Compressing and Swelling To Study the Structure of Extremely Soft Bottlebrush Networks Prepared by ROMP

Joel M. Sarapas,* Edwin P. Chan, Emma M. Rettner, and Kathryn L. Beers*

Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Supporting Information

ABSTRACT: To fully explore bottlebrush polymer networks as potential model materials, a robust and versatile synthetic platform is required. Ring-opening metathesis polymerization is a highly controlled, rapid, and functional group tolerant polymerization technique that has been used extensively for bottlebrush polymer generation but to this point has not been used to synthesize bottlebrush polymer networks. We polymerized a mononorbornene macromonomer and dinorbornene cross-linker (both poly(n-butyl acrylate)) with Grubbs’ third-generation catalyst to achieve bottlebrush networks and in turn demonstrated control over network properties as the ratio of macromonomer and cross-linker was varied. Macromonomer to cross-linker ratios ([MM]/[XL]) of 10 to 100 were investigated, of which all derivative networks yielded gel fractions over 90%. Because of its amenability toward small samples, contact adhesion testing was used to quantify dry-state shear modulus G, which ranged from 1 to 10 kPa, reinforcing that bottlebrush polymer networks can achieve low moduli in the dry state compared to other polymer network materials through the mitigation of entanglements. A scaling relationship was found such that G ∼ ([MM]/[XL])−0.81, indicating that macromonomer to cross-linker ratio is a good estimator of cross-linking density. The swelling ratio in toluene, Q, was compared to dry-state modulus to test the universal scaling relationship for linear networks G ∼ Q−1.75, and a measured exponent of −1.71 indicated good agreement. The synthetic platform outlined here represents a highly flexible route to a myriad of different bottlebrush networks and will increase the accessibility of materials critical to applications ranging from fundamental to biomedical.

INTRODUCTION

Because of their unique physical and solution properties, bottlebrush polymers have been of significant interest to the materials community for over 20 years. Consisting of densely grafted (generally oligomeric) chains extending from a polymer backbone, these materials are themselves often large enough such that single molecules can be visualized by conventional atomic force microscopy (AFM). Because of their size, with microdomains on the length scale of visible light, bottlebrush block polymers are capable of self-assembling into photonic crystals. Conversely, bottlebrush polymers containing block polymer side chains can be used as a hydrophobic core–hydrophilic corona drug carrier or as templates for well-defined nanostructures such as cylinders or spheres. The latter has been achieved by Rzayev and co-workers by grafting through a macromonomer containing an inner degradable block and an outer cross-linkable block. The interesting and highly tunable architecture of bottlebrush materials has also been the study of numerous rheological and mechanical studies. Their wide side chain diameter, as dictated by both side chain length and grafting density, forces the backbone of a bottlebrush polymer into an extended conformation to maximize side chain freedom. This extended conformation suppresses the formation of entanglements, which is analogous to the traditional strategy of swelling a polymer network with solvent. In this way, dry networks largely free of entanglements can be generated.

In traditional polymer networks, mechanical properties are largely controlled by the effective cross-linking density. Both chemical and physical cross-links contribute to overall network properties, and in many networks, physical cross-links in the form of entanglements can influence, or even dominate, the overall mechanical behavior. This is best understood by considering a network composed of a soft, flexible polymer with a low critical molar mass for entanglements to form. At a high chemical cross-link density, i.e., molar mass between cross-links (Mc) < molar mass between entanglements (Me), the material is stiff, and its mechanics are primarily dictated by Mc. If the chemical cross-links are diluted out, the material becomes softer, and the modulus reaches a plateau value as the elasticity is largely controlled by Mc. If Mc, a property dependent on polymer chemistry and architecture, is increased such that little to no entanglements are formed between network cross-links, then material properties should be governed exclusively by polymer chemistry and covalent cross-linking density.

Received: January 4, 2018
Revised: February 26, 2018
Published: March 14, 2018
By cross-linking individual bottlebrush polymers, a network with a bottlebrush architecture and properties can be achieved. A comparison of traditional bulk polymer networks, swollen gels, and bottlebrush networks is portrayed in Figure 1.

Figure 1. Bulk polymer network (left) with both chemical cross-links (red dots) and entanglements (blue circles). Swollen polymer gel (center), where entanglements are largely diluted out by solvent. Bottlebrush polymer network (right), effectively entanglement free, with cross-linking chains being depicted in red.

Because the bottlebrush architecture results in extremely high \( M_c \) values, these elastomers are effectively entanglement-free and can exhibit extremely low shear moduli \( (G) \), in fact the lowest reported in a solvent-free material.27,28 These ultrasoft elastomers are important from a fundamental perspective as they permit measurements on nearly entanglement free materials in the absence of a solvent, which generally complicates measurements and properties due to syneresis. Bottlebrush networks are also highly appealing for biomedical applications due to their tunable modulus within the range of many biologically relevant values.

The first report of bottlebrush elastomers was by Matyjaszewski and co-workers, where they demonstrated the cross-linking of a double-grafted oligo-ethylene glycol methacrylate, ultimately yielding extremely soft materials (shear modulus \( G \approx 10^4 \) Pa).26 Exploration into bottlebrush thermoplastic elastomers has also been performed.29,30 Very recently, a radical polymerization grafting-through approach was used targeting poly(dimethylsiloxane) (PDMS) and poly(n-butyl acrylate) (PnBA) macromonomers, highlighting possibilities for biological mimetic materials.31 Specifically targeting soft materials, Weitz and co-workers generated PDMS bottlebrush networks through hydrosilylation.32 Sheiko and co-workers recently published a thorough structure–property relationship between bottlebrush side chain length and \( M_c \), in addition to comparing PDMS bottlebrush elastomers to conventional hydrogels.32a Several examples of higher glass transition temperature \( (T_g) \) bottlebrush networks are also present in recent literature.32a,33

In generating and studying soft bulk bottlebrush materials, there is a critical need for a versatile synthetic platform, allowing for a wide variety of chemistries and cross-linking densities to be achieved. To date, most strategies, including those above, have focused almost exclusively on polymer-specific cross-linking techniques, wherein cross-linking density is also hard to cleanly control. Here, we propose utilizing a grafting-through ring-opening metathesis polymerization (ROMP) method (Figure 2), allowing for relatively good control over cross-linking density, as will be shown later, and accessibility to most monomers amenable to atom transfer radical polymerization (ATRP) and other controlled radical polymerizations. We selected ROMP as the polymerization approach because of its controlled nature, while enabling extremely high polymerization rates (even of high molar mass macromonomers), as well as imparting functional group tolerance, allowing for numerous applications to ultimately be targeted.

Recently, ROMP has seen an immense increase in use to generate bottlebrush materials due to the incredible rates of reactions when polymerizing particularly strained alkenes, such as norbornenes.35–39 Norbornene-functionalized macromonomers have been obtained from either controlled polymerization (atom-transfer radical polymerization, reversible addition−fragmentation chain-transfer polymerization, ring-opening polymerization) from a norbornene-functionalized initiator or end-functionalization of a well-defined polymer with a norbornene.40,41 Patton and Advincula32 as well as Woolley and co-workers43 have shown that monomer selection has a significant impact on the quality of macromonomer realized through ATRP or RAFT from a norbornene initiator, with acrylates usually resulting in significant (≥10%) dimerized products. We are primarily interested in soft materials accessible through radical polymerization; thus, a synthetic route amenable to controlled norbornene-functionalized oligoacrylates is ideal. Xia et al. originally reported the use of ATRP followed by azide substitution and azide−alkyne click as a route to efficiently achieve highly functionalized, ROMP targetable macromonomers.44 Because any dimerized polymer generated during polymerization would not contain two norbornenes by this method, it is an ideal route to access high purity macromonomer required to precisely control the ratio of macromonomer and cross-linking in this platform. Xia and co-workers also recently demonstrated that dimerization of macromonomers leads to bottlebrush polymers with broader molar mass distributions, though they did not observe network formation.32 Using mono- and difunctional oligoacrylates (representing macromonomer and cross-linker) generated through this method, we synthesized a series of bottlebrush networks with varying cross-linking density and dramatically different stiffness parameters. Exploiting controlled polymerizations in this way can lead to an even greater variety in bottlebrush network materials and is a promising platform for both fundamental studies and biomimetics.

By applying such a versatile bottlebrush polymer network platform to conventional network and gel physics, we can begin to verify universal network scaling theories as a function of network architecture. To demonstrate the power of this system as well as how a brush architecture impacts material properties, we investigate modulus and swelling ratio as a function of cross-linking density and show that the resulting scaling laws are in good agreement with the corresponding linear network prediction. As such, this synthetic platform is a promising
approach to continue correlating linear and bottlebrush polymer networks.

### RESULTS AND DISCUSSION

**Macromonomer and Network Synthesis.** In this study, poly(n-butyl acrylate) (PnBA) was used as the brush chemistry due to its soft, tacky nature at room temperature, which will yield especially soft bulk networks in the absence (or near absence) of entanglements. Moreover, PnBA linear bottlebrushes have been thoroughly examined for $M_n$ dependence on grafting length, albeit in an all-ATRP system.\(^{28}\) For this network series, a macromonomer (MM) of 4 kg/mol was selected, which has been shown to be long enough to yield a sterically confined brush polymer, yet not so long that polymerization rate and conversion drop substantially.\(^{28}\) Conversely, a 22 kg/mol dinorbornyl cross-linker (XL) was used, to ensure that after the first end of this cross-linker was incorporated into a growing chain the opposing end would still be accessible by a second, distinct growing chain and not imbedded in the brush structure. We acknowledge the possibility that this cross-linker molecule could entangle after polymerizing, either on its own or with neighboring cross-linkers. In most samples it is dilute, so this effect should be minimal; however, because of this we refrain from referring to these materials as entirely entanglement-free. This cross-linker was obtained by the ATRP of nBA from a difunctional alkyl bromide ATRP initiator, whereas the macromonomer was generated with a monoalkyl bromide (Figure 3). These materials underwent quantitative azidation with sodium azide in DMF and were then further functionalized with a norbornyl methyl ester alkyne under CuAAC conditions. The norbornyl methyl ester moiety was selected as the bottlebrush anchor group due to the particularly rapid polymerization kinetics of this group, as recently highlighted in a report from Matson and co-workers.\(^{36}\) The exo-norbornene alkyne was prepared in two steps from exo-norbornene carboxylic acid.\(^{1}H\) NMR and GPC were used to demonstrate both quantitative end-functionalization and polymer stability. The PnBA MM was polymerized by ROMP using Grubbs’ third-generation catalyst (G3) to confirm activity and purity and resulted in a clean high molar mass peak by GPC as well as quantitative norbornene consumption by $^{1}H$ NMR.

To achieve bottlebrush polymer networks, both MM and XL were dissolved in freshly distilled THF to a final total norbornene concentration ([norb] = [MM] + 2[XL]) of 0.05 M. The ratio of [MM] and [XL] should correlate to an average degree of polymerization between cross-links, provided that no cross-linkers partake in looping events. We have no clear way to demonstrate whether or not this happens; thus, the ratio [MM]/[XL] is used here to differentiate between samples instead of degree of polymerization between cross-links. [MM]/[XL] values of 10, 25, 40, 50, 70, and 100 were targeted, both to test the dynamic range of the platform and to yield a wide family of samples, ideally spanning an order of magnitude in properties. To gel the materials, a stock solution of G3 was rapidly added to the solution in an argon glovebox by syringe and mixed at a predetermined ratio, determined by the targeted cross-linking density. At a minimum, the [norb]/[G3] ratio was at least twice that of [MM]/[XL] in order to ensure percolation rather than local cross-linking would occur. All samples rapidly became viscous, achieving qualitative gelation within 10 m. After 18 h, unreacted MM and XL were extracted with methanol washes and massed, yielding gel fraction values (Table 1). It is notable that all samples, including the [MM]/[XL] = 100 samples, had high gel fractions, over 90%. The most widely used method to generate soft bottlebrush networks—hydrosilylation of mono- and disilyl hydrides to a vinylsilane PDMS backbone—is a grafting-to technique and results in networks with gel fractions ranging from 76 to 94%.\(^{27}\) Notably, gel fractions above 90% were achievable with the PDMS system only when more cross-linker than macromonomer was used. Because a grafting-through approach is used here, in conjunction with the extremely reactive norbornyl methyl ester and G3, significantly higher gel fractions were reliably achieved. This allows for precision materials of well-defined molecular architecture and brush density to be achieved, which is critical for our fundamental understanding of this class of materials.

**Swelling and Contact Adhesion Testing.** As a simple method to study chain extensibility, swelling studies were

![Figure 3. Synthetic approach to mononorbornene macromonomer MM (top) and dinorbornene cross-linker XL (bottom).](image-url)
performed for all samples. Toluene was selected as the solvent both because it is a good solvent for PnBA and because the Flory–Huggins interaction parameter for PnBA and toluene at room temperature in the infinite dilution has been reported ($\chi = 0.07$). The infinite dilution $\chi$ approximation is reasonable for our materials since the most tightly cross-linked networks in this study swell significantly ($\phi_p < 0.1$). To validate this assumption, the mass fraction of norbornene linker, up to the triazole moiety, is shown for each sample condition in Table S2. At most, samples are 6 mass % norbornene linker. After washing with methanol, samples were vacuum-dried, weighed, and swollen to equilibrium with toluene. Samples were weighed again, and mass fractions were converted to volume fractions based on PnBA and toluene room temperature densities. These swelling ratios are tabulated in Table 1. A clear upward trend can be seen at lower [MM]/[XL] ratios, while higher ratios, notably 50, 70, and 100, plateau off at a swelling ratio of roughly 35. It is likely that swelling is achieved in these materials both by the swelling of the bottlebrush backbone and side chains and also by the 22 kg/mol cross-linking chains.

The mass fraction of this swellable cross-linking strand is especially large at lower [MM]/[XL] ratios, helping to explain the high swelling observed for these materials. This strand likely exists in two distinct conformations: segments that are imbedded in the brush architecture behave as other brush strands, while portions of the chain outside of the brush corona have significantly more degrees of freedom and thus swell differently. If we assume loop-free cross-linking, the [MM]/[XL] = 10 samples have swelling contributions from both the norbornene brush repeat units along the bottlebrush backbone and the nonimbedded segments of the cross-linker, which comprises 23% of the total sample by mass (Table S2). These two contributions yield an increased composite swelling ratio. Notably, the mass percent of nonimbedded chain drops off rapidly at higher [MM]/[XL] ratios. As stated earlier, it is also possible that cross-linking chains are participating in looping events, which would increase the effective number of monomer units between cross-links.

Shear modulus, $G$, as determined by contact adhesion testing, is plotted against the [MM]/[XL] ratio in Figure 4. Since the bottlebrush architecture spatially frustrates the formation of entanglements, extremely soft, solvent-free samples can be synthesized, which is demonstrated in our materials with $G$ values ranging from 1 to 10 kPa, in the same range as the softest bulk polymer networks reported. An exponential dependence of $G$ on [MM]/[XL] was found, with an exponent of $-0.81$ when fitting all available data. For an elastomer, $G$ scales as the following:

$$G \sim (M^-1_c + M^-1_e)$$

(1)

As stated previously, we are hesitant to equate [MM]/[XL] to $M_c$, because the dinorbornene cross-linker has the potential to loop. We are probing a regime of networks where the expected molar mass between cross-links is significantly lower than the entanglement molar mass of the system, the $M^-1_c$ term should minimize, and $G$ should simply scale as $M^-1_e$. The deviation we observe here, i.e., an exponent of $-0.81$ instead of $-1.0$, is evidence that, indeed, the [MM]/[XL] ratio is not a perfect descriptor of cross-linking density but that certainly network properties such as modulus can be tuned using this ratio as a handle for property control.

It is worth noting that by excluding the series of samples at [MM]/[XL] = 10, an exponent of $-1.03$ is obtained, suggesting a deviation from the expected trend at particularly high cross-linking densities. At lower cross-linking densities, [MM]/[XL] trends as expected with $M_c$ (Figure S5), while in a higher cross-linking density network, measured properties may be a composite of multiple structural heterogeneities. Specifically, such heterogeneities could manifest as looping events, consecutive cross-linker insertion, failure to incorporate both ends into the propagating network, or entanglement of the longer linear cross-linking segments. If a cross-linker chain forms a loop or does not react at both ends, rather than contributing to cross-linking, the effective cross-linking density would be lower than predicted, and a lower modulus would result. This fits the observed data. Moreover, because cross-linking chains are incorporated at an average spacing of [MM]/[XL] repeat units, the likelihood of polymerizing consecutive cross-linkers is highest in this sample. Areas with high cross-linking density, i.e., heterogeneities mentioned above, would not behave ideally and could promote entanglement between adjacent cross-linking chains or behave as an $f = 4$ cross-linker (instead of two distinct $f = 3$ cross-linkers), ultimately diluting the cross-linking density. Finally, there is a distinct possibility that cross-linking chains participating in a single addition, not limited to the [MM]/[XL] = 10 network. This possibility can lead to complications as it reduces the number of chemical cross-links but presents a new side chain with substantial molar mass not tethered at one end that can potentially form entanglements. While this could possibly affect our materials, we see extremely high conversion in the case of the linear bottlebrush sample and therefore expect very few of these events.

The data described above, i.e., shear modulus $G$ and swelling ratio $Q$, can be related to one another through the following network relationship:

$$G(Q = 1) = \frac{kT}{\xi^3}(1 - 2\chi)^{0.69}Q^{-1.75}$$

(2)

where $G(Q = 1)$ is the dry-state shear modulus, $\xi$ is the correlation length, $\chi$ is the polymer–solvent interaction.
parameter, and \( Q \) is the swelling ratio. A room temperature interaction parameter for PnBA and toluene was measured by Saeki et al. in the extreme dilution, \( \chi \approx 0.07^{45} \) By plotting dry-state shear modulus versus the swelling ratio in toluene, it is possible to test whether or not bottlebrush networks generated through the ROMP platform follow this relationship for linear polymer networks. Indeed, as shown in Figure 5, an exponent of \(-1.71\) is obtained, in extremely good agreement with the predicted value of \(-1.75\).

![Figure 5](image)  
**Figure 5.** Dry-state shear modulus versus equilibrium swelling ratio in toluene. Swelling ratio is given in volume fraction.

With an understanding that this relationship holds for bottlebrush networks, the correlation length \( \xi \) can also be estimated. A value of 18.3 Å is obtained, which when compared to computational predictions is lower than anticipated. A relationship proposed by Dobrynin and co-workers using molecular dynamics simulations relates \( \xi \) to the Kuhn length of the individual monomer repeat units, \( b_i \), as

\[
\xi = b_i \sqrt{n_{ac} + 1}
\]

where \( n_{ac} \) is the length of each brush arm.\(^{36,47}\) In our case, this relationship simplifies roughly to \( \xi = 6b_i \). An issue arises in that two discrete chemistries are being interrogated with this measurement: the backbone polynorbornene and the cross-linker PnBA. The Kuhn length for PnBA is approximately 6 Å, while that of polynorbornene can be estimated by measurements of its functionalized and hydrogenated derivatives to be around 13 Å.\(^{36}\) It is thus challenging to map eq 3 directly onto the ROMP system demonstrated here, though considering only the PnBA effects would yield a Kuhn length of 36 Å, or roughly twice that of what we measured. Even so, the measured \( \xi \) here is in relatively good agreement with other polynorbornene bottlebrush polymer systems, where the lower values were rationalized through a lower grafting density compared to their all-ATRP counterparts.\(^{23,49–51}\) Moreover, it seems this observation gives credence to the hypothesis that the 22 kg/mol PnBA cross-linker is contributing significantly to swelling; in fact, if lower swelling ratios were observed, a substantially higher Kuhn length would be extracted. Thus, it is very likely that the observed Kuhn length for this system is an average of all the chains that contribute to network elasticity, including both the bottlebrush norbornene backbone and the long, linear cross-linkers.

### CONCLUSIONS

A series of bottlebrush polymer networks with PnBA as the brush chemistry were synthesized through a grafting-through ROMP method, utilizing mononorbornene macromonomers to form bottlebrush strands and dinorbornene cross-linkers to facilitate network formation. A norbornyl methyl ester was used as the anchor group to promote reactivity. Different ratios of macromonomer and cross-linker were used during gelation to yield materials with varying molar mass between cross-links. Ratios of macromonomer to cross-linker \([\text{MM}] / [\text{XL}]\) targeted were 10, 25, 40, 50, 70, and 100, with gel fractions over 90% in all cases. Contact adhesion was used to measure modulus of the resulting samples, and a scaling relationship of \(-0.81\) was found between \([\text{MM}] / [\text{XL}]\) and shear modulus \(G\). Excluding the highest density of cross-linking, where the formation of loops is most likely, a scaling relationship of \(-1.03\) was found, indicating very good agreement with rubber elasticity and demonstrating that \([\text{MM}] / [\text{XL}]\) is a good predictor for cross-linking density. Moreover, the extremely low modulus values associated with bottlebrush networks were reproduced here, with \(G\) ranging from 1 to 10 kPa. Swelling studies were performed in toluene, a good solvent for PnBA with a known room temperature interaction parameter. Samples swelled significantly, up to a swelling ratio \(Q\) of 36. This was rationalized in part by the ability of the cross-linking chain to partake in swelling as well as the bottlebrush backbone. A scaling relationship was also determined for \(G\) and \(Q\), with a determined exponent of \(-1.71\), in extremely good agreement with the predicted value of \(-1.75\) in a good solvent. A statistical segment length of 18.3 Å was determined, which is lower than predicted by simulation studies, likely due to the impact of the flexible cross-linking chain. Ongoing studies include varying the length of the difunctional cross-linking chain in order to better understand the contributions of this segment to the overall mechanical properties of these networks.

To meet the rapidly increasing demands for extremely soft, entanglement-free materials, a robust and versatile synthetic platform will be required. ROMP is shown here as a synthetically versatile and accessible route, producing networks with the fidelity and tunability to meet these demands and continue progress in a quickly expanding field.

### METHODS

**General.** Air- and water-sensitive procedures were carried out under an inert argon atmosphere, while all ROMP polymerizations and network formations were conducted in an argon glovebox. An Avance II 600 MHz Bruker spectrometer equipped with a broadband inverse room temperature probe was used to record all nuclear magnetic resonance (NMR) spectra. Gel permeation chromatography (GPC) data were obtained using a Waters instrument equipped with three mixed bed columns (HR0.5, HR3, and HR4) at a flow rate of 1 mL/min and a constant temperature of 25 °C relative to polystyrene standards.

**Materials.** Grubbs’ second-generation catalyst, \(\text{exo-5}\)-norbornene carboxylic acid, 4-pentyonic acid, 2.4 mol/L lithium aluminum hydride in tetrahydrofuran (THF), \((\text{dimethylamino})\text{pyridine}, (3-\text{dimethylamino})\text{propyl})-N′-ethylcarboximide hydrochloride, sodium azide, \(n\)-butyl acrylate, copper(I) bromide, \(\text{N,N,N′,N′-pentamethyldiethylenetriamine} (\text{PMDETA})\), ethyl bromoisobutyrate, bromoisobutyryl bromide, 2-bromopyrrolidine, \(\text{N,N-dimethylformamide} (\text{DMF})\), THF, and \(\text{N,N,N′-triethylamine} (\text{TEA})\) were purchased from...
Sigma-Aldrich. Ethylene glycol, DCM, and acetone were purchased from Fisher Scientific. THF was distilled under argon over sodium, while DCM was dried over 4 Å molecular sieves before use. Copper(I) bromide was purified by alternating washes of acetic acid and ethanol. n-Butyl acrylate was passed through a short basic alumina plug before use. The 2-bromopyridine version of Grubbs' third-generation catalyst was prepared according to the literature.\(^\text{36}\) exo-5-Norbornenemethanol was prepared according to previous procedures.\(^\text{38}\)

**Macromonomer Synthesis.** exo-5-Norbornenemethylpent-4-ynoate: norbornenemethanol (1.06 g, 8.54 mmol), pent-4-ynoic acid (0.838 g, 8.54 mmol), and (+)-dimethylamino)pyridine (0.104 g, 0.85 mmol) were added to a dry 100 mL round-bottom flask and dissolved in 16.8 (0.5 mol/L) of dry DCM. 1-ethyl-3-(3-(dimethylamino)-propyl)carbodiimide hydrochloride was added in one portion, and the reaction was stirred for 18 h under argon. The reaction was diluted with 50 mL of DCM, washed with 2 × 50 mL of 1 mol/L HCl, 1 × 50 mL of saturated NaHCO\(_3\), and 1 × 50 mL of brine, dried over Na\(_2\)SO\(_4\), and concentrated by rotary evaporation. The resulting residue was purified by column chromatography (silica, 9:1 hexanes:ethyl acetate) to yield the norbornene alkyne coupling reagent as a clear oil.\(^\text{1H NMR (600 Mz, CDCl\(_3\))}: \delta 6.09 (2H, m), \delta 4.19 (1H, dd, J\(_{1,2}\) = 10.8 Hz, J\(_{2,3}\) = 6.4 Hz), \delta 4.01 (1H, dd, J\(_{1,2}\) = 10.8, J\(_{2,3}\) = Hz, 9.3), \delta 2.84 (1H, s), \delta 2.71 (1H, s), \delta 2.58 (2H, m), \delta 2.52 (2H, m), \delta 2.58 (2H, m), \delta 1.98 (1H, t, J\(_{2,3}\) = 2.5 Hz), \delta 1.73 (1H, m), \delta 1.35 (1H, m), \delta 1.31 (1H, m), \delta 1.28 (1H, m), \delta 1.16 (1H, m).\(^\text{13C NMR (150 Mz, CDCl\(_3\))}: \delta 172.0, \delta 137.1, \delta 136.3, \delta 82.7, \delta 69.1, \delta 69.0, \delta 45.1, \delta 43.8, \delta 41.7, \delta 38.1, \delta 35.6, \delta 29.7, \delta 14.6. See Figures S6 and S7 for full spectra.\(^\text{Poly(n-butyl acrylate) macromonomer (MM) and cross-linker (XL): PaNB was synthesized by ATRP, as previously reported.\(^\text{19}\) Briefly, the macromonomer was generated by polymerization of n-butyl acrylate in acetone at a 1:1 ratio to volume at 50 °C for 18 h, with typical conversions of 50%. Ethyl bromoisobutyrate was used as the initiator, CuBr as the copper source, and PMDETA as the ligand. A ratio of 1:1 mole by volume was used for initiator to copper. The cross-linker was polymerized in DMF at a ratio of 1:1 ratio to volume by 75 °C. After 1 h, a conversion of 85% was observed. Both macromonomer and cross-linker were precipitated up to six times in 90:10 methanol-water ratio by volume, until no unreacted monomer was observed by \(^1\)H NMR. The terminal bromide was displaced with sodium azide and functionalized with norbornene by CuAAC as previously reported by Xia et al.\(^\text{7}\) Slight adjustments to these procedures included a slight excess of norbornene alkyne was used (1.3 equiv), and the final norbornene macromonomer and cross-linker were precipitated in 90:10 methanol-water ratio by volume until no residual alkyne was observed (generally 2×). MM and XL GPC traces and \(^1\)H NMR spectra can be found in the Supporting Information (Figures S1 and S2).\(^\text{Linear brush test polymerization: in an argon glovebox, 0.108 g of MM was dissolved in 0.33 mL of distilled THF in a scintillation vial. Grubbs' third-generation catalyst was added (0.119 mg) as a stock solution in 0.1 mL of dry THF to bring the final solution to a concentration of [norbornene] = 0.05 mol/L. After 1 h, the polymerization was quenched with a drop of ethyl vinyl ether. The sample was assessed for conversion by both \(^1\)H NMR and GPC (Figures S3 and S4).\(^\text{Bottlebrush network synthesis and swelling: a generalized synthesis for all bottlebrush networks is described here. A predetermined amount of MM and XL was added to a 1 dram vial, with total sample mass ranging from 0.10 to 0.12 g. Samples were brought into an argon glovebox and dissolved in distilled THF such that the anticipated norbornene concentration upon addition of G3 stock solution was 0.05 mol/L. A stock solution of G3 was added in 0.1 mL volume, and samples were mixed rapidly by syringe. After 18 h, samples were removed from the box, a drop of ethyl vinyl ether was added, and samples were delaminated from the vial walls with methanol. Samples were transferred to a 20 mL scintillation vial and washed with methanol over 3 days. The wash was collected, dried, and used to calculate gel fraction. Samples were dried in vacuo at 40 °C, massed, swollen to equilibrium in toluene to calculate toluene swelling ratio, and deswollen with methanol. Samples were transferred to glass slides dried in vacuo at 40 °C before contact adhesion testing. Contact adhesion testing: the shear modulus of the bottlebrush networks was quantified using contact adhesion testing. A cylindrical glass probe, of radius a = 1 mm, was brought into contact at a crosshead speed of 5 μm/s in order to indent with the sample up to a load of 0.5 g. Samples were prepared to be 1.5 mm tall and 7.5 mm in diameter in the dry state. The modulus was measured in the dry state. The linear portion of the load–displacement curve while the probe was in full contact with the sample was used to calculate stiffness and ultimately translated to shear modulus G by assuming the networks are incompressible (ν = 0.5) through the following relationships: \(^K = 2E^*a\) \(^E = (1 - \nu^2)E^*\) \(^G = \frac{E}{2(1 + \nu)}\) where K is stiffness, \(E^*\) is the plane-strain modulus, \(E\) is Young’s modulus, \(\nu\) is Poisson’s ratio, and G is shear modulus. Because the samples were thin, a correction factor established by Crosby and co-workers was applied to take into account substrate effects.\(^\text{34}\) **Supporting Information** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00018. NMR spectra, GPC traces, as well as network precursor molecular weight data and network compositional data (PDF) **AUTHOR INFORMATION**

**Corresponding Author**
*E-mail kathryn.beers@nist.gov* (K.L.B.).

**ORCID**
Joel M. Sarapas: 0000-0002-6548-4101
Edwin P. Chan: 0000-0003-4832-6299

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
J. Sarapas acknowledges support from the NRC fellowship program. E. Rettner acknowledges support from the NIST SURF program. The authors thank V. Prabhu and A. Forster for their help in preparing the manuscript. The equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.

**REFERENCES**


