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

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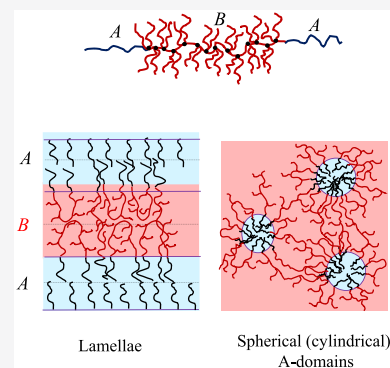


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Supporting Information

4 **ABSTRACT:** A theory describing the equilibrium morphology and structural properties of
5 solvent-free mesophases of ABA triblock copolymers comprised of comblike blocks is
6 developed using a strong-stretching self-consistent field (SS-SCF) analytical approach with
7 architecture-dependent parameters of the molecular potential. Morphological phase
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.



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 solvents^{1–5} 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}

35 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.⁶⁴

In our recent study,³⁶ we applied the parabolic potential
65 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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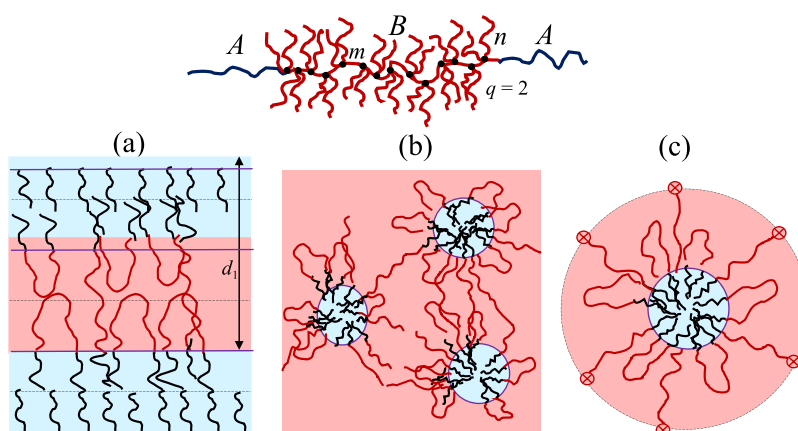


Figure 1. Schematic of the ABA block copolymer with a central comb-shaped block, and microphase-segregated structures in melts. Lamellar (a) and nonplanar (spherical, cylindrical) morphologies (b). Wigner–Seitz cell with half bridges attached to its boundary (c). Side chains of comb-shaped block are 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
78 development of dead zones in convex brushes with nonplanar
79 morphologies,^{37–41} their presence was ignored in our previous
80 study³⁶ due to conjecture that branching leads to a shrinkage
81 of the dead zones^{24,43} and thus that their effect on the
82 equilibrium parameters of superstructures is minor.

83 In this paper, we quantitatively evaluate the effect of dead
84 zones on the structural properties of microphase-segregated
85 melts by implementing the two-layer model that was originally
86 formulated for solvated cylindrical and spherical brushes of
87 linear polymers.⁴¹ We supplement the analytical model with
88 the numerical Scheutjens–Fleer self-consistent field (SF-SCF)
89 simulations of convex solvent-free brushes of comblike
90 polymers with systematically varied lengths of side chains
91 and spacers.

92 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.

98 Similarly to AB diblocks, triblock copolymers ABA with
99 branched blocks give rise to spherical, cylindrical, and lamellar
100 superstructures. More complex structures, e.g., a double
101 gyroid,⁴² are also possible. The major difference between
102 microphase-segregated melts of AB and ABA block copolymers
103 arises due to formation of B bridges by central blocks of ABA
104 copolymers. In contrast to B loops returning to the same
105 domains, B bridges connect neighboring domains giving rise to
106 a physical network with architecture-dependent elasticity.
107 While the presence of B bridges mildly affects the equilibrium
108 dimensions of the domains and interdomain distances, the
109 network elasticity is governed by both the fraction of bridges
110 and the architecture of B blocks.

111 In our previous papers,^{45,47} we analyzed how the grafting
112 density and length of the side chains affect the equilibrium
113 fraction of B bridges in lamellar mesophases of ABA block

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

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

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

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: 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 $q \geq 1$ 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

$$173 \quad N = P(m + qn) = M(1 + qn/m) \quad (1)$$

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 $D = Nv/s$
180 from the surface.

181 Following the strong stretching self-consistent field (SS-
182 SCF) approach formulated earlier,³⁶ the molecular potential
183 $U(z)$ in a solvent-free brush exhibits a parabolic dependence
184 on distance z from the grafting surface

$$185 \quad \frac{U(z)}{k_B T} = \frac{3}{2lb} \kappa^2 (D^2 - z^2) \quad (2)$$

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

198 The topological coefficient κ in eq 2 depends on the
199 architectural parameters of the polymers with $q \geq 1$: 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

$$207 \quad \kappa = \frac{\pi}{2N} \left(1 + \frac{qn}{m}\right)^{1/2} = \frac{\pi}{2M} \left(1 + \frac{nq}{m}\right)^{-1/2}, \quad (3)$$

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

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

$$\eta = \frac{\kappa}{\kappa_{\text{lin}}} = \frac{2\kappa N}{\pi} \quad (4) \quad 211$$

which is approximated as 212

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

for comblike polymers with $M \gg (mn/q)^{1/2}$ (locally un-
extended backbones). In conventional comblike polymers, $q =$
1. 216

The topological ratio η for bottlebrush (bb) polymers with
locally extended backbones was also discussed earlier.³⁶ The
onset of local backbone extension (i.e., the onset of the
bottlebrush regime for comb-shaped polymer) is governed by
dense packing of the backbone segment with associated side
chains in volume V with radius $r_0 = (lbn)^{1/2}$ equal to the
Gaussian size of side chain, that is 223

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

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

$$m_* \approx \frac{3}{4\pi} \frac{v}{(lb)^{3/2}} qn^{1/2} \quad (7) \quad 226$$

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

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

with the numerical coefficient $\alpha \simeq 1$. In this scenario, the
topological coefficient $\kappa = \pi\eta_{\text{bottlebrush}}/(2N)$ in eq 2 should be
renormalized according to eq 8. 233

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

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

A simplified two-layer model accounting for dead zones in
solvated convex brushes of linear chains⁴¹ combined the power
law decay in polymer density inside the dead zone with the
planar-like distribution of chain segments in the brush
peripheral region. Matching the polymer density profiles in
the spherical (or cylindrical) dead zone and the planar-like
peripheral layer, supplemented with length conservation of
chain segments in both layers, relates the dead zone width, z_0 ,
to the curvature of the grafting surface. It was demonstrated⁴¹
and confirmed by more accurate calculations³⁹ that an inferior
solvent strength leads to the increased relative extension of the
dead zone, suggesting that dead zones could occupy a
significant part of strongly curved solvent-free brushes of
comb-shaped polymers. 260

261 To evaluate the effect of dead zones on the properties of
 262 microphase-segregated melts of copolymers with comb-shaped
 263 blocks, we extend the original two-layer model⁴¹ to dry,
 264 solvent-free brushes. In contrast to brushes swollen in solvent,
 265 matching of polymer volume fractions $\varphi(z)$ at $z = z_0$ occurs in
 266 a solvent-free brush automatically because $\varphi(z) = 1$ every-
 267 where in both layers. In this case, z_0 is specified by matching
 268 the average elastic tensions at the boundary between the two
 269 layers. A detailed description of the two-layer model of dry
 270 brushes is presented in the SI. Here, we formulate the results
 271 relevant to further discussion.

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

$$276 \quad \frac{i\nu N}{s_i R_i} = \left(1 + \frac{D_i}{R_i}\right)^i - 1 \quad (9)$$

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

$$283 \quad \omega_i = \frac{D_i}{R_i}; \quad y_i = \frac{z_0}{D_i} \quad (10)$$

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 (i
 287 $= 2$) geometries

$$288 \quad y_3 = \frac{z_0}{D_3} = \left[\frac{1}{2} \left(\frac{\omega_3}{3} + 1 - \frac{\pi^2}{4} \right) + \sqrt{\frac{1}{4} \left(\frac{\omega_3}{3} + 1 - \frac{\pi^2}{4} \right)^2 + \left(\frac{\pi^2}{8} - \frac{1}{3} \right) \left(\frac{\omega_3^2}{3} + \omega_3 + 1 - \frac{\pi^2}{8} \right)} \right] \div \left[\omega_3 \left(\frac{\pi^2}{8} - \frac{1}{3} \right) \right] \quad (11)$$

289 and

$$290 \quad y_2 = \frac{z_0}{D_2} = \frac{2 + \omega_2 - \frac{\pi^2}{4}}{\omega_2 \left(\frac{\pi^2}{4} - 1 \right)} \quad (12)$$

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

$$292 \quad \omega_i < \omega_{i,0} = \left(\frac{D_i}{R_i} \right)_0 = \begin{cases} -\frac{3}{2} + \sqrt{\frac{3\pi^2}{8} - \frac{3}{4}} \approx 0.218 & i = 3 \\ \frac{\pi^2}{4} - 2 \approx 0.467 & i = 2 \end{cases} \quad (13)$$

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

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

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

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

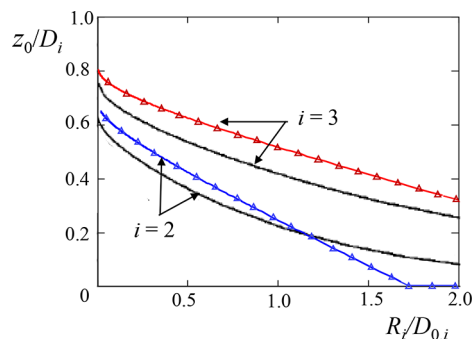


Figure 2. Relative extension of the curvature-induced dead zone, z_0/D_i , in a convex dry brush with thickness D_i , formed by linear chains with DP N , tethered to a convex surface with radius R_i and grafting area s_i per chain. $D_{0,i} = \nu N/s_i$ is the thickness of a planar brush with grafting 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 12) as a function of the reduced curvature

$$302 \quad \frac{R_i}{D_0} = \frac{R_i s_i}{\nu N} = \frac{i}{(1 + \omega_i)^i - 1} \quad (15) \quad 303$$

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

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

$$319 \quad F_{el} = F_{el,in} + F_{el,out} \quad (16)$$

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

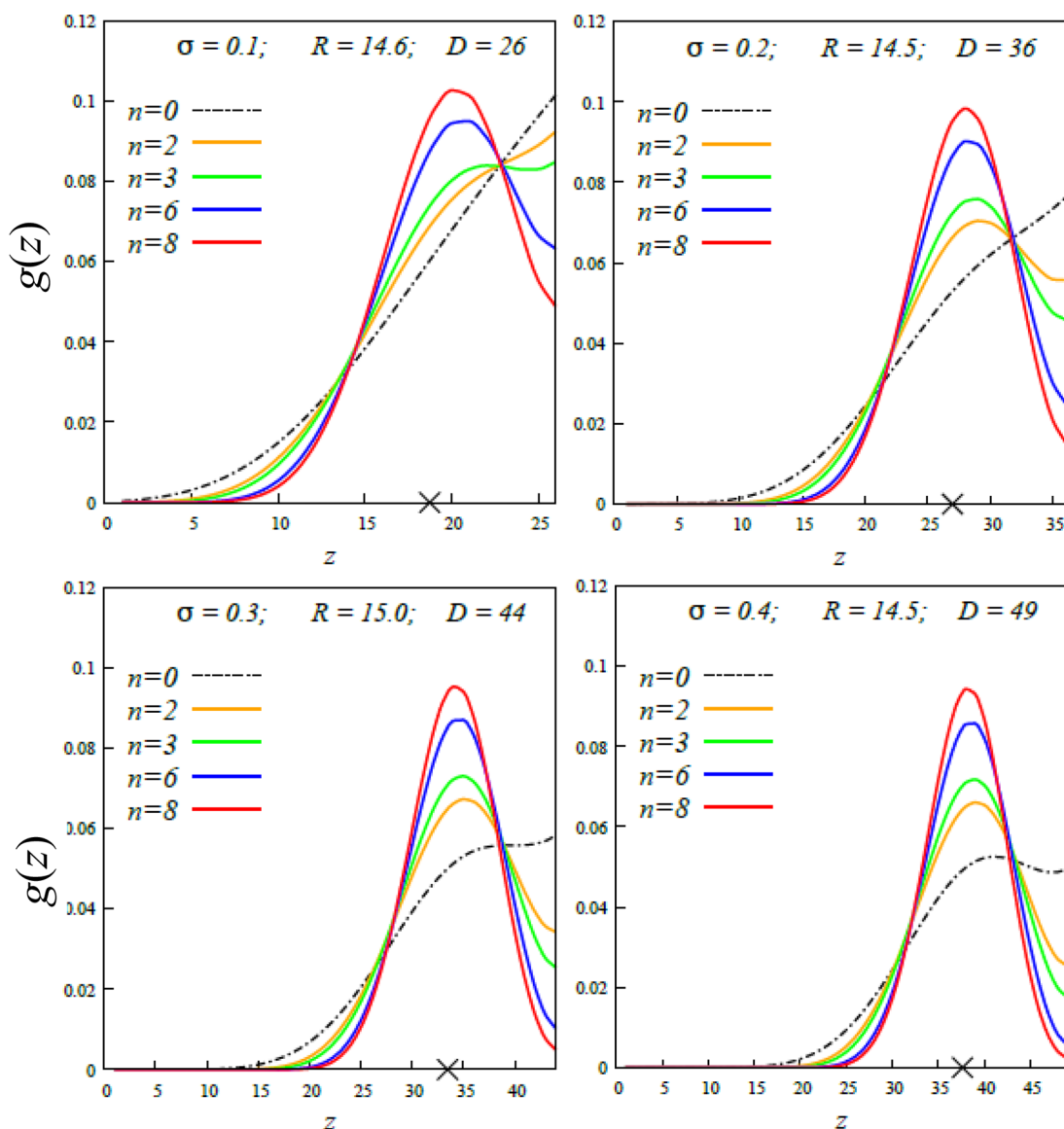


Figure 3. Fraction $g(z)$ of middle points in the spherical ($i = 3$) brush of loops formed by comblike polymer with fixed DP $N = M(1 + n/m) = 1000$ as a function of distance z from the surface. $m = 2$ values of other parameters (σ , R , D , n) are indicated in the plots. Theoretical thickness z_0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

$$\frac{F_{el}}{k_B T} = \frac{v\eta^2 R_i}{lb s_i} \times \begin{cases} \frac{3}{2} \frac{y_i}{y_i + \omega_i} + \frac{27\pi^2 \omega_3^3 (1 - y_3)^3 [(1 + y_3 \omega_3)^2 / 3 + \omega_3 (1 + y_3 \omega_3) (1 - y_3) / 2 + \omega_3^2 (1 - y_3)^2 / 5]}{8 [(1 + \omega_3)^3 - (1 + \omega_3 y_3)^3]^2} & i = 3 \\ \frac{3}{2} \ln \left(\frac{y_i + \omega_i}{y_i} \right) + \frac{3\pi^2 \omega_2^3 (1 - y_2)^3 [(1 + y_2 \omega_2) / 3 + \omega_2 (1 - y_2) / 4]}{2 [(1 + \omega_2)^2 - (1 + \omega_2 y_2)^2]^2} & i = 2 \end{cases} \quad (17)$$

322

323

324 **2.2. SF-SCF Modeling of Convex Solvent-Free**
 325 **Brushes of Comb-Shaped Polymers.** The details of the
 326 SF-SCF method have been described in detail in our previous
 327 publications.^{45,47} Here, we present the scf data to merely
 328 confront the relevant analytical predictions. As before, we
 329 implement monomer size a as the unit length to make R , D , z_0 ,
 330 and grafting density $\sigma = s^{-1}$ dimensionless. More results of the
 331 numerical scf modeling and computer DPD simulations of

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

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

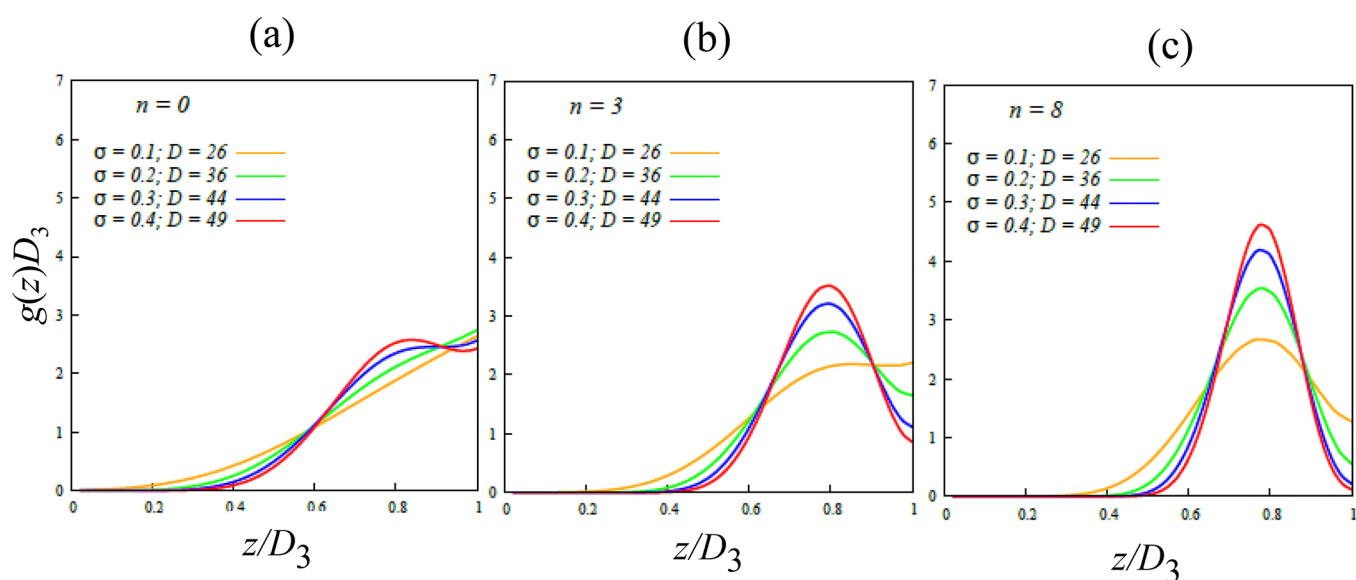


Figure 4. Normalized fraction $g(z)D_3$ of middle points in the brush of loops with fixed DP $N = 1000$ as a function of reduced distance z/D_3 from the surface of the spherical substrate with radius $R_3 = 15$ at different grafting densities σ . DP of the side chain $n = 0$ (a), 3 (b), and 8 (c).

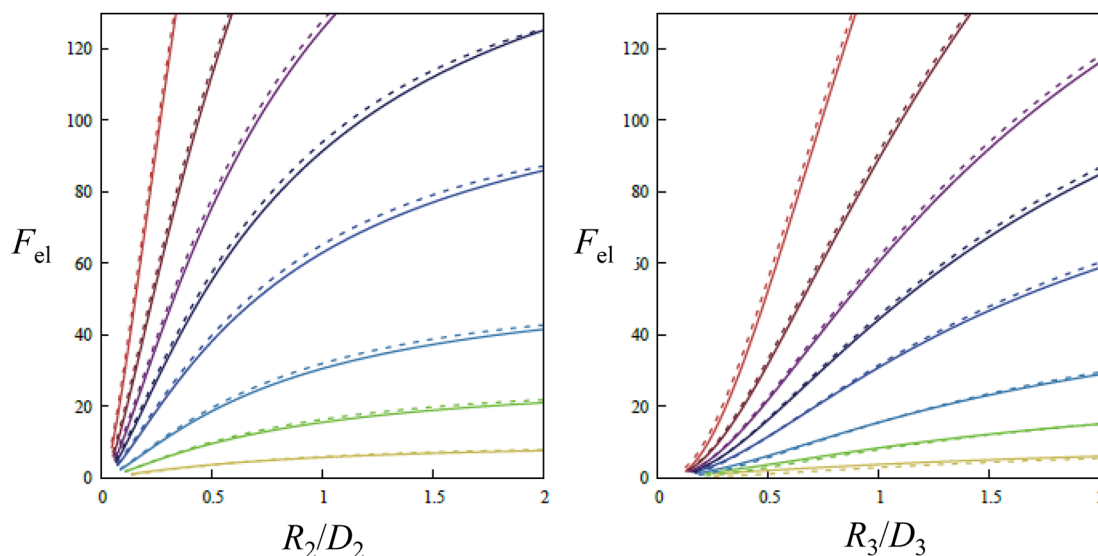


Figure 5. Free energy F_{el} per molecule (in $k_B T$ units) in the cylindrical ($i = 2$, left) and spherical ($i = 3$, right) solvent-free brushes of loops formed by comblike polymer as a function of ratio R_i/D_i . Solid and dashed lines indicate scf data and analytical predictions calculated according 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 .

350 According to the two-layer model, the relative width of the
 351 outer (planar-like) sublayer depends only on the ratio R_i/D_i ,
 352 and therefore, at a fixed surface radius, $R_i = \text{const}$, the
 353 distribution $g(z)$ of loop middle points (end points of the
 354 equivalent linear chains) depends only on the reduced distance
 355 z/D_i . Therefore, the two-layer model predicts a universal shape
 356 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
 Figure 4, we present $g(z)D_3$ as a function of z/D_3 in a spherical
 brush ($i = 3$) for comb-shaped polymer DP $N = 1000$ and
 varied lengths of the side chains, $n = 0$ (Figure 4a), $n = 3$
 (Figure 4b), and $n = 8$ (Figure 4c). An increase in n and the
 concomitant decrease in $M = N/(1 + n/m)$ lead to localization
 of the normalized distribution $g(z)D_3$ around the same
 maximum (consistent with the analytical model). However,
 in contrast to the theoretical predictions, the position of the
 maximum in $g(z)D_3$ is shifted to smaller values of $z/D_3 \approx 0.8 <$
 1 . This shift could be rationalized as follows. In the case of
 comb-shaped polymers, the maximum in $g(z)D_3$ dependence is
 expected to shift to the left due to accommodation of the side
 chains that ensure dense packing of monomer units in the
 vicinity of the brush external boundary. This feature of comb-
 shaped polymers is not accounted for in the analytical model

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 .

381 However, in spite of all of the discrepancies, the two-layer
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 COPOLYMER: TWO-LAYER MODEL OF THE MATRIX

397 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

$$\beta = \frac{l_A b_A v_B}{l_B b_B v_A} \quad (18) \quad 403$$

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

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

$$s_i = iN_A v_A / R_i \quad (19) \quad 423$$

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

$$\frac{F_{B,i}}{k_B T} = \frac{R_i^2}{l_A b_A N_A} \beta \eta_B^2 c_i(\omega_i, \gamma_i) \quad (20) \quad 426$$

427 with

$$c_3(\omega_3, \gamma_3) = \begin{cases} \frac{1}{2} \frac{\omega_3 \gamma_3}{1 + \omega_3 \gamma_3} + \frac{9\pi^2}{8} \omega_3^3 (1 - \gamma_3)^3 \frac{[(1 + \gamma_3 \omega_3)^2/3 + \omega_3(1 + \gamma_3 \omega_3)(1 - \gamma_3)/2 + \omega_3^2(1 - \gamma_3)^2/5]}{[(1 + \omega_3)^3 - (1 + \omega_3 \gamma_3)^3]^2} & \omega_3 > \omega_{3,0} \\ \frac{9\pi^2}{8} \omega_3^3 \frac{[1/3 + \omega_3/2 + \omega_3^2/5]}{[(1 + \omega_3)^3 - 1]^2} & \omega_3 < \omega_{3,0} \end{cases} \quad (21) \quad 428$$

429 and

$$c_2(\omega_2, \gamma_2) = \begin{cases} \frac{3}{4} \ln(1 + \omega_2 \gamma_2) + \frac{3\pi^2}{4} \omega_2^3 (1 - \gamma_2)^3 \frac{[(1 + \gamma_2 \omega_2)/3 + \omega_2(1 - \gamma_2)/4]}{[(1 + \omega_2)^2 - (1 + \omega_2 \gamma_2)^2]^2} & \omega_2 > \omega_{2,0} \\ \frac{3\pi^2}{4} \omega_2^3 \frac{[1/3 + \omega_2/4]}{[(1 + \omega_2)^2 - 1]^2} & \omega_2 < \omega_{2,0} \end{cases} \quad (22) \quad 432$$

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

3.2. Free Energy per AB Block Copolymer Molecule.

435 Compared to the free energy of the diblock copolymer
436 calculated in the SS-SCF approximation,³⁶ the free energy F_i
437 per diblock AB copolymer in the two-layer model of the B
438 matrix is reformulated as

$$\begin{aligned} \frac{F_i}{k_B T} &= \frac{F_{A/B}}{k_B T} + \frac{F_{A,i}}{k_B T} + \frac{F_{B,i}}{k_B T} \\ &= \frac{i\gamma N_A v_A}{l_A^2 R_i} + \frac{R_i^2}{l_A b_A N_A} [b_i \eta_A^2 + \beta \eta_B^2 c_i(\omega_i, \gamma_i)] \end{aligned} \quad (23) \quad 441$$

442 with the numerical coefficients

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

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

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

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

relates x to ω_i as

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

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

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

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

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

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460

while at a large curvature of A domains (i.e., at $\omega_i > \omega_{i,0}$) 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 in a planar morphology ($i = 1$), $G_1(x) \equiv g_1(x)$ at any x .

Minimization of F_i with respect to R_i in eq 23 gives

$$R_i = \left(\frac{i\gamma N_A^2 v_A b_A}{2\Phi_i(x) l_A} \right)^{1/3}; \quad D_i = R_i [(1+x)^{1/i} - 1], \quad i = 1, 2, 3 \quad (29)$$

466

467 and

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

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469 with

$$\Phi_i(x) = b_i \eta_A^2 + \beta \eta_B^2 G_i(x) \quad (31)$$

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4. FRACTION OF BRIDGES IN MESOPHASES OF ABA BLOCK COPOLYMER

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

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

480

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

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

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

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

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

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

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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

$$X_{B,i} \approx \frac{1}{1 + \left(1 + \frac{72 \Delta F_{B,i}(x)}{\pi^4 k_B T} \right)^{1/3}}, \quad i = 2, 3 \quad (37)$$

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$$\left(\frac{\Delta F_{B,i}(x)}{k_B T} \right)_{z_0=0} = \beta \eta_B^2 N_A^{1/3} \left(\frac{\gamma^{2/3} \nu_A^{2/3}}{b_A^{5/3} l_A^{1/3}} \right) \begin{cases} \left[\frac{\pi^2}{2^{10/3} x} \left[\frac{\pi^2}{8} + \beta \eta_B^2 g_1(x) \right] \right]^{-2/3} & i = 1 \\ \frac{1}{2} [(1+x)^{1/2} - 1] \left[\frac{\pi^2}{16} + \beta \eta_B^2 g_2(x) \right]^{-2/3} & i = 2 \\ \frac{1}{(12)^{1/3}} [(1+x)^{1/3} - 1] \left[\frac{3\pi^2}{80} + \beta \eta_B^2 g_3(x) \right]^{-2/3} & i = 3 \end{cases} \quad (38)$$

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

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

522 In Figure 6, we present the equilibrium fraction $X_{B,i}$ of B
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.

541 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, $\eta_B = 2$ (Figure
544 7a) and $\eta_B = 5$ (Figure 7b). Transitions between morphologies
545 are accompanied by jumps in $X_{B,i}$. As shown in Figures 6 and 7,

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

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according to the two-layer model, fraction $X_{B,3}$ of bridges
approaches 0.5 at $f_B \rightarrow 1$ and weakly depends of η_B .

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

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

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

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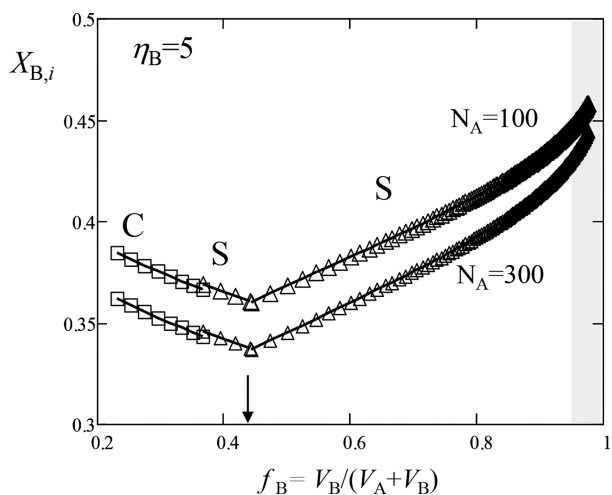


Figure 6. Equilibrium fraction $X_{B,i}$ of B bridges in cylindrical (C) and spherical (S) morphologies formed by ABA triblock copolymer with linear A and comb-shaped B blocks as a function of volume fraction f_B of the B component for two values of N_A (indicated near the curves). $\eta_B = 5$, $\eta_A = 1$. 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.

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

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

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

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

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In Figure 8, we present binodals calculated with the SS-SCF parabolic potential framework ($Y_{LC,par}$ and $Y_{CS,par}$) presented earlier in ref 36) and binodals Y'_{LC} and Y'_{CS} calculated for fixed end points of B backbones in lamellar ($i = 1$), cylindrical ($i = 2$), and spherical ($i = 3$) morphologies. The latter correspond to $y_i = 1$ in eq 20 and are indicated by filled triangles. Below we refer to the model with end points of backbones fixed at external boundaries of Wigner–Zetitz cells as an “extended Semenov’s model” in analogy with his original model of spherical and cylindrical matrices in microphase-segregated block copolymers with linear blocks.³⁷ If the free ends of backbones spread in lamellar layers then the corresponding L–C binodal, Y''_{LC} , is shown by the line with unfilled circles. As shown in Figure 13, for linear B blocks ($\eta_B = \eta_A = 1$) and $\beta = 1$, the transition compositions f_{LC} and f_{CS} (corresponding to respective intersections of $Y_{LC,par}$, $Y_{CS,par}$ and Y''_{LC} , Y'_{CS} with the x axis) are quite close in the SS-SCF framework ($f_{LC} \approx 0.704$, $f_{CS} \approx 0.886$) and Semenov’s model³⁷ ($f_{LC} \approx 0.717$, $f_{CS} \approx 0.874$). The latter model allows for distribution of the free end

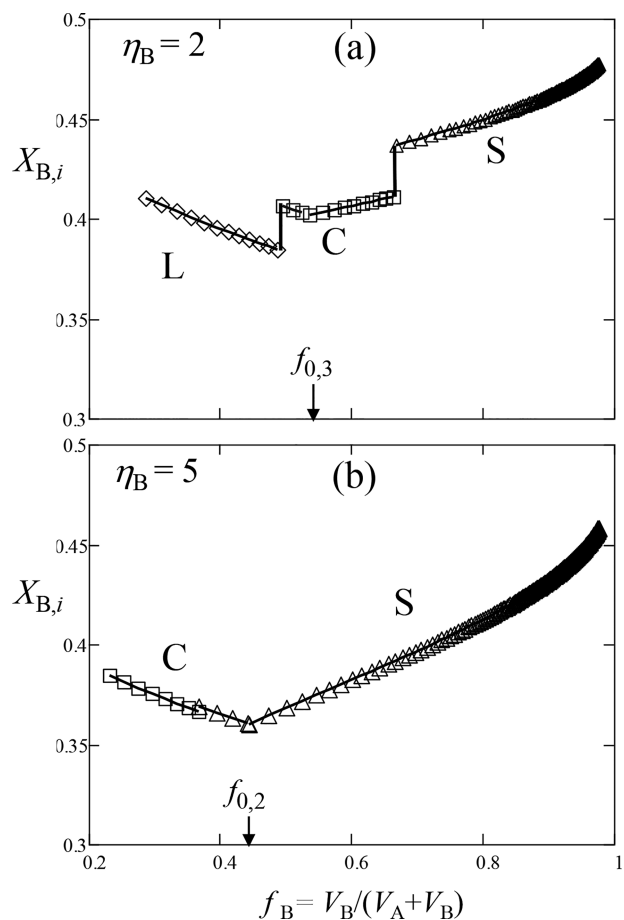


Figure 7. Equilibrium fraction $X_{B,i}$ of B bridges in lamellar (L), cylindrical (C), and spherical (S) morphologies formed by triblock ABA copolymer with linear A and comblike B blocks as a function of volume fraction f_B of the B component for $\eta_B = 2$ (a) and $\eta_B = 5$ (b), $\eta_A = 1$. 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 blocks in cylindrical and spherical morphologies. In the case of fixed end points of linear B blocks in lamellae, f_{LC} decreases to $f_{LC} \approx 0.615$.

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

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

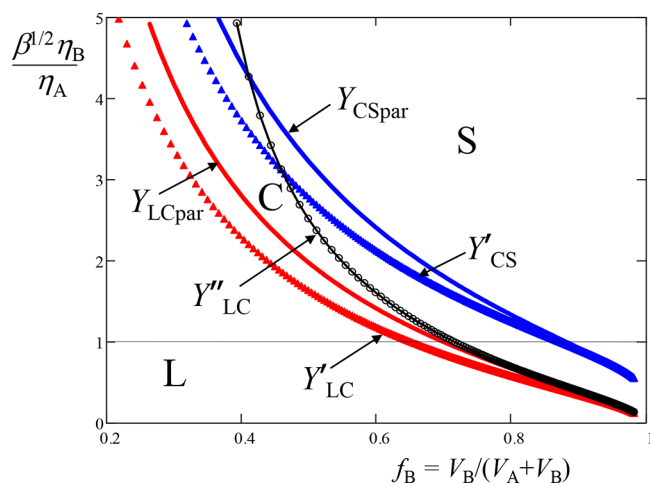


Figure 8. Binodals $Y = \beta^{1/2} \eta_B / \eta_A$ separating spherical (S), cylindrical (C), and lamellar (L) morphologies as a function of $f_B = V_B / (V_A + V_B)$, calculated with a parabolic potential framework ($Y_{CS,par}$, $Y_{LC,par}$ shown by solid lines) and an extended Semenov model (Y'_{CS} , 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.

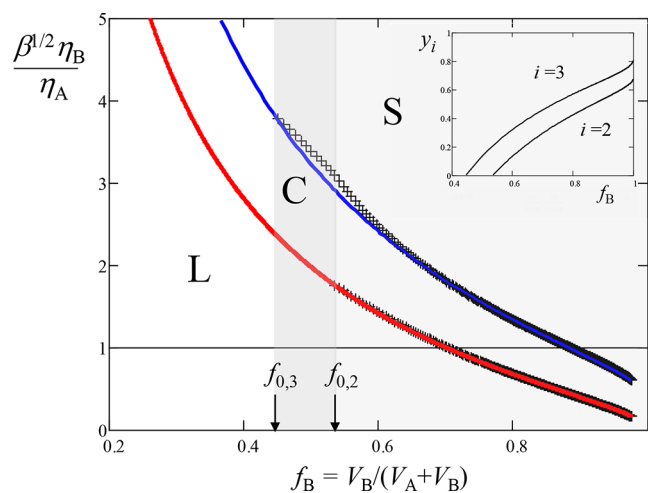


Figure 9. Binodals separating spherical (S), cylindrical (C), and lamellar (L) morphologies calculated with a parabolic potential framework (solid lines) and with a two-layer model (crosses). Arrows indicate block copolymer compositions, $f_{0,3} = 0.446$ and $f_{0,2} = 0.536$ corresponding to the onset 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.

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

623 In Figure 9, we present L–C and C–S binodals as a function
 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 $Y_{LC,par}$ and $Y_{CS,par}$
 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 decrease³⁹ in
 640 the width of the dead zone at small curvatures.

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 $\sim 2\%$. 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

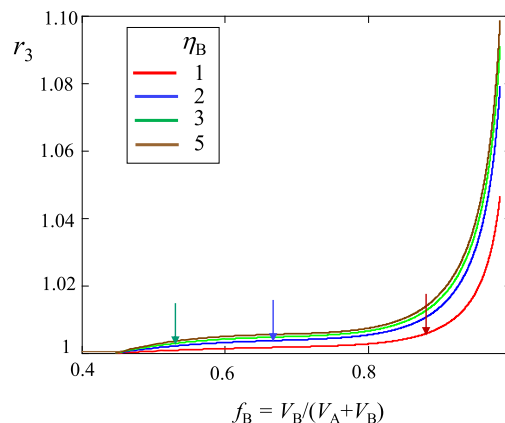


Figure 10. Ratio $r_3 = R_{3,par} / R_3$ of spherical domain radii calculated with a parabolic potential ($R_{3,par}$) and two-layer model (R_3) as a function of diblock copolymer composition f_B and topological ratio η_B of matrix block $\eta_A = 1$, $\beta = 1$. Onsets of thermodynamic stability for 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 $f_B \lesssim 0.97$ 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. 660

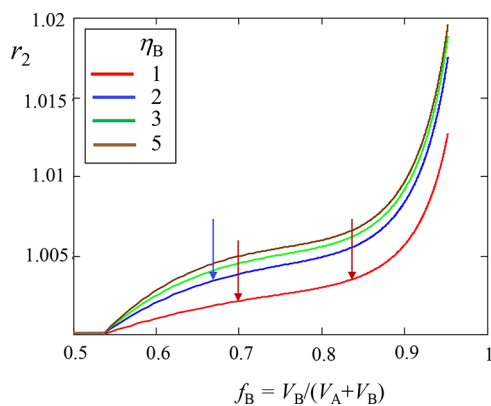


Figure 11. Ratio $r_2 = R_{2,\text{par}}/R_2$ of cylindrical domain radii calculated with a parabolic potential ($R_{2,\text{par}}$) and two-layer model (R_2) as a function of diblock copolymer composition f_B and topological ratio η_B of matrix block $\eta_A = 1$, $\beta = 1$. Cylinders are thermodynamically 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.

677 In localizing these copolymers in the morphological diagram
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 $\approx r_0$.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 $R_0 \approx r_0 N_0^{1/2}$. 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, α_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.

695 It should be emphasized, however, that superblob
696 impermeability arises due to conformational losses associated
697 with extra stretching of the side chains upon superblob
698 interpenetration. Therefore, the concept of an impermeable
699 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 ($v_B = 136 \text{ \AA}^3$, $l_B = 2.5 \text{ \AA}$, $b_A = 13 \text{ \AA}$)
704 gives $m_{B^*} \approx 0.67$ 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 $m_{B^*} \approx 1$ are found at the crossover between comblike and
707 bottlebrush regimes.
708

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 $i = 3$).
719

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 $R_3^{\text{exp}}(\text{\AA})$ 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 n_B

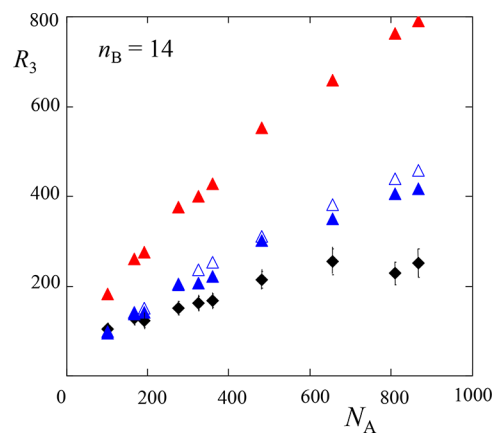


Figure 12. Radii $R_3(\text{\AA})$ of the A domain in a microphase-segregated melt of triblock copolymer ABA with molecular brush B block as a function of DP N_A of linear block A . In the B block, $n_B = 14$, $m_B = 1$, $\beta = 1.26$. Experimental R_3 for PMMA–PDMS–PMMA copolymers^{16,49} are indicated 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 $\beta = 1.26$, $v_A = 141 \text{ \AA}^3$, $l_A = 2.5 \text{ \AA}$, and $b_A = 17 \text{ \AA}$.
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

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.

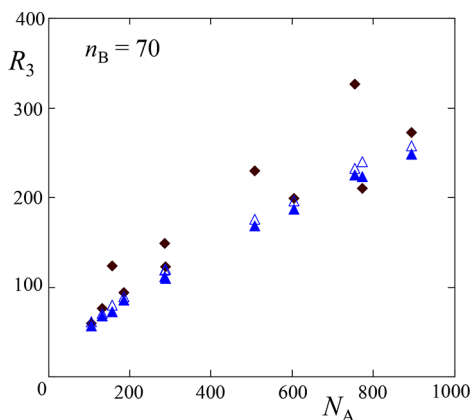


Figure 13. Radii R_3 (Å) of A domains in a microphase-segregated melt of triblock copolymer ABA with a comb-shaped B block with $n_B = 70$ as a function of DP N_A of a linear block. Experimental radii $R_{3, \text{exp}}$ are shown by diamonds. Theoretical values of R_3 calculated with the SS-SCF parabolic 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 $m_B = 1$.

f13 741 In Figure 13, we compare R_3^{exp} for PMMA–PDMS–PMMA
 742 samples with $n_B = 70$ (diamonds) to the theoretically predicted
 743 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 $n_B = 14$
 745 (Figure 12), modeling the B block as a linear chain of
 746 impermeable superblobs considerably overestimates R_3^{exp} (not
 747 shown in Figure 13). Notably, in both series, the backbones in
 748 the B blocks are strongly elongated, even approaching the
 749 backbone contour length in some samples with $n_B = 70$.
 750 However, the two-layer model partially compensates for the
 751 nonlinear elasticity of the backbones via overestimated
 752 elongation near the surfaces of the A domains (see SI).

f14 753 In Figure 14, we present the normalized domain radius
 754 $R_{\text{norm}} = \left(\frac{2\Phi_3(x)l_A}{3\gamma v_A b_A}\right)^{1/3} R_3^{\text{exp}}$ 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 asymptote $R_{\text{norm}}^{\text{theor}}$ correlate with the shift from a
 766 comblike to a bottlebrush regime for the B block upon

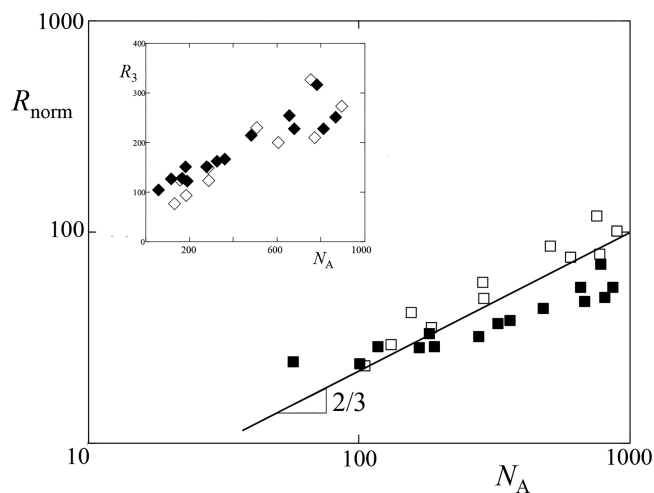


Figure 14. Normalized radius $R_{\text{norm}} = R_3^{\text{exp}}[(2l_A\Phi_3)/(3\gamma v_A b_A)]^{1/3}$ of the A domain in a microphase-segregated melt of triblock copolymer ABA with molecular brush B block as a function of DP N_A of the linear block. Topological ratio for B blocks was calculated as $\eta_B = (1 + n_B/m_B)^{1/2}$ 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^{exp} (error bars are not shown).

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

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

801 In Figure 15, the experimentally measured period d_1^{exp} of the
 802 lamellae is presented as a function of DP N_A of the PS block.
 803 Black squares correspond to positions of the main peak in the
 804 SAX scattering intensity curves; white squares with error bars
 805 indicate the data from TEM for selected samples. The
 806 theoretical values of period $d_1^{\text{theor}} = 2(R_1 + D_1)$ were calcu-
 807 lated using eq 29, that is, $d_{1,\text{bb}}^{\text{theor}}$ (blue filled triangles) and
 808 $d_{1,\text{cb}(m=1)}^{\text{theor}}$ (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).

817 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.

831 The presented examples of lamellar¹³ and spherical¹⁶
 832 mesophases illustrate that treatment of comb-shaped blocks
 833 as comblike with $\eta_i = (1 + n_i/m_i)^{1/2}$ leads to a better
 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
 840 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
 844 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.

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

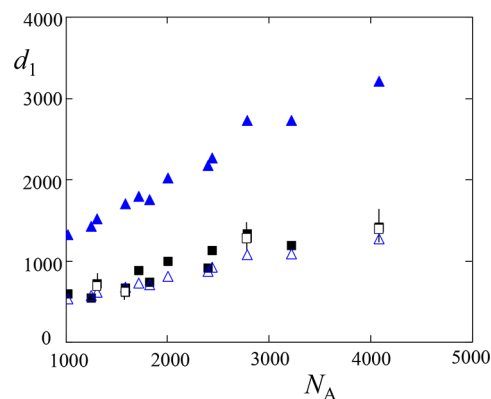


Figure 15. Period d_1 (Å) in a microphase-segregated melt of AB diblock copolymer PS–PDMD with lamellar morphology ($i = 1$) as a function of DP N_A of PS block. Both blocks constitute molecular brushes: in PS block $n_A = 65$, and in PDMS block $n_B = 29$ or 48 (see Table S2 with data in SI). Experimental 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
 $X_{B,i}$ 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. 895

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 **SI** Supporting Information

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

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

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941 Notes

942 The authors declare no competing financial interest.

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947 ■ REFERENCES

948 (1) Wurm, F.; Frey, H. Linear-dendritic block copolymers: the state
949 of the art and exciting perspectives. *Prog. Polym. Sci.* **2011**, *36*, 1–52.

(2) Blasco, E.; Pinol, M.; Oriol, L. Responsive Linear-Dendritic
Block Copolymers. *Macromol. Rapid Commun.* **2014**, *35* (12), 1090–
1115. 951

(3) Garcia-Juan, H.; Nogales, A.; Blasco, E.; Martinez, J. C.; Sics, I.;
Ezquerro, T. A.; Pinol, M.; Oriol, L. Self-assembly of thermo and light
responsive amphiphilic linear dendritic block copolymers. *Eur. Polym.*
J. **2016**, *81*, 621–633. 952–956

(4) Mirsharghi, S.; Knudsen, K. D.; Bagherifam, S.; Nystrom, B.;
Boas, U. Preparation and self-assembly of amphiphilic polylysine
dendrons. *New J. Chem.* **2016**, *40*, 3597–3611. 957–959

(5) Fan, X.; Zhao, Y.; Xu, W.; Li, L. Linear-Dendritic Block
Copolymer for Drug and Gene Delivery. *Mater. Sci. Eng., C* **2016**, *62*,
943–959. 960–962

(6) Rzaev, J. Synthesis of polystyrene-poly(lactide) bottlebrush
block copolymers and their melt self-assembly into large domain
nanostructures. *Macromolecules* **2009**, *42*, 2135–2141. 963–965

(7) Liberman-Martin, A. L.; Chu, C. K.; Grubbs, R. H. Application
of Bottlebrush Block Copolymers as Photonic Crystals. *Macromol.*
Rapid Commun. **2017**, *38*, 1700058. 966–968

(8) Song, D. P.; Zhao, T. H.; Guidetti, G.; Vignolini, S.; Parker, R.
M. Hierarchical Photonic Pigments via the Confined Self-Assembly of
Bottlebrush Block Copolymers. *ACS Nano* **2019**, *13*, 1764–1771. 969–971

(9) Bolton, J.; Bailey, T. S.; Rzaev, J. Large pore size nanoporous
materials from self-assembly of asymmetric bottlebrush block
copolymers. *Nano Lett.* **2011**, *11*, 998–1001. 972–974

(10) Gai, Y.; Song, D.-P.; Yavitt, B. M.; Watkins, J. J. Polystyrene-
block-poly(ethylene oxide) Bottlebrush Block Copolymer Morphology
Transitions: Influence of Side Chain Length and Volume Fraction.
Macromolecules **2017**, *50*, 1503–1511. 975–978

(11) Runge, M. B.; Bowden, N. B. Synthesis of High Molecular
Weight Comb Block Copolymers and Their Assembly into Ordered
Morphologies in the Solid State. *J. Am. Chem. Soc.* **2007**, *129*, 10551–
10560. 979–982

(12) Runge, M. B.; Lipscomb, C. E.; Ditzler, L. R.; Mahanthappa, M.
K.; Tivanski, A. V.; Bowden, N. B. Investigation of the Assembly of
Comb Block Copolymers in the Solid State. *Macromolecules* **2008**, *41*,
7687–7694. 983–986

(13) Fei, H.-F.; Yavitt, B. M.; Hu, X.; Kopanati, G.; Ribbe, A.;
Watkins, J. J. Influence of Molecular Architecture and Chain
Flexibility on the Phase Map of Polystyrene-block-poly-
(dimethylsiloxane) Brush Block Copolymers. *Macromolecules* **2019**,
52, 6449–6457. 987–991

(14) Sunday, D. F.; Chang, A. B.; Liman, C. D.; Gann, E.;
Delongchamp, D. M.; Thomsen, L.; Matsen, M. W.; Grubbs, R. H.;
Scoles, C. L. Self-Assembly of ABC Bottlebrush Triblock Terpolymers
with Evidence for Looped Backbone Conformations. *Macromolecules*
2018, *51* (18), 7178–7185. 992–996

(15) Bolton, J.; Rzaev, J. Synthesis and Melt Self-Assembly of PS-
PMMA-PLA Triblock Bottlebrush Copolymers. *Macromolecules* **2014**,
47, 2864–2874. 997–999

(16) Vatanikhah-Varnosfaderani, M.; Keith, A. N.; Cong, Y.; Liang,
H.; Rosenthal, M.; Sztucki, M.; Clair, C.; Magonov, S.; Ivanov, D. A.;
Dobrynin, A. V.; Sheiko, S. S. Chameleon-like elastomers with
molecularly encoded strain-adaptive stiffening and coloration. *Science*
2018, *359*, 1509–1513. 1000–1004

(17) Yuan, J.; Müller, A. H. E.; Matyjaszewski, K.; Sheiko, S. In
Polymer Science: A Comprehensive Reference; Matyjaszewski, K., Möller,
M., Eds.; Elsevier: Amsterdam, 2012. 1005–1007

(18) Tu, S.; Choudhury, C. K.; Luzinov, I.; Kuksenok, O. Recent
advances towards applications of molecular bottlebrushes and their
conjugates. *Curr. Opin. Solid State Mater. Sci.* **2019**, *23*, 50. 1008–1010

(19) Xie, G.; Martinez, M. R.; Olszewski, M.; Sheiko, S. S.;
Matyjaszewski, K. Molecular Bottlebrushes as Novel Materials.
Biomacromolecules **2019**, *20* (1), 27–54. 1011–1013

(20) Gillich, T.; Benetti, E. M.; Rakhmatullina, E.; Konradi, R.; Li,
W.; Zhang, A.; Schlüter, A. D.; Textor, M. Self-Assembly of Focal
Point Oligo-Catechol Ethylene Glycol Dendrons on Titanium Oxide
Surfaces: Adsorption Kinetics, Surface Characterization, and Non-
fouling Properties. *J. Am. Chem. Soc.* **2011**, *133*, 10940–10950. 1014–1018

- 1019 (21) Yeh, P. Y. J.; Kainthan, R. K.; Zou, Y.; Chiao, M.;
1020 Kizhakkedathu, J. N. Self-assembled monothiol-terminated hyper-
1021 branched polyglycerols on a gold surface: a comparative study on the
1022 structure, morphology, and protein adsorption characteristics with
1023 linear poly(ethylene glycol). *Langmuir* **2008**, *24*, 4907–4916.
- 1024 (22) Gillich, T.; Acikgoz, C.; Isa, L.; Schluter, A. D.; Spencer, N. D.;
1025 Textor, M. PEG-Stabilized Core-Shell Nanoparticles: Impact of
1026 Linear versus Dendritic Polymer Shell Architecture on Colloidal
1027 Properties and the Reversibility of Temperature-Induced Aggregation.
1028 *ACS Nano* **2013**, *7*, 316–329.
- 1029 (23) Pickett, G. T. Classical Path Analysis of end-Grafted
1030 Dendrimers: Dendrimer Forest. *Macromolecules* **2001**, *34*, 8784–
1031 8791.
- 1032 (24) Zook, T. C.; Pickett, G. T. Hollow-Core Dendrimers Revised.
1033 *Physical review letters* **2003**, *90* (1), 015502.
- 1034 (25) Kröger, M.; Peleg, O.; Halperin, A. From Dendrimers to
1035 Dendronized Polymers and Forests: Scaling Theory and its
1036 Limitations. *Macromolecules* **2010**, *43*, 6213–6224.
- 1037 (26) Gergidis, L. N.; Kalogirou, A.; Vlahos, C. Dendritic Brushes
1038 under Good Solvent Conditions: A Simulation Study. *Langmuir* **2012**,
1039 *28*, 17176–17185.
- 1040 (27) Polotsky, A. A.; Gillich, T.; Borisov, O. V.; Leermakers, F. A.
1041 M.; Textor, M.; Birshtein, T. M. Dendritic versus Linear Polymer
1042 Brushes: Self-Consistent Field Modelling, Scaling Theory, and
1043 Experiment. *Macromolecules* **2010**, *43*, 9555–9566.
- 1044 (28) Borisov, O. V.; Polotsky, A. A.; Rud, O. V.; Zhulina, E. B.;
1045 Leermakers, F. A. M.; Birshtein, T. M. Dendron Brushes and
1046 Dendronized Polymers: A Theoretical Outlook. *Soft Matter* **2014**, *10*,
1047 2093–2101.
- 1048 (29) Li, C.-W.; Merlitz, H.; Wu, C.-X.; Sommer, J.-U. The structure
1049 of brushes made of dendrimers: Recent Advances. *Polymer* **2016**, *98*,
1050 437–447.
- 1051 (30) Leermakers, F. A. M.; Zhulina, E. B.; Borisov, O. V. Interaction
1052 forces and lubrication of dendronized surfaces. *Curr. Opin. Colloid*
1053 *Interface Sci.* **2017**, *27*, 50–56.
- 1054 (31) Polotsky, A. A.; Leermakers, F. A. M.; Zhulina, E. B.; Birshtein,
1055 T. M. On the Two-Population Structure of Brushes Made of Arm-
1056 Grafted Polymer Stars. *Macromolecules* **2012**, *45*, 7260–7273.
- 1057 (32) Zhulina, E. B.; Leermakers, F. A. M.; Borisov, O. V. Theory of
1058 brushes formed by Ψ -shaped macromolecules at solid-liquid
1059 interfaces. *Langmuir* **2015**, *31* (23), 6514–6522.
- 1060 (33) Lebedeva, I. O.; Zhulina, E. B.; Borisov, O. V. Theory of
1061 Linear-dendritic Block Copolymer Micelles. *ACS Macro Lett.* **2018**, *7*
1062 (1), 42–46.
- 1063 (34) Lebedeva, I. O.; Zhulina, E. B.; Leermakers, F. A. M.; Borisov,
1064 O. V. Dendron and Hyperbranched Polymer Brushes in Good and
1065 Poor Solvents. *Langmuir* **2017**, *33*, 1315–1325.
- 1066 (35) Borisov, O. V.; Zhulina, E. B.; Polotsky, A. A.; Leermakers, F.
1067 A. M.; Birshtein, T. M. Interactions between Brushes of Root-tethered
1068 Dendrons. *Macromolecules* **2014**, *47* (19), 6932–6945.
- 1069 (36) Zhulina, E. B.; Sheiko, S. S.; Dobrynin, A. V.; Borisov, O. V.
1070 Microphase segregation in the melts of bottlebrush block copolymers.
1071 *Macromolecules* **2020**, *53* (7), 2582–2593.
- 1072 (37) Semenov, A. N. Contribution to the Theory of Microphase
1073 Layering in Block-Copolymer Melts. *Sov. Phys. JETP* **1985**, *61*, 733–
1074 742.
- 1075 (38) Ball, R. C.; Marko, J. F.; Milner, S. T.; Witten, T. A. Polymers
1076 Grafted to a Convex Surface. *Macromolecules* **1991**, *24*, 693–703.
- 1077 (39) Belyi, V. A. Exclusion Zone of Convex Brushes in the Strong-
1078 Stretching Limit. *J. Chem. Phys.* **2004**, *121*, 6547.
- 1079 (40) Dimitriev, M. S.; Grason, G. M. End-exclusion zones in strongly
1080 stretched, molten polymer brushes of arbitrary shape. *J. Chem. Phys.*
1081 **2021**, *155*, 224901.
- 1082 (41) Wijmans, C. M.; Zhulina, E. B. Polymer Brushes at Curved
1083 Surfaces. *Macromolecules* **1993**, *26* (26), 7214–7224.
- 1084 (42) Park, S. J.; Cheong, G. K.; Bates, F. S.; Dorfman, K. D. Stability
1085 of the Double Gyroid Phase in Bottlebrush Diblock Copolymer Melts.
1086 *Macromolecules* **2021**, *54*, 9063–9070.
- (43) Rud, O. V.; Polotsky, A. A.; Gillich, T.; Borisov, O. V.;
1087 Leermakers, F. A. M.; Textor, M.; Birshtein, T. M. Dendritic Spherical
1088 Polymer Brushes: Theory and Self-Consistent Field Modelling.
1089 *Macromolecules* **2013**, *46*, 4651–4662.
- (44) Tian, Y.; Ina, M.; Cao, Z.; Sheiko, S. S.; Dobrynin, A. V. How
1091 to Measure Work of Adhesion and Surface Tension of Soft Polymeric
1092 Materials. *Macromolecules* **2018**, *51* (11), 4059–4067.
- (45) Mikhailov, I. V.; Zhulina, E. B.; Borisov, O. V. Brushes and
1094 lamellar mesophases of comb-shaped (co)polymers: a self-consistent
1095 field theory. *Phys. Chem. Chem. Phys.* **2020**, *22*, 23385–23398.
- (46) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.;
1097 Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall:
1098 London, 1993.
- (47) Mikhailov, I. V.; Leermakers, F. A. M.; Darinskii, A. A.; Zhulina,
1100 E. B.; Borisov, O. V. Theory of microphase segregation in ABA
1101 triblock comb-shaped copolymers: lamellar mesophase. *Macro-*
1102 *molecules* **2021**, *54*, 4747–4759.
- (48) Zhulina, E. B.; Leermakers, F. A. M.; Borisov, O. V. Brushes of
1104 Cycled Macromolecules: Structure and Lubricating Properties.
1105 *Macromolecules* **2016**, *49* (22), 8758–8767.
- (49) Clair, C.; Lallam, A.; Rosenthal, M.; Sztucki, M.; Vatankhah-
1107 Varnosfaderani, M.; Keith, A. N.; Cong, Y.; Liang, H.; Dobrynin, A.
1108 V.; Sheiko, S. S.; Ivanov, D. A. Strained Bottlebrushes in Super-Soft
1109 Physical Networks. *ACS Macro Lett.* **2019**, *8* (5), 530–534.
- (50) Liang, H.; Wang, Z.; Dobrynin, A. V. Strain-Adaptive Self-
1111 Assembled Networks of Linear-Bottlebrush-Linear Copolymers.
1112 *Macromolecules* **2019**, *52*, 8617–8624.
- (51) Wessels, M. J.; Jayaraman, A. Molecular dynamic simulation
1114 study of linear, bottlebrush, and star-like amphiphilic block polymer
1115 assembly in solution. *Soft Matter* **2019**, *15*, 3987–3998.
- (52) Paturej, J. J.; Sheiko, S. S.; Panyukov, S.; Rubinstein, M.
1117 Molecular Structure of Bottlebrush Polymers in Melts. *Science*
1118 *Advances* **2016**, *2* (11), No. e1601448. 1119