 - 1} \approx 0.681 & i = 2\\ \frac{1/6 + \sqrt{1/36 + (\pi^2/8 - 1/3)/3}}{\pi^2/8 - 1/3} \approx 0.821\\ i = 3 \end{cases} \approx 0.821$$
(14) 294

Notably, eq 10 does not comprise the architectural parameters 295 of comb-shaped polymers and is applicable to linear polymers 296 as well. 297

In Figure 2, we present the reduced width of the dead zone, 298 f2 $y_i = z_0/D_i$, in spherical (i = 3) and cylindrical (i = 2) dry 299



Figure 2. Relative extension of the curvature-induced dead zone, z_0/D_i in a convex dry brush with thickness D_i , formed by linear chains with DP N, tethered to a convex surface with radius R_i and grafting area s_i per chain. $D_{0,i} = Nv/s_i$ is the thickness of a planar brush with grafting area s_i per chain. Lines with symbols show z_0/D_i calculated with the two-layer model. Solid black curves are exact z_0/D_i according to ref 39.

brushes (lines with symbols calculated according to eqs 11 and 300 12) as a function of the reduced curvature 301

$$\frac{R_i}{D_0} = \frac{R_i s_i}{Nv} = \frac{i}{(1+\omega_i)^i - 1}$$
(15) 302

Here, $D_0 = Nv/s_i$ is the thickness of the planar solvent-free 303 layer with grafting area s_i per chain. As it is seen in Figure 2, at 304 strong curvature of a spherical surface, $R_3/D_0 \leq 2$, the ratio $z_0/305$ D_3 is rather close to the exact dependence³⁹ calculated for 306 linear chains (shown by the upper solid lines in Figure 2). The 307 correspondence between the approximate and the exact values 308 of z_0/D_2 (lower solid line) at strong curvatures for a cylindrical 309 geometry is reasonable as well. The maximal extensions of 310 dead zones, $y_{3,max} \approx 0.82$ and $y_{2,max} \approx 0.68$, are close to the 311 exact values, 0.71 and 0.63, respectively.³⁹ However, at weak 312 curvatures ($\omega_i < \omega_{i,0}$), in contrast to the predicted exponential 313 decay,³⁹ z_0 exactly equals zero in the two-layer model. 314

In the two-layer model, the elastic free energy $F_{\rm el}$ per chain 315 in a convex brush of comb-shaped polymers comprises the 316 elastic contributions due to the dead zone region $(F_{\rm el,in})$ and 317 the planar-like peripheral layer $(F_{\rm el,out})$ 318

$$F_{\rm el} = F_{\rm el,in} + F_{\rm el,out} \tag{16}_{319}$$

The elastic free energy F_{el} per molecule is calculated in the SI 320 and is given by 321



Figure 3. Fraction g(z) of middle points in the spherical (i = 3) brush of loops formed by comblike polymer with fixed DP N = M(1 + n/m) = 1000 as a function of distance *z* from the surface. m = 2 values of other parameters (σ , *R*, *D*, *n*) are indicated in the plots. Theoretical thickness z_0 of the dead zone is indicated by cross on the *z* axis.

$$\frac{F_{\rm el}}{k_{\rm B}T} = \frac{\upsilon\eta^2}{lb} \frac{R_i}{s_i} \times \begin{cases} \frac{3}{2} \frac{y_i}{y_i + \omega_i} + \frac{27\pi^2}{8} \frac{\omega_3^3 (1 - y_3)^3 [(1 + y_3\omega_3)^2/3 + \omega_3 (1 + y_3\omega_3)(1 - y_3)/2 + \omega_3^2 (1 - y_3)^2/5]}{[(1 + \omega_3)^3 - (1 + \omega_3 y_3)^3]^2} & i = 3\\ \frac{3}{2} \ln\left(\frac{y_i + \omega_i}{y_i}\right) + \frac{3\pi^2}{2} \frac{\omega_2^3 (1 - y_2)^3 [(1 + y_2\omega_2)/3 + \omega_2 (1 - y_2)/4]}{[(1 + \omega_2)^2 - (1 + \omega_2 y_2)^2]^2} & i = 2 \end{cases}$$

$$(17)$$

322 323

2.2. SF-SCF Modeling of Convex Solvent-Free Brushes of Comb-Shaped Polymers. The details of the Brushes of the set of the set of the set of the set of the Brushes of the set of the Brushes of the set of

microphase-segregated melts of comb-shaped polymers will be 332 presented in a subsequent publication. 333

In Figure 3, we illustrate the development of a dead zone in 334 f3 a spherical (i = 3) solvent-free brush formed by loops of comb- 335 shaped polymer. In the SF-SCF approach, a brush of loops 336 with backbone DP *M* and grafting density σ is equivalent to the 337 brush of linear chains with DP *M*/2 and grafting density 2σ . In 338 Figure 3, the normalized to unity fraction g(z) of middle points 339 of the loops is presented as a function of distance *z* from the 340



Figure 4. Normalized fraction $g(z)D_3$ of middle points in the brush of loops with fixed DP N = 1000 as a function of reduced distance z/D_3 from the surface of the spherical substrate with radius $R_3 = 15$ at different grafting densities σ . DP of the side chain n = 0 (a), 3 (b), and 8 (c).



Figure 5. Free energy F_{el} per molecule (in k_BT units) in the cylindrical (i = 2, left) and spherical (i = 3, right) solvent-free brushes of loops formed by comblike polymer as a function of ratio R_i/D_i . Solid and dashed lines indicate scf data and analytical predictions calculated according to eq 20 (two-layer model), respectively. In both plots backbone DP M = 400, grafting density of loops $\sigma = 0.1$, m = 2, and n = 1, 3, 5, 8, 10, 12, 15, and 20 (curves indicated by different colors with n increasing from bottom to top).

341 surface at a fixed loop DP N = 1000, m = 2, $R_3 \approx 15$, and varied 342 system parameters (indicated in the plots with subscript 3 343 omitted to avoid crowding). The theoretical thickness z_0 (eq 344 11) is indicated by a cross on the *z* axis. As it is seen in Figure 345 3, an increase in DP *n* of the side chains leads to the stretching 346 of polymer backbones with DP M = N(1 + n/m), the 347 concomitant development of the maximum in g(z) depend-348 ence, and the extension of the dead zone. A similar effect is 349 invoked by the increase in the grafting density σ .

According to the two-layer model, the relative width of the ss1 outer (planar-like) sublayer depends only on the ratio R_i/D_i , ss2 and therefore, at a fixed surface radius, R_i = const, the distribution g(z) of loop middle points (end points of the ss4 equivalent linear chains) depends only on the reduced distance ss5 z/D_i . Therefore, the two-layer model predicts a universal shape ss6 of the normalized distribution $g(z)D_i$ as a function of z/D_i with a maximum at the external boundary of the brush, $z/D_i = 1$. In 357 Figure 4, we present $g(z)D_3$ as a function of z/D_3 in a spherical 358 f4 brush (i = 3) for comb-shaped polymer DP N = 1000 and 359 varied lengths of the side chains, n = 0 (Figure 4a), n = 3 360 (Figure 4b), and n = 8 (Figure 4c). An increase in n and the 361 concomitant decrease in M = N/(1 + n/m) lead to localization 362 of the normalized distribution $g(z)D_3$ around the same 363 maximum (consistent with the analytical model). However, 364 in contrast to the theoretical predictions, the position of the 365 maximum in $g(z)D_3$ is shifted to smaller values of $z/D_3 \approx 0.8 < 366$ 1. This shift could be rationalized as follows. In the case of 367 comb-shaped polymers, the maximum in $g(z)D_3$ dependence is 368 expected to shift to the left due to accommodation of the side 369 chains that ensure dense packing of monomer units in the 370 vicinity of the brush external boundary. This feature of comb- 371 shaped polymers is not accounted for in the analytical model 372

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³⁷³ but is revealed in the scf numerical calculations. Simulta-³⁷⁴ neously, an increase in n leads to stronger stretching of the ³⁷⁵ backbones and the approach to their limiting extension. As a ³⁷⁶ result, the maximum tends to shift in the opposite direction, ³⁷⁷ i.e., closer to the brush external boundary. Due to these two ³⁷⁸ counteracting factors, the location of the maximum could ³⁷⁹ remain virtually unchanged upon increasing n but the scf width ³⁸⁰ of the dead zone decreases compared to the theoretical z_0 .

However, in spite of all of the discrepancies, the two-layer 381 382 model is capable of adequately reproducing the behavior of the 383 elastic free energy in convex brushes of comb-shaped polymers. 384 Notably, the latter is of utmost important for the subsequent 385 analysis of microphase segregation. In Figure 5, we present the 386 elastic free energy F_{el} per molecule as a function of R_i/D_i in the 387 cylindrical (i = 2) and spherical (i = 3) convex solvent-free 388 brushes formed by loops with a fixed backbone DP M = 400. 389 The solid lines indicate the scf numerical data, while the 390 dashed lines are calculated according eq 17 (two-layer model). ³⁹¹ In both plots, the grafting density $\sigma = 0.1$, m = 2, and variations $_{392}$ in *n* lead to the corresponding decrease in the backbone DP M 393 = N/(1 + n/m). As shown in Figure 5, the difference between 394 the analytical and the numerical values of F_{el} is reasonably 395 small which justifies the applicability of the two-layer model of 396 the matrix in curved geometries.

3. MICROPHASE-SEGREGATED MELT OF ABA 397 COPOLYMER: TWO-LAYER MODEL OF THE 398 MATRIX

³⁹⁹ Let triblock copolymer *ABA* have DP N_A of blocks *A* and DP ⁴⁰⁰ $2N_B$ of the central block *B*. The structural parameters v_j , l_j of ⁴⁰¹ the monomer units in the blocks and Kuhn segments b_j (j = A, ⁴⁰² *B*), specify the ratio³⁶

$$\beta = \frac{l_A b_A v_B}{l_B b_B v_A} \tag{18}_{403}$$

Transformation of the *ABA* triblock copolymer in two diblock 404 copolymer molecules *AB* with DP N_B of block *B* does not 405 significantly change the equilibrium parameters of the *A* 406 domains and *B* matrix in the strong segregation limit as the 407 account of bridging invokes only minor correction to the free 408 energy of the *B* block. For example, in a planar case (*i* = 1), the 409 relative increase in the elastic free energy of the *B* block due to 410 the presence of $X_{B,1}$ bridges per grafting area s_1 is estimated as 411 $O(X_{B,1}^4) < 1\%$ at the maximal value of $X_{B,1} = 0.5$.⁴⁵ However, 412 the development of dead zones in cylindrical and spherical 413 morphologies might more strongly affect the elastic free energy 414 of *B* blocks (as well as the sizes of *A* domains), and we adopt 415 the two-layer model of convex brushes to describe the *B* 416 matrix.

3.1. Elastic Free Energy of Comb-Shaped Block B. If N 418 and R_i introduced in the previous section are assimilated to DP 419 N_B of block *B* in the *AB* diblock copolymer and radius of the *A* 420 domain then the grafting area s_i per chain is related to the 421 domain radius R_i as 422

$$s_i = i N_A v_A / R_i \tag{19}_{423}$$

and the total elastic free energy of the *B* block in the two-layer 424 model is formulated as 425

$$\frac{F_{B,i}}{k_{\rm B}T} = \frac{R_i^2}{l_A b_A N_A} \beta \eta_{\rm B}^2 c_i(\omega_i, y_i)$$
(20) 426

with

$$c_{3}(\omega_{3}, y_{3}) = \begin{cases} \frac{1}{2} \frac{\omega_{3}y_{3}}{1 + \omega_{3}y_{3}} + \frac{9\pi^{2}}{8} \omega_{3}^{3}(1 - y_{3})^{3} \frac{\left[(1 + y_{3}\omega_{3})^{2}/3 + \omega_{3}(1 + y_{3}\omega_{3})(1 - y_{3})/2 + \omega_{3}^{2}(1 - y_{3})^{2}/5\right]}{\left[(1 + \omega_{3})^{3} - (1 + \omega_{3}y_{3})^{3}\right]^{2}} & \omega_{3} > \omega_{3,0} \\ \frac{9\pi^{2}}{8} \omega_{3}^{3} \frac{\left[1/3 + \omega_{3}/2 + \omega_{3}^{2}/5\right]}{\left[(1 + \omega_{3})^{3} - 1\right]^{2}} & \omega_{3} < \omega_{3,0} \end{cases}$$

$$(21)$$

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f5

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$$c_{2}(\omega_{2}, y_{2}) = \begin{cases} \frac{3}{4} \ln(1 + \omega_{2}y_{2}) + \frac{3\pi^{2}}{4} \omega_{2}^{3}(1 - y_{2})^{3} \frac{\left[(1 + y_{2}\omega_{2})/3 + \omega_{2}(1 - y_{2})/4\right]}{\left[(1 + \omega_{2})^{2} - (1 + \omega_{2}y_{2})^{2}\right]^{2}} & \omega_{2} > \omega_{2,0} \\ \frac{3\pi^{2}}{4} \omega_{2}^{3} \frac{\left[1/3 + \omega_{2}/4\right]}{\left[(1 + \omega_{2})^{2} - 1\right]^{2}} & \omega_{2} < \omega_{2,0} \end{cases}$$

$$(22)$$

and

432 433

434 Here, y_i is related to ω_i via eqs 11 and 12 and $\omega_{i,0}$ is specified in 435 eq 13.

3.2. Free Energy per *AB* **Block Copolymer Molecule.**

Compared to the free energy of the diblock copolymer

calculated in the SS-SCF approximation,³⁶ the free energy F_i ⁴³⁸ per diblock *AB* copolymer in the two-layer model of the *B*

⁴³⁹

440 matrix is reformulated as

 $\frac{F_{i}}{k_{\rm B}T} = \frac{F_{A/B}}{k_{\rm B}T} + \frac{F_{A,i}}{k_{\rm B}T} + \frac{F_{B,i}}{k_{\rm B}T}$ $= \frac{i\gamma N_{\rm A}v_{\rm A}}{l_{\rm A}^{2}R_{i}} + \frac{R_{i}^{2}}{l_{\rm A}b_{\rm A}N_{\rm A}} [b_{i}\eta_{\rm A}^{2} + \beta\eta_{\rm B}^{2}c_{i}(\omega_{i}, y_{i})]$ (23) 441

with the numerical coefficients

427

431

$$\mathbf{b}_{i} = \begin{cases} \pi^{2}/8, & i = 1 \\ \pi^{2}/16, & i = 2 \\ 3\pi^{2}/80, & i = 3 \end{cases}$$
(24)

444 and functions c_i specified by eqs 21 and 22. Here, the surface 445 free energy $F_{A/B}$ and the elastic free energy $F_{A,i}$ of the domain-446 forming block A are not changed, while $F_{B,i}$ is modified to account for the dead zone. 447

Introduction of volumes $V_i = v_i N_i$ (i = A, B) and the ratio 448

$$x = \frac{V_B}{V_A} = \frac{v_B N_B}{v_A N_A}$$
(25)

relates x to ω_i as

450

$$\omega_i(x) = (1+x)^{1/i} - 1 \tag{26}_{451}$$

and $y_i(\omega_i)$ and $c_i(\omega_i, y_i)$ in eqs 21 and 22 become functions of x 452 as 453

$$y_i(\omega_i) \to y_i(x) \text{ and } c_i(\omega_i, y_i) = G_i(x)$$
 (27) 452

At a small curvature of A domains ($\omega_i < \omega_{i,0}$, no dead zones 455 in the B matrix), functions $G_i(x)$ coincide with the 456 morphology-dependent functions $g_i(x)$ calculated in the 457 parabolic potential framework³⁶ 458

$$G_{i}(x) = g_{i}(x) = \frac{\pi^{2}}{8} \begin{cases} x, & i = 1 \\ 6x^{-2}[(1+x)^{1/2} - 1]^{4} \left[\frac{1}{4} + \frac{1}{3}[(1+x)^{1/2} - 1]^{-1}\right], & i = 2 \\ 9x^{-2}[(1+x)^{1/3} - 1]^{5} \left[\frac{1}{5} + \frac{1}{2}[(1+x)^{1/3} - 1]^{-1} + \frac{1}{3}[(1+x)^{1/3} - 1]^{-2}\right], & i = 3 \end{cases}$$
(28)

459 460

443

461 while at a large curvature of A domains (i.e., at $\omega_i > \omega_{i,0}$) 462 functions $G_i(x)$ are specified by eqs 26, 12, 11, 22,21, and 27. Notably, due to the absence of a curvature-induced dead zone 463 in a planar morphology (i = 1), $G_1(x) \equiv g_1(x)$ at any x. 464 Minimization of F_i with respect to R_i in eq 23 gives 465

$$R_{i} = \left(\frac{i\gamma N_{A}^{2} v_{A} b_{A}}{2\Phi_{i}(x) l_{A}}\right)^{1/3}; D_{i} = R_{i}[(1+x)^{1/i} - 1], i = 1, 2, 3$$
(29)

466

468

480

467 and

$$\frac{F_i}{k_{\rm B}T} = 3\left(\frac{i}{2}\right)^{2/3} N_A^{1/3} \Phi_i(x)^{1/3} \left(\frac{\gamma^{2/3} v_A^{2/3}}{l_A^{5/3} b_A^{1/3}}\right)$$
(30)

469 with

$$_{470} \quad \Phi_i(x) = b_i \eta_A^2 + \beta \eta_B^2 G_i(x) \tag{31}$$

4. FRACTION OF BRIDGES IN MESOPHASES OF ABA **BLOCK COPOLYMER** 471

472 To estimate the equilibrium fraction $X_{B,i}$ of bridging comb-473 shaped B blocks in spherical (i = 3) and cylindrical (i = 2)⁴⁷⁴ morphologies, we use the previously implemented approach⁴⁷ 475 to calculate fraction $X_{B,1}$ of the bridges in lamellae (i = 1). As 476 we demonstrated earlier,⁴⁷ the equilibrium fraction of bridges 477 formed by blocks B in a planar geometry (i = 1) is related to 478 the elastic free energy $F_{B,1}(x)$ of B subchains (that is, loops cut 479 into two equal parts) as

$$X_{B,1} \approx \frac{1}{1 + \left(1 + \frac{72}{\pi^4} \frac{F_{B,1}(x)}{k_B T}\right)^{1/3}}$$
(32)

481 Here, the elastic free energy per B subchain with DP N_B is 482 specified as³⁶

$$\frac{F_{B,1}(x)}{k_{B}T} = \frac{\pi^{2}}{8} \eta_{B}^{2} \frac{D_{1}^{2}}{l_{B}b_{B}N_{B}} = \frac{\pi^{2}}{8} x\beta \eta_{B}^{2} \frac{R_{1}^{2}}{l_{A}b_{A}N_{A}} = \frac{\pi^{2}}{8} x\beta \eta_{B}^{2} N_{A}^{1/3} \frac{1}{2^{2/3}} \left(\frac{\gamma^{2/3} v_{A}^{2/3}}{l_{A}^{1/3} b_{A}^{5/3}} \right) \left(\frac{\pi^{2}}{8} + \frac{\pi^{2}}{8} \beta \eta_{B}^{2} x \right)^{-2/3}$$
(33) 48.

In contrast to lamellae, the free ends of B subchains in 484 nonplanar morphologies are distributed only in the peripheral 485 layers while the segments of B subchains in dead zones are 486 stretched equally. Therefore, the difference in the elastic free 487 energies of loops and bridges is associated merely with the 488 difference in the free energies of segments of B subchains with 489 free and pinched end points at the outer boundary of the 490 peripheral layer (edge of the Wigner-Seitz cell). 491

In the two-layer model, the peripheral layers in spherical (i = 492)3) and cylindrical (i = 2) morphologies are assimilated to 493 planar brushes of subchains with DP $N_{\rm B,out}$ 494

$$N_{B,\text{out}} = \left[\left(1 + \frac{D_i}{R_i} \right)^i - \left(1 + \frac{z_0}{R_i} \right)^i \right] \frac{s_i R_i}{iv}$$
(34) 495

tethered with area $s_{\text{eff}} = \frac{\pi^2}{8} s_i (1 + z_0/R_i)^{i-1}$. The elastic free 496 energy $\Delta F_{B,i}(x)$ of chain segments in the peripheral layer with 497 thickness $(D_i - z_0)$ is formulated (see SI) as 498

.

$$\frac{\Delta F_{B,i}(x)}{k_{\rm B}T} = \frac{\pi^2}{8} \eta_B^2 \frac{(D_i - z_0)^2}{l_B b_B N_{B,out}} = \frac{\pi^2}{8} \eta_B^2 \frac{(D_i - z_0) v_B}{l_B b_B s_{eff}} = \eta_B^2 \frac{(D_i - z_0) v_B}{l_B b_B s_i (1 + z_0/R_i)^{i-1}}$$
(35) 499

Using eq 19 for surface area s_i per molecule in morphology i 500 and eq 29 one finds 501

$$\frac{\Delta F_{B,i}(x)}{k_{\rm B}T} = \beta \eta_{\rm B}^2 \left(\frac{\gamma^{2/3} v_A^{2/3}}{b_A^{5/3} l_A^{1/3}} \right) N_A^{1/3} \begin{cases} \frac{\omega_2 (1-y_2)}{2[1+\omega_2(x)y_2(x)]} \left[\frac{\pi^2}{16} + \beta n_{\rm B}^2 G_2(x) \right]^{-2/3} & i=2\\ \frac{\omega_3 (1-y_3)}{(12)^{1/3} [1+\omega_3(x)y_3(x)]^2} \left[\frac{3\pi^2}{80} + \beta n_{\rm B}^2 G_3(x) \right]^{-2/3} & i=3 \end{cases}$$
(36)

502 503

504 The equilibrium fraction $X_{B,i}$ of bridges in spherical (i = 3) and 505 cylindrical (i = 2) morphologies of the *ABA* copolymer is then 506 evaluated as

$$X_{B,i} \approx \frac{1}{1 + \left(1 + \frac{72}{\pi^4} \frac{\Delta F_{B,i}(x)}{k_{\rm B}T}\right)^{1/3}}, i = 2, 3$$

507 (37)

When the dead zone is absent (i.e., $z_0 = 0$), $\Delta F_{B,i}(x)$ reduces ⁵⁰⁸ to the elastic free energy of *B* subchains in a planar layer with ⁵⁰⁹ effective grafting area $s_{\text{eff}} = s_i(\pi^2/8)$ for i = 2, 3 and $s_{\text{eff}} = s_1$ for i_{510} = 1, calculated in the parabolic potential framework ⁵¹¹

$$\left(\frac{\Delta F_{B,i}(x)}{k_{B}T}\right)_{z_{0}=0} = \beta \eta_{B}^{2} N_{A}^{1/3} \left(\frac{\gamma^{2/3} v_{A}^{2/3}}{b_{A}^{5/3} l_{A}^{1/3}}\right) \left\{\frac{\frac{\pi^{2}}{2^{10/3}} x \left[\frac{\pi^{2}}{8} + \beta \eta_{B}^{2} g_{1}(x)\right]^{-2/3}}{16} + \beta n_{B}^{2} g_{2}(x)\right]^{-2/3} \quad i = 1$$

$$\left(\frac{1}{2} \left[(1+x)^{1/2} - 1\right] \left[\frac{\pi^{2}}{16} + \beta n_{B}^{2} g_{2}(x)\right]^{-2/3} \quad i = 2$$

$$\left(\frac{1}{(12)^{1/3}} \left[(1+x)^{1/3} - 1\right] \left[\frac{3\pi^{2}}{80} + \beta n_{B}^{2} g_{3}(x)\right]^{-2/3} \quad i = 3$$

$$(38)$$

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513

514 with $g_i(x)$ specified in eq 28.

Using eq 37 with $\Delta F_{B,i}(x)$ formulated in eq 36 for $z_0 > 0$ or s_{16} eq 38 for $z_0 = 0$, one finds the equilibrium fraction $X_{B,i}$ of B s_{17} bridges in planar, cylindrical, and spherical morphologies. The s_{18} latter is an important factor in the mechanical properties of s_{19} microphase-segregated melts. Notably, in all three morpholo s_{20} gies, the two-layer model predicts a larger elastic free energy of s_{21} bridges compared to loops, making $X_{B,i} < 0.5$.

In Figure 6, we present the equilibrium fraction $X_{B,i}$ of B 522 523 bridges as a function of the volume fraction f_B of the B $_{524}$ component for two values of N_A . Triangles indicate a spherical 525 morphology and squares a cylindrical one. In the absence of a 526 dead zone (to the left of f_B indicated by arrow), an increase in $_{527} f_B$ leads to the decrease in fractions of bridges, $X_{B,2}$ and $X_{B,3}$. 528 The onset of the dead zone in a spherical morphology 529 (indicated by arrow), and further increase in the extension of 530 the dead zone with increasing f_B leads to the increase in $X_{B,3}$ 531 due to progressive accumulation of the free ends of B 532 subchains closer to the boundaries of Wigner-Seitz cells. 533 Therefore, according to the two-layer model, the equilibrium ₅₃₄ fraction $X_{B,i}$ of bridges in cylindrical (i = 2) and spherical (i =535 3) geometries passes through a minimum upon the onset of a 536 dead zone. Notably, a kink in $X_{B,i}$ at the onset of a dead zone is 537 related to approximations imposed in the two-layer model to 538 find z_0 . We anticipate that rigorously calculated z_0 would 539 smooth the kink while preserving the minimum in $X_{B,i}(f_B)$ 540 dependence.

In Figure 7, the equilibrium fraction of bridges $X_{B,i}$ is 542 presented as a function of f_B for triblock copolymers with N_A = 543 100 and different topological ratios for *B* blocks, η_B = 2 (Figure 544 7a) and η_B = 5 (Figure 7b). Transitions between morphologies 545 are accompanied by jumps in $X_{B,i}$. As shown in Figures 6 and 7, according to the two-layer model, fraction $X_{B,3}$ of bridges 546 approaches 0.5 at $f_B \rightarrow 1$ and weakly depends of η_B . 547

The predicted trends in the behavior of $X_{B,3}$ are consistent 548 with MD simulations^{50,51} of self-assembling ABA networks 549 with spherical domains. Both the simulations and the two-layer 550 model predict the decrease in $X_{B,3}$ upon increasing N_A and the 551 increase in fraction $X_{B,3}$ of bridges upon increasing $f_B \approx N_B = 552$ $M_B(1 + n_B/m_B)$. However, MD simulations of dry networks⁵⁰ 553 revealed the values of $X_{B,3} > 0.5$, pointing at a smaller elastic 554 free energy of bridges compared to loops, while the two-layer 555 model predicts $X_{B,3}$ < 0.5. The discrepancy could arise due to 556 relatively short copolymer blocks in MD simulations.⁵⁰ The 557 short backbones in microphase-segregated structures are more 558 stretched than long ones, decreasing the difference between 559 the elastic free energies of loops and bridges. The filling 560 constraints ($\varphi_B = 1$ everywhere in *B* matrix) and penalties due 561 to backward turns in the stretched loops might favor a bridging 562 conformation of the *B* block, leading to $X_{B,3} > 0.5$. However, 563 the MD simulations of self-assembling ABA networks with 564 swollen in solvent *B* blocks⁵¹ indicated $X_{B,3} < 0.5$ and were also 565 consistent with the predicted increase in fraction $X_{B,3}$ of 566 bridges upon increasing f_B . 567 f6f7

5. BINODALS IN THE TWO-LAYER MODEL OF THE B MATRIX

In the cylindrical geometry (i = 2), the dead zone in the *B* layer 569 emerges at $x = x_{0,2} \approx 1.153$ (or equivalently at $f_B = f_{2,0} \approx 570$ 0.536), while for spheres (i = 3), the onset of the dead zone is 571 shifted to $x_{0,3} \approx 0.806$ (or $f_B = f_{0,3} \approx 0.446$). Therefore, 572 depending on the ratio $x = V_B/V_A$, equations for binodals $Y_{\rm LC}$ 573 and $Y_{\rm CS}$ (specified, respectively, as $F_1 = F_2$ and $F_2 = F_3$) are 574 modified in the two-layer model as

568



Figure 6. Equilibrium fraction $X_{B,i}$ of *B* bridges in cylindrical (C) and spherical (S) morphologies formed by *ABA* triblock copolymer with linear *A* and comb-shaped *B* blocks as a function of volume fraction f_B of the *B* component for two values of N_A (indicated near the curves). $\eta_B = 5$, $\eta_A = 1$. Squares correspond to cylinders (i = 2) and triangles to spheres (i = 3). Onset of dead zone occurs in spherical morphology at $f_B = f_{0,3} = 0.446$ shown by arrow. In shaded area, chain segments in the peripheral layer loose stretching.

$$Y_{LC} = \beta^{1/2} \left(\frac{\eta_B}{\eta_A} \right)_{LC}$$

= $\sqrt{4b_2 - b_1} \cdot \begin{cases} 1/\sqrt{g_1(x) - 4g_2(x)} & x < x_{0,2} = 1.153 \\ 1/\sqrt{g_1(x) - 4G_2(x)} & x > x_{0,2} \end{cases}$ (39)

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¥

$$Y_{CS} = \beta^{1/2} \left(\frac{\eta_B}{\eta_A} \right)_{CS}$$

$$= \sqrt{9b_3 - 4b_2} \cdot \begin{cases} 1/\sqrt{4g_2(x) - 9g_3(x)} & x < x_{0,3} = 0.806 \\ 1/\sqrt{4g_2(x) - 9G_3(x)} & x_{0,2} > x > x_{0,3} \\ 1/\sqrt{4G_2(x) - 9G_3(x)} & x > x_{0,2} \end{cases}$$
(40)

577





Figure 7. Equilibrium fraction $X_{B,i}$ of *B* bridges in lamellar (L), cylindrical (C), and spherical (S) morphologies formed by triblock *ABA* copolymer with linear *A* and comblike *B* blocks as a function of volume fraction f_B of the *B* component for $\eta_B = 2$ (a) and $\eta_B = 5$ (b), $\eta_A = 1$. Diamonds correspond to lamellae (*i* = 1), squares to cylinders (*i* = 2), and triangles to spheres (*i* = 3). Onsets of dead zone $f_B = f_{0,2} = 0.54$ for *i* = 2 and $f_B = f_{0,3} = 0.45$ for *i* = 3 are shown by arrows. Transitions between morphologies are accompanied by jumps in $X_{B,i}$.

points of linear *B* blocks in lamellae and fixed end points of *B* 597 blocks in cylindrical and spherical morphologies. In the case of 598 fixed end points of linear *B* blocks in lamellae, $f_{\rm LC}$ decreases to 599 $f_{\rm LC} \approx 0.615$.

Branching of *B* blocks and an increase in η_B lead to 601 progressive deviations of Y'_{LC} , Y''_{LC} from $Y_{LC,par}$ and Y'_{CS} from 602 $Y_{CS,par}$. If the end points of the *B* backbones in the lamellar 603 morphology remain free, the L–C binodal Y''_{LC} intersects Y'_{CS} at 604 $\eta_B \approx 3$, indicating destabilization of the cylindrical morphol- 605 ogy. This discrepancy is directly related to different 606 approximations for end-point distributions of backbones in 607 planar (i = 1) and nonplanar (i = 2, 3) morphologies. If the 608 end points of backbones in the *B* layers are fixed at the outer 609 boundaries of the Wigner–Seitz cells in all of the geometries 610 (including lamellae) then the L–C binodal Y'_{LC} is located 611 below $Y_{LC,par}$, providing the corridor of stability for the 612 cylindrical morphology. 613

Clearly, the L–C binodal $Y_{\rm LC}$ calculated with the two-layer 614 model of the *B* matrix must be located between $Y_{\rm LC,par}$ (no 615 dead zone, $z_0 = 0$) and $Y''_{\rm LC}$ (dead zone extends to the whole *B* 616 layer, $z_0 = D_2$), being closer to $Y''_{\rm LC}$ at $f_B \leq f_{CL} \approx 0.717$ and 617 approaching $Y_{\rm LC,par}$ upon decreasing f_B (and concomitant 618



Figure 8. Binodals $Y = \beta^{1/2} \eta_B / \eta_A$ separating spherical (S), cylindrical (C), and lamellar (L) morphologies as a function of $f_B = V_B / (V_A + V_B)$, calculated with a parabolic potential framework $(Y_{CS,par'}, Y_{LC,par'})$ shown by solid lines) and an extended Semenov model $(Y'_{CS}, Y'_{LC}, shown by triangles)$. Y''_{LC} (line with unfilled circles) indicates binodal between lamellae with unrestricted free ends of *B* backbones and cylinders with ends of *B* backbones fixed at the outer boundary of the Wigner–Zeit cell. Intersections of binodals with the black line $\beta^{1/2} \eta_B / \eta_A = 1$ correspond to morphological transitions in topologically symmetrical (including linear–linear) block copolymers. Binodals for inverted structures (*B* domains in the *A* matrix) are not shown.

619 decrease in z_0), that is, $Y_{\rm LC}$ should shift to the right of $Y_{\rm LC,par}$ 620 due to the presence of a dead zone. A similar shift to the right 621 of $Y_{\rm CS,par}$ is expected for C–S binodal $Y_{\rm CS}$ due to larger 622 extension of the dead zone in the spherical morphology.

- In Figure 9, we present L-C and C-S binodals as a function 623 624 of volume fraction $f_B = V_B/(V_A + V_B)$ of the B component, 625 calculated with the two-layer model of the B matrix (eqs 39 626 and 40). Solid lines indicate binodals $Y_{\rm LC,par}$ and $\hat{Y}_{\rm CS,par}$ 627 obtained in the parabolic potential framework³⁶ (first lines in 628 eqs 39 and 40, extended to all x). Symbols (crosses) indicate 629 sections of binodals Y_{LC} and Y_{CS} corrected for dead zones, i.e., 630 emerging at $f_B > f_{0,2} \approx 0.536$ for i = 2 (the second line in eq 631 39), and $f_B > f_{0,3} \approx 0.446$ for i = 3 (the second and third lines 632 in eq 40). The values of $f_{0,2}$ and $f_{0,3}$ do not depend on the ⁶³³ modes of branching of the *B* blocks (i.e., do not depend on η_B) 634 and are shown by arrows. Clearly, deviations of corrected 635 binodals from $Y_{LC,par}$ and $Y_{CS,par}$ are small (numerical estimates 636 are presented in the SI). Although the two-layer model ignores 637 the presence of a curvature-induced dead zone at $f_B < f_{0,2}$ and $_{638} f_B < f_{0,3}$, we believe that corrections to $Y_{LC,par}$ and $Y_{CS,par}$ $_{639}$ remain small there as well due to an exponential decrease $_{39}^{39}$ in 640 the width of the dead zone at small curvatures.
- f10f11

641 In Figures 10 and 11, we present ratios $r_i(\eta_B, x) = R_{i,par}/R_i$ of 642 the domain radius $R_{i,par}$ calculated using the parabolic potential 643 framework and R_i calculated with the two-layer model of the *B* 644 matrix for spherical (i = 3) and cylindrical (i = 2)645 morphologies, respectively, as a function of $f_B = x/(1 + x) =$ 646 $v_B N_B/(v_A N_A + v_B N_B)$. As shown in Figure 11, the two-layer 647 model predicts almost no affect of dead zone on r_2 in the range 648 of stability of cylindrical domains: $R_{2,par}$ exceeds R_2 by less than 649 1%. The effect of dead zones on R_3 is stronger. An increase in 650 ratio $r_3 = R_{3,par}/R_3$ in the range of $f_B < 0.9$ in Figure 10 651 indicates the decrease in R_3 by less than ~2%. At larger $f_B >$ 652 0.9, the radius of the *A* domain R_3 declines sharply. However, 653 progressive branching of *B* blocks (i.e., an increase in η_B) shifts



Figure 9. Binodals separating spherical (S), cylindrical (C), and lamellar (L) morphologies calculated with a parabolic potential framework (solid lines) and with a two-layer model (crosses). Arrows indicate block copolymer compositions, $f_{0,3} = 0.446$ and $f_{0,2} = 0.536$ corresponding to the onset of dead zone formation in the two-layer model. At $f_B < f_{0,3}$ (white area), no dead zones in the *B* layers, at $f_{0,3} < f_B < f_{0,2}$, dead zones emerge only in spherical morphology (dark gray area), while at $f_B > f_{0,2}$, dead zones emerge in both cylindrical and spherical morphologies (light gray area). (Inset) Relative width $y_i = z_0/D_i$ of dead zones in spherical (i = 3) and cylindrical (i = 2) *B* layers. Intersections of binodals with the black line $\beta^{1/2}\eta_B/\eta_A = 1$ correspond to morphological transitions in topologically symmetrical (including linear–linear) block copolymers. Binodals for inverted structures (*B* domains in *A* matrix) are not shown.



Figure 10. Ratio $r_3 = R_{3,par}/R_3$ of spherical domain radii calculated with a parabolic potential $(R_{3,par})$ and two-layer model (R_3) as a function of diblock copolymer composition f_B and topological ratio η_B of matrix block $\eta_A = 1$, $\beta = 1$. Onsets of thermodynamic stability for spherical morphology are indicated by arrows: $f_B = 0.525$, 0.666, and 0.883 for $\eta_B = 3$, 2, and 1, respectively. For $\eta_B = 5$, arrow at $f_B = 0.366$ is not shown. To the right of each arrow spherical domains are stable and to the left metastable.

the onset of stability of spherical domains (indicated by arrows 654 in Figure 10) to smaller values of f_B , providing a wider interval 655 of stability for the spherical morphology. Therefore, the 656 difference between $R_{3,par}$ and R_3 in a wide range of $f_B \leq 0.97$ is 657 predicted to be less than 10%, supporting the application of the 658 SS-SCF framework to calculate the equilibrium parameters of 659 the spherical and cylindrical domains.



Figure 11. Ratio $r_2 = R_{2,par}/R_2$ of cylindrical domain radii calculated with a parabolic potential $(R_{2,par})$ and two-layer model (R_2) as a function of diblock copolymer composition f_B and topological ratio η_B of matrix block $\eta_A = 1$, $\beta = 1$. Cylinders are thermodynamically stable between the two arrows located at $f_B = 0.701$ and 0.883 for $\eta_B = 1$ and to the left of the arrow at $f_B = 0.666$ for $\eta_B = 2$. No thermodynamically stable cylinders at $f_B > 0.5$ for $\eta_B = 3$ and $\eta_B = 5$.

6. COMPARISON TO EXPERIMENTS

⁶⁶¹ In our previous publication³⁶ we checked the predicted ⁶⁶² exponent 2/3 in the molecular mass dependence of the ⁶⁶³ domain size, $R_i(N_A)$, for sets of chemically different *AB* and ⁶⁶⁴ *ABA* copolymers with bottlebrush *B* blocks. Here, we perform ⁶⁶⁵ a more refined comparison between the theoretical predictions ⁶⁶⁶ and the experimental data.

667 Microphase-segregated triblock *ABA* copolymers, PMMA– 668 PDMS–PMMA, with bottlebrush PDMS and linear PMMA 669 blocks were experimentally examined in the series of papers by 670 Sheiko et al.^{16,19,49} These copolymers had high volume 671 fractions f_B of PDMS (*B* component) and gave rise to 672 spherical PMMA domains in the PDMS matrix upon 673 evaporation of nonselective solvent toluene. The data for 674 series of samples with $m_B = 1$ and $n_B = 14$ and 70 are collected 675 in Table S1 in the SI in the upper and lower panels, 676 respectively.

In localizing these copolymers in the morphological diagram 677 678 of states³⁶ we treated the PDMS block as a bottlebrush 679 polymer with $q_B = 1$ and $\beta \approx 1.26$ for the PDMS/PMMA pair, 680 that is, the PDMS block was envisioned as a linear chain of N_0 ⁶⁸¹ impermeable superblobs with radius $r_0 = (l_B b_B n_B)^{1/2}$ and ⁶⁸² effective Kuhn length $\simeq r_0$.⁵² While the backbone in each 683 superblob is strongly elongated, the bottlebrush conformations 684 in the melts remain Gaussian on larger scales with the ₆₈₅ backbone average end-to-end distance $R_0 \simeq r_0 N_0^{1/2}$. On the 686 basis of this model, the topological coefficient η_B for the PDMS 687 block with $n_B = 14$ was estimated via eq 8 with the numerical 688 coefficient $\alpha_B = 0.5$ to give $\eta_B \approx 1.13$ and position $\beta^{1/2} \eta_B \approx$ 689 1.27 for this PMMA-PDMS-PMMA series in the morpho-690 logical diagram.³⁶ Notably, $\alpha_{\rm B}$ served as an adjustable 691 parameter to match the theoretical value of the C-S binodal 692 to the experimental volume fraction $f_B \approx 0.82$, corresponding 693 to first detection of PMMA domains with nonspherical 694 geometry.

It should be emphasized, however, that superblob impermeability arises due to conformational losses associated with extra stretching of the side chains upon superblob interpenetration. Therefore, the concept of an impermeable superblob becomes progressively more accurate for barbwire polymers with $m_B = 1$ and increasing $q_B > 1$, i.e., with side 700 chains stretching beyond the Gaussian size, r_0 . The superblobs 701 in conventional bottlebrushes with $q_B = 1$ still experience 702 interpenetration, and estimation of m_{B^*} according to eq 7 for 703 the PDMS parameters ($v_B = 136 \text{ Å}^3$, $l_B = 2.5 \text{ Å}$, $b_A = 13 \text{ Å}$) 704 gives $m_{B^*} \simeq 0.67$ for $n_B = 14$ and $m_{B^*} \approx 1.51$ for $n_B = 70$. 705 Therefore, according to eq 7, experimental PDMS blocks with 706 $m_{B^*} \simeq 1$ are found at the crossover between comblike and 707 bottlebrush regimes.

An alternative option in analyzing the experimental data is to 709 use η_B corresponding to the scale-independent Gaussian 710 elasticity of the backbone in the *B* block. In this scenario, 711 $\eta_B \approx (1 + n_B/m_B)^{1/2}$ for comb-shaped blocks with long 712 backbones yielding $\eta_B \approx 3.87$ for $m_B = 1$ and 14. Below, we 713 use both expressions for η_B (eqs 5 and 8) in confronting the 714 theoretical predictions to the experimental data. Due to large 715 content of PDMS in the PMMA–PDMS-PMMA block 716 copolymers ($f_B > 0.8$), we apply the two-layer model of the 717 *B* matrix to calculate the equilibrium radius R_3 of the *A* domain 718 (eqs 29 and 31 for i = 3).

The structural parameters of the microphase-segregated melt 720 of PMMA–PDMS–PMMA (*ABA*) copolymer with a spherical 721 morphology^{16,19,49} are collected in Table S1 in the SI. The 722 experimentally measured¹⁹ radius $R_3^{exp}(\text{Å})$ of the PMMA A 723 domains in a series of samples with $n_B = 14$ (upper panel in 724 Table S1) is presented in Figure 12 as a function of DP N_A of 725 fil2



Figure 12. Radii $R_3(Å)$ of the *A* domain in a microphase-segregated melt of triblock copolymer *ABA* with molecular brush *B* block as a function of DP N_A of linear block *A*. In the *B* block, $n_B = 14$, $m_B = 1$, $\beta = 1.26$. Experimental R_3 for PMMA–PDMS–PMMA copolymers^{16,49} are indicated by diamonds with error bars. Red filled triangles indicate theoretically calculated R_3 (eq 29) for the *B* block treated as a bottlebrush with $\eta_B = 1.13$; blue filled triangles correspond to treatment of the *B* block as comblike with $\eta_B = (1 + n_B/m_B)^{1/2} = 15^{1/2}$ in the two-layer model. Unfilled triangles indicate theoretical values of R_3 in the SS-SCF parabolic potential framework.

the PMMA block (black diamonds with error bars). Filled 726 triangles indicate R_3^{theor} calculated according to eqs 29 and 31 727 with $\eta_B = 1.13$ and 3.87, respectively, for values of parameters γ 728 = 0.37,⁴⁴ β = 1.26, v_A = 141 Å ³, l_A = 2.5 Å, and b_A = 17 Å. 729 Unfilled blue triangles indicate R_3^{theor} calculated in the 730 parabolic SS-SCF approximation (eqs 29 and 31 with G_3 = 731 g_3). As shown in Figure 12, modeling the PDMS block *B* as a 732 bottlebrush polymer, i.e., as a linear chain of impermeable 733

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⁷³⁴ superblobs with $\eta_B = 1.13$ (red filled triangles), strongly ⁷³⁵ overestimates the domain radius R_3^{exp} , while the scale-⁷³⁶ independent Gaussian backbone elasticity ($\eta_B = 3.87$, blue ⁷³⁷ filled triangles) leads to a better correspondence with the ⁷³⁸ experimental data. The difference between filled and unfilled ⁷³⁹ blue triangles (i.e., between predictions of the SS-SCF model ⁷⁴⁰ and the two-layer model) is minor.



Figure 13. Radii $R_3(\text{Å})$ of *A* domains in a microphase-segregated melt of triblock copolymer *ABA* with a comb-shaped *B* block with $n_B = 70$ as a function of DP N_A of a linear block. Experimental radii R_3 , exp are shown by diamonds. Theoretical values of R_3 calculated with the SS-SCF parabolic potential framework and the extended Semenov's model are indicated by filled and unfilled triangles, respectively. *B* blocks were treated as comblike polymers with $\eta_B = (1 + n_B/m_B)^{1/2}$ and $m_B = 1$.

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In Figure 13, we compare R_3^{exp} for PMMA–PDMS-PMMA r42 samples with $n_B = 70$ (diamonds) to the theoretically predicted r43 R_3^{theor} calculated according to eqs 29 and 31 with $\eta_B = (1 + 744 \ 70)^{1/2} \approx 8.43$ (triangles). Similarly to the series with $n_B = 14$ r45 (Figure 12), modeling the *B* block as a linear chain of r46 impermeable superblobs considerably overestimates R_3^{exp} (not r47 shown in Figure 13). Notably, in both series, the backbones in r48 the *B* blocks are strongly elongated, even approaching the r49 backbone contour length in some samples with $n_B = 70$. r50 However, the two-layer model partially compensates for the r51 nonlinear elasticity of the backbones via overestimated r52 elongation near the surfaces of the *A* domains (see SI).

753 In Figure 14, we present the normalized domain radius $R_{\text{norm}} = \left(\frac{2\Phi_3(x)l_A}{3\gamma v_A b_A}\right)^{1/3} R_3^{\exp}$ as a function of N_A . The data for 755 samples with stronger stretched backbones ($n_B = 70$, unfilled 756 symbols) and less stretched backbones ($n_B = 14$, filled 757 symbols) fall predominantly above and below the theoretical 758 asymptote, $R_{\text{norm}}^{\text{theor}} = N_A^{2/3}$ (shown by the straight line with 759 slope 2/3). One would expect that samples with stronger 760 elongated backbones (i.e., series with $n_B = 70$) would deviate 761 below $R_{\text{norm}}^{\text{theor}}$ due to smaller values of the equilibrium domain 762 radius. In contrast, the majority of samples with $n_B = 70$ 763 demonstrate a larger domain radius than predicted by the two-764 layer model. The deviations of the data for $n_B = 70$ above the 765 theoretical asymptore $R_{\text{norm}}^{\text{theor}}$ correlate with the shift from a 766 comblike to a bottlebrush regime for the *B* block upon



Figure 14. Normalized radius $R_{\text{norm}} = R_3^{(\text{exp})} [(2l_A \Phi_3)/(3\gamma v_A b_A)]^{1/3}$ of the *A* domain in a microphase-segregated melt of triblock copolymer *ABA* with molecular brush *B* block as a function of DP N_A of the linear block. Topological ratio for *B* blocks was calculated as $\eta_B = (1 + n_B/m_B)^{1/2}$ with $m_B = 1$. Filled and unfilled symbols correspond to $n_B = 14$ and 70, respectively. Straight line is the theoretically predicted asymptote, $R_{\text{norm}} = N_A^{2/3}$. (Inset) Raw data for $R_3^{(\text{exp})}$ (error bars are not shown).

increasing n_B . The discrepancy could also arise due to a lack of 767 equilibration of the self-assembling networks of the *ABA* block 768 copolymers. At the same time, the relative deviations from the 769 asymptotic dependence $R_{\text{norm}}^{\text{theor}} = N_A^{2/3}$ are moderate in both 770 cases, indicating that the two-layer model with a scale- 771 independent elasticity of *B* blocks could still describe the 772 structure of microphase-segregated *ABA* melts with reasonable 773 accuracy.

To illustrate that implementation of the scale-independent 775 Gaussian elasticity for backbones allows for better agreement 776 with the experiments, we present here also the data for PS- 777 PDMS (AB) diblock copolymers with comb-shaped blocks¹³ 778 that self-assemble in lamellar structures (i = 1). All of the 779 selected samples (listed in Table S2 in SI) have one side chain 780 per monomer unit of norbornene backbone in each block, and 781 both backbones have DP $M_i > n_i^{1/2}$. The latter condition ₇₈₂ allows us to use eq 5, which is asymptotically valid in the limit 783 of $M_i \gg n_i^{1/2}$. Equation 5 for the topological coefficient with q_i 784 = 1 and m_i = 1 is applicable to both blocks if they are treated as 785 comblike homopolymers with equal sizes of monomer units in 786 the backbone and side chain.⁴⁵ If, however, both blocks are 787 treated as bottlebrushes, their topological ratios are calculated 788 as $\eta_i = \alpha_i (l_i b_i)^{3/4} v_i^{-1/2} n_i^{1/4}$ (eq 8) with numerical coefficients 789 $\alpha_i \simeq 1$. Evaluation of m_* (eq 7) for samples listed in Table S2 790 indicated that the PS blocks (with $m_* = 0.76$ for $n_A = 29$, and 791 $m_* = 1.14$ for $n_A = 48$) as well as the PDMS block (with $m_* = 792$ 1.41 for $n_B = 65$) were at the crossover between the comblike 793 and the bottlebrush regimes, and we used both eqs 8 and 5 to 794 calculate the lamellae periodicity. Notably, the planar geometry 795 of the lamellae eliminates curvature-induced dead zones, while 796 the effect of the architecture-induced dead zones decreases 797 upon increasing backbone length, M_{i} , which justifies 798 application of the SS-SCF model to evaluate the periodicity 799 of the lamellar structures. 800

In Figure 15, the experimentally measured period d_1^{exp} of the 801 $_{802}$ lamellae is presented as a function of DP N_A of the PS block. 803 Black squares correspond to positions of the main pick in the 804 SAX scattering intensity curves; white squares with error bars 805 indicate the data from TEM for selected samples. The the theoretical values of period $d_1^{\text{theor}} = 2(R_1 + D_1)$ were calcu-⁸⁰⁷ lated using eq 29, that is, $d_{1,bb}^{\text{theor}}$ (blue filled triangles) and $_{808} d_{1,cb(m=1)}^{\text{theor}}$ (blue unfilled triangles) were obtained by treating 809 both blocks either as bottlebrushes or as comblike polymers, 810 respectively. Similarly to the case of the PMMA-PDMS-811 PMMA triblock copolymer in Figure 14, treatment of the 812 branched blocks as linear chains of impermeable superblobs 813 significantly overestimates the dimensions of microphase-814 segregated domains, and the experimental and theoretical 815 periods are found in better agreement if the blocks are treated 816 as comblike polymers (see also Figure S5 in SI).

As it follows from Table S2 in the SI, the backbones in both 818 blocks were strongly stretched in the lamellae, particularly at 819 small values of M_i . Nonetheless, the parabolic potential 820 framework SS-SCF reasonably describes the experimental 821 data. Notably, in the theoretical model, the sizes of the 822 monomer units in the backbones and side chains are presumed 823 to be equal. The norbornene monomer unit in the backbone of 824 the PS–PDMS diblock is however approximately two times 825 longer than the monomer units in the PS and PDMS side 826 chains. This difference could be roughly accounted for by 827 assigning $m_i = 2$ in the theoretical estimates of d_1^{theor} . The set of 828 d_1^{theor} for $m_i = 2$ (which doubles the distance between 829 neighboring grafts on the norbornene backbone) is shown in 830 Figure S6 in the SI.

The presented examples of lamellar¹³ and spherical¹⁶ 831 832 mesophases illustrate that treatment of comb-shaped blocks as comblike with $\eta_i = (1 + n_i/m_i)^{1/2}$ leads to a better 833 834 correspondence between the theoretically predicted and the 835 experimentally measured structural parameters of super-836 structures. However, such change in treatment of the blocks 837 leads to concomitant relocation of the PS-PDMS and 838 PMMA-PDMS-PMMA series in the morphological diagram 839 presented earlier.³⁶ Relocation of the PS–PDMS series makes samples with shorter PS side chains $(n_A = 29)$ closer to the L-841 C boundary but still keeps it in the lamellae stability region. All 842 of the PMMA-PDMS-PMMA samples move deeper in the 843 stability region of the spherical morphology. The predicted s44 onset of the cylindrical morphology for a series with $n_B = 14$ ⁸⁴⁵ (and $\eta_B \approx 3.87$) then significantly decreases compared to the ⁸⁴⁶ experimental $f_B \approx 0.82$ at which cylindrical PMMA domains 847 were first detected in addition to spherical ones.

7. CONCLUSIONS

848 In this study, we examined the equilibrium fraction of bridges 849 and the effect of dead zones in microphase-segregated melts of 850 *ABA* block copolymers comprising comb-shaped blocks. The 851 curvature-induced dead zones were described via the two-layer 852 model of the matrix in a Wigner–Seitz cell.

The development of curvature-induced dead zones and variations in the architecture of the *ABA* triblock copolymer affect the fraction of *B* bridges connecting neighboring *A* domains in cylindrical and spherical morphologies (Figures 6 as 7 and 7). At a small curvature of the domains (i.e., in the absence of dead zones in the two-layer model), the equilibrium fraction



Figure 15. Period $d_1(\hat{A})$ in a microphase-segregated melt of *AB* diblock copolymer PS–PDMD with lamellar morphology (i = 1) as a function of DP N_A of PS block. Both blocks constitute molecular brushes: in PS block $n_A = 65$, and in PDMS block $n_B = 29$ or 48 (see Table S2 with data in SI). Experimental values of d_1 (SAXS) are shown by black squares, theoretical values of $d_1 = 2(R_1 + D_1)$ were calculated by treating both blocks as either bottlebrushes with $\eta_i = \alpha_i (l_i b_i)^{3/4} v_i^{-1/2} n_i^{1/4}$ (i = A, B) and numerical coefficients $\alpha_A = 0.65$ and $\alpha_B = 0.5$ (solid blue triangles) or comblike with $\eta_i = (1 + n_i/m_i)^{1/2}$ and $m_i = 1$ (unfilled blue triangles). $\gamma = 0.37$. White squares with error bars are TEM data for selected samples.

 $X_{B,i}$ of the bridges was calculated as in a planar layer. Here, $X_{B,i}$ 859 decreases upon increasing volume fraction f_B of the B block 860 due to the increasing difference between the elastic free 861 energies of the loops and bridges.⁴⁷ The onset of a dead zone 862 and the increase in its width z_0 upon further increasing f_B lead 863 to progressive accumulation of the median points of the loops 864 closer to the external boundary of the Wigner-Seitz cell, 865 decreasing the difference between the elastic free energies of 866 the loops and bridges. As a result, the equilibrium fraction $X_{B,i}$ 867 of the bridges increases with increasing f_{B} , passing through a 868 minimum at the onset of the dead zone. An increase in the 869 branching of the central B block in the ABA block copolymer 870 leads to a reverse effect: the equilibrium fraction of the bridges 871 decreases upon increasing η_B . Although the fraction of bridges, 872 $X_{B,\nu}$ was estimated using an approximate (two-layer) model of 873 the matrix, the dependence of $X_{B,i}(f_B)$ is expected to remain 874 nonmonotonic in a more rigorous calculation due to the 875 exponential decrease in the width of the dead zone at small 876 curvatures. 877

We demonstrated that in a wide range of block copolymer 878 compositions, the account of curvature-induced dead zones 879 leads to minor changes in the structural parameters of the 880 domains (Figures 10 and 11) and the positions of the binodals 881 (Figures 8 and 9) compared to the parabolic potential 882 framework SS-SCF used by us previously.³⁶ 883

The developed theoretical model invoking linear elasticity of 884 the blocks allows for direct calculation of the domain sizes and 885 interdomain distances in microphase-segregated melts of *AB* 886 and *ABA* block copolymers as a function of DPs of the blocks 887 and their architectural parameters. In spite of the strong 888 elongation of the backbones of the branched blocks in the 889 experimental systems, the structural parameters of the 890 microphase-segregated melts could be still reasonably 891 described by the two-layer model. Deviations between theory 892 and experiments on self-assembling networks of *ABA* 893 copolymers with spherical *A* domains^{16,19,49} were moderate 894 when the central *B* block was treated as a comblike polymer.

896 Notably, the discrepancy between theory and experiments 897 could also arise due to the lack of full equilibration of 898 mesophases upon evaporation of nonselective solvent. A good 899 correspondence between theory and experiment was also 900 found for lamellar mesophases formed by *AB* diblock 901 copolymers with comb-shaped blocks¹³ when the latter were 902 treated as comblike polymers. Although the backbones in both 903 blocks were strongly stretched, the SS-SCF modeling provided 904 a reasonable description of the lamellae period when the blocks 905 were treated as comblike polymers. We emphasize that in the 906 treatment of comb-shaped blocks as comblike polymers and in 907 a comparison between the theoretical and the experimental 908 data we did not implement adjustable prefactors and used the 909 values of the model parameters reported in the literature.

910 ASSOCIATED CONTENT

911 **Supporting Information**

912 The Supporting Information is available free of charge at 913 https://pubs.acs.org/doi/10.1021/acs.macromol.2c00418.

Detailed derivation of the free energy within a two-layer 914 model for convex dry brushes of comblike macro-915 molecules; analysis of the quantitative effect of the dead 916 zones on the phase diagram for the microphase-917 separated melt of block copolymers comprising comb-918 like blocks; comparison of the theoretical predictions to 919 experimental data, including tables with experimentally 920 measured structural properties of the copolymers and 921 922 values of adjustable parameters (PDF)

923 AUTHOR INFORMATION

924 Corresponding Author

- 925 Oleg V. Borisov Institute of Macromolecular Compounds of
 926 the Russian Academy of Sciences, St. Petersburg 199004,
- Russia; Institut des Sciences Analytiques et de Physico-Chimie
- pour l'Environnement et les Matériaux, UMR 5254 CNRS
- 929 UPPA, Pau 64053, France; [©] orcid.org/0000-0002-9281-
- 930 9093; Email: oleg.borisov@uiv-pau.fr

931 Authors

- 932 Ekaterina B. Zhulina Institute of Macromolecular
- 933 Compounds of the Russian Academy of Sciences, St.
- 934
 Petersburg 199004, Russia; o orcid.org/0000-0001-9139

 935
 3484
- Ivan V. Mikhailov Institute of Macromolecular Compounds
 of the Russian Academy of Sciences, St. Petersburg 199004,
- 938 Russia

939 Complete contact information is available at: 940 https://pubs.acs.org/10.1021/acs.macromol.2c00418

941 Notes

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