

Brush Architecture and Network Elasticity: Path to the Design of Mechanically Diverse Elastomers

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ABSTRACT: We unveil universal correlations between architectural parameters and nonlinear elastic properties of brush polymer networks. A comprehensive library of poly(*n*-butyl acrylate), poly(dimethylsiloxane), and polyisobutylene brush networks was synthesized with systematically varied side chain length ($\sim n_{sc}$), grafting density ($\sim n_{g}^{-1}$), and backbone degree of polymerization between cross-links (n_{x}). This allowed experimental verification of theoretical scaling relationships between mechanical properties (shear modulus and strain-stiffening), architectural parameters [n_{sc} , n_{g} , n_{x}], and microstructure from in situ small-angle X-ray scattering in both comb and bottlebrush conformational regimes. These results can be used as a foundation for the programmable design of mechanically diverse solvent-free elastic materials.

Supporting Information

■ INTRODUCTION

Brush-like elastomers made by grafting long side chains to a linear backbone demonstrate a broad range of mechanical properties with Young's modulus on par with those of linear chain gels ($E_0 \sim 10^2 - 10^7$ Pa) and large reversible deformations (~10×) due to suppression of chain entanglements.¹⁻¹⁰ The absence of solvent resolves issues with leaching and evaporation pertinent to polymer gels.¹⁰⁻¹⁷ These supersoft yet solvent-free elastic materials have been explored for applications such as stimuli response,¹⁸ 3D printing,¹⁹ in vivo injectability,²⁰ self-healing,^{21,22} structural coloration,²³ dielectric actuation,^{24,25} and drug delivery.^{26,27}

It is well established that grafting side chains to a linear backbone plays a dual role as it (i) dilutes and disentangles the stress supporting strands allowing for unprecedented softness down to $E_0 \sim 10^2$ Pa and (ii) induces steric repulsion between side chains with increasing grafting density leading to preextension of the network strands in as-prepared elastomers.^{2,3,28-32} The dual effect of the side chains manifests itself with intense strain-stiffening whereby initially soft materials rapidly stiffen with deformation (Figure 1). Depending on brush network architecture, the modulus may increase up to 2 orders of magnitude within a short strain interval of 50%.²³ This behavior is qualitatively different from that of linear chain networks with flexible strands that exhibit a relatively weak modulus variation with deformation. The initial modulus and strain-stiffening of brush networks can be controlled independent of each other by varying three architectural parameters: degree of polymerization (DP) of side chains n_{sc} , DP of spacer between neighboring side chains $n_{g'}$ and DP of the backbone between cross-links n_{x} .⁴ In contrast, mechanical



elongation, $\lambda = L/L_0$

Figure 1. Comparison of nonlinear deformation in brush networks to linear chain networks. For uniform networks, the elongation at break (λ_{max}) is inversely proportional to $\sqrt{\beta}$ (eq 8).

properties of linear chain networks, such as shear modulus $G \cong E_0/3$ and elongation at break $\lambda_{\text{max}} = L/L_0$, are largely determined by a single structural parameter n_{x^1} as $G \sim 1/n_x$ and $\lambda_{\text{max}} \sim \sqrt{n_x}$.

Architectural network optimization by diluting and stiffening the backbone has empowered the synthesis of supersoft elastic materials capable of reproducing the characteristic strainstiffening behavior of soft biological tissues.^{4,6,23,33-36} While

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Figure 2. (a) A brush macromolecule with low grafting density of side chains is presented as a chain of blobs of size R_{sc} that host monomeric units of the surrounding brushes (bleached lines). (b) Conformations of side chains and backbone in different brush regimes depicted in panel c. Adapted from ref 37. (c) Diagram of states of brush macromolecules in a melt with monomer projection length *l*, Kuhn length of side chains *b*, and monomer excluded volume ν (logarithmic scales). SBB: stretched backbone subregime, SSC: tretched side-chain subregime, and RSC: rodlike side-chain subregime. The boundary between the accessible regimes and the so-called forbidden region is defined by $\varphi^{-1} \leq n_{sc}/n_g^{max} + 1$ for $n_g^{max} = 1$. Adapted from ref 32. For graft copolymer with chemically dissimilar backbone and side chains, the regime boundaries depend on the corresponding molecular parameters $l_i\nu_i$ and b_i^{39} .

Table	1.	Parameters	of	Brush	Networks	in	Different	Conformational	Regimes
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brush regime	comb	SBB	SSC
boundaries	$\frac{\varphi^{-1}}{\Phi^*} \le \frac{(bl)^{3/2}}{\nu} n_{\rm sc}^{1/2}$	$\frac{(bl)^{3/2}}{\nu} \eta_{\rm sc}^{1/2} \le \frac{\varphi^{-1}}{\Phi^*} \le \frac{bl^2}{\nu} \eta_{\rm sc}$	$\frac{bl^2}{\nu}n_{\rm sc} \leq \frac{\varphi^{-1}}{\Phi^*}$
b_K (ref 32)	Ь	$\frac{\nu}{l^{3/2}b^{1/2}}\frac{\varphi^{-1}}{n_{\rm sc}^{1/2}\Phi^*}$	$\frac{\nu^{1/2}}{l^{1/2}} \left(\frac{\varphi^{-1}}{\Phi^*} \right)^{1/2}$
G (eq 11)	$k_{ m B}Trac{l}{ u b_{ m K}}arphieta$	$k_{ m B}Trac{l}{vb}arphieta$	
α (eq 4)	$\frac{b}{n_{x}l}$	$\frac{b_{\mathrm{K}}}{n_{\mathrm{x}}l}$	
β (eq 7)	α	$\alpha \left(1 - \frac{\alpha}{2} \left(1 - \exp\left(-\frac{\alpha}{2}\right)\right)\right)$	$\left(\frac{2}{\alpha}\right)$

"SBB: stretched backbone regime, SSC: stretched side-chain regime, ρ : polymer bulk density, *l*: projection length of the repeat unit, *v*: excluded volume of the repeat unit, *b*: Kuhn length of a linear chain, $b_{\rm K}$: Kuhn length of brush backbone, $k_{\rm B}$: Boltzmann constant, *T* is the absolute temperature, and Φ^* : value of the crowding parameter at crossover to bottlebrush regime.^{32,37,39}

these studies showed potential of using molecular architecture for materials design, the complete picture of the structure– property correlations of brush networks is far from complete. To address this problem, we synthesized a comprehensive library of poly(*n*-butyl acrylate) (PBA), poly-(dimethylsiloxane) (PDMS), and polyisobutylene (PIB) networks with brushlike strands and studied their structural and mechanical properties. We begin with a brief overview of brush conformations in an undeformed network, corresponding diagram of states, and nonlinear network elasticity model.^{31–38}

MODEL OF BRUSH NETWORKS

Conformation Regimes of Network Strands and Diagram of States. Conformations of brush strands in an undeformed network are determined by the $n_{\rm sc}$ and the brush compositional parameter, φ^{-1} , which describes the partitioning of polymer volume between side chains and backbone as³⁷

$$\varphi^{-1} = 1 + \frac{n_{\rm sc}}{n_{\rm g}} \tag{1a}$$

The φ^{-1} may also be viewed as an average DP of side chain per repeat unit of the backbone, which is linearly proportional to mass grafting density under the assumption that both the

backbone and side chains are made of identical repeat units with projection length l, volume v, and bare Kuhn length b. For heteropolymers, or graft copolymers, with chemically dissimilar backbone and side chains, the compositional parameter is given by

$$\varphi^{-1} = 1 + \frac{v_{sc} n_{sc}}{v_{bb} n_{g}}$$
(1b)

where v_{sc} and v_{bb} are volumes of side-chain and backbone repeat units.³⁹

At low grafting densities $(n_g \gg n_{sc})$, loosely grafted side chains allow an overlap of neighboring brush macromolecules without perturbing their Gaussian conformation (Figure 2a). In this comb regime, brush backbones behave as conventional linear polymer chains. As grafting density increases $(n_g < n_{sc})$, side chains are forced to withdraw from the pervaded volume occupied by neighboring brush molecules, effectively resulting in segregation of the side chains belonging to the same macromolecules and the formation of soft filaments with a thickness of the order of the side chain size, R_{sc} (Figure 2b). This segregation is quantified by the so-called crowding parameter, which defines the degree of mutual interpenetration between side chains belonging to different brush macro-molecules: $^{\rm 37}$

$$\Phi \cong \begin{cases} \frac{\nu}{(bl)^{3/2}} \varphi^{-1} n_{\rm sc}^{-1/2}, \text{ for flexible side chains } (n_{\rm sc} \ge b/l) \\ \frac{\nu}{l^3} \varphi^{-1} n_{\rm sc}^{-2}, \text{ for rodlike side chains } (n_{\rm sc} < b/l) \end{cases}$$
(2)

The condition $\Phi^* \cong 1$ in the scaling approach framework defines the crossover between the comb ($\Phi < \Phi^*$) and bottlebrush ($\Phi > \Phi^*$), which is designated as a bold solid line in the diagram of states of brush polymers constructed in terms of $n_{\rm sc}$ and φ^{-1} (Figure 2c).³² The bottlebrush regime has three subregimes: stretched-backbone (SBB), stretched-side-chain (SSC), and rodlike side-chain (RSC) bottlebrush subregimes. These subregimes reflect the effect of the grafting density or DP of the side chains on the backbone and side-chain conformation. The upper boundary of the bottlebrush regime is determined by backbone chemical structure, which determines a maximum number of the side chains $n_{\rm g}^{\rm max}$ per backbone monomer such that $\varphi^{-1} \leq n_{\rm sc}/n_{\rm g}^{\rm max} + 1$.

Analysis of the brush conformations in different regimes indicates that brushlike strands can be viewed as semiflexible chains with the effective Kuhn length, $b_{\rm K}$, which depends on φ^{-1} , $n_{\rm sc}$ bare Kuhn length b, repeat unit projection length l, and excluded volume v (Table 1).^{32,37,39} In the comb regime, the backbone conformations of loosely grafted strands with relatively short side chains are similar to those of linear chains with the Kuhn length $b_{\rm K} \cong b$. Upon increasing the grafting density and/or side-chain length, steric repulsion between side chains leads to backbone extension and stiffening. In the SBB subregime, the backbone extends with an effective Kuhn length $b_{\rm K} \cong \frac{v}{l^{3/2}b^{1/2}}\frac{\varphi^{-1}}{n_{\rm sc}^{-1/2}\Phi^{*}}$, yet the side chains remain coiled. As the backbone approaches a full extension, the further increase of grafting density at $n_{\rm g} \leq v/(bl^2)$ prompts extension of side chains. In this SSC subregime, the effective Kuhn length of the backbone is $b_{\rm K} \cong \frac{v^{1/2}}{l^{1/2}}(\varphi^{-1}/\Phi^{*})^{1/2}.^{32,37,39}$

For semiflexible chains, the mean-square end-to-end distance is equal to

$$\langle R_{\rm in}^2 \rangle = \alpha R_{\rm max}^2 \left(1 - \frac{\alpha}{2} \left(1 - \exp\left(-\frac{2}{\alpha}\right) \right) \right)$$
(3)

where $R_{\rm max}$ is the contour length of the backbone and parameter

$$\alpha^{-1} \equiv n_{\rm x} l/b_{\rm K} = R_{\rm max}/b_{\rm K} \tag{4}$$

is equal to the number of Kuhn segments per strand and defines strand flexibility.

Mechanical Properties of Networks in Different Brush Regimes. Mechanical stress in polymer networks made of either entangled or unentangled semiflexible strands undergoing uniaxial deformation with the elongation ratio λ is given by the following expression^{34,35}

$$\sigma_{\rm true}(\lambda) = (\lambda^2 - \lambda^{-1}) \left(\frac{G_{\rm e}}{\lambda} + \frac{G}{3} \left(1 + 2 \left(1 - \frac{\beta(\lambda^2 + 2\lambda^{-1})}{3} \right)^{-2} \right) \right)$$
(5)

where G_e is the entanglement modulus. For unentangled networks, two parameters, G and β , define the network

elasticity and control the shape of the stress-deformation curve.^{6,34} The former is the network structural shear modulus

$$G \cong k_{\rm B} T \rho_{\rm s} \frac{\langle R_{\rm in}^2 \rangle}{b_{\rm K} R_{\rm max}} \tag{6}$$

where $k_{\rm B}$ is the Boltzmann constant, *T* is absolute temperature, $\rho_{\rm s} = V_{\rm strand}^{-1}$ is the cross-link density, i.e., number of mechanically active strands per unit volume, $V_{\rm strand} = v n_{\rm x} \varphi^{-1}$, and $\langle R_{\rm in}^2 \rangle$ is given by eq 3.

The strain-stiffening (firmness) parameter, β , describes the extension of network strands (eq 3) relative to their contour length, $R_{\text{max}} = n_x l$,

$$\beta \equiv \frac{\langle R_{\rm in}^2 \rangle}{R_{\rm max}^2} = \alpha \left(1 - \frac{\alpha}{2} \left(1 - \exp\left(-\frac{2}{\alpha}\right) \right) \right)$$
(7)

and predicts the extensibility (elongation at break) $\lambda_{max} = L/L_0$ of uniform networks as

$$\lambda_{\max} \cong \frac{R_{\max}}{\sqrt{\langle R_{\inf}^2 \rangle}} = \frac{1}{\sqrt{\beta}}$$
(8)

Note, however, that networks with a broad mesh size distribution may undergo premature rupture prior to reaching the theoretical limit: $\lambda_{\rm max} < 1/\sqrt{\beta}$.

For long and/or flexible brush strands $(h_x \gg b_K)$, the backbone adopts a Gaussian conformation with $\langle R_{\rm in}^2 \rangle \cong b_K R_{\rm max}$ and $\alpha^{-1} \ll 1$ (eq 4). In this case, parameters G and β reduce to

$$G \cong k_{\rm B} T \rho_{\rm s} \cong \frac{k_{\rm B} T}{\nu n_{\rm x} (1 + n_{\rm sc}/n_{\rm g})} \tag{9}$$

$$\beta = \frac{\langle R_{\text{in}}^2 \rangle}{R_{\text{max}}^2} \cong \frac{b_{\text{K}} R_{\text{max}}}{R_{\text{max}}^2} = \frac{b_{\text{K}}}{n_{\text{x}} l} = \alpha$$
(10)

where *G* for brush elastomers diverts from the conventional $G \cong k_{\rm B}T/vn_{\rm x}$ for linear networks due to dilution of network strands by the grafted side chains as $\rho_{\rm s} \sim \varphi = (1 + n_{\rm sc}/n_{\rm g})^{-1}$. By solving eq 10 for $n_{\rm x}$ and substituting it into eq 9, we can express the modulus as

$$G \cong \frac{k_{\rm B} T \beta l}{v b_{\rm K} (1 + n_{\rm sc}/n_{\rm g})} \tag{11}$$

This expression provides a direct correlation between the *G* and β , also eliminating explicit dependence of the *G* on n_{xy} , which is typically unknown for synthetic polymer networks.

In summation, each brush regime is characterized by the effective backbone Kuhn length, $b_{\rm K}$, which provides explicit dependence of the elastomer mechanical properties (*G* and β) on the architectural triplet $[n_{\rm sc}, n_{\rm g}, n_{\rm x}]$ as well as chemistry specific parameters (l, b, v) (Table 1).^{32,37,39}

EXPERIMENTAL STUDIES OF BRUSH NETWORKS

Synthesis of Brush Networks. To study the nonlinear elastic deformation in different brush regimes, we synthesized several series of brush elastomers by systematically varying n_{sc} , n_{g} , and n_{x} (Experimental Section and Supporting Information section S1). The effect of different chemistries on mechanical properties was examined by preparing networks with PBA, PIB, and PDMS side chains.

The PBA macromonomers and cross-linkers with defined degrees of polymerization (DP) were synthesized by monoand difunctionally initiated ATRP (dispersity, D < 1.12, Figure S3) followed by postpolymerization substitution of the terminal, secondary bromine with a methacrylate. The PIB macromonomer was derived from methylvinylidene-functionalized oligomer (D = 1.9) following a two-step methacrylation while PDMS macromonomers (D = 1.41) were commercially available (Figure 3; see the Experimental Section for full



Figure 3. Side-chain macromonomer synthesis. (a) PBA side-chain macromonomer synthesis from monomer (Figures S1–S3). (b) Twostep methacrylation of PIB oligomer (Figures S4–S6). (c) PDMS macromonomer was commercially available. See the Supporting Information for photocuring of macromonomer resin to form brush elastomers.

synthesis of macromonomers). Macromonomers were mixed with appropriate spacer monomers, solvent, and initiator with cross-linkers of DP ~ $2n_{\rm sc}$. In the case of the dense bottlebrushes ($n_{\rm g} = 2$) with longer side chains ($n_{\rm sc} = 41$), the cross-linker DP was increased to ~ $3n_{\rm sc}$ to alleviate polymerization constraints from steric repulsion of densely grafted side chains.⁴⁰ Reagents underwent overnight UV-curing after injection into an elastomer mold to form 1 mm thick films with glass transition temperatures below room temperature.

The possibility of phase separation was considered for chemically dissimilar backbone and side chains in combs with near equimolar ratios of side chain and backbone spacers. To avoid phase separation, PBA brush networks are built of chemically identical side chains, spacer molecules, and crosslinkers. In contrast, the PIB and PDMS systems having polyacrylate backbones are generally prone to phase separation depending on grafting density. In densely grafted bottlebrushes, where the side-chain fraction is predominant (>85 wt %), we did not observe any sign of phase separation such as multiple glass transitions, turbidity, or microdomains in SAXS curves. However, studies of PIB and PDMS combs should proceed with caution with that potential complication in mind.

The assignment of PBA, PIB, and PDMS networks with different n_{sc} and φ^{-1} combinations to the specific brush regimes is depicted by symbols in the diagram of states (Figure 4). Unlike the diagram in Figure 2c, the universal coordinates in Figure 4 account for the difference in chemical composition and use the crossover crowding parameter $\Phi^* = 0.7$ determined by computer simulations.^{37,39} The crossover lines between different regimes in Figure 4 are calculated by using molecular parameters summarized in Table 3.³²

Scattering from Brush Networks. Small-angle X-ray scattering (SAXS) studies were conducted to verify brush

elastomer structure and demonstrate the effects of side-chain length and grafting density on brush dimensions (Supporting Information, section S3). Side-chain grafting leads to enhanced electron density at the backbone junctions as well as limited interpenetration of the segments from the neighboring chains, which in turn generates contrast in X-ray scattering even in homopolymer (e.g., all-PBA) brush networks (Figures S14 and S15). In the case of the most densely grafted side chains (n_{g} = 1), the scattering peak located at $q^* \approx 1-3 \text{ nm}^{-1}$ is clearly visible as it progressively shifts toward larger q^* values with decreasing $n_{\rm sc}$ (Figure 5a).^{38,41-43} With increasing $n_{\rm g}$ at a fixed $n_{\rm sc}$ = 11, the peak gradually vanishes and becomes indiscernible at $n_{g} > 5$ due to diminishing enhancement of the backbone electron density by grafting junctions and increasing interpenetration between the neighboring chains (Figure 5b). For $n_{\rm sc}$ = 41, the peak respectively disappears at higher $n_{\rm g}$ > 10 (Figure S16). Note that the peaks partially overlap with the WAXS peak originated from the interatomic correlations. Therefore, to obtain peak location at q^* , the scattering function was represented by a sum of analytical functions pertaining to the WAXS halo and the asymmetric shape of the bottlebrush peak (Figure S17).

Two different interpretations have been proposed to correlate peak location and brush chain conformations in a melt state. The first perception is to consider q^* as an intermolecular correlation peak corresponding to the average distance $d = 2\pi/q^*$ between the neighboring bottlebrush backbones.^{41,42} This interpretation would be appropriate if brushes acted as rigid cylinders, where the peak position scales with grafting density as $q^* \sim d^{-1} \sim \sqrt{\varphi}$. For dense bottlebrushes ($n_{\rm g}$ = 1 and $\varphi^{-1} \cong n_{\rm sc}$ (eq 1)), this scaling relation can be approximated with $d \sim \sqrt{n_{sc}}$, assuming the backbone conformation (length per side chain) does not depend on $n_{\rm sc}$. The data approach the $\varphi^{-1/2}$ dependence for the dense $(n_{\rm g}$ = 1) PBA bottlebrushes (Figure 5c), while deviation from this scaling behavior for $n_{\rm g}$ > 1 may be ascribed to backbone contraction within the bottlebrush envelope. However, this molecular packing interpretation cannot be fully validated through the existence of a single correlation peak.

The second interpretation of q^* considers brushlike macromolecules as copolymers in a melt with backbone fluctuations being coupled with fluctuations of covalently connected side chains imposed by the incompressibility condition.^{42–48} Accordingly, any fluctuation of the backbone electron density is accompanied by an opposite fluctuation of the side chains to maintain constant melt density resulting in characteristic length scale $d \cong (n_{\rm g} n_{\rm sc} b_{\rm K} b_{\rm I}^2)^{1/4}$. This leads to a softer power law $d \sim n_{\rm sc}^{-3/8}$ in the SBB bottlebrush subregime and $d \sim n_{\rm sc}^{-1/4}$ in the comb regime.⁴⁹

This investigation reveals that both interpretations of the scattering results are possible depending on side-chain conformations. To highlight the existence of two different regimes, we plot the PBA brush elastomer SAXS data as d/b_K vs the dimensionless parameter $(n_g n_{sc} b l^2 / b_K^{-3})^{1/4}$, which confirms nearly constant $d/b_K \cong 1$ for $(n_g n_{sc} b l^2 / b_K^{-3})^{1/4} < 1$ followed by a linear increase of the d/b_K ratio (Figure 5d). For bottlebrushes with densely grafted side chains $n_g = 1$ and 2 (SSC regime), stretching of the side chains suppresses their fluctuations, resulting in direct coupling of the backbone fluctuations such that $d \cong b_K$. In this case, bottlebrushes may be considered flexible cylinders that scatter according to the

Table 2. Structural Parameters and Mechanical Properties of Brush Elastomers

PBA1115099	side-chain chemistry	$n_{\rm sc}^{a}$	n_g^b	n _x ^c	G (kPa) ^d	G _e (kPa) [€]	β^{f}	$E_0 \ (\mathrm{kPa})^g$	brush regime ^h
11 11 100 5.4 0.16 20.7 8C 11 2 50 21.2 0.00 87.5 8C 11 2 200 5.4 0.08 18.6 SC 11 3 30 28.5 3.3 0.18 12.2 SB/comb 11 3 200 7.2 4.4 0.09 37.8 SB/comb 11 3 200 7.2 4.4 0.09 37.8 Comb 11 5 200 2.1 3.9 0.01 18.1 Comb 11 10 100 27.1 8.1 0.06 17.4 Comb 11 10 100 27.1 8.1 0.03 17.4 Comb 12 2 20 10.1 0.3 44.2 SC SC 13 100 2.2 0.09 7.52 SC SC 14 100 3.8 8.8 0.22 18.9 SC 13 100 18.3 .007 9.92 SB 14 2 50 18.3 8.8 0.22 18.9 13 100 18.3	PBA	11	1	50	9.9		0.22	42.4	RSC
11 1 200 2.5 0.10 87.5 85C 11 2 100 10.3 0.14 38.2 85C 11 2 100 10.3 0.14 18.6 85C 11 3 50 25.5 3.3 0.18 123.2 SBM/comb 11 3 100 15.3 3.8 0.13 93.9 SBM/comb 11 3 100 27.2 4.4 0.95 37.8 SBM/comb 11 5 100 27.1 8.1 0.01 18.1 comb 11 5 100 27.1 8.1 0.03 74.2 comb 13 10 200 15.5 9.1 0.03 74.2 comb 14 10 200 16.1 0.03 74.2 SSC 15.3 10 10.1 10.3 18.4 20.1 75.2 SSC 13 4 50 15.3 0.14 15.2 SSC 14 200 3 0.07 99.2 SBM 15.3 10 1.8 0.21 SSC SSC 14 100 1.8		11	1	100	5.4		0.16	20.7	RSC
11 2 50 21.2 0.20 8.75 SSC 11 2 200 5.4 0.08 18.6 SSC 11 3 50 22.5 3.8 0.15 69.0 SBM/comb 11 3 200 7.2 4.4 0.99 37.8 SBM/comb 11 5 200 2.1 3.9 0.01 18.1 comb 11 5 200 2.1 3.9 0.01 18.1 comb 11 10 100 27.1 8.1 0.06 12.4 comb 123 2 50 10.1 0.3 14.2 SSC 23 4 100 8.4 0.16 32.2 SSB 23 4 100 3.4 0.16 32.2 SSB 23 10 100 19.5 7.7 0.17 99.2 comb 23 10 100 13.		11	1	200	2.5		0.10	8.7	RSC
11 2 100 10.3 0.14 38.2 SC 11 3 50 28.5 3.3 0.18 123.2 SRP/comb 11 3 100 15.3 3.8 0.18 123.2 SRP/comb 11 3 100 7.2 4.4 0.09 37.8 SRP/comb 11 5 100 8.2 2.5 0.05 33.9 comb 11 5 100 7.1 8.1 0.06 18.1 comb 11 10 50 46.5 7.3 0.11 18.8 comb 12 10 50 10.1 0.33 74.2 comb 13 10 200 15 9.1 0.3 74.2 comb 14 20 3 0.11 18.52 SSC SSC 13 10 50 18.3 0.16 32.2 SRP 14 10 50 38 8.8 0.22 I88.2 comb 15 10.1 74 88 10.2 18.1 10.1 74 SRP 14 2 100 1.8 0.14 6.6 SSC		11	2	50	21.2		0.20	87.5	SSC
11 2 200 5.4 0.08 18.6 SCC 11 3 100 15.3 3.8 0.15 SBP/comb 11 3 100 62.3 2.5 0.05 33.9 comb 11 5 100 62.2 2.0 0.05 33.9 comb 11 5 200 2.1 3.9 0.01 18.1 comb 11 10 100 27.1 8.1 0.06 17.4 comb 123 2 200 15 9.1 0.3 74.2 SCC 23 4 100 5 0.07 76.2 SRB 23 4 100 8.4 0.16 32.22 SRB 23 10 100 19.5 7.7 0.17 99.22 comb 23 10 100 1.8 0.16 0.23 SCS/SBB 24 100 1.8		11	2	100	10.3		0.14	38.2	SSC
11 3 50 28.5 3.3 0.18 123.2 SBB/comb 11 3 100 15.3 3.8 0.15 69.0 SBB/comb 11 5 100 7.2 4.4 0.09 37.8 SBB/comb 11 5 100 2.1 3.9 0.01 18.1 comb 11 10 50 46.5 7.3 0.11 18.5.3 comb 11 10 100 2.71 8.1 0.06 11.2 comb 23 2 100 5 9.1 0.03 74.2 comb 23 2 100 15 9.1 0.03 74.2 SEC 23 2 100 18.3 0.01 18.3 comb SEC 23 4 100 8.4 0.16 32.2 SEB 23 10 100 19.5 7.7 0.16 19.2 comb 23 10 100 1.8 0.4 6.6 SEC/SBB 41 2 100 1.8 0.4 6.6 SEC/SBB 41 10 2.5 1.3 0.06 0.08 <		11	2	200	5.4		0.08	18.6	SSC
11 3 100 15.3 3.8 0.15 99.0 SBB/comb 11 3 200 7.2 4.44 0.09 7.3 SBB/comb 11 5 100 8.2 2.5 0.05 33.9 comb 11 10 50 4.65 7.3 0.01 18.1 comb 11 10 100 27.1 8.1 0.06 11.2.4 comb 23 2 50 10.1 -0.3 7.4.2 comb 23 2 100 5 -0.03 7.4.2 comb 23 4 50 8.2 0.2.2 0.09 7.52 SB 23 4 100 8.4 0.01 7.7 0.17 9.02 comb 23 10 100 1.8 0.14 6.6 SC/SB 23 10 100 1.8 0.14 6.6 SC/SB 24		11	3	50	28.5	3.3	0.18	123.2	SBB/comb
11 3 200 7.2 4.4 0.09 37.8 SBB/comb 11 5 200 2.1 3.9 0.01 18.1 comb 11 10 50 44.5 7.3 0.11 18.5 comb 11 10 100 27.1 8.1 0.06 11.4 comb 13 10 200 15 9.1 0.03 74.2 comb 23 2 100 5 0.14 18.52 SSC 23 4 200 3 0.01 7.92 SBB 23 4 100 8.4 0.16 32.22 SBB 23 10 50 3.8 8.8 0.22 18.9.32 comb 23 10 200 10.3 1.8 0.06 39.02 comb 24 10 5.5 7.7 0.7 1.7 9.0 SB 23 10 </td <td></td> <td>11</td> <td>3</td> <td>100</td> <td>15.3</td> <td>3.8</td> <td>0.15</td> <td>69.0</td> <td>SBB/comb</td>		11	3	100	15.3	3.8	0.15	69.0	SBB/comb
11 5 100 8.2 2.5 0.05 3.39 comb 11 10 50 2.11 3.9 0.01 18.1 comb 11 10 100 27.1 8.1 0.06 112.4 comb 11 10 200 15 9.1 0.03 74.2 comb 23 2 100 5 0.01 0.23 44.2 SC 23 2 200 2.2 0.09 7.52 SE 23 4 100 8.4 0.01 32.22 SB 23 10 50 3.8 8.8 0.07 9.92 comb 23 10 100 19.5 7.7 0.17 99.2 comb 41 2 0.0 1.8 0.1 1.4 6.6 SC/SB 41 2 0.0 1.8 0.1 7.4 SB 141 10		11	3	200	7.2	4.4	0.09	37.8	SBB/comb
1152002.13.90.0118.1comb11105044.57.30.1118.58comb11102001.59.10.037.4.2comb2325010.10.234.2.4SSC2322002.20.1418.52SSC2345018.30.217.692SBB2340.08.40.163.222SB2340.08.40.163.222SB2310503.88.80.22189.32comb231020010.31.80.0639.02comb23102001.80.146.6SSC/SBB4122000.60.882.0SSC/SBB4122000.60.882.0SSC/SBB4151002.10.117.4SB4151002.10.130.845.9comb41105020.36.90.1799.9comb1811003.80.2018.5SSCSSC1811003.80.0913.5SSCSSC1811003.80.0013.5SSCSSC1910.001.240.054.00SSC1811003.9 <td></td> <td>11</td> <td>5</td> <td>100</td> <td>8.2</td> <td>2.5</td> <td>0.05</td> <td>33.9</td> <td>comb</td>		11	5	100	8.2	2.5	0.05	33.9	comb
11 10 50 46.5 7.3 0.11 185.8 comb 11 10 100 27.1 8.1 0.06 11.4 comb 23 2 50 10.1 0.23 44.2 SSC 23 2 100 5 0.04 415.2 SSC 23 4 100 8.4 0.016 32.22 SBB 23 4 100 8.4 0.16 32.22 SBB 23 4 0.00 3 8.8 0.22 SBB 23 10 100 19.5 7.7 0.17 99.22 comb 23 10 200 10.3 1.8 0.03 18.4 SSC/SBB 23 10 200 1.42 0.03 18.4 SSC/SBB 41 2 200 0.6 0.23 18.4 SSC/SBB 41 10 50 2.5 8.8		11	5	200	2.1	3.9	0.01	18.1	comb
111010027.18.10.0611.2.4comb1312200159.10.0374.2comb23210050.1418.52SSC2320002.20.0165.2SBC23450018.30.217.692SBB2341008.40.079.92SBB23100.0019.57.70.179.92SBC231010019.57.70.179.92Comb23102001.31.80.063.90.2comb23102001.80.146.6SSC/SBB2421001.80.146.6SSC/SBB4122000.60.082.0SSC/SBB4151002.10.130.0845.9comb41502.36.90.1799.9comb4110502.36.90.1799.9comb411000.236.90.1799.9comb1811003.820.0613.5SSC/SBB1811001.240.054.00SSC1811001.240.054.00SSC1811003.820.077.6comb1810.002.70.086.3		11	10	50	46.5	7.3	0.11	185.8	comb
1110200159.10.0374.2comb2325010.10.2344.2SSC2322002.20.097.52SSC234508.40.163.22SBB2341008.40.163.22SBB2310503.88.80.22189.32comb231010019.57.70.1799.22comb23102001.80.146.6SSC/SBB412504.20.2318.4SSC/SBB4122000.60.295.7SBF4152.510.60.29SSC/SBBSSC/SBB4122000.60.146.6SSC/SBB41102537.58.80.22187.2comb41102537.58.80.22187.2comb4110001.30.044.59comb3.614100.031.240.054.00SSC1811003.20.0777.6SSC1811002.20.070.084.93comb1811001.20.0777.6SSC1811002.20.0777.6SSC18100.230.070.084.00		11	10	100	27.1	8.1	0.06	112.4	comb
232500.10.2344.2SSC232000\$.20.0418.52SSC2345018.30.2176.92SBB2341008.40.079.92SBB23420030.079.92SBB2310503.88.80.22189.32comb231020010.31.80.0639.02comb231020010.31.80.0639.02comb412504.20.2318.4SSC/SBB4122000.60.082.0SSC/SBB4151002.10.117.4SBB4110251.30.0845.9comb411010012.51.30.0845.9comb41101003.90.1013.5SSC/SBB41100.01.40.114.0SSC1813001.40.114.0SSC1813001.40.114.0SSC1810.03.90.1013.5SSC/SBB1810.03.90.1013.5SSC/SBB1810.03.90.1013.5SSC/SBB1810.03.90.1013.5SSC/SBB181		11	10	200	15	9.1	0.03	74.2	comb
23210050.1418.52SSC2322000.20.097.52SSC2341008.40.163.2.2SBB2342003.88.80.22189.32comb2310503.88.80.22189.32comb231020010.57.70.1799.22comb23102001.80.0639.02comb412504.20.2318.4SSC/SBB4122000.60.29S2.7SBB4152510.60.29S2.7SBB4110253.7.58.80.22SSC4110253.30.845.9comb4110202.36.90.1799.9comb41100.03.820.2015.7SSC1811003.820.2015.7SSC1812001.40.054.00SSC1812001.40.054.00SSC18161004.20.06136comb18161002.20.077.7.6Comb18161002.20.077.7.6SSC18100.7.50.099.3comb1816100 <t< td=""><td></td><td>23</td><td>2</td><td>50</td><td>10.1</td><td></td><td>0.23</td><td>44.2</td><td>SSC</td></t<>		23	2	50	10.1		0.23	44.2	SSC
2322002.20.097.52SSC2345018.30.2176.92SBB23420030.079.92SBB231050388.80.22189.3.2comb231010019.57.70.1799.2.2comb231020010.31.80.0639.0.2comb412504.20.2318.4SSC/SBB4122000.60.092.0SSC/SBB4151002.10.117.4SBB4151002.10.117.4SBB41105020.36.90.1799.9comb41105020.36.90.1799.9comb1811003.820.2015.7SSC1812001.40.114.90SSC1813001.240.054.00SSC1810.03.90.1013.5SSC/SBB18161004.20.06136comb18160.07.7.6comb141.670.086.9.31841002.80.077.6comb1418160.02.01.75.5CSSB18160.02.00.038.15		23	2	100	5		0.14	18.52	SSC
2345018.30.217.69.2SBB2341008.40.163.2.2SBB231050388.80.22189.3.2comb231020010.31.80.679.9.2comb231020010.31.80.619.0.2comb412504.20.318.4SSC/SBB4122000.60.082.0SSC/SBB4152510.60.29S.7SBB41102537.58.80.22187.2comb41100.02.10.117.4SBB41101003.820.2015.7SSC41101003.820.2015.7SSC1812001.40.114.90SSC1812001.40.114.90SSC1811003.90.077.7.6comb1812001.240.054.00SSC18161004.20.036.9.3comb18160.02.20.1724.2SSC1841001.70.086.9.3comb18160.02.60.038.15SSC/SBB1841002.60.077.6comb18		23	2	200	2.2		0.09	7.52	SSC
2341008.40.1632.22SBB23420030079.92SBD231010019.57.70.179.9.2comb231020010.31.80.6639.02comb23102001.80.146.6SSC/SBB4121001.80.146.6SSC/SBB4121002.10.117.4SBB4151002.10.117.4SBB4110502.036.90.179.9.9comb41101002.51.30.0845.9comb1811003.8.20.0215.7SSC1811003.8.20.054.00SSC1811003.70.056.70SSC1811003.60.077.6comb1811003.60.077.6comb1811003.60.077.6comb1811002.40.06136comb1811002.60.038.9.3comb1811002.60.077.6comb1811002.60.077.6comb1811002.60.077.6comb181100 <td></td> <td>23</td> <td>4</td> <td>50</td> <td>18.3</td> <td></td> <td>0.21</td> <td>76.92</td> <td>SBB</td>		23	4	50	18.3		0.21	76.92	SBB
23420030.079.92SBB231050388.80.22189.32comb231020010.31.80.0639.02comb231020010.31.80.0639.02comb412504.20.2318.4SSC/SBB4122000.60.082.0SSC/SBB4152510.60.2952.7SB4151002.10.117.4SBB41105023.58.80.22187.2comb41105023.51.30.0845.9comb141010012.51.30.0845.9comb1811003.820.054.00SSC1812001.40.114.90SSC1813001.240.054.00SSC181610023.60.0777.6comb18810020.70.0869.3comb181610023.60.038.15SSC/SBB18181001.10.083.70SSC18161002.60.038.15SSC/SBB18161002.60.038.15SSC/SBB18161002.60.038.15SS		23	4	100	8.4		0.16	32.22	SBB
231050388.80.22189.32comb231010019.57.70.1799.22comb412504.20.2318.4SSC/SBB4121001.80.146.6SSC/SBB4122000.60.082.0SSC/SBB4152.510.60.2952.7SBB4151002.10.117.4SBB41105020.36.90.1799.9comb41105020.36.90.1799.9comb1811003.820.0845.9comb1813001.240.054.00SSC1813001.240.054.00SSC18130023.60.077.6comb1816100420.06136comb181610017.50.0869.3comb181610017.50.0869.3comb18161002.80.119.87SSC18161002.80.1724.2SSC18161002.80.1724.2SSC18161002.80.1724.5SSC18161002.80.1724.5SSC1816 </td <td></td> <td>23</td> <td>4</td> <td>200</td> <td>3</td> <td></td> <td>0.07</td> <td>9.92</td> <td>SBB</td>		23	4	200	3		0.07	9.92	SBB
231010019.57.70.1799.22comb231020010.31.80.0639.02comb412504.20.031.80.146.6SSC/SBB4122000.60.082.0SSC/SBB4151002.10.117.4SBB41102537.58.80.22187.2comb411010012.51.30.0845.9comb1811003.820.2015.7SSC1811003.820.2015.7SSC1813001.240.054.00SSC1813001.240.054.00SSC18181003.70.0869.3comb1816100420.06136comb181610023.60.0777.6comb1814167100.2343.7SSC1411002.80.119.8SSC/SBB1414001.10.083.70SSC1414001.10.038.15SSC/SBB1414001.10.038.15SSC/SBB1414001.10.038.15SSC/SBB1414001.10.038.15 <td></td> <td>23</td> <td>10</td> <td>50</td> <td>38</td> <td>8.8</td> <td>0.22</td> <td>189.32</td> <td>comb</td>		23	10	50	38	8.8	0.22	189.32	comb
231020010.31.80.0639.02comb412504.20.2318.4SSC/SBB4122000.60.082.0SSC/SBB4152510.60.295.27SBB415002.10.117.4SBB41102537.58.80.22187.2comb41105020.36.90.1799.9comb41105020.36.90.1799.9comb1811003.820.2015.7SSC1813001.240.054.00SSC/SBB1813001.240.054.00SSC/SBB18410023.60.077.7.6comb18410023.60.077.7.6comb1816100420.06136comb181610017.50.0869.3comb14167100.2343.7SSC1414001.10.083.70SSC1414001.10.038.15SC/SBB1414001.10.038.15SC/SBB1414001.10.038.15SC/SBB1414001.10.038.15SC/SBB14 <td></td> <td>23</td> <td>10</td> <td>100</td> <td>19.5</td> <td>7.7</td> <td>0.17</td> <td>99.22</td> <td>comb</td>		23	10	100	19.5	7.7	0.17	99.22	comb
412504.20.2318.4SSC/SBB4121001.80.146.6SSC/SBB412200.60.095.2.7SB4151002.10.117.4SB41102537.58.80.22187.2comb41105020.36.90.1799.9comb411010012.51.30.0845.9comb1811003.820.2015.7SSC1812001.40.114.90SSC1813001.240.054.00SSC1813001.240.054.00SSC1816100420.06136comb18161002.3.60.0777.6comb18141000.2.343.7SSCSSC18141002.3.60.0777.6comb18141002.3.60.0777.6SSC1412002.80.119.87SSC1412002.80.119.87SSC1410.06.20.038.15SSC/SBB1410.02.60.038.5C/SBB1410.01.40.031.50SC/SBB1410.01.4		23	10	200	10.3	1.8	0.06	39.02	comb
4121001.80.146.6SSC/SBB4122000.60.082.0SSE4152510.60.29S.2.7SSB4151002.10.117.4SBE41102537.58.80.22187.2comb41105020.36.90.1799.9comb411010012.51.30.0845.9comb1811003.820.0015.7SSC1812001.40.114.90SSC1812001.240.054.00SSC1816100420.06136comb23810020.70.0869.3comb181610420.06136comb23810020.70.0869.3comb14167100.2343.7SSC1411006.20.1724.2SSC1412002.60.038.15SSC/SBB142120010.023.08SSC/SBB1421001.170.023.08SSC/SBB1421001.40.023.08SSC/SBB1446008.20.072.5.5SBC/SBB144600 <td></td> <td>41</td> <td>2</td> <td>50</td> <td>4.2</td> <td></td> <td>0.23</td> <td>18.4</td> <td>SSC/SBB</td>		41	2	50	4.2		0.23	18.4	SSC/SBB
4122000.60.082.0SSC/SBB4152510.60.2952.7SBB4151002.10.117.4SBB41102537.58.80.22187.2comb41105020.36.90.1799.9comb411010012.51.30.0845.9comb1811003.820.2015.7SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.0013.5SSC/SBB1841008.70.0929.6SBB1816100420.06136comb23810020.70.0869.3comb14167100.2343.7SSC141006.20.0777.6SSC1412002.80.119.87SSC1410.02.60.038.15SSC/SBB1412002.80.119.87SSC1410.02.60.038.15SSC/SBB1410.02.60.038.15SSC/SBB1446008.20.072.5.5SBF/comb144600		41	2	100	1.8		0.14	6.6	SSC/SBB
4152510.60.2952.7SBB4151002.10.117.4SBB41102537.58.80.22187.2comb41105020.36.90.1799.9comb411010012.51.30.0845.9comb1811003.820.2015.7SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SB18410023.60.0777.6comb1816100420.06136comb23810020.70.0869.3comb1411006.20.1724.2SSC1411006.20.1724.2SSC1410.02.60.038.15SSC/SBB1412002.60.038.15SSC/SBB1446008.20.023.08SSC/SBB1446008.20.023.08SSC/SBB1446008.20.023.08SSC/SBB1446008.20.023.08SSC/SBB1446		41	2	200	0.6		0.08	2.0	SSC/SBB
4151002.10.117.4SBB41102537.58.80.22187.2comb41105020.36.90.1799.9comb41101001.251.30.0845.9comb1811003.820.2015.7SSC1812001.40.114.90SSC1812001.40.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SBB18161004.20.06136comb23810020.70.0869.3comb14167100.2343.7SSC1411006.20.1724.2SSC1414001.10.083.70SSC1412002.60.038.15SSC/SBB14144001.10.083.70SSC142120010.023.08SSC/SBB1446002.60.038.15SSC/SBB14830047.80.033150comb1486001.170.2725.58SSC1486001.430.02244.2comb148600<		41	5	25	10.6		0.29	52.7	SBB
41102537.58.80.22187.2comb41105020.36.90.1799.9comb411010012.51.30.0845.9comb18110012.51.30.0215.7SSC1811501.770.156.70SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SBB18810023.60.0777.6comb1816100420.06136comb181610017.50.0959.3comb14167100.2343.7SSC1412002.60.119.87SSC1412002.60.038.15SSC/SBB1412002.60.038.15SSC/SBB1412002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.038.15SSC/SBB1446008.430.02244.2comb1486001.170.2725.58SSC14<		41	5	100	2.1		0.11	7.4	SBB
41 10 50 20.3 6.9 0.17 99.9 comb 41 10 100 12.5 1.3 0.08 45.9 comb PIB 18 1 100 3.82 0.20 15.7 SSC 18 1 100 1.4 0.15 6.70 SSC 18 1 200 1.4 0.05 4.00 SSC 18 1 300 1.24 0.05 4.00 SSC 18 2 100 3.9 0.10 13.5 SSC/SBB 18 4 100 8.7 0.09 29.6 SBB 18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 14 1 67 10 0.23 43.7 SSC 14 1 100 6.2 0.17 24.2 SSC		41	10	25	37.5	8.8	0.22	187.2	comb
PIB411010012.51.30.0845.9combPIB1811003.820.2015.7SSC1811001.770.156.70SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SBB18810023.60.077.7.6comb23810020.70.0869.3comb23810020.70.0869.3comb14167100.2343.7SSC1412002.80.119.87SSC1412002.80.119.87SSC1414001.10.083.70SSC142120010.023.08SSC/SBB142120010.023.08SSC/SBB14430047.80.033150comb14860014.30.02244.2comb14860014.30.02244.2comb1486001.170.2725.58SSC1486001.130.02244.2comb148600 <td></td> <td>41</td> <td>10</td> <td>50</td> <td>20.3</td> <td>6.9</td> <td>0.17</td> <td>99.9</td> <td>comb</td>		41	10	50	20.3	6.9	0.17	99.9	comb
PIB1811003.820.2015.7SSC1811501.770.156.70SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SB1841008.70.0929.6SB1816100420.06136comb181610020.70.0869.3comb18161017.50.0959.3comb14167100.2343.7SSC1412002.80.119.87SSC1412002.80.119.87SSC/SBB1446008.20.02725.5SB/comb1446008.20.02725.5SB/comb14830047.80.033150comb14860014.30.02244.2comb14860014.30.2622.00SSC/SBB1486001.170.2725.58SSC1486001.430.02244.2comb1486001.430.02244.2comb1486001.430.2622.00SSC1486000.37<		41	10	100	12.5	1.3	0.08	45.9	comb
1811501.770.156.70SSC1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SB18810023.60.077.7.6comb23810020.70.0869.3comb23810020.70.0869.3comb14167100.2343.7SSC1412002.80.119.87SSC1412002.80.119.87SSC1426002.60.038.15SSC/SBB1422120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb1486001.170.2725.58SSC1486001.430.02244.2comb1486001.430.02244.2comb1486001.430.02244.2comb1486001.430.0222.00SSC151000.170.2531.70 <td>PIB</td> <td>18</td> <td>1</td> <td>100</td> <td>3.82</td> <td></td> <td>0.20</td> <td>15.7</td> <td>SSC</td>	PIB	18	1	100	3.82		0.20	15.7	SSC
1812001.40.114.90SSC1813001.240.054.00SSC1821003.90.1013.5SSC/SBB1841008.70.0929.6SB18810023.60.0777.6comb23810020.70.0869.3comb23810017.50.0959.3comb41810017.50.0959.3comb14167100.2343.7SSC1412002.80.119.87SSC1412002.60.038.15SSC/SBB1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb1486001.170.2725.58SSC/SBB1486001.430.02244.2comb1486001.430.2622.00SSC7011000.170.2531.70SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		18	1	150	1.77		0.15	6.70	SSC
18 1 300 1.24 0.05 4.00 SSC 18 2 100 3.9 0.10 13.5 SSC/SBB 18 4 100 8.7 0.09 29.6 SBB 18 8 100 23.6 0.07 77.6 comb 18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 14 1 67 10 0.23 43.7 SSC 14 1 100 62 0.17 24.2 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 400 1.1 0.02 3.08 SSC/SBB 14 2 600 2.6 0.03 8.15 SSC/SBB 14 4 600 8.2 0.027 2.5.5 SBB/comb 14 8<		18	1	200	1.4		0.11	4.90	SSC
18 2 100 3.9 0.10 13.5 SSC/SBB 18 4 100 8.7 0.09 29.6 SBB 18 8 100 23.6 0.07 77.6 comb 18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 23 8 100 20.7 0.08 69.3 comb 14 1 67 10 0.23 3.7 SSC 14 1 100 6.2 0.17 24.2 SSC 14 1 200 2.8 0.11 9.87 SSC/SBB 14 2 600 2.6 0.03 8.15 SSC/SBB 14 2 1200 1 0.022 3.08 SSC/SBB 14 4 600 8.2 0.033 150 comb 14 8 </td <td></td> <td>18</td> <td>1</td> <td>300</td> <td>1.24</td> <td></td> <td>0.05</td> <td>4.00</td> <td>SSC</td>		18	1	300	1.24		0.05	4.00	SSC
18 4 100 8.7 0.09 29.6 SBB 18 8 100 23.6 0.07 77.6 comb 18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 41 8 100 17.5 0.09 59.3 comb 14 1 67 10 0.23 43.7 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 400 1.1 0.08 3.70 SSC 14 2 600 2.6 0.03 8.15 SSC/SBB 14 4 600 8.2 0.027 25.5 SBE/comb 14 8 300 47.8 0.033 150 comb 14 8		18	2	100	3.9		0.10	13.5	SSC/SBB
18 8 100 23.6 0.07 77.6 comb 18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 41 8 100 17.5 0.09 59.3 comb 14 1 67 10 0.23 43.7 SSC 14 1 200 2.8 0.17 24.2 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 400 1.1 0.08 3.70 SSC 14 2 600 2.6 0.03 8.15 SSC/SBB 14 2 1200 1 0.022 3.08 SSC/SBB 14 4 600 8.30 0.43 0.022 44.2 comb 14 8 300 47.8 0.033 150 comb 14 </td <td></td> <td>18</td> <td>4</td> <td>100</td> <td>8.7</td> <td></td> <td>0.09</td> <td>29.6</td> <td>SBB</td>		18	4	100	8.7		0.09	29.6	SBB
18 16 100 42 0.06 136 comb 23 8 100 20.7 0.08 69.3 comb 41 8 100 17.5 0.09 59.3 comb 14 1 67 10 0.23 43.7 SSC 14 1 100 6.2 0.17 24.2 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 400 1.1 0.08 3.70 SSC 14 2 600 2.6 0.03 8.15 SSC/SBB 14 2 600 2.6 0.03 8.15 SSC/SBB 14 4 600 8.2 0.027 25.5 SBB/comb 14 8 300 47.8 0.033 150 comb 14 8 600 1.17 0.272 5.58 SSC 70 1 </td <td></td> <td>18</td> <td>8</td> <td>100</td> <td>23.6</td> <td></td> <td>0.07</td> <td>77.6</td> <td>comb</td>		18	8	100	23.6		0.07	77.6	comb
23 8 100 20.7 0.08 69.3 comb 41 8 100 17.5 0.09 59.3 comb PDMS 14 1 67 10 0.23 43.7 SSC 14 1 100 6.2 0.17 24.2 SSC 14 1 200 2.8 0.11 9.87 SSC 14 1 400 1.1 0.08 3.70 SSC/SBB 14 2 600 2.6 0.03 8.15 SSC/SBB 14 2 1200 1 0.02 3.08 SSC/SBB 14 2 1200 1 0.021 3.08 SSC/SBB 14 4 600 8.2 0.027 25.5 SBB/comb 14 8 300 47.8 0.033 150 comb 14 8 600 1.17 0.272 5.58 SSC		18	16	100	42		0.06	136	comb
PDMS41810017.50.0959.3comb14167100.2343.7SSC1411006.20.1724.2SSC1412002.80.119.87SSC1414001.10.083.70SSC1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.2725.58SSC7011001.170.2725.58SSC7013000.430.2622.00SSC7016000.370.2531.70SSC7016000.220.1270.80SSC		23	8	100	20.7		0.08	69.3	comb
PDMS14167100.2343.7SSC1411006.20.1724.2SSC1412002.80.119.87SSC1414001.10.083.70SSC1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		41	8	100	17.5		0.09	59.3	comb
1411006.20.1724.2SSC1412002.80.119.87SSC1414001.10.083.70SSC1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7016000.370.2531.70SSC7016000.220.1270.80SSC	PDMS	14	1	67	10		0.23	43.7	SSC
1412002.80.119.87SSC1414001.10.083.70SSC1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	1	100	6.2		0.17	24.2	SSC
1414001.10.083.70SSC1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	1	200	2.8		0.11	9.87	SSC
1426002.60.038.15SSC/SBB142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	1	400	1.1		0.08	3.70	SSC
142120010.023.08SSC/SBB1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	2	600	2.6		0.03	8.15	SSC/SBB
1446008.20.02725.5SBB/comb14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	2	1200	1		0.02	3.08	SSC/SBB
14830047.80.033150comb14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	4	600	8.2		0.027	25.5	SBB/comb
14860014.30.02244.2comb7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	8	300	47.8		0.033	150	comb
7011001.170.2725.58SSC7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		14	8	600	14.3		0.022	44.2	comb
7013000.430.2622.00SSC7014000.370.2531.70SSC7016000.220.1270.80SSC		70	1	100	1.17		0.272	5.58	SSC
7014000.370.2531.70SSC7016000.220.1270.80SSC		70	1	300	0.43		0.262	2.00	SSC
70 1 600 0.22 0.127 0.80 SSC		70	1	400	0.37		0.253	1.70	SSC
		70	1	600	0.22		0.127	0.80	SSC

^{*a*}Degree of polymerization (DP) of side chains. ^{*b*}DP of backbone spacers between side chains. ^{*c*}Targeted DP of brush backbone between crosslinks defined by molar fraction of cross-linker, e.g., $n_x = 200$ corresponds to 0.25 mol %. ^{*d*}Shear moduli determined by fitting stress–elongation curves with eq 5. ^{*c*}Entanglement plateau moduli determined by fitting stress–elongation curves with eq 5. ^{*f*}Strain-stiffening parameter determined by fitting stress–elongation curves with eq 5. ^{*g*}Young's modulus (eq 12). ^{*h*}Brush regimes according to the diagram of states in Figure 4. If a brush structure is in the crossover between, e.g., SSC and SBB regimes, it is designated as SSC/SBB.



Figure 4. Diagram of states for different conformation regimes with brush strands of different chemical compositions: PBA (black squares), PIB (red circles), and PDMS (blue triangles) (Table 1). The crossover boundaries between regimes are given by $\varphi^{-1} = (bl)^{3/2}v^{-1}n_{\rm sc}^{-1/2}\Phi^*$ (comb/SBB), $\varphi^{-1} = bl^2v^{-1}n_{\rm sc}\Phi^*$ (SBB/SSC), and $\varphi^{-1} = l^3v^{-1}n_{\rm sc}^{-2}\Phi^*$ (SSC/RSC). The crossover boundaries are calculated by setting the crowding parameter $\Phi^* = 0.7$ as determined by computer simulations.^{37,39} The low boundary (solid red) for forbidden region $\varphi^{-1} = 1 + n_{\rm sc}$ calculated with $n_{\rm g} = 1$ (eq 1a) shown as different gradient: PBA (dark gray), PIB (medium gray), and PDMS (light gray).

Table 3. Molecular Parameters^a

В
11
5
4

 ${}^{a}M_{0}$, v, and l are respectively the molar mass, volume, and projection length of the repeat unit. ρ is the polymer bulk density, and b is the Kuhn length.

first interpretation. However, in the SBB and comb regimes, the side chains adopt Gaussian conformations, and the scattering peak results from coupled fluctuations of both the backbones and side chains manifested as $d \cong (n_g n_{sc} b_K b l^2)^{1/4}$. Note that some samples are in a crossover between the different brush regimes, resulting a mixed scattering behavior.

Mechanical Properties of Brush Networks. The interplay of n_{g} and n_{sc} plays a pivotal role in regulating elastic response to deformation. In the following, we first describe the deformation behavior (Figure 6) of the brush elastomers and then discuss the corresponding structure-property correlations (Figure 7). Uniaxial tensile tests were performed at a low strain rate of $\dot{\varepsilon} = 0.005 \text{ s}^{-1}$ to ensure that the deformation was applied in the deformation regime where the modulus is independent of the strain rate (Figures S7-S13). All brush elastomers exhibit the characteristic strong strain-stiffening imposed by the finite extensibility of network strands, which is defined by β (eqs 7 and 10). The initial slope of the stresselongation curves, E_0 , decreases with increasing n_{sc} at fixed n_g = 2 (Figure 6a) and with decreasing n_g at fixed $n_{sc} = 11$ (Figure 6b). However, the curvature, i.e., strain-stiffening parameter β , shows a monotonic increase with such variations in architectural parameters. These correlations are discussed in more detail in the next section.

Analysis of the SAXS from elastomers under stress shows that the intensity of the bottlebrush peak becomes more concentrated in the plane (i.e., the equator) perpendicular to the direction of force (Figure 6c). This behavior is consistent with alignment of the backbones upon deformation and is further corroborated in Figure 6d showing the Herman's orientation factor, calculated from azimuthal variations in the scattering intensities in Figure 6c, as a function of the network deformation. The slope of the optical law is rather high, 0.06, approximately an order of magnitude higher than the value of typical natural rubber elastomers⁵⁰ with similar molecular weights between the cross-links, e.g., $M_c = 64$ kg/mol for a sample [11, 1, 100].

Structure–Property Correlations. Mechanical properties of brush elastomers defined by G, β , and E_0 were obtained by fitting stress–elongation curves to eq 5 as illustrated in Figure 7a. It is important to emphasize that the equation of state (eq 5) fits the stress–elongation profile all the way up to sample rupture at $\lambda = \lambda_{max}$, the elongation at break. The fitting provides G and β which jointly elicit the Young's modulus of networks with entangled and unentangled strands, respectively, by extrapolating eq 5 to $\lambda \rightarrow 1$ as

$$E_0 = G \left(1 + \frac{3G_e}{G} + 2(1 - \beta)^{-2} \right)$$
(12)

The strong nonlinear deformation response of brush elastomers is highlighted by plotting the instantaneous deformation dependent modulus

$$G(I_{\rm l}) \equiv \sigma_{\rm true} / (\lambda^2 - \lambda^{-1})$$
⁽¹³⁾

where the plateau at $\lambda \rightarrow 1$ corresponds to $E_0/3$ for incompressible networks (Figure 7b and Figure S8).

To demonstrate the effect of specific architectural parameters on the network mechanical properties, we plot direct correlations between G, β , and φ^{-1} at a constant n_x (Figure 7c). Both structural shear modulus $G(\varphi^{-1})$ and firmness $\beta(\varphi^{-1})$ show nonlinear monotonic variations as brush architectures evolve from comb to bottlebrush conformation with increasing φ^{-1} , the fraction of the repeat units belonging to the side chains. The softness (G) and firmness (β) of brush elastomers exhibit opposite trends, respectively decreasing and increasing upon augmentation of side-chain length ($\sim n_{sc}$) and grafting density ($\sim n_g^{-1}$). The inverse relationship of E_0 and β to $n_{\rm sc}/n_{\rm g} \sim \varphi^{-1}$ is because increasing $n_{\rm sc}$ and $n_{\rm g}$ concurrently makes the network strand bulkier and less flexible. Specifically, an increase in φ^{-1} leads to a decrease in cross-link density $\rho_{\rm s} \sim V_{\rm strand}^{-1} \sim 1/\varphi^{-1}$ and strand extension $\langle R_{\rm in}^2 \rangle \sim b_{\rm K} \sim \varphi^{-1}$ (eq 9 and Table 1). Combined variations in architectural parameters n_{sc} , n_{g} , and n_{x} allow coverage of a broad range of softness and firmness represented by $E_0 = 1.6 -$ 184 kPa and β = 0.03–0.27, respectively. From obtained values of β , we estimate an upper limit for strand extension using eq 8, which effectively corresponds to the molecular elongation at break, $\lambda_{max,theo}$. The agreement between $\lambda_{max,theo}$ and the macroscopic elongation-at-break, $\lambda_{\max, exp}$, suggests that the prepared networks have uniform mesh size distribution (Figure 7d).

The n_x of polymer networks is currently ill-defined. To address this issue, we use a universal representation which eliminates n_x (eq 11) and enables definition of different brush networks by using chemistry specific parameters [l, b, v] and



Figure 5. Evolution of the small-angle X-ray scattering (SAXS) curves corresponding to undeformed PBA brush networks at fixed $n_x = 100$ (a) with $n_{g} = 1$ and various n_{sc} 's and (b) with $n_{sc} = 11$ and various n_{g} 's. (c) Dependence of the characteristic length scale $d = 2\pi/q^*$ associated with the peak position q^* in the scattering function on the brush compositional parameter (eq 1a). (d) Dependence of the normalized characteristic length scale $d/b_K = 2\pi/q^*b_K$ on the dimensionless parameter $(n_g n_{sc} bl^2/b_K^3)^{1/4}$. The effective backbone Kuhn length b_K was calculated by using equations for the designated brush regimes (see Table 1) for PBA elastomers with molecular parameters provided in Table 3 and the crowding parameter, $\Phi^* = 0.7$.^{37,39} Samples with $n_g = 2$ were located in a crossover between the SSC and SBB regimes where b_K values were calculated by using the SSC equation for $n_{sc} = 11$, SBB equation for $n_{sc} = 41$, and a mean of corresponding values in SSC and SBB for $n_{sc} = 23$.

two architectural parameters $[n_{scr}, n_g]$. The experimentally determined values of the structural shear modulus *G* and strain-stiffening parameter β for brush elastomers with PBA, PDMS, and PIB side chains were plotted with respect to expected architectural correlations and chemistry specific prefactors outlined in Table 3. Both combs (Figure 7e) and bottlebrushes (Figure 7f) are consistent with theoretical predictions.

CONCLUSION

In this study, we demonstrate that mechanical properties of brush networks can be controlled through variations in the DP of the side chains, n_{sc} , and the spacer between them, n_{g} independent of the specific chemistry of the repeat units. This is based on the unique correlation between effective Kuhn length, $b_{\rm K}$, of the brush strands and their molecular architecture in the different conformation regimes corresponding to comb and bottlebrush macromolecules. The disparity in $b_{\rm K}$ for each conformational state results in an incongruent macromolecular contribution to mechanical properties. Precise synthesis of brush elastomers yielded a library of networks with diverse mechanical profiles. Results from the mechanical testing of the elastomer library experimentally verify the theoretical framework for predicting mechanical response of brush elastomers in each conformational regime. We have also shown that networks with brush-like strands must be treated with respect to the complex interplay of architecture and chemistry rather than as one homogeneous group of elastomers. Furthermore, through the input of precise architectural parameters $[n_{sc}, n_{g}, n_{x}]$ and chemistry specific

parameters [l, b, v], the established structure-property correlations can be used to design polymeric networks for use in biomedical implants, soft electronics, and soft robotics. The established structure-property correlations for networks with brush-like strands could build a foundation for architecture driven design of networks with a particular nonlinear elastic response to deformation.

EXPERIMENTAL SECTION

Materials. 1,6-Hexanediol dimethacrylate (>90%), phenylbis-(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, 97%), ethyl α boromoisobutyrate (EBiB, 98%), ethylene bis(2-bromoisobutyrate) (2-BiB, 97%), copper(II) bromide (CuBr₂, 99.99%), tris[2-(dimethylamino)ethyl]amine (Me6TREN), methacrylic acid (99%), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), potassium tert-butoxide (98%), and tetrabutylammonium bromide (TBAB, 98%) were used as received from Sigma-Aldrich. n-Butyl acrylate (n-BA, 99%) was obtained from Sigma-Aldrich and purified by passing through a column of basic alumina (Sigma-Aldrich, activated, basic, Brockman I) to remove inhibitor. Methylvinyledene-terminated polyisobutylene (RB HR-PIB) oligomers with average molar masses of 1000, 1300, and 2300 ($D \sim 1.9$) were obtained from RB products and used as received. Acetonitrile, anhydrous methanol, dichloromethane, acetone, anisole, and N,N-dimethylacetamide were used as received from Sigma-Aldrich. In addition, α,ω -methacryloxypropylterminated poly(dimethylsiloxane) (DMS-R18, average molar mass of 5000 g/mol, D = 1.15) and monomethacryloxypropyl-terminated polydimethylsiloxane (MCR-M11 and MCR-M17) were obtained from Gelest and purified by using basic alumina columns to remove inhibitor.

Synthesis of Potassium Methacrylate. Approximately 25 g of potassium *tert*-butoxide was dissolved in 50 mL of THF in a sealed



Figure 6. Strand conformational analysis of brush elastomers under deformation. Samples were subjected to uniaxial extension (T = 22 °C and $\dot{e} = 0.005$ s⁻¹), and the true stress, $\sigma_{true} = \sigma_{eng}\lambda$, is plotted as a function of elongation, $\lambda = L/L_0$, from the initial sample length L_0 to its instantaneous length L for brush networks with (a) fixed $n_g = 2$ and varying n_{sc} and (b) fixed $n_{sc} = 11$ and different n_g . All samples in panel a belong to the SSC bottlebrush subregime, while the samples with different grafting densities in panel b traverse the state diagram from comb to SBB to SSC regimes (Figure 4 and Table 2). (c) Evolution of the azimuthal SAXS intensity profiles with network deformation for brush elastomers with [11, 1, 100]. (d) Optical law (Herman's orientation factor) for brush elastomers overlaid on the corresponding stress-strain curve.

250 mL round-bottom flask equipped with a stir bar. An equal molar portion of methacrylic acid was added dropwise over the course of 10 min stirring in an ice bath, generating a white potassium methacrylate precipitate. The reaction mixture was then shaken vigorously for 5 min and left to equilibrate to room temperature overnight. The precipitate was separated by passing the mixture through a porous glass filter and washed immediately with an addition 25 mL of anhydrous THF. Solvent was removed under vacuum, and the potassium methacrylate was stored for later use.

Synthesis of Butyl Acrylate by SARA ATRP. Poly(*n*-butyl acrylate) with different degrees of polymerization was synthesized by supplemental activation reducing agent (SARA) atom transfer radical polymerization (ATRP) followed by a postpolymerization functionalization displacing the bromine end group with potassium methacrylate. To a 500 mL air-free Schlenk flask, 120 g (0.94 mol) of butyl acrylate was combined with Me₆TREN (10 μ L, 37 μ mol), CuBr₂ (8 mg, 36 µmol), and EBiB, 15.2, 7.3, or 3.7 g (0.078, 0.037, or 0.019 mol) depending on desired n_{sc} and diluted with an equal volume of acetonitrile. The reaction mixture was cooled with an ice bath, and oxygen was removed by bubbling nitrogen gas for 1 h. The polymerization was initiated by adding a stir bar equipped with a clean Cu⁰ wire and transferring to a 45 °C mineral oil bath. The reaction was monitored by ¹H NMR and stopped near 80% conversion with the addition of chloroform (Figure S1). Excess catalyst was removed by washing in water ~11 times, and excess solvent was removed by rotary evaporation at 45 °C under reduced pressure.

Synthesis of Poly(*n*-butyl acrylate) Macromonomers. The previously synthesized poly(n-butyl acrylate) was dissolved in 7 parts of *N*,*N*-dimethylacetamide. Potassium methacrylate was added in large excess (>3 mol equiv), and the reaction was left to stir for 3 days, turning a faint yellow color. To purify, the mixture of 1 part chloroform and 1 part water was added, separating the mixture into two separate phases. The aqueous phase was discarded, and the remaining organic component was added 11 times with water until

clear. Solvent was removed by rotary evaporation. See NMR spectra in Figure S2 and GPC analysis in Figure S3.

Synthesis of Poly(n-butyl acrylate) Macro-Cross-Linker by SARA ATRP. Poly(n-butyl acrylate) macro-cross-linkers were synthesized by using an equivalent procedure to the poly(n-butyl acrylate) macromonomers. The one exception is that a difunctional 2-BiB ATRP initiator was used to polymerize n-BA such that the corresponding macromonomer was functionalized at both ends of the polymer chain. This difunctional poly(n-butyl acrylate) macro-crosslinker was also synthesized on a much smaller due to relatively small amount of it used during synthesis. The $n_{\rm sc}$ = 80 cross-linker was synthesized by combining 24 g (0.19 mol) of n-butyl acrylate, Me_6TREN (2 μL , 7.4 μmol), $CuBr_2$ (1.6 mg, 7.2 μmol), and 2-BiB (0.67 g, 1.9 μ mol) and diluting the mixture to 50% with acetonitrile. The reaction was then cooled in an ice bath and degassed for 1 h with bubbling nitrogen gas. The polymerization was initiated by the addition of a Cu⁰ wire and transferred to a 45 °C oil bath until the reaction reached ~80% conversion. The reaction was then terminated by the addition of 50 mL of chloroform and washed 11 times in water. Solvent was removed by rotary evaporation at 45 °C under reduced pressure. The cleaned polymer was then functionalized by the addition of 7 parts N,N-dimethylacetamide and a large excess of potassium methacrylate and left stirring for 72 h. 50 mL of chloroform and 100 mL of water were then added, separating the polymer into the organic phase. The organic phase was then washed in water 11 times until it became clear. Solvent was again removed by rotary evaporation at 45 °C under reduced pressure.

Anti-Markovnikov Bromination of HR-PIB 1000 n_{sc} = 18. A 250 mL round-bottom flask was prepared with a stir bar and 50 g (0.05 mmol) of RB HR-PIB (M_n = 1000 g/mol, $D \sim 1.9$) dissolved in hexane (150 mL) and placed in an ice bath. The solution was bubbled with air for 30 min at 0 °C, and 24.3 g of 33% w/w HBr (0.1 mol) in EtOAc was added dropwise to the flask with vigorous stirring. The solution reacted for 2 h at 0 °C and followed by RT overnight.



Figure 7. Structure-property correlations. (a) Dependence of true stress in the PBA brush elastomer [11, 2, 200] on uniaxial elongation ratio. Dotted line corresponds to the best fit to eq 5 with structural modulus G = 5.5 kPa and strain-stiffening parameter $\beta = 0.08$, yielding a Young's modulus of $E_0 = 18.6$ kPa (eq 12). (b) Deformation-dependent instantaneous shear modulus from (a). The plateau is consistent with $E_0 = 18.6$ kPa. (c) G and β as a function of φ^{-1} for PBA brush networks with $n_x = 200$ (Table 2). (d) Measured elongation at break is consistent with the maximal strand extension estimated from the value of the firmness parameter (eq 8). (e) Cross-correlation plot for comb regime for different chemical compositions of side chains: PBA (\Box), PBI (O), and PDMS (\triangle). (f) Cross-correlation plot for SSC regime. Dashed lines in panels d, e, and f show agreement with the expected scaling dependences.

Stirring was ceased, and the resultant anti-Markovnikov brominefunctionalized PIB oligomer was washed with H_2O/Na_2CO_3 twice (dried with anhydrous MgSO₄) and extracted with a SiO₂ column. The hexanes were evaporated by bubbling with air, yielding 88% functionalized polymer (determined by ¹H NMR, Figure S4). No residual olefin residue was present, suggesting higher yield. This synthesis applies to RB HR PIB-1300 (n_{sc} = 23) and RB HR PIB-2300 (n_{sc} = 41) with molar ratios respectively applied.

Synthesis of PIB ($n_{sc} = 18$) Macromonomer. The functionalized oligomer was dissolved in THF (350 mL) and transferred to a clean 500 mL round-bottom flask equipped with a stir bar. The solution was charged with 3.01 g of KOMA (0.25 mol) and 80.5 g of TBAB (0.25 mol) and was run for 36 h at 45 °C. The solution was centrifuged to remove residual salt and unreacted reagent. Subsequently, the solution was condensed by bubbling with air and washed with H₂O/hexane twice. The organic layer was separated, dried with anhydrous MgSO₄, and ran through a SiO₂ column revealing PIB ($n_{sc} = 18$) macromonomer product (96% yield). Again, no residual peaks were present from the α -hydrogens, suggesting higher yield. ¹H NMR of the synthetic progression is shown in Figure S4. This synthesis applies to RB HR PIB-1300 ($n_{sc} = 23$) and RB HR PIB-2300 ($n_{sc} = 41$) with molar ratios respectively applied (Figures S5 and S6).

Synthesis of Brush Elastomers (Supporting Information, Section S1). A scintillation vial was charged with the desired molar

ratios of PBA, PIB, or PDMS macromonomers, spacer monomers, and cross-linkers according to targeted n_x and n_g values. While the n_g values were verified previously by ¹H NMR of un-cross-linked brush polymers, the reported n_x values are calculated from the shear modulus of the prepared networks (Table 2), and molar ratios of cross-linker to macromonomer/spacer correspond to input estimated n_x . The vial was covered in aluminum foil and placed in an ice bath to prevent autoinitiation. Furthermore, ~7.0 mg of BAPO was added to the vial. The vial was rapidly fixed with a rubber septum and bubbled with nitrogen for 30 min. The deoxygenized solution was injected into a nitrogen-flushed, handmade glass mold and set to cure in a nitrogen chamber overnight (18–24 h). The polymers were removed from the mold and swollen in toluene twice to remove unreacted macromonomer (gel fraction >90%). The brush elastomers were dried overnight in a fume hood followed by 2 h in the oven at 60 °C.

Uniaxial Tensile Stress–Strain Measurements. Tensile testing was performed on a TA Instruments RSA-G2 Solids Analyzer DMA at $\dot{\epsilon} = 0.005 \text{ s}^{-1}$. Samples were cut into a dog bone shape with bridge dimensions of 12 mm × 2 mm × ~1 mm and tested at 22 °C. Samples were stretched until rupture, revealing the full mechanical profile (see Supporting Information, section 2, for all data).

Small-Angle X-ray Scattering (SAXS). The SAXS measurements were performed at the ID02 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The experiments were conducted in transmission geometry by using a

photon energy of 12.46 keV. The recorded 2D data were centered, calibrated, regrouped, and reduced to 1D by using the SAXS utilities platform described elsewhere.⁵¹ The analysis of the SAXS data was performed by using the SANS data reduction and analysis package provided by NIST⁵² for the Igor Pro environment (WaveMetrics Ltd.).

The monochromatic incident X-ray beam was collimated on the sample to a footprint of $100 \times 200 \ \mu m^2$ ($V \times H$). The total photon flux was estimated to be 9×10^{11} photons/s, allowing for acquisition times of <100 ms. The accessed *q* values, with $|q| = 4\pi \sin(\Theta)/\lambda$, where Θ is the Bragg angle and λ is the wavelength, cover a range from 7.0×10^{-3} to 5.0 nm⁻¹. A Rayonix MX-170HS implemented in a 35 m long vacuum flight tube was applied for recording of SAXS intensities at two different sample-to-detector distances of 1.5 and 10.0 m. For optimization of the scattering signal, a binning of 2×2 pixels was applied, resulting in an effective pixel size of 89 μ m in both directions.

The in situ mechanical and structural measurements were performed with the help of a custom-made stretching device compatible with the ID02 beamline environment. The stretching device allowed for computer-controlled synchronized motion of the two symmetrical fixtures in which the dog-bone-shaped sample was clamped. For each deformation, the position of the X-ray beam on the sample was refined by scanning it along two perpendicular directions. The structural irreversibility in the loading/unloading cycles in the linear regime was specifically checked and found negligible for all the samples studied.

Additional SAXS measurements were conducted with the help of a laboratory Xenocs Xeuss SAXS/WAXS system equipped with a GeniX3D copper microfocus tube operating at 60 kV and 0.59 mA. Samples were placed in an evacuated chamber and illuminated with monochromatic X-rays in transmission geometry. The scattered intensity was recorded by using a Dectris Pilatus 300K detector located 2.2 m downstream from the sample position.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c00006.

Network synthesis, mechanical testing, scattering data analysis (PDF)

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Author Contributions

M.M. synthesized and characterized PIB networks; B.J.M. synthesized and characterized PBA networks; E.D. assisted with the synthesis of PIB and PDMS networks; Y.T. and A.V.D. provided theoretical analysis of mechanical properties; E.B., A.V.M., and D.A.I. conducted X-ray studies and data analysis; K.M. developed the concept of bottlebrush elastomers, S.S.S. is the principal investigator and corresponding author; M.M., A.V.D., and S.S.S were primary writers of the manuscript. All authors discussed the results and provided feedback on the manuscript.

Notes

The authors declare no competing financial interest.

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