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Strained Bottlebrushes in Super-Soft Physical Networks

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ABSTRACT: ABA triblock copolymers composed of a poly(dimethylsiloxane) (PDMS) bottlebrush central block and linear poly(methyl methacrylate) (PMMA) terminal blocks self-assemble into a physical network of PDMS bottlebrush strands connected by PMMA spherical domains. A combination of Small- and Ultra-Small-Angle X-ray scattering techniques was used to concurrently examine dimensions of PMMA spherical domains and PDMS bottlebrush strands both in the bulk and at the PMMA-PDMS interface. In agreement with scaling model predictions, the degrees of polymerization of the bottlebrush backbone (n_{bb}) and PMMA block (n_A) correlate with the measured PMMA domain size and area per molecule at the PMMA-PDMS interface as $D_A \propto (n_{bb}n_A)^{1/3}$ and $S \propto n_A^{2/3}n_{bb}^{-1/3}$, respectively. In the bulk, bottlebrush strands are extended due to steric repulsion between the side chains and unfavorable interactions between the different blocks. At the PMMA-PDMS interface with large curvature, packing constraints could require additional bottlebrush backbone extension and alignment of side chains along the backbone in the direction perpendicular to the interface.

Brush-like polymers enable the design of super-soft and hyperelastic elastomers, in which side chains grafted onto network strands act as both entanglement diluents and mechanical property regulators.[1] Precise and independent tuning of side-chain degree of polymerization and grafting density yields materials with Young's moduli down to $\sim 10^2$ Pa and elongation-at-break up to 10.[2] These low moduli are typically achieved in swollen networks such as hydrogels, yet brush-like elastomers require no solvent and thus are immune from property degradation, caused by solvent evaporation or leakage upon deformation.

While chemically crosslinked bottlebrush networks replicate the modulus of polymeric gels and biological tissues, they fail to recreate tissue's extreme strain-stiffening behavior.[2] For instance, the Young's modulus of soft tissues such as brain and lung ($\sim 10^2$ - 10^3 Pa) is rapidly followed by two-three orders of magnitude increase during deformation. To

enhance material strain-stiffening, we designed physical networks that self-assemble from **ABA**-triblock copolymers with chemically and physically distinct linear **A**-blocks and bottlebrush **B**-blocks (**Figure 1a**).[3] As a result of strong segregation of the blocks, at rest, network strands are stretched beyond what is observed in chemically crosslinked elastomers leading to significant enhancement of the strain-stiffening behavior. Although the overall extension of polymer chains in block-copolymer systems is well established,[4] the backbone conformation inside the cylindrical envelope of bottlebrush strands remains unknown. **In contrast to our previous publications [1-3], the present Letter is focused on elucidating the elastomer morphology (strand conformation).**

To characterize conformation of bottlebrush blocks in the microphase-separated **ABA** networks, we employed a combination of Small- and Ultra-Small Angle X-ray scattering

(SAXS and USAXS) that span length scales from Angstroms to micrometers. For this study, a series of **ABA** triblock copolymers with systematically varied degrees of polymerization (DP) of a central poly(dimethylsiloxane) (PDMS)-based bottlebrush block (**B**) (n_{bb}) and poly(methyl methacrylate) (PMMA) linear terminal blocks (**A**) (n_A) was

synthesized (**Table 1**). Each monomeric unit of the bottlebrush backbone carries one PDMS side chain with an effective DP of $n_{sc} = 14$ determined as $n_{sc} = M_{sc}/M_0$, where $M_{sc} = 1024 \text{ g/mol}$ and $M_0 = 74 \text{ g/mol}$ are molar masses of macromonomer and PDMS monomer, respectively.

Figure 1. a): Microphase separation of (a) **ABA** bottlebrush copolymers results in formation of a (b) physical network composed of hard PMMA spheres imbedded in a soft matrix of PDMS bottlebrush blocks. Hexagonal packing of PMMA hard spheres covered with soft PDMS shells represents an idealized structure (see text for details). Longer PMMA-blocks may result in non-spherical morphologies [3] that are not discussed in this paper. (c) Schematics representing the conformation of the bottlebrush block anchored on a spherical PMMA domain. For a strongly curved interface the cross-section of the bottlebrush block increases with distance from the PMMA domain surface from S_{interf} to S_{bulk} .

Table 1: Parameters of the **ABA** (linear-bottlebrush-linear) systems.

Sample ¹⁾	n_{bb} ²⁾	n_A ²⁾	$\phi_{A, ch}$ ⁴⁾	D_A , ⁵⁾ nm	RSD ⁶⁾	d_3 , ⁷⁾ nm	Q ⁸⁾	S_{interf} , ⁹⁾ nm ²
300_1	302	100	0.051	20.8	0.12	42.9	333	4.1
300_2	302	166	0.082	25.5	0.11	45.0	373	5.5
300_3	302	276	0.130	30.2	0.10	45.7	372	7.7
900_1	938	190	0.032	24.3	0.12	55.5	280	6.6
900_2	938	325	0.053	32.3	0.09	59.3	386	8.5
900_3	938	656	0.102	50.9	0.11	78.8	749	10.9
900_4	938	1235	0.177	/	/	141.0	/	/
1200_1	1065	360	0.052	33.4	0.09	66.4	384	9.1
1200_2	1065	480	0.068	42.8	0.09	79.1	609	9.5
1200_3	1065	810	0.110	45.7	0.11	77.4	438	15.0
1500_3	1483	867	0.087	50.3	0.13	85.9	546	14.6
1800_3 ⁹⁾	1765	780	0.067	/	/	122.3	/	/

¹⁾All samples had degree of polymerization (DP) of the side chains of bottlebrush block $n_{sc}=14$ separated by $n_g = 1$. DPs of the backbone of the bottlebrush block ²⁾ and the PMMA linear block ³⁾ were determined by ¹H-NMR within a standard deviation of 5% and 2%, respectively (**Figures S1** and **S2**), as well as with AFM (**Figures S3A, S3B** and **Table S1**). ⁴⁾Volume fraction of PMMA block is determined from chemical composition of **ABA** bottlebrushes. ⁵⁾Diameter of PMMA spherical domains is determined from the form-factor of spheres (**Figure 2**). ⁶⁾Relative standard deviation of D_A . ⁷⁾Position of the main interference

peak (see text for details). ⁸⁾ Aggregation number determined as $Q = \pi D_A^3 / (6 n_A v_A)$, where $v_A = 0.141 \text{ nm}^3$ is volume of methyl methacrylate. ⁹⁾ Area per bottlebrush strand at the interface with PMMA spherical domains.

The significant difference in the solubility parameter between PMMA and PDMS and correspondingly large value of the Flory-Huggins interaction parameter ($\chi=0.2$) results in strong segregation between the PMMA and PDMS blocks.[5] The PMMA-blocks (**A**) form spherical domains linked together by PDMS bottlebrush strands (**B**) (**Figure 1b**). This arrangement close to the interface may be viewed as a brush-on-brush system, where side chains are grafted to the bottlebrush backbone, which in turn is anchored at the **A-B** interface (**Figure 1c**).

Selected series of USAXS-SAXS curves are shown in **Figure 2**. The left panel displays scattering curves that correspond to samples with the same bottlebrush block ($n_{bb} = 938$) and variable length of the terminal PMMA blocks ($n_A = 190, 325, 656, \text{ and } 1235$). The right panel shows curves corresponding to **ABA** samples with an approximate n_A of the PMMA block and variable n_{bb} of the PDMS bottlebrush block. These curves exhibit several characteristic features: (i) a strong interference maximum in the USAXS region corresponding to the spatial arrangement of the PMMA spheres (d_3), (ii) a series of ripples (d_2) that correspond to the form-factor of the PMMA spheres at higher angles, and (iii) a single peak (d_1) due to scattering from bottlebrushes caused by the electron-density contrast between the brush backbone and that of the side chains.

To verify the assignments of d_1 and d_2 , we monitored the variation of the peaks positions upon swelling in different solvents. The d_1 peak consistently shifts to smaller angles when swollen in PDMS-selective solvents such as *n*-hexane and linear PDMS oligomers, however, its location remains unchanged when swollen in dimethylformamide a poor solvent for PDMS. (**Figures S4.1 and S4.2**). In contrast, the d_2 -peak is not affected by swelling in PDMS-selective solvents due to their immiscibility with PMMA. In addition, the intensity of the d_1 -peak exhibits orientation during in-situ stretching, with the intensity maxima being located in the plane perpendicular to the stretching direction (**Figure S5**). Note that the d_1 -peak was previously reported for polymer brushes with crystallizable side chains[9], bottlebrushes with *n*-butyl acrylate side chains [10], and α -olefin bottlebrushes [11].

For quantitative analysis of the USAXS-SAXS curves, we present the scattering intensity $I(q)$ as:

$$I(q) \sim P^2(q)S(q) \quad (1)$$

where $S(q)$ is the structure factor and $P(q)$ is the form-factor of spherical domains which, for homogeneous monodisperse spheres, has the following form $P(q) = 3[\sin(qR) - qR\cos(qR)]/(qR)^3$. In eq 1 q stands for the norm of the scattering vector defined as $|q| = 4\pi \cdot \sin(\Theta)/\lambda$, where Θ is the Bragg angle and λ – wavelength. The polydispersity effect was incorporated by a convolution of eq 1 with the Gaussian size distribution functions. After extracting the PMMA sphere diameter (D_A) and its polydispersity, the $S(q)$ functions were analyzed. The obtained $S(q)$

curves with a well-defined main interference maximum indicate that there is no long-range order in arrangement of the PMMA spheres. Therefore, the $S(q)$ curves were fitted to Kinning and Thomas model,[7] which accounts for both the hard-core [8] and soft interaction potentials in liquid-like systems. This fitting reproduces the lowest angle peak and in some cases the secondary peak (**Figure S6**). The obtained effective radius of the particles includes the hard sphere (i.e., PMMA), as well as a size of the surrounding soft shell.[7] The thickness of the covering layer varies between 7.7 and 16.8 nm, which correlates with the length of the bottlebrush blocks. This analysis provides the inter-domain distance distribution as a function of the backbone DP (n_{bb}). These results are also consistent with AFM observations (**Figures S3A,B**).

Evaluation of the local backbone conformation was performed by using the well-defined form-factor $P(q)$ and the brush peak (d_1). Position of the d_1 -peak corresponding to the backbone-to-backbone separation reflects packing of bottlebrushes in the melt that fills the space between the PMMA domains far from the **A-B** interface. Due to strong steric repulsion, side chains do not overlap and bottlebrushes behave as filaments with a persistence length on the order of their diameter.[1,12,13] We can use average distance between backbones $d_1 = 3.4 \text{ nm}$ to estimate the local backbone conformation inside the bottlebrush envelope. Indeed, from distance d_1 the average area per side chain is equal to $S_{bulk} \cong \sqrt{3}d_1^2/2 \cong 10 \text{ nm}^2$. Using the volume $V_{sc} = M_{sc}/(N_{Av}\rho) = 1.73 \text{ nm}^3$ occupied by a side chain with a molar mass of the side chain $M_{sc} = 1024 \text{ g/mol}$ and density of bottlebrush $\rho = 0.97 \text{ g/cm}^3$, the distance between neighboring side chains along the bottlebrush backbone is estimated as $l_{bulk} = V_{sc}/S_{bulk} = 0.17 \text{ nm}$. Note that l_{bulk} is smaller than the backbone monomer projection length $l_0 = 0.25 \text{ nm}$. This points out to a moderate extension of the backbone inside the bottlebrush envelope.

The spatial organization of the bottlebrush blocks at the **A-B** interface can be obtained by approximating scattering of PMMA domains by the form-factor of polydisperse solid spheres (see **Table 1** for sphere diameter (D_A) and its dispersity). This directly gives the aggregation number $Q = \pi D_A^3 / (6 v_A n_A)$ and the average area per molecule (S_{interf}) at the surface of the PMMA domains as:

$$S_{interf} = \frac{\pi D_A^2}{Q} = \frac{6 v_A n_A}{D_A} \quad (2)$$

where $v_A = 0.141 \text{ nm}^3$ is the PMMA monomer volume. In the framework of the scaling approach based on the balance of the block's interfacial and stretching free energies, the diameter of PMMA spheres is related to the block's degrees of polymerization [3] as

$$D_A \cong (n_{bb} n_A v_A)^{1/3} \quad (3)$$

By substituting eq 2 into eq 3, the following scaling relation for the molecular area at the **A-B** interface is estimated to be:

$$S_{interf} \sim n_A^{2/3} n_{bb}^{-1/3} \quad (4)$$

It can be seen that relationships (3) and (4) hold within ca. 18% precision for all of the studied systems (**Figure 3**).

Figure 2. USAXS-SAXS curves corresponding to different series of **ABA** bottlebrush copolymer with (A) invariable **B** block and (B) approximately invariable **A** block. The fits with the form-factor of PMMA spheres are shown by the dashed lines. Note that the **A**₁₂₃₅**B**₉₃₈**A**₁₂₃₅ sample with the longest **A** block does not display well-defined ripples of the spherical form-factor, which is ascribed to a transition to a non-spherical morphology as supported by AFM.[3]

Comparing the average area in the bulk with that at the **A-B** interface, we can identify **ABA** systems with locally perturbed bottlebrush conformation. This is illustrated in **Figure 3B** by a dashed line $S_{interf} \sim S_{bulk}$. For **ABAs** with longer **A**-blocks and correspondingly larger domain sizes D_A , S_{interf} approaches and then becomes bigger than the bulk value of $S_{interf} \sim S_{bulk} \approx 8.5 \div 15 \text{ nm}^2$. However, systems with shorter **A**-blocks (smaller domains with higher curvature) demonstrate progressive decrease of the bottlebrush footprint at the **A-B** interface down to 4.1 nm^2 (**Table 1**). This results in additional local stretching of the bottlebrush block including stretching and alignment of side chains along the backbone.

We can estimate how far from the interface the deformation of the bottlebrush block should persist. To do so, we introduce a dimensionless crowding parameter Φ - ratio of the volume occupied by sections of the bottlebrush block $V_{bb}(\Delta)$ within a spherical shell of thickness Δ around **A** domains to the volume of the spherical shell $V_{sh}(\Delta)$. In our analysis of the bottlebrush packing in the vicinity of the **A** domains, we assumed that the bottlebrush backbones are aligned in radial direction to reduce their footprint (**Figure 1C**). The volume occupied by bottlebrushes is equal to $V_{bb}(\Delta) = QV_{sc}\Delta/l_0$ (where $l_0 = 0.25 \text{ nm}$ is the monomer projection length). Taking into account the explicit expression for the volume of the spherical shell and substituting

Note that the main source of error in this case is associated with uncertainty in the molecular parameters of the studied plastomers.

for the aggregation number $Q = 4\pi R_A^3/(3 v_A n_A)$ in terms of the spherical domain size, R_A , we obtain:

$$\Phi(\Delta) = \frac{R_A^3 V_{sc}}{n_A l_0 v_A} (3R_A^2 + 3R_A\Delta + \Delta^2)^{-1} \quad (5)$$

The value of the crowding parameter $\Phi > 1$ indicates that all monomers belonging to the side chains cannot be packed within a spherical shell and should be expelled. The value of the crowding parameter at the surface of the spherical domain $\Phi(0)$ is larger than unity only for 300-x series and one 900-1 data set (see **Table S3**). Thus, for these systems, packing of the bottlebrushes close to **A-B** interface could require stretching of the backbone and stretching and alignment of the side chains along the bottlebrush backbone. Such additional straining of the bottlebrush as compared to the conformation in the bulk will continue until $\Phi \approx 1$. The thickness of the spherical shell Δ^* at crossover to the bulk-like behavior is obtained by solving eq 5 for Δ with crowding parameter $\Phi = 1$. We can extend this analysis to the case when backbones maintain their original bulk conformations close to interface and side chains are aligned along the direction normal to the interface. In this case we substitute $l_{bulk} = 0.17 \text{ nm}$ instead of the monomer projection length l_0 in eq 5. The results of these calculations are summarized in **Table S3**. We would like to point out that direct probing of the brush conformation at

interface could be obtained from neutron scattering experiments,[14] unfortunately, precise deuteration of the bottlebrushes remains a challenging synthetic task.

In conclusion, the combination of USAXS and SAXS techniques highlights the hierarchical organization of linear-bottlebrush-linear PMMA-PDMS-PMMA triblock copolymer physical networks. A new feature is the dependence of bottlebrush conformation on the distance from the PMMA-PDMS **A-B** interface and the interface curvature. Close to the interface with a diameter of $D_A < 27\text{ nm}$, the backbones are aligned in the radial direction while side chains are stretched and aligned with the backbones in order to satisfy local packing constraints. (**Figure 1C**). Far from the interface, bottlebrushes behave as flexible filaments with moderately extended backbones. A similar conformational behavior on both sides of the **A-B** interface should also be expected for other types of block-copolymer with brush-like blocks [15-17]. We hope our results will inspire investigation of bottlebrush conformation in such systems.

Figure 3. (A) Scaling dependences for the PMMA domain diameter D_A and (B) the molecular area at the **A-B** interface S_{intf} as a function of degrees of polymerization of the PMMA linear block (n_A) and PDMS bottlebrush backbone (n_{bb}).

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Materials and synthesis, NMR characterization of the bottlebrush copolymers, molecular and structural parameters of the studied bottlebrush copolymers, AFM characterization, SAXS data treatment and analysis, structure evolution of the bottlebrush copolymers upon swelling in selective solvents, orientation of the brush

peak upon stretching, fitting of the structure factor with the Kinning-Thomas model, and analysis of packing of the bottlebrushes (PDF).

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