Chemical Botany: Bottlebrush Polymers in Materials Science

Intanon Lapkriengkri,[†] Kaitlin R. Albanese,[‡#] Andrew Rhode,[†] Austin Cunniff,[†] Angela A. Pitenis,[†#]* Michael L. Chabinyc,[†#]* and Christopher M. Bates[†#]*

[†]*Materials Department, University of California, Santa Barbara, CA 93106.* [‡]*Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106, United States.* [#]*Materials Research Laboratory, University of California, Santa Barbara, CA 93106.*

To whom correspondence should be addressed:
apitenis@ucsb.edu, chabinyc@engineering.ucsb.edu, cbates@ucsb.edu

ABSTRACT

The bottlebrush polymer architecture provides unique opportunities to tune the structure and properties of soft materials with applications ranging from rubbers to thin films and composites. This review addresses recent developments and future opportunities in the field with an emphasis on materials science enabled by contemporary bottlebrush chemistry.

INTRODUCTION

The recent explosion of techniques to control polymerization reactions has unleashed a cornucopia of choices in the design of soft materials.[1] Unsurprisingly, this newfound level of control has significant implications for manipulating the properties of polymers in ways not possible in the not-so-distant past.[2–4] This review focuses on the materials science of a branched architecture known as 'bottlebrush' polymers. The term bottlebrush refers to macromolecules that contain two key ingredients: (i) a polymeric backbone, and (ii) polymeric side chains that protrude from many, if not all, of the backbone repeat units.[5–7] Discrete bottlebrushes—which, given the synthetic breakthroughs alluded to above, are remarkably accessible—can be thought of as situated at one extreme along a continuous spectrum of grafting density, with classical linear polymers at the other and combs somewhere in between (**Figure 1**). Detailed theory[5,8] and experiments[6,7,9,10]

have carefully studied the transitions between these conceptually distinct regimes and interested readers are referred to the literature for more information. Here, our goal is to discuss bottlebrush polymers in detail, as this versatile molecular building block provides exciting opportunities to tune the properties of materials in ways that are difficult, if not impossible, with other systems. Emphasis is placed on current and future *applications* enabled by the bottlebrush architecture rather than synthetic strategies or solution-phase chemistry alone. For readers interested in these riveting areas, we again refer to other contemporary literature.[6,11–14]

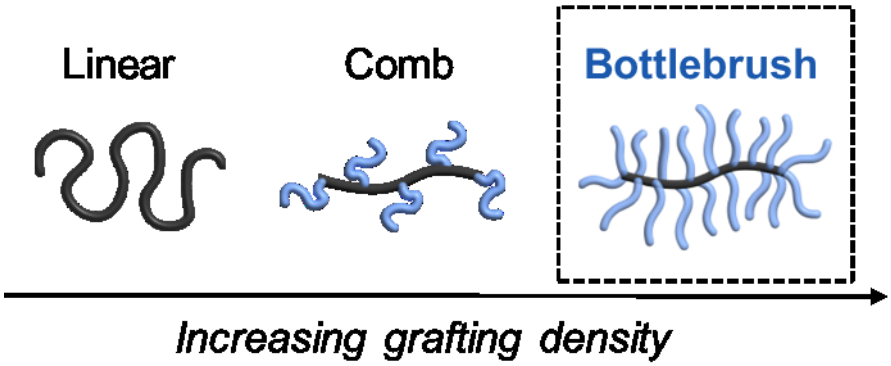

Figure 1. Transition from linear to bottlebrush polymers upon increasing grafting density.

Although we do not dwell on the multitude of synthetic techniques that have been developed to create bottlebrushes, it is important to appreciate there are a number of options available depending on target material properties and constituent chemistry. In particular, strategies to build the backbone and attached side chains fall under three broad categories: grafting-to, grafting-from, and grafting-through polymerization.[11–13] These approaches can be used individually or together to build bottlebrushes of varying complexity ranging from a single type of side chain to blocky,[15–18] statistical,[19,20] or gradient sequences[21] of different chemistry and/or degrees of polymerization. Below, we dive into the benefits and potential applications of materials

derived from these intricate yet synthetically accessible building blocks. Our overarching goal is to highlight state-of-the-art materials with unique properties that emerge from the bottlebrush architecture, as well as future opportunities in which this molecular motif may prove enabling. Consequently, the remainder of this review is organized loosely by application. Bon voyage!

Bottlebrush elastomers

The thermal properties of bottlebrushes are typically dominated by the choice of side-chain chemistry, which often constitutes >95% of the molecule by weight or volume.[22] Consequently, if one selects side chains with a low glass-transition temperature ($T_g \ll 20$ °C) and no crystallinity, crosslinking will yield elastomers in analogy with linear systems (**Figure 2**).[3] However, the properties of these so-called 'bottlebrush elastomers' vary considerably from linear analogues. Sheiko, Dobrynin, and coworkers have published an eloquent series of papers discussing one unique property of these materials: the elastic modulus reaches as low as 0.1–10 kPa, even with gel fractions >90%—several orders of magnitude smaller than linear elastomers.[3,4,23] While similar moduli can be achieved in highly swollen hydrogels,[24] these bottlebrush elastomers are soft and solvent-free. The physical underpinning of this behavior relates to a lack of entanglements—which act as transient physical crosslinks that limit softness—as the densely grafted side chains cause backbone stiffening and a substantial increase in the main-chain entanglement molecular weight.[9,25] Typically, designs targeting this type of softening will similarly select side-chain lengths that are smaller than their respective entanglement molecular weight to maximize the effect.[26]

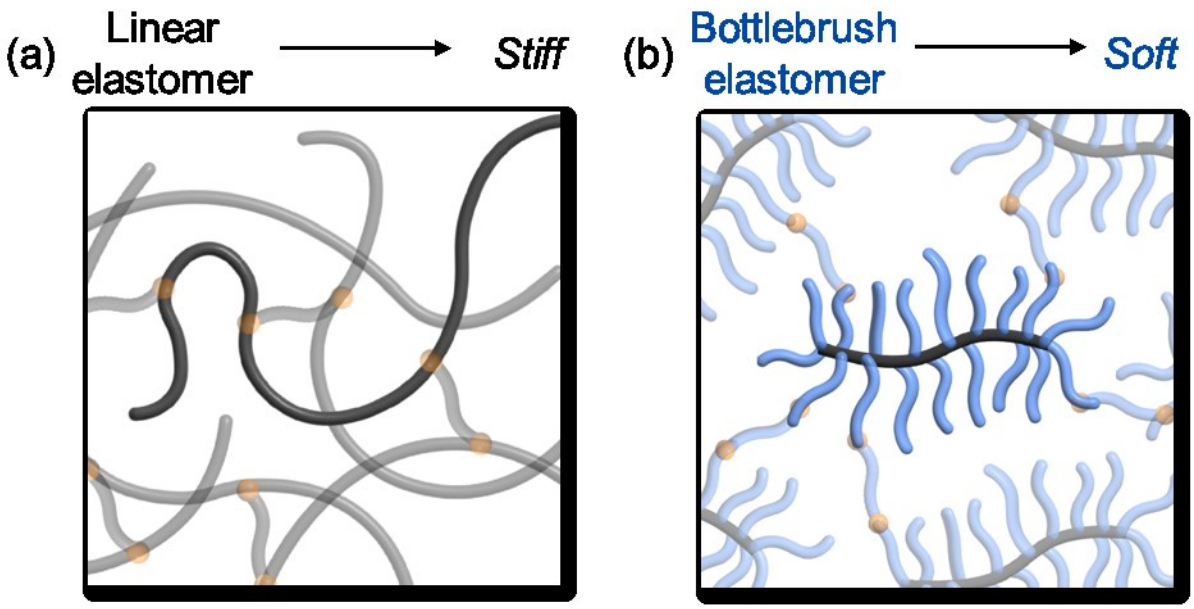

Figure 2. Illustration highlighting the distinct network architecture of **(a)** linear and **(b)** bottlebrush elastomers.

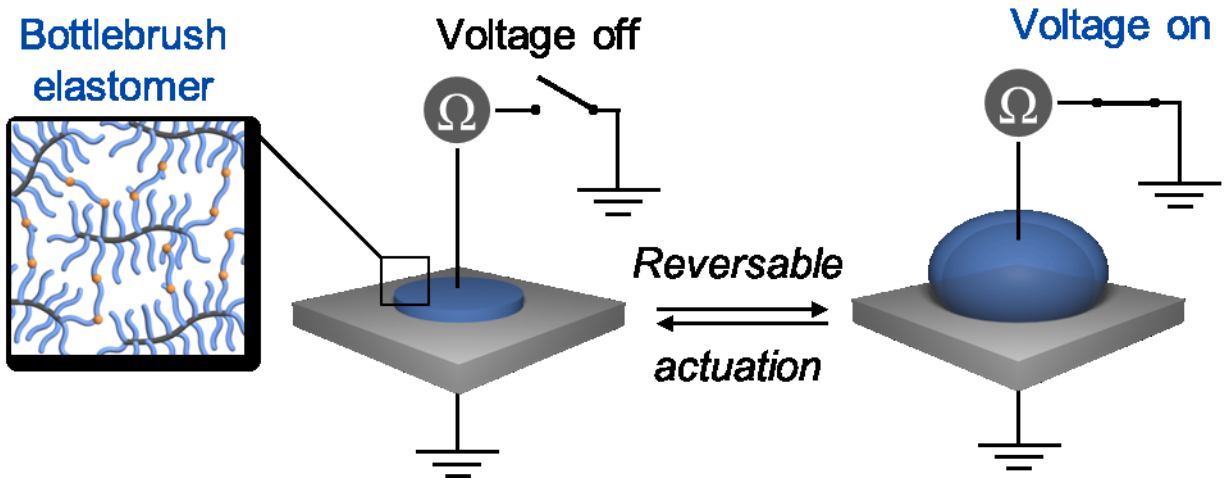

Figure 3. Reversible dielectric actuators with unique performance made possible by using crosslinked bottlebrush elastomers.[27]

Bottlebrush elastomers have pushed the boundary of possibilities for applications where a low modulus and elasticity are attractive features, but in which the presence of solvent may not be desirable, *e.g.* because of concerns over failure, leaching, or evaporation. For example, devices

that operate as a parallel plate capacitor with an elastic dielectric flanked by two electrodes can exhibit better performance when the intermediate layer is softer and more deformable. Vatankhah-Varnoosfaderani and coworkers demonstrated the advantage of using bottlebrush elastomers in this context by creating efficient actuators that move in response to an applied electrical signal by reversibly deforming the super-soft bottlebrush elastomer layer (**Figure 3**).[27] Similarly, Reynolds *et al.* highlighted the use of bottlebrush elastomers in capacitive pressure sensors (**Figure 4**),[28] where applied pressure causes a measurable change in induced charge that is more pronounce with softer materials. Bottlebrush networks with a range of moduli ($G' \approx 6$–100 kPa)[28] showed a ~22-fold increase in sensitivity under small loads (< 10 kPa) and ~53-fold increase at moderate ones (>10 kPa) compared to commercially available Sylgard 184 ($G' = 520$ kPa, **Figure 3a**).[28] For both the actuator and pressure sensor, improved performance is related to a difference in modulus as rationalized by the classical theory of rubber elasticity;[29] increased deformation (actuator) or sensitivity (sensor) is directly proportional to the inverse of the shear modulus. Another advantage that contributes to performance in these contexts is the pre-stretched nature of the backbone which causes strain-stiffening that prevents electrical breakdown without a potential downside of solvent leakage in analogous hydrogel materials.

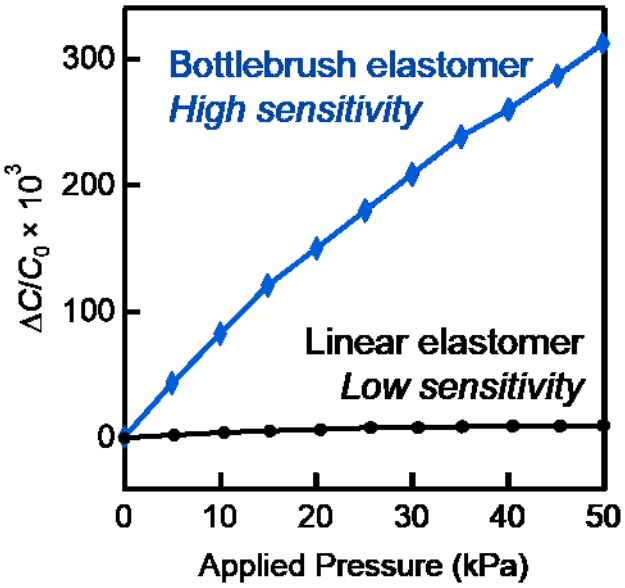

Figure 4. Bottlebrush elastomers improve the sensitivity of capacitive pressure sensors.[28]

The intrinsically soft nature of bottlebrushes has also been exploited in pressure-sensitive adhesives (PSA). PSAs require a delicate balance of viscoelasticity to quickly adhere to surfaces upon contact but detach cleanly without leaving residue after use.[30,31] Because the requisite Dahlquist criterion ($G' \approx 0.1$ MPa) is lower than the plateau modulus of a typical elastomer ($G' \approx 1$ MPa), linear PSA formulations are softened through the addition of small-molecule plasticizers (**Figure 5a**).[32] Arrington *et al.* used dynamically crosslinked bottlebrush polymers containing disulfide bonds at the ends of side chains to circumvent the use of leachable additives in PSAs (**Figure 5b**).[33] They showed up to a 10× difference in storage modulus at the bonding ($G' \approx 1$ kPa, 0.01 Hz) and debonding ($G' \approx 10$ kPa, 100 Hz) frequencies, akin to physical properties observed in traditional PSAs. Maw *et al.* built on this idea and systematically synthesized bottlebrushes of different side-chain lengths and grafting densities. Through such fine-tuning, they were able to demonstrate the potential of bottlebrush PSAs to meet the requirements for different types of PSAs, from general purpose to high-shear variants.[34]

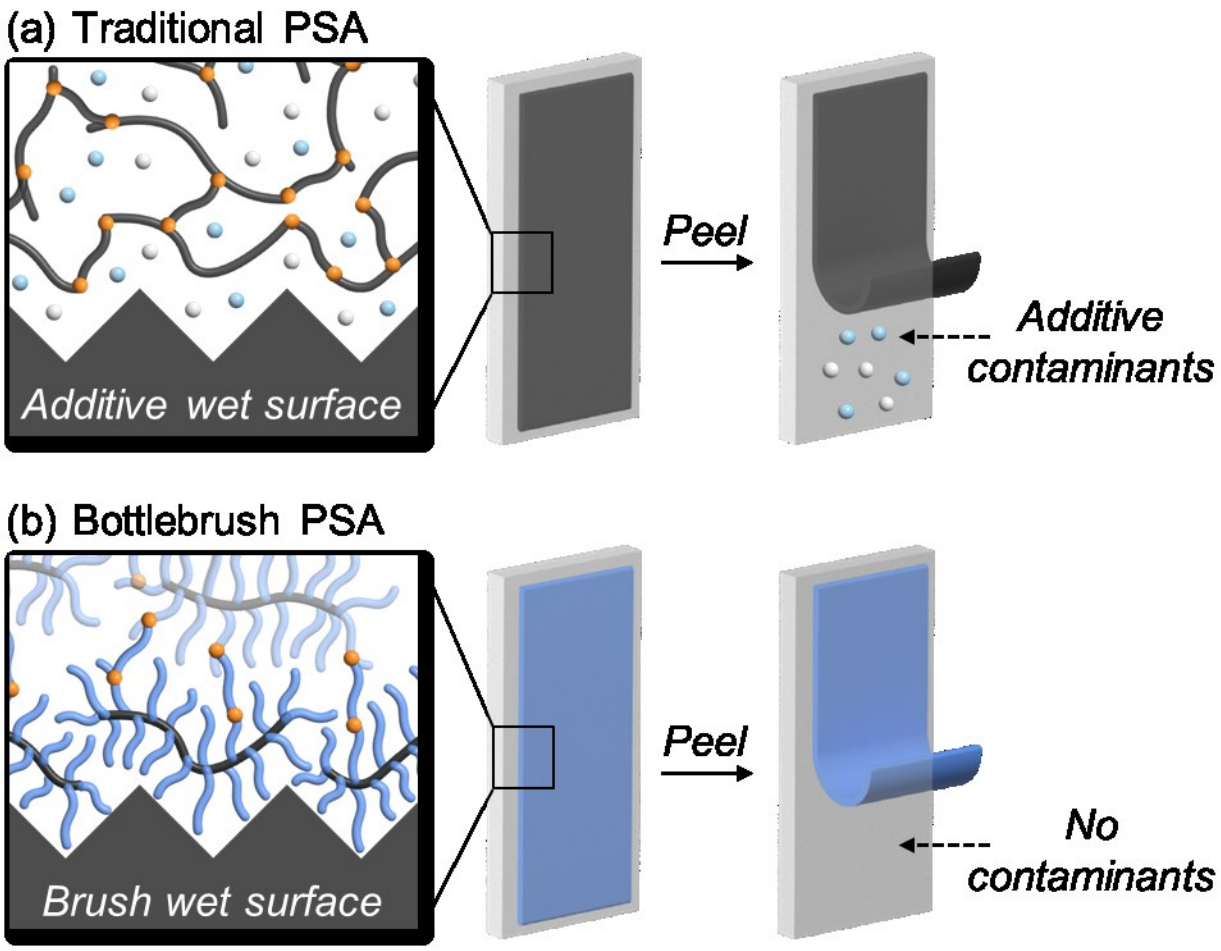

Figure 5. Bottlebrush pressure-sensitive adhesives can achieve similar performance as traditional linear materials without containing additives that contribute to residue formation.[32,34]

Another intriguing idea is the similarity in mechanical properties between bottlebrush elastomers and various types of human tissue.[23,35] Interesting possibilities extend beyond the low-deformation limit of softness (*e.g.* Young's modulus, dynamic shear moduli) to include control over strain stiffening and firmness. Keith *et al.* demonstrated this versatility by independently manipulating both backbone and side-chain lengths to tailor the stress–strain behavior of bottlebrush elastomers as inspired by biology.[23] Extending the design of these materials to include two types of side chains distributed statistically along the backbone provides additional control

over mechanical properties through microphase separation. For example, copolymerizing a combination of hard (T_g > 25 °C) and soft (T_g < 25 °C) side chains can yield a modulus similar to human aorta with high extensibility (up to 300%) and tensile strength (≈ 5 MPa) as shown by Dashtimighadam *et al*.[35]

There are also compelling reasons to use crosslinked bottlebrush elastomers in composites. For example, a common method to obtain soft and electrically conductive materials involves dispersing conductive additives (*e.g.* carbon nanotubes,[36] doped polymers,[37–39] or liquid metals[40–42]) into a polymer matrix. However, there is an inherent tradeoff between softness and conductivity in this approach as the additive tends to be stiff; larger loadings of additive, to achieve percolation and associated high conductivities, increases the modulus. In contrast, bottlebrush elastomers circumvent this limitation by lowering the modulus of the pristine matrix by 1–2 orders of magnitude. Various strategies can be used to efficiently disperse conductive additives such as carbon nanotubes into bottlebrush elastomers as described by Self *et al.*[43] and Xu *et al.*[44] **Figure 6** illustrates the general concept and provides a comparison of properties among different electrically conductive composites; it is evident that bottlebrush-based materials occupy a unique region for these solvent-free examples, although there is still considerable room for improvement in electrical conductivity.[37]

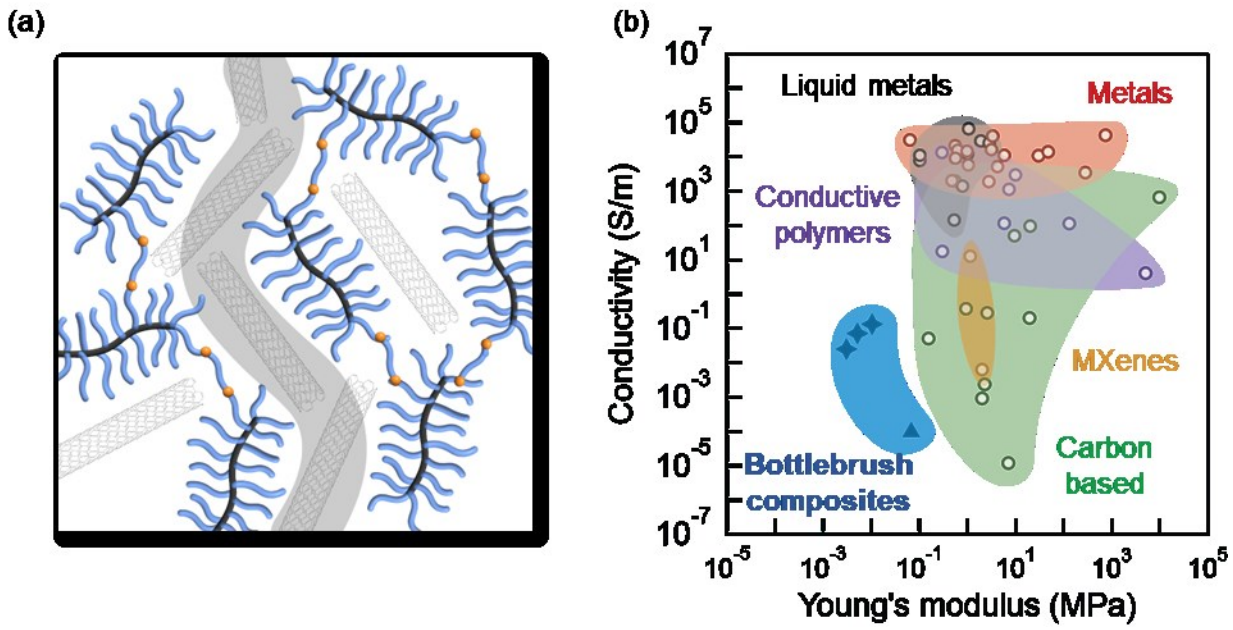

Figure 6. (a) Illustration of an electrically conductive bottlebrush–carbon-nanotube composite. (b) Ashby plot comparing the properties of elastomers containing different conductive additives.[44]

We close this section on bottlebrush elastomers with a brief comment about crosslinking chemistry. Clearly, this is an important consideration when designing materials, particularly with an eye towards applications. Broadly speaking, there are two conceptual strategies that can be used to form bottlebrush elastomers: (1) pre-synthesize bottlebrushes, formulate them with crosslinker (plus any other desired additives), and solidify on demand, or (2) crosslink during the polymerization that forms bottlebrushes. Neither strategy is inherently better, although each may lend itself to different applications. For example, pre-synthesizing bottlebrushes allows a researcher to rigorously hold the backbone and side-chain lengths constant while studying the impact of crosslinker (and/or additive) loading during formulation. However, it is worth appreciating that uncrosslinked bottlebrushes tend to be very high molecular weight (M), and even though they likely remain unentangled, viscosity still increases linearly as M^1. In contrast,

crosslinking during polymerization can avoid challenges related to viscosity; for example, grafting-through polymerization only necessitates the use of monofunctional macromonomers with the molecular weight of a single side chain (and multi-functional crosslinker of similar size). The price paid is difficulty in rigorously controlling and characterizing the average backbone degree of polymerization between crosslinks. If selecting the two-step process of approach (1), note that recent literature has described a number of robust thermal[45] and photo-crosslinking[22] chemistries that are versatile, scalable, and easy to access, even for non-experts in synthesis.[25]

3D printing

An application gaining significant traction in academia and industry is known as 3D printing, *i.e.* additive manufacturing. These terms encompass a growing number of techniques that can be used to exquisitely sculpt the three-dimensional structure of materials. Various flavors of 3D printing include powder bed manufacturing for ceramics,[46] selective laser sintering of metals,[47,48] and methods geared toward soft materials such as extrusion[49] and digital-light processing.[50] 3D printing has the potential to transform manufacturing as an efficient way to rapidly fashion highly customizable and intricate objects that are difficult or impossible to obtain via traditional processing techniques like molding.[51] This is especially true in the context of soft materials, with applications across a wide range of fields, from bespoke consumer products to biomedicine and next-generation technological devices.[52,53]

Design criteria for materials that are applied to additive manufacturing of course consider end-use performance but also compatibility with a given printing technique. Building on the compelling properties described above, recent work has developed strategies to 3D print super-

soft bottlebrush elastomers through two complementary strategies: vat photopolymerization and direct-ink writing.

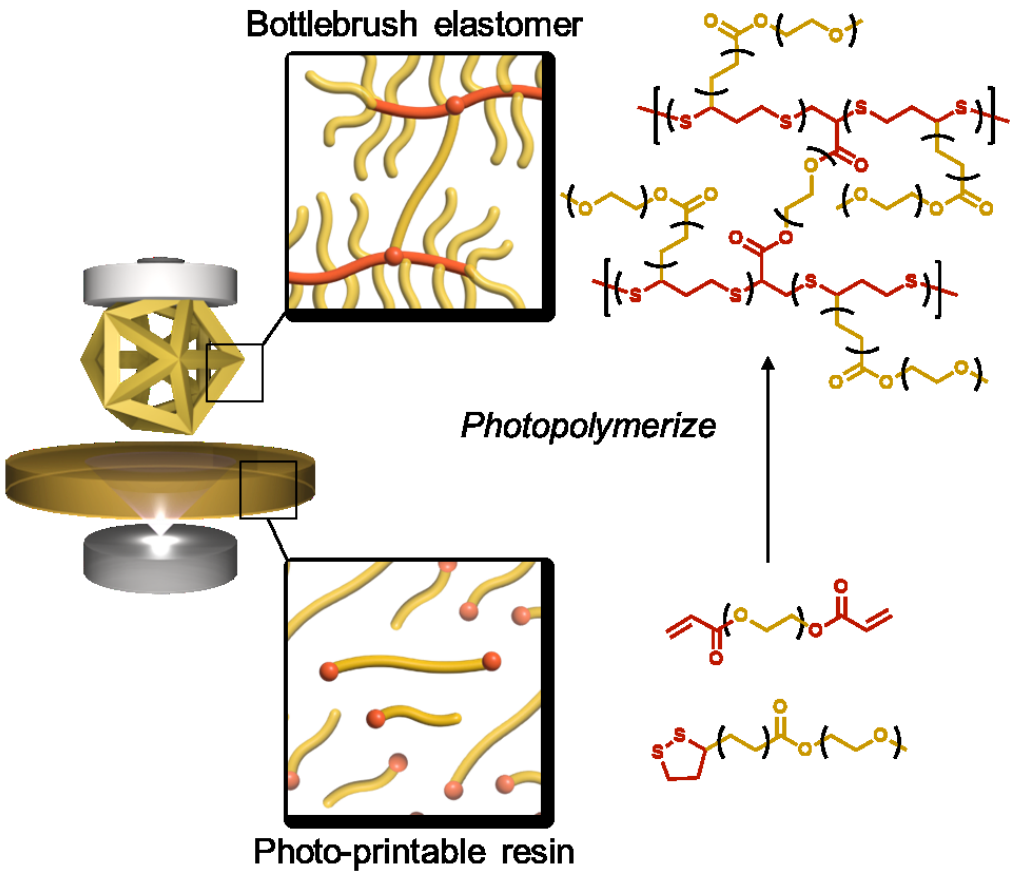

Figure 7. Digital-light processing (DLP) of bottlebrush elastomers using light to polymerize the backbone and crosslink the material simultaneously. Although a specific chemistry is depicted, one could envision extending this concept to other types of side-chain chemistry, backbones, and thus materials with different physical properties.

Choi *et al.* developed a resin containing an α-lipoic acid macromonomer and diacrylate crosslinker that copolymerize under 385 nm light to form bottlebrush networks (**Figure 7a**).[54] A key consideration in the design of this resin builds on concepts described earlier: pre-formed bottlebrushes would likely be too viscous to provide the right fluid dynamics within the resin bath.

The choice of polymerizable functionality is also important as fast curing is desired in a layer-by-layer digital-light process. Optimized resins rapidly cured 50 μm layers in 1.5 s with a light intensity of 13 mW cm^{-2}. The mechanical properties of printed parts were tunable by changing the ratio between macromonomer and crosslinker, resulting in materials with shear moduli ranging from 100−1000 kPa. Recent work has demonstrated a significant enhancement in toughness at optimized compositions using similar materials that should also be printable by this simple technique.[55]

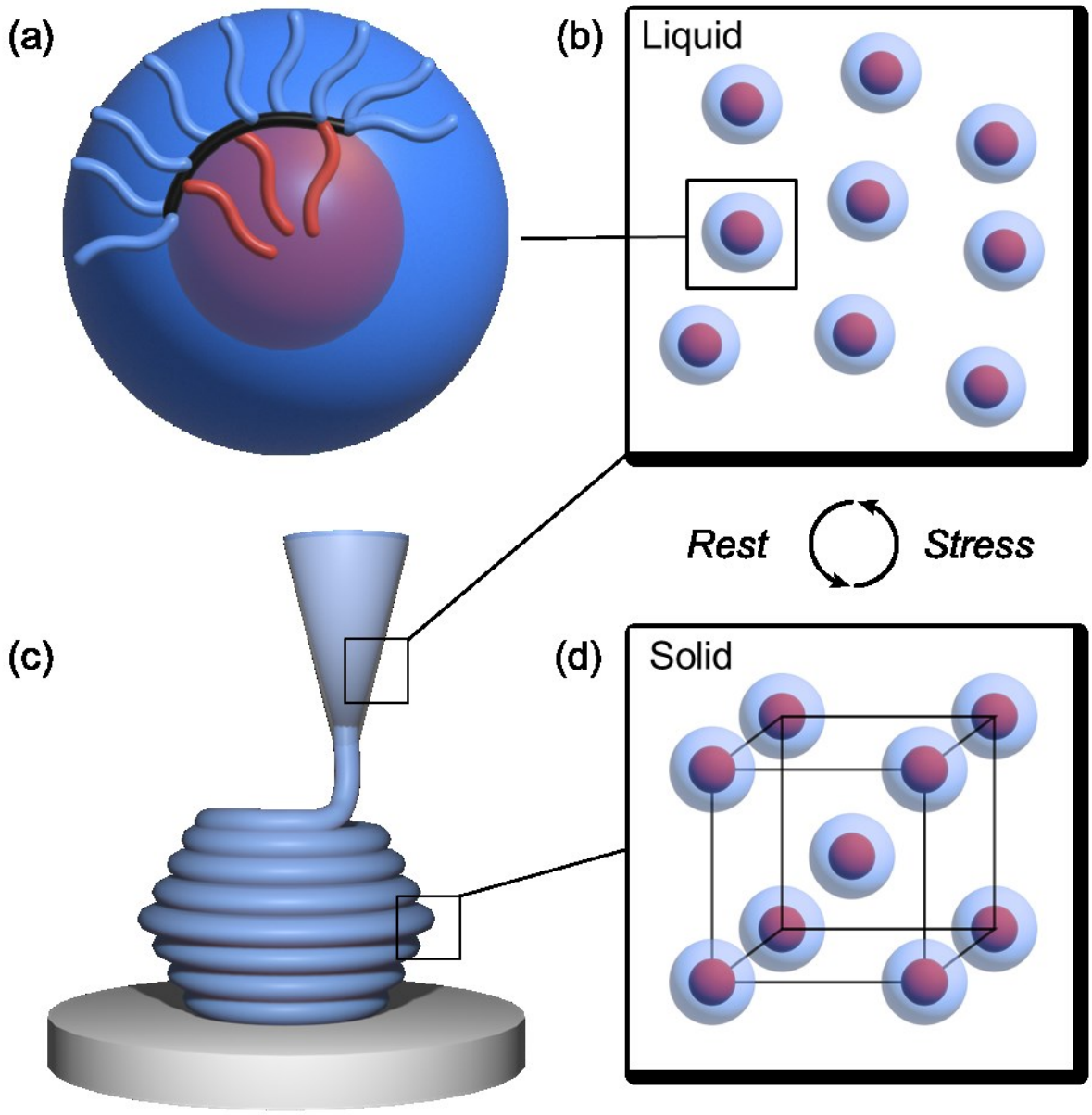

Figure 8. Room-temperature 3D printing of bottlebrush copolymers by extrusion (direct-ink write) is enabled via molecular self-assembly into micelles that exhibit a fast and reversible yielding transition.

Bottlebrush elastomers can also be printed by extrusion at room temperature through a process known as direct-ink write. This technique relies on resins with different design criteria

than digital light processing. The general concept is similar to a scenario most of us are familiar with on a daily basis: squeezing toothpaste out of its tube. An ideal resin for direct-ink write liquifies in the syringe under applied force and flows but quickly resolidifies after exiting to hold the desired shape of a part. The normalized force required to traverse this solid–liquid transition is known as a yield stress. A variety of strategies are commonly used to finesse the yield stress of resins for direct-ink writing to balance the ease of extrusion with part fidelity; examples include adding solvent and/or particles that can reversibly jam. Xie *et al.* developed a different approach that relies on self-assembly using statistical bottlebrush copolymers containing two types of side chains: poly(ethylene oxide) and poly(dimethylsiloxane) (PDMS).[56] At appropriate volume fractions, these bottlebrushes form micelles with a yielding transition that corresponds to lattice disordering (**Figure 8**). This process is fast and reversible at room temperature, facilitating direct-ink writing. The addition of photocrosslinker—designed to be soluble in the PDMS matrix—enabled crosslinking after printing to form elastomers with light. Nian *et al.* also leveraged self-assembly in the design of hybrid ABA triblock bottlebrushes containing hard linear A blocks flanking a bottlebrush B block.[57] Similar to conventional thermoplastic elastomers, the outer A blocks form spherical domains that anchor the bottlebrushes together via physical crosslinks. This clever design allows the material to retain its shape and be extremely soft at the same time. These materials can be printed by adding a small amount of volatile solvent to disrupt self-assembly during extrusion, which quickly reappears upon evaporation. The authors reported printed materials with Young's moduli of 10^2−10^4 Pa while retaining good extensibility (≈100−600%).

Photonic crystals

One of the earliest examples of applying bottlebrush polymers relates to photonic crystals—materials that reflect certain colors of light based on a (hopefully controlled) photonic bandgap. Nature regularly exploits this concept to express specific colors in a variety of contexts, *e.g.* the magnificent metallic gold found on flower beetles and the blue wings/green tails of magpies.[58] These colorful properties arise from a periodic arrangement of materials with different dielectric constants, where their periodicity and refractive-index contrast influence the wavelength(s) of light that cannot propagate.[59] The simplest photonic crystal, referred to as a Bragg stack, comprises layers of high and low refractive index materials forming periodic lamellae in one dimension. Realizing the similarities of this structure with traditional (linear) block copolymer self-assembly, Bowden showed that bottlebrush block copolymers—having two types of side chains arranged in a blocky sequence—can also form lamellae.[60] Importantly, these lamellae have enormous domain spacings compared to linear variants because the backbone orients perpendicular to the block–block interface (**Figure 9**). By fine-tuning the backbone degree of polymerization during synthesis, polymeric materials can be made with predictable band gaps that reflect colors across the entire visible spectrum (≈ 400−700 nm). In a beautiful series of papers, Miyake and coworkers demonstrated exquisite control over the properties of photonic bottlebrushes through synthesis and blending, highlighting their potential use as paints to minimize energy inefficiencies in buildings.[61–64] Notably, reflected wavelengths can be extended beyond the visible range by adding homopolymer that further dilates domain spacings into the near infrared regime (>800 nm). Recent efforts have considered new methods to control the structure[65] and processability[66,67] of bottlebrush-based photonic crystals, as well as demonstrated their utility in applications such as pigments[68] and 3D printing.[69]

Clearly, a number of the applications just discussed rely on molecular self-assembly to manipulate material properties and processability. A brief comment is therefore warranted regarding apparent constraints in self-assembly that are important to appreciate for bottlebrush systems. Bottlebrushes with a blocky sequence of side chains form stunning lamellae almost instantaneously,[70] often with upwards of 10 X-ray diffraction peaks.[71] In contrast, morphologies with any interfacial curvature, such as cylinders, yield *significantly* less-clear diffraction patterns,[19] and well-defined spherical morphologies may be absent entirely.[72] Although this behavior is not fully understood, it likely relates to difficulty packing bulky bottlebrush molecules—both the backbone and attached side chains—uniformly within the interior of each micelle (inspect, for example, the steric bulk evident in **Figure 9**). This intuitive explanation might lead one to wonder whether statistical bottlebrush copolymers could somehow avoid this energetically unfavorable scenario because the backbone itself wraps around the block–block interface, making the side-chain arrangement more reminiscent of linear diblock copolymers (recall the micelle depiction in **Figure 8**). Indeed, statistical bottlebrush copolymers are known to form high-quality spherical[19,35,56] and network phases.[73] However, the photonic "magic" is lost in these materials because the domain spacing is, once again, controlled by the length of two side chains, not the backbone. There are a considerable number of interesting photonic structures in two and three dimensions—for example, single gyroid with a complete photonic band gap—that are simply not accessible at the present point in time. Can clever molecular design somehow overcome this conundrum and achievable independently tunable morphologies and domain spacings, perhaps through the appropriate choice of backbone length, side-chain degrees of polymerization, formulation (*e.g.* blending), and chemistry? Such an expansive set of design parameters almost demands a close collaboration between theorists and experimentalists to both predict what will

happen on thermodynamic grounds and test what is actually possible based on kinetic limitations in real experiments.

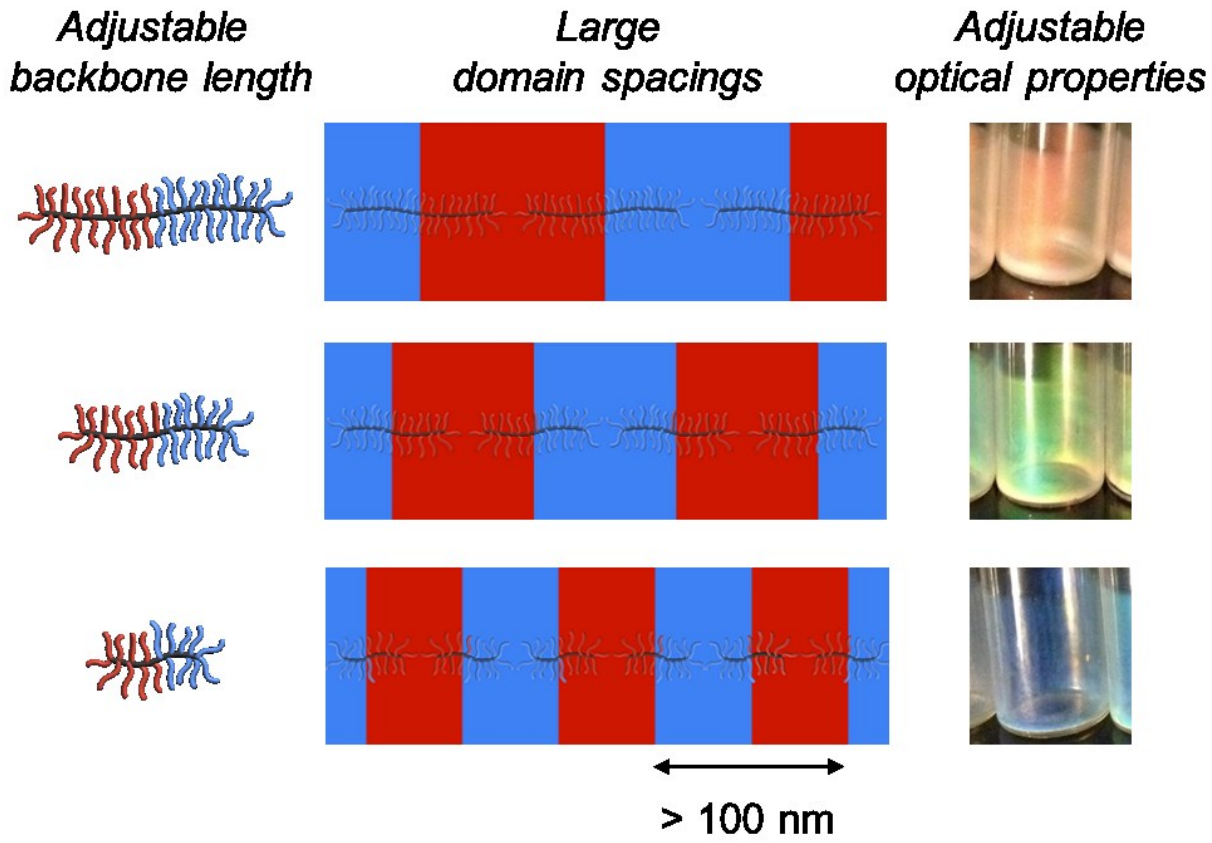

Figure 9. Block bottlebrushes self-assemble into nanostructures with unusually large domain sizes. As shown, lamellae that form Bragg stacks with domain spacings on the order of visible light result in the efficient reflection of select and tunable colors.[63,74] High-resolution photographs courtesy of Garret Miyake.

Additives

The bottlebrush architecture also offers enticing opportunities to tune the performance of materials beyond bulk properties. One example involves the use of bottlebrushes as additives. This strategy is broadly appealing from a business perspective because any bottlebrush, irrespective of chemistry, is almost certainly more expensive than existing commercially available materials.

There are also compelling performance advantages that warrant studying bottlebrushes as additives. Polymers that contain branching are predicted to preferentially accumulate at surfaces due to entropic effects; in this regard, bottlebrushes can be thought of as highly branched and controllable building blocks. Verduzco and Stein have studied this phenomenon in a series of papers that focus on characterizing thin films of linear–bottlebrush blends, primarily using secondary-ion mass spectrometry.[75–79] For example, Mitra *et al.* reported a systematic study of nearly athermal blends ($\chi \approx 10^{-4}$) of polystyrene bottlebrush and deuterated polystyrene linear homopolymer.[79] They found that surface segregation strongly depends on the ratio N_{homo}/N_{sc}, where N_{homo} is the homopolymer degree of polymerization and N_{sc} that of the side chains. When $N_{homo}/N_{sc} \leq 1.6$, bottlebrushes are homogeneously dispersed in the blend, and no phase separation is observed, even after annealing for 7 days at 165 °C. In contrast, when $N_{homo}/N_{sc} \geq 8$, bottlebrushes completely localize at the substrate and air interfaces. **Figure 10** summarizes these findings. This work has significant implications in the design of materials because surface segregation is usually dominated by enthalpic effects. For example, materials that contain fluorine typically enrich at an air interface to reduce interfacial tension. The bottlebrush architecture therefore provides a mechanism to counteract enthalpic preferences and manipulate interfaces in new ways. A cute demonstration of this was recently reported in the context of block copolymer lithography, where a perpendicular orientation of thin-film lamellae or cylinders is desired but preferential enthalpic interactions at the air and/or substrate interfaces usually drive morphologies to be parallel. Kim *et al.* demonstrated that small amounts of statistical bottlebrush copolymer (with a carefully selected composition) blended into the block copolymer layer spontaneously segregates to the air and substrate interfaces, rendering both neutral. The perpendicular features that form during this thermal annealing process are typically much more challenging to access,[80]

for example, through multi-step processes involving the deposition of surface treatments[81] and top coats.[82]

We emphasize there will likely be other examples beyond thin films where bottlebrush polymers provide value as additives in more traditional materials without incurring exorbitant additional expense. One recent example from Yamauchi *et al.* demonstrated the ability of poly(*n*-butyl acrylate) bottlebrush to increase the fracture toughness of a linear poly(*n*-butyl acrylate) plastic by >100% with just 10 wt% of the additive.[83] While the mechanism underpinning this interesting behavior remains somewhat mysterious, the general idea represents an exciting future direction in the field.

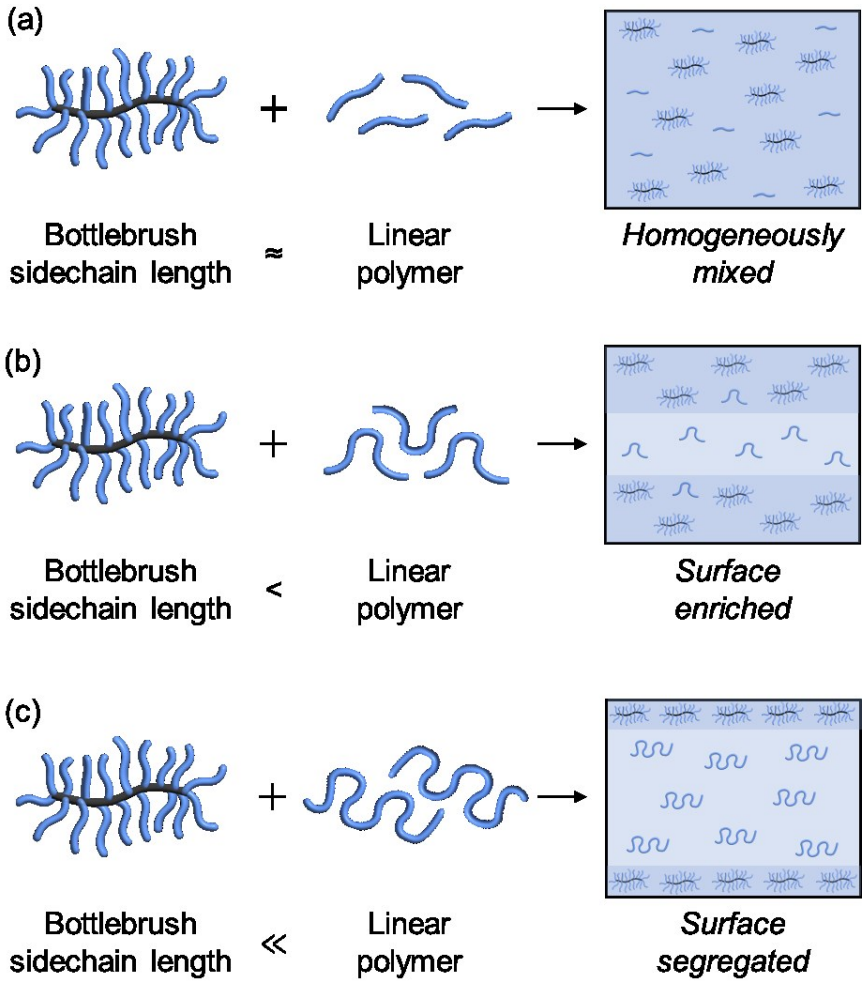

Figure 10. The bottlebrush architecture drives surface enrichment in polymer blends with a magnitude that depends on relative degrees of polymerization.[79]

Lubrication and Wear

Surfaces also play a key role in the lubricity and wear of materials. A hint that the bottlebrush architecture may prove useful in improving lubricity lies in its similarity with the structure of natural lubricating glycoproteins, such as lubricin in the synovial fluid near articular cartilage.[84] Lubricin contains densely grafted, hydrophilic, polymeric side chains sandwiched between cartilage-binding domains on either end (**Figure 11a**). These hydrophilic side chains swell with water, creating a lubricating layer at the cartilage surface. Steric repulsion of the side chains and the presence of a hydration shell further contribute to low friction.[85,86] Membrane-bound and gel-forming mucins are other examples of lubricating glycoproteins with a similar structure to bottlebrush polymers. Mucins protect all moist epithelial cell layers lining ocular surfaces, the respiratory system, and gastrointestinal tracts from stress-induced damage. Although lubricating proteins can make effective aqueous lubricants, they are difficult to synthesize due to their complex structure containing many amino acids.[86]

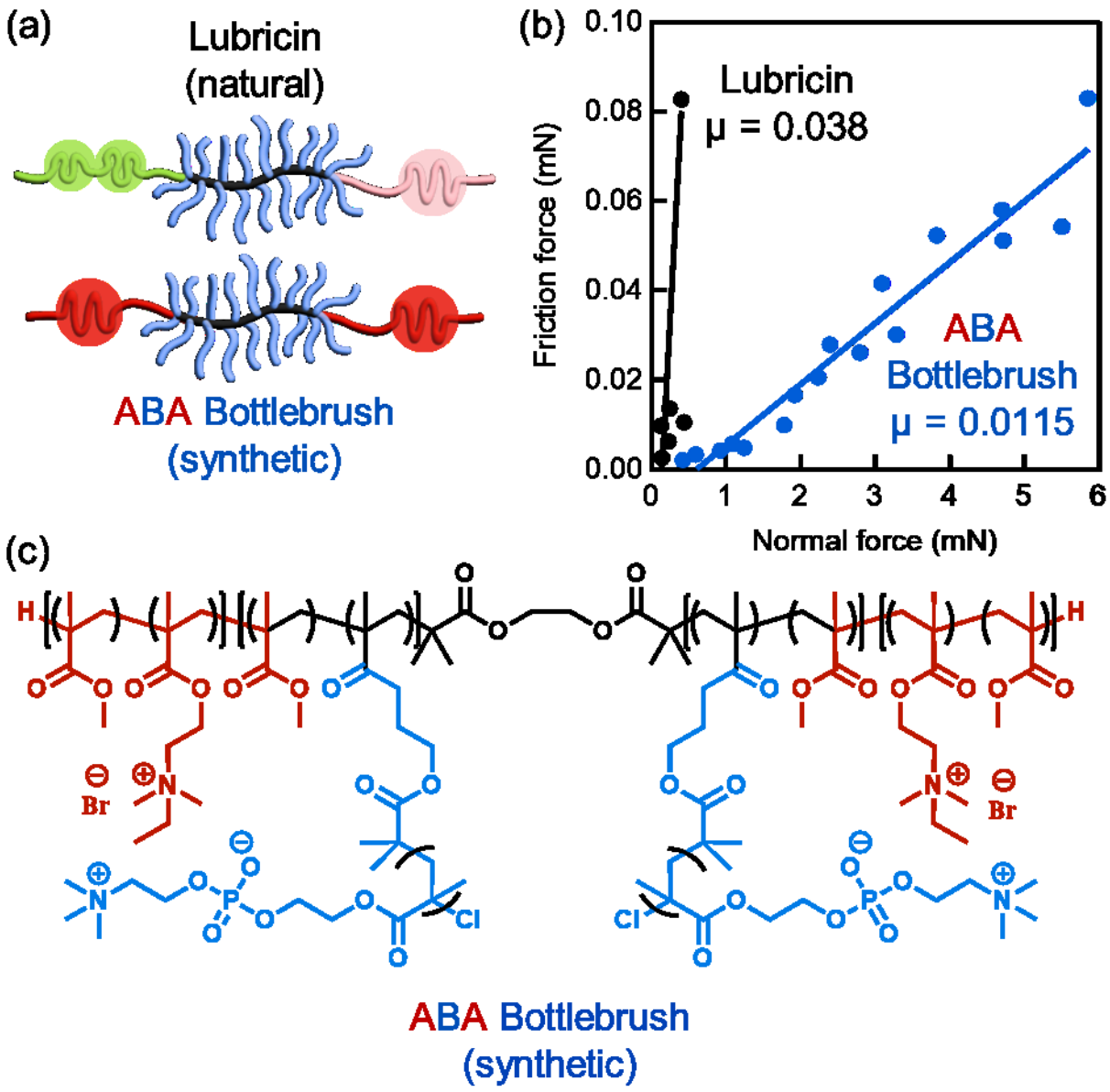

Figure 11. Efficient surface lubrication from bottlebrush polymers. (a) Similarities between natural lubricin and a synthetic ABA bottlebrush architecture. (b) Friction force measurements as a function of applied normal force. A linear fit was used to estimate the friction coefficient (μ). (c) An ABA triblock bottlebrush mimicking the general structure of lubricin.[84,87]

Enter synthetic bottlebrushes that mimic the salient structural features of naturally occurring lubricating proteins but as a more accessible material platform. **Figure 11** shows an

example of a bottlebrush that was inspired by lubricin, with linear outer blocks and a bottlebrush mid-block. The water retention and osmotic repulsion of the hydrophilic poly(2-methacryloyloxyethylphosphorylcholine) side chains leads to exceptionally low friction[88,89,90] while the outer blocks were designed to bind mica. Self-mated or "gemini" interactions were measured on a surface-force apparatus between coated mica surfaces. Friction coefficients around μ = 0.0115 in phosphate-buffered saline (PBS) at physiologically relevant pressures up to 2.1 MPa[84] are approaching those across whole joints *in vivo*, reported to be as low as μ = 0.001 and maintained at this value at high contact pressures up to approximately 10 MPa.[85] Olszewski *et al.* demonstrated that lubricating bottlebrushes can be engineered to have low cytotoxicity, which is encouraging for their potential use in restoring damaged cartilage.[91] These conclusions seem to be general for other systems and more complex mixtures of multivalent ions.[92] Andresen Equiliuz, *et al.* combined bottlebrush lubricants with the linear polymer fibronectin to further improve wear resistance with respect to that of a bottlebrush alone. This result was attributed to fibronectin mediating stronger binding of the bottlebrush to mica, forming a dense layer that prevented removal under high pressures. Similarly, Moon *et al.* demonstrated that the addition of other linear polymers, namely hyaluronic acid or poly(vinyl alcohol), improved the wear resistance of a hydrophilic bottlebrush coating based on 2-hydroxyethyl methacrylate.[90] Clearly, the tunability and accessibility of synthetic bottlebrushes provides an exciting platform to tune the properties of biocompatible lubricants and wear-resistant surfaces with implications for new implants and consumer products.

Hydrogels

Bottlebrushes swollen with water, so-called hydrogels, are an interesting material platform beyond applications in surface science. This area remains ripe for research as historically bottlebrushes have been advertised as solvent-free analogues of hydrogels. Of course, there may also be compelling reasons why bottlebrush hydrogels are enabling in other contexts. Indeed, the architectural tunability emphasized throughout this article facilitates the manipulation of hydrogel properties such as gel dynamics,[93] viscoelasticity, and load bearing characteristics,[94] often without needing to adjust crosslink density. Such decoupling creates unique opportunities to tailor the properties of bottlebrush hydrogels for applications where hydrogels remain popular. An elegant example by the Sheiko group designed linear–bottlebrush–linear triblocks as injectable hydrogels (**Figure 12**)[95] based on an analogous mechanism of physical crosslinking as described earlier in the 3D printing section. This architecture resulted in low solution viscosity that facilitates injectability while also integrating thermo-responsivity to drive gelation at body temperatures. The resulting bottlebrush hydrogel matched the deformation mechanics of biological tissue. This ABA architecture shares similarities with the ABC triblock bottlebrush copolymers reported by Vohidov *et al.* that self-assemble into uniform (~100 nm) micelles which encapsulate a range of therapeutic agents[96] and rapidly gel after injection.

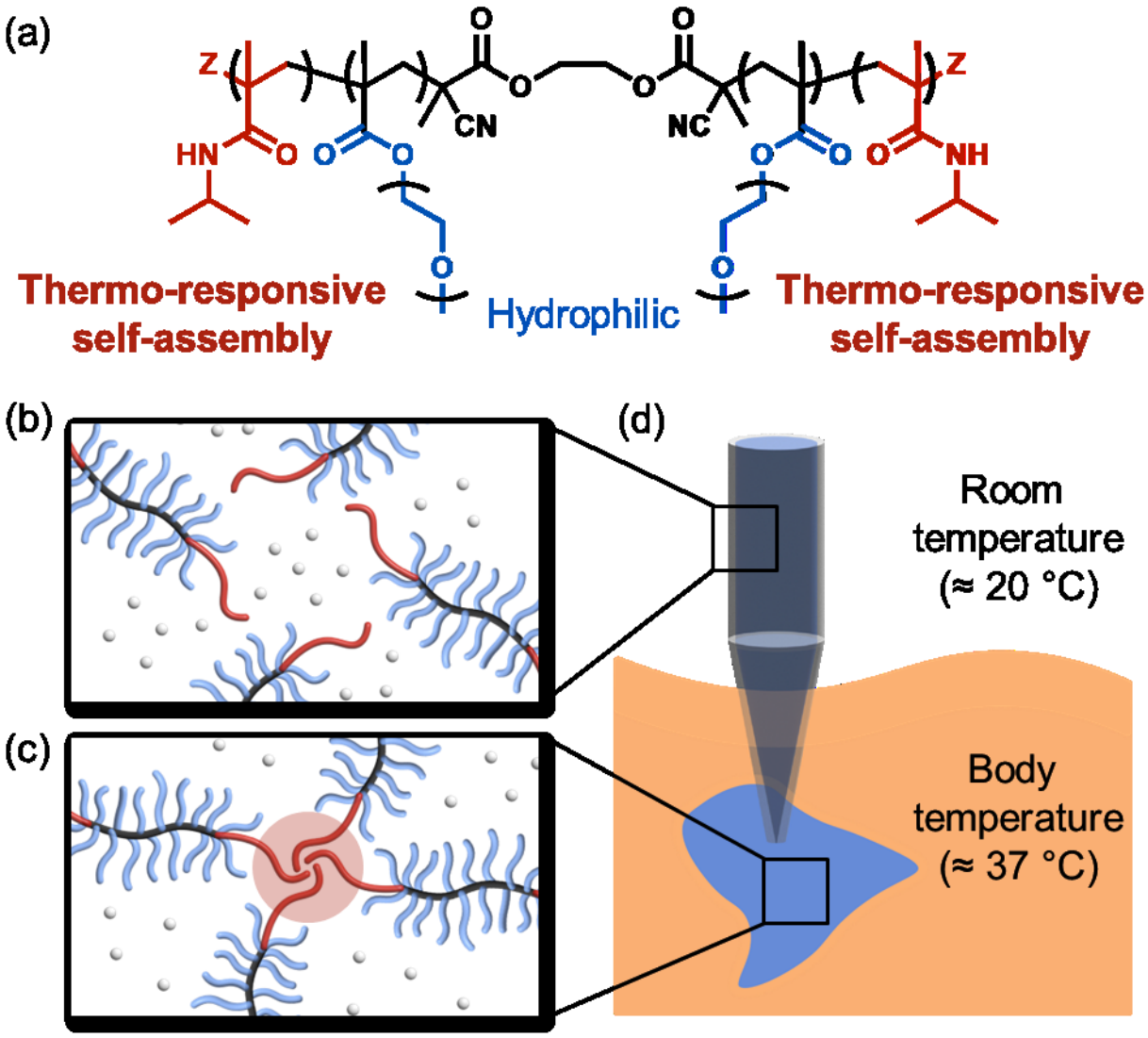

Figure 12. Injectable bottlebrush hydrogels as a tissue-mimetic platform for medicine.[95]

Conclusions and Future Outlook

The bottlebrush architecture is a powerful platform for tuning the structure and properties of materials. Throughout this paper, we have highlighted select applications meant to convey the breadth of exciting opportunities and enabling performance advantages that can be achieved through contemporary materials design. These are by no means all-encompassing and we fully anticipate bracing future developments in entirely unanticipated new directions as well.

A major driver in the growing popularity of synthetic bottlebrush polymers, and materials derived therefrom, is their synthetic accessibility. Even non-experts can perform the requisite (macro)monomer and polymer synthesis using simple and robust techniques,[25] *e.g.* (un)controlled free-radical polymerization and/or ring-opening metathesis polymerization. Thanks to detailed efforts by Sheiko, Dobrynin, Matyjaszewski, and coworkers,[3,4,27,34,35,95] the structure–property relationships that connect architectural parameters such as backbone degree of polymerization and side-chain length with physical material properties like low-deformation moduli are now well-established. So, what is left to do? As alluded to throughout this review, we still see significant opportunities in both fundamental science and applied engineering. The same level of synthetic control that has made bottlebrush homopolymers popular also provides a route to sculpt the molecular structure of more complex copolymers with implications for properties that are not so obvious. How do sequence, side-chain chemistry, and formulation interplay to control the processability and properties of multi-component materials over a vast range of length scales, from nanometers to microns? We have already seen glimpses of the power in designing self-assembling systems beyond simple homopolymers, with unique sets of properties emerging that prove advantageous in applications ranging from 3D printing to biomedicine and flexible electronics.[37] When considering the design of materials in this highly multidimensional phase space, it is tempting to ask whether contemporary data science tools including artificial intelligence and machine learning can somehow be used to navigate the synthesis–characterization–theory pursuit more efficiently. We see significant rewards in store for more tightly coupling these synergistic but often isolated efforts, for example, in realizing photonic crystals with a full three-dimensional photonic band gap that spontaneously arises from self-assembly. Finally, in the realm of engineering, we challenge researchers in the field to think carefully about their value proposition:

can an unavoidable increase in cost associated with including bottlebrushes be justified given the target properties and importance of a given application? This question is one of the many reasons we find applications involving surfaces and additives so appealing—they require minimal material for an outsized impact. To summarize, bottlebrush polymers represent a striking marriage of chemistry, materials, and engineering. Bon retour!

AUTHOR INFORMATION

Corresponding Authors

*Email: cbates@ucsb.edu (C.M.B)

*Email: chabiny@ucsb.edu (M.L.C.)

*Email: apitenis@ucsb.edu (A.A.P.)

Author Contributions

All authors contributed to the writing of this manuscript.

Notes

The authors declare no competing financial interest.

Funding

The writing of this manuscript was supported by the National Science Foundation through the LEAP-HI (CMMI-2053760, M.L.C., C.M.B.) and DMREF (A.A.P., DMR-2323715) programs. C.M.B. also thanks The Camille and Henry Dreyfus Foundation for partial support. I.L. is grateful for a DPST fellowship from the Institute for the Promotion of Teaching Science and Technology, Thailand.

References

(1) McLeish, T. C. Polymer Architecture Influence on Rheology. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2* (6), 678–682. https://doi.org/10.1016/S1359-0286(97)80009-5.

(2) Levi, A. E.; Lequieu, J.; Horne, J. D.; Bates, M. W.; Ren, J. M.; Delaney, K. T.; Fredrickson, G. H.; Bates, C. M. Miktoarm Stars via Grafting-Through Copolymerization: Self-Assembly and the Star-to-Bottlebrush Transition. *Macromolecules* **2019**, *52* (4), 1794–1802. https://doi.org/10.1021/acs.macromol.8b02321.

(3) Daniel, W. F. M.; Burdyńska, J.; Vatankhah-Varnoosfaderani, M.; Matyjaszewski, K.; Paturej, J.; Rubinstein, M.; Dobrynin, A. V.; Sheiko, S. S. Solvent-Free, Supersoft and Superelastic Bottlebrush Melts and Networks. *Nat. Mater.* **2016**, *15* (2), 183–189. https://doi.org/10.1038/nmat4508.

(4) Xie, G.; Martinez, M. R.; Olszewski, M.; Sheiko, S. S.; Matyjaszewski, K. Molecular Bottlebrushes as Novel Materials. *Biomacromolecules* **2019**, *20* (1), 27–54. https://doi.org/10.1021/acs.biomac.8b01171.

(5) Paturej, J.; Sheiko, S. S.; Panyukov, S.; Rubinstein, M. Molecular Structure of Bottlebrush Polymers in Melts. *Sci. Adv.* **2016**, *2* (11), e1601478. https://doi.org/10.1126/sciadv.1601478.

(6) Dalsin, S. J.; Hillmyer, M. A.; Bates, F. S. Molecular Weight Dependence of Zero-Shear Viscosity in Atactic Polypropylene Bottlebrush Polymers. *ACS Macro Lett.* **2014**, *3* (5), 423–427. https://doi.org/10.1021/mz500082h.

(7) Sunday, D. F.; Burns, A. B.; Martin, T. B.; Chang, A. B.; Grubbs, R. H. Relationship between Graft Density and the Dilute Solution Structure of Bottlebrush Polymers: An Inter-Chemistry Comparison and Scaling Analysis. *Macromolecules* **2023**. https://doi.org/10.1021/acs.macromol.3c01436.

(8) B. Zhulina, E.; S. Sheiko, S.; V. Borisov, O. Theoretical Advances in Molecular Bottlebrushes and Comblike (Co)Polymers: Solutions, Gels, and Self-Assembly. *Soft Matter* **2022**, *18* (46), 8714–8732. https://doi.org/10.1039/D2SM01141G.

(9) Zografos, A.; All, H. A.; Chang, A. B.; Hillmyer, M. A.; Bates, F. S. Star-to-Bottlebrush Transition in Extensional and Shear Deformation of Unentangled Polymer Melts. *Macromolecules* **2023**, *56* (6), 2406–2417. https://doi.org/10.1021/acs.macromol.3c00015.

(10) Abbasi, M.; Faust, L.; Wilhelm, M. Comb and Bottlebrush Polymers with Superior Rheological and Mechanical Properties. *Adv. Mater.* **2019**, *31* (26), 1806484. https://doi.org/10.1002/adma.201806484.

(11) Xie, R.; Lapkriengkri, I.; Pramanik, N. B.; Mukherjee, S.; Blankenship, J. R.; Albanese, K.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Hydrogen-Bonding Bottlebrush Networks: Self-Healing Materials from Super-Soft to Stiff. *Macromolecules* **2022**, *55* (23), 10513–10521. https://doi.org/10.1021/acs.macromol.2c01886.

(12) Clauss, Z. S.; Wardzala, C. L.; Schlirf, A. E.; Wright, N. S.; Saini, S. S.; Onoa, B.; Bustamante, C.; Kramer, J. R. Tunable, Biodegradable Grafting-from Glycopolypeptide Bottlebrush Polymers. *Nat. Commun.* **2021**, *12* (1), 6472. https://doi.org/10.1038/s41467-021-26808-5.

(13) Tanaka, J.; Häkkinen, S.; Boeck, P. T.; Cong, Y.; Perrier, S.; Sheiko, S. S.; You, W. Orthogonal Cationic and Radical RAFT Polymerizations to Prepare Bottlebrush Polymers. *Angew. Chem.* **2020**, *132* (18), 7270–7275. https://doi.org/10.1002/ange.202000700.

(14) Shanmugam, S.; Cuthbert, J.; Kowalewski, T.; Boyer, C.; Matyjaszewski, K. Catalyst-Free Selective Photoactivation of RAFT Polymerization: A Facile Route for Preparation of

Comblike and Bottlebrush Polymers. *Macromolecules* **2018**, *51* (19), 7776–7784. https://doi.org/10.1021/acs.macromol.8b01708.
(15) Bates, C. M.; Chang, A. B.; Momčilović, N.; Jones, S. C.; Grubbs, R. H. ABA Triblock Brush Polymers: Synthesis, Self-Assembly, Conductivity, and Rheological Properties. *Macromolecules* **2015**, *48* (14), 4967–4973. https://doi.org/10.1021/acs.macromol.5b00880.
(16) Rzayev, J. Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication. *ACS Macro Lett.* **2012**, *1* (9), 1146–1149. https://doi.org/10.1021/mz300402x.
(17) Verduzco, R.; Li, X.; Pesek, S. L.; Stein, G. E. Structure, Function, Self-Assembly, and Applications of Bottlebrush Copolymers. *Chem. Soc. Rev.* **2015**, *44* (8), 2405–2420. https://doi.org/10.1039/C4CS00329B.
(18) Tonge, C. M.; Sauvé, E. R.; Cheng, S.; Howard, T. A.; Hudson, Z. M. Multiblock Bottlebrush Nanofibers from Organic Electronic Materials. *J. Am. Chem. Soc.* **2018**, *140* (37), 11599–11603. https://doi.org/10.1021/jacs.8b07915.
(19) Xie, R.; Mukherjee, S.; Levi, A. E.; Self, J. L.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Yielding Behavior of Bottlebrush and Linear Block Copolymers. *Macromolecules* **2021**, *54* (12), 5636–5647. https://doi.org/10.1021/acs.macromol.1c00557.
(20) Hyun Kim, K.; Nam, J.; Choi, J.; Seo, M.; Bang, J. From Macromonomers to Bottlebrush Copolymers with Sequence Control: Synthesis, Properties, and Applications. *Polym. Chem.* **2022**, *13* (16), 2224–2261. https://doi.org/10.1039/D2PY00126H.
(21) Lord, S. J.; Sheiko, S. S.; LaRue, I.; Lee, H.-I.; Matyjaszewski, K. Tadpole Conformation of Gradient Polymer Brushes. *Macromolecules* **2004**, *37* (11), 4235–4240. https://doi.org/10.1021/ma035989z.
(22) Mukherjee, S.; Xie, R.; Reynolds, V. G.; Uchiyama, T.; Levi, A. E.; Valois, E.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Universal Approach to Photo-Crosslink Bottlebrush Polymers. *Macromolecules* **2020**, *53* (3), 1090–1097. https://doi.org/10.1021/acs.macromol.9b02210.
(23) Keith, A. N.; Vatankhah-Varnosfaderani, M.; Clair, C.; Fahimipour, F.; Dashtimoghadam, E.; Lallam, A.; Sztucki, M.; Ivanov, D. A.; Liang, H.; Dobrynin, A. V.; Sheiko, S. S. Bottlebrush Bridge between Soft Gels and Firm Tissues. *ACS Cent. Sci.* **2020**, *6* (3), 413–419. https://doi.org/10.1021/acscentsci.9b01216.
(24) Yuk, H.; Lu, B.; Zhao, X. Hydrogel Bioelectronics. *Chem. Soc. Rev.* **2019**, *48* (6), 1642–1667. https://doi.org/10.1039/C8CS00595H.
(25) Cai, L.-H.; Kodger, T. E.; Guerra, R. E.; Pegoraro, A. F.; Rubinstein, M.; Weitz, D. A. Soft Poly(Dimethylsiloxane) Elastomers from Architecture-Driven Entanglement Free Design. *Adv. Mater.* **2015**, *27* (35), 5132–5140. https://doi.org/10.1002/adma.201502771.
(26) Hu, M.; Xia, Y.; McKenna, G. B.; Kornfield, J. A.; Grubbs, R. H. Linear Rheological Response of a Series of Densely Branched Brush Polymers. *Macromolecules* **2011**, *44* (17), 6935–6943. https://doi.org/10.1021/ma2009673.
(27) Vatankhah-Varnoosfaderani, M.; Daniel, W. F. M.; Zhushma, A. P.; Li, Q.; Morgan, B. J.; Matyjaszewski, K.; Armstrong, D. P.; Spontak, R. J.; Dobrynin, A. V.; Sheiko, S. S. Bottlebrush Elastomers: A New Platform for Freestanding Electroactuation. *Adv. Mater.* **2017**, *29* (2), 1604209. https://doi.org/10.1002/adma.201604209.
(28) Reynolds, V. G.; Mukherjee, S.; Xie, R.; Levi, A. E.; Atassi, A.; Uchiyama, T.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Super-Soft Solvent-Free Bottlebrush Elastomers for Touch Sensing. *Mater. Horiz.* **2020**, *7* (1), 181–187. https://doi.org/10.1039/C9MH00951E.
(29) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press, 2003.

(30) Yarusso, D. J. 13 - Effect of Rheology on PSA Performance. In *Adhesion Science and Engineering*; Dillard, D. A., Pocius, A. V., Chaudhury, M., Eds.; Elsevier Science B.V.: Amsterdam, 2002; pp 499–533. https://doi.org/10.1016/B978-0-444-51140-9.50040-8.
(31) Packham, D. E. Chapter 7 - Surface Roughness and Adhesion. In *Adhesion Science and Engineering*; Dillard, D. A., Pocius, A. V., Chaudhury, M., Eds.; Elsevier Science B.V.: Amsterdam, 2002; pp 317–349. https://doi.org/10.1016/B978-044451140-9/50007-X.
(32) Dadashi-Silab, S.; Stache, E. E. Sticky or Not: Adhesion by Architectural Design. *ACS Cent. Sci.* **2023**, *9* (2), 134–136. https://doi.org/10.1021/acscentsci.3c00104.
(33) Arrington, K. J.; Radzinski, S. C.; Drummey, K. J.; Long, T. E.; Matson, J. B. Reversibly Cross-Linkable Bottlebrush Polymers as Pressure-Sensitive Adhesives. *ACS Appl. Mater. Interfaces* **2018**, *10* (31), 26662–26668. https://doi.org/10.1021/acsami.8b08480.
(34) Maw, M.; Dashtimoghadam, E.; Keith, A. N.; Morgan, B. J.; Tanas, A. K.; Nikitina, E.; Ivanov, D. A.; Vatankhah-Varnosfaderani, M.; Dobrynin, A. V.; Sheiko, S. S. Sticky Architecture: Encoding Pressure Sensitive Adhesion in Polymer Networks. *ACS Cent. Sci.* **2023**, *9* (2), 197–205. https://doi.org/10.1021/acscentsci.2c01407.
(35) Dashtimoghadam, E.; Maw, M.; Keith, A. N.; Vashahi, F.; Kempkes, V.; Gordievskaya, Y. D.; Kramarenko, E. Y.; Bersenev, E. A.; Nikitina, E. A.; Ivanov, D. A.; Tian, Y.; Dobrynin, A. V.; Vatankhah-Varnosfaderani, M.; Sheiko, S. S. Super-Soft, Firm, and Strong Elastomers toward Replication of Tissue Viscoelastic Response. *Mater. Horiz.* **2022**, *9* (12), 3022–3030. https://doi.org/10.1039/D2MH00844K.
(36) Ponnamma, D.; Sadasivuni, K. K.; Grohens, Y.; Guo, Q.; Thomas, S. Carbon Nanotube Based Elastomer Composites – an Approach towards Multifunctional Materials. *J. Mater. Chem. C* **2014**, *2* (40), 8446–8485. https://doi.org/10.1039/C4TC01037J.
(37) Le, M. L.; Lapkriengkri, I.; Albanese, K. R.; Nguyen, P. H.; Tran, C.; Blankenship, J. R.; Segalman, R. A.; Bates, C. M.; Chabinyc, M. L. Engineering Soft, Elastic, and Conductive Polymers for Stretchable Electronics Using Ionic Compatibilization. *Chem. Mater.* **2023**. https://doi.org/10.1021/acs.chemmater.3c01685.
(38) Kim, N.; Lienemann, S.; Petsagkourakis, I.; Alemu Mengistie, D.; Kee, S.; Ederth, T.; Gueskine, V.; Leclère, P.; Lazzaroni, R.; Crispin, X.; Tybrandt, K. Elastic Conducting Polymer Composites in Thermoelectric Modules. *Nat. Commun.* **2020**, *11* (1), 1424. https://doi.org/10.1038/s41467-020-15135-w.
(39) Yang, Y.; Zhao, G.; Cheng, X.; Deng, H.; Fu, Q. Stretchable and Healable Conductive Elastomer Based on PEDOT:PSS/Natural Rubber for Self-Powered Temperature and Strain Sensing. *ACS Appl. Mater. Interfaces* **2021**, *13* (12), 14599–14611. https://doi.org/10.1021/acsami.1c00879.
(40) Xu, Y.; Su, Y.; Xu, X.; Arends, B.; Zhao, G.; Ackerman, D. N.; Huang, H.; Reid, St. P.; Santarpia, J. L.; Kim, C.; Chen, Z.; Mahmoud, S.; Ling, Y.; Brown, A.; Chen, Q.; Huang, G.; Xie, J.; Yan, Z. Porous Liquid Metal–Elastomer Composites with High Leakage Resistance and Antimicrobial Property for Skin-Interfaced Bioelectronics. *Sci. Adv.* **2023**, *9* (1), eadf0575. https://doi.org/10.1126/sciadv.adf0575.
(41) Markvicka, E. J.; Bartlett, M. D.; Huang, X.; Majidi, C. An Autonomously Electrically Self-Healing Liquid Metal–Elastomer Composite for Robust Soft-Matter Robotics and Electronics. *Nat. Mater.* **2018**, *17* (7), 618–624. https://doi.org/10.1038/s41563-018-0084-7.
(42) Tutika, R.; Kmiec, S.; Haque, A. B. M. T.; Martin, S. W.; Bartlett, M. D. Liquid Metal–Elastomer Soft Composites with Independently Controllable and Highly Tunable Droplet Size

and Volume Loading. *ACS Appl. Mater. Interfaces* **2019**, *11* (19), 17873–17883. https://doi.org/10.1021/acsami.9b04569.
(43) Self, J. L.; Reynolds, V. G.; Blankenship, J.; Mee, E.; Guo, J.; Albanese, K.; Xie, R.; Hawker, C. J.; de Alaniz, J. R.; Chabinyc, M. L.; Bates, C. M. Carbon Nanotube Composites with Bottlebrush Elastomers for Compliant Electrodes. *ACS Polym. Au* **2022**, *2* (1), 27–34. https://doi.org/10.1021/acspolymersau.1c00034.
(44) Xu, P.; Wang, S.; Lin, A.; Min, H.-K.; Zhou, Z.; Dou, W.; Sun, Y.; Huang, X.; Tran, H.; Liu, X. Conductive and Elastic Bottlebrush Elastomers for Ultrasoft Electronics. *Nat. Commun.* **2023**, *14* (1), 623. https://doi.org/10.1038/s41467-023-36214-8.
(45) Self, J. L.; Sample, C. S.; Levi, A. E.; Li, K.; Xie, R.; de Alaniz, J. R.; Bates, C. M. Dynamic Bottlebrush Polymer Networks: Self-Healing in Super-Soft Materials. *J. Am. Chem. Soc.* **2020**, *142* (16), 7567–7573. https://doi.org/10.1021/jacs.0c01467.
(46) Oropeza, D.; Roberts, R.; Hart, A. J. A Rapid Development Workflow for Binder Inks for Additive Manufacturing with Application to Polymer and Reactive Binder Ink Formulation. *J. Manuf. Process.* **2022**, *73*, 471–482. https://doi.org/10.1016/j.jmapro.2021.10.068.
(47) Das, S. Physical Aspects of Process Control in Selective Laser Sintering of Metals. *Adv. Eng. Mater.* **2003**, *5* (10), 701–711. https://doi.org/10.1002/adem.200310099.
(48) Gunasekaran, J.; Sevvel, P.; John Solomon, I. Metallic Materials Fabrication by Selective Laser Melting: A Review. *Mater. Today Proc.* **2021**, *37*, 252–256. https://doi.org/10.1016/j.matpr.2020.05.162.
(49) Garcia, R. V.; Murphy, E. A.; Sinha, N. J.; Okayama, Y.; Urueña, J. M.; Helgeson, M. E.; Bates, C. M.; Hawker, C. J.; Murphy, R. D.; Read de Alaniz, J. Tailoring Writability and Performance of Star Block Copolypeptides Hydrogels through Side-Chain Design. *Small n/a* (n/a), 2302794. https://doi.org/10.1002/smll.202302794.
(50) Robinson, L. L.; Self, J. L.; Fusi, A. D.; Bates, M. W.; Read de Alaniz, J.; Hawker, C. J.; Bates, C. M.; Sample, C. S. Chemical and Mechanical Tunability of 3D-Printed Dynamic Covalent Networks Based on Boronate Esters. *ACS Macro Lett.* **2021**, *10* (7), 857–863. https://doi.org/10.1021/acsmacrolett.1c00257.
(51) Shahrubudin, N.; Lee, T. C.; Ramlan, R. An Overview on 3D Printing Technology: Technological, Materials, and Applications. *Procedia Manuf.* **2019**, *35*, 1286–1296. https://doi.org/10.1016/j.promfg.2019.06.089.
(52) Capel, A. J.; Rimington, R. P.; Lewis, M. P.; Christie, S. D. R. 3D Printing for Chemical, Pharmaceutical and Biological Applications. *Nat. Rev. Chem.* **2018**, *2* (12), 422–436. https://doi.org/10.1038/s41570-018-0058-y.
(53) Wallin, T. J.; Pikul, J.; Shepherd, R. F. 3D Printing of Soft Robotic Systems. *Nat. Rev. Mater.* **2018**, *3* (6), 84–100. https://doi.org/10.1038/s41578-018-0002-2.
(54) Choi, C.; Okayama, Y.; Morris, P. T.; Robinson, L. L.; Gerst, M.; Speros, J. C.; Hawker, C. J.; Read de Alaniz, J.; Bates, C. M. Digital Light Processing of Dynamic Bottlebrush Materials. *Adv. Funct. Mater.* **2022**, *32* (25), 2200883. https://doi.org/10.1002/adfm.202200883.
(55) Tan, Y.; Chen, H.; Kang, W.; Wang, X. Versatile Light-Mediated Synthesis of Dry Ion-Conducting Dynamic Bottlebrush Networks with High Elasticity, Interfacial Adhesiveness, and Flame Retardancy. *Macromolecules* **2022**, *55* (21), 9715–9725. https://doi.org/10.1021/acs.macromol.2c01234.

(56) Xie, R.; Mukherjee, S.; Levi, A. E.; Reynolds, V. G.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Room Temperature 3D Printing of Super-Soft and Solvent-Free Elastomers. *Sci. Adv.* **2020**, *6* (46), eabc6900. https://doi.org/10.1126/sciadv.abc6900.

(57) Nian, S.; Zhu, J.; Zhang, H.; Gong, Z.; Freychet, G.; Zhernenkov, M.; Xu, B.; Cai, L.-H. Three-Dimensional Printable, Extremely Soft, Stretchable, and Reversible Elastomers from Molecular Architecture-Directed Assembly. *Chem. Mater.* **2021**, *33* (7), 2436–2445. https://doi.org/10.1021/acs.chemmater.0c04659.

(58) Vigneron, J. P.; Simonis, P. Natural Photonic Crystals. *Phys. B Condens. Matter* **2012**, *407* (20), 4032–4036. https://doi.org/10.1016/j.physb.2011.12.130.

(59) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. Photonic Crystals. *Solid State Commun.* **1997**, *102* (2), 165–173. https://doi.org/10.1016/S0038-1098(96)00716-8.

(60) Runge, M. B.; Bowden, N. B. Synthesis of High Molecular Weight Comb Block Copolymers and Their Assembly into Ordered Morphologies in the Solid State. *J. Am. Chem. Soc.* **2007**, *129* (34), 10551–10560. https://doi.org/10.1021/ja072929q.

(61) Sveinbjörnsson, B. R.; Weitekamp, R. A.; Miyake, G. M.; Xia, Y.; Atwater, H. A.; Grubbs, R. H. Rapid Self-Assembly of Brush Block Copolymers to Photonic Crystals. *Proc. Natl. Acad. Sci.* **2012**, *109* (36), 14332–14336. https://doi.org/10.1073/pnas.1213055109.

(62) Piunova, V. A.; Miyake, G. M.; Daeffler, C. S.; Weitekamp, R. A.; Grubbs, R. H. Highly Ordered Dielectric Mirrors via the Self-Assembly of Dendronized Block Copolymers. *J. Am. Chem. Soc.* **2013**, *135* (41), 15609–15616. https://doi.org/10.1021/ja4081502.

(63) Miyake, G. M.; Piunova, V. A.; Weitekamp, R. A.; Grubbs, R. H. Precisely Tunable Photonic Crystals From Rapidly Self-Assembling Brush Block Copolymer Blends. *Angew. Chem. Int. Ed.* **2012**, *51* (45), 11246–11248. https://doi.org/10.1002/anie.201205743.

(64) Miyake, G. M.; Weitekamp, R. A.; Piunova, V. A.; Grubbs, R. H. Synthesis of Isocyanate-Based Brush Block Copolymers and Their Rapid Self-Assembly to Infrared-Reflecting Photonic Crystals. *J. Am. Chem. Soc.* **2012**, *134* (34), 14249–14254. https://doi.org/10.1021/ja306430k.

(65) Lequieu, J.; Quah, T.; Delaney, K. T.; Fredrickson, G. H. Complete Photonic Band Gaps with Nonfrustrated ABC Bottlebrush Block Polymers. *ACS Macro Lett.* **2020**, *9* (7), 1074–1080. https://doi.org/10.1021/acsmacrolett.0c00380.

(66) Liberman-Martin, A. L.; Chang, A. B.; Chu, C. K.; Siddique, R. H.; Lee, B.; Grubbs, R. H. Processing Effects on the Self-Assembly of Brush Block Polymer Photonic Crystals. *ACS Macro Lett.* **2021**, *10* (12), 1480–1486. https://doi.org/10.1021/acsmacrolett.1c00579.

(67) Patel, B. B.; Pan, T.; Chang, Y.; Walsh, D. J.; Kwok, J. J.; Park, K. S.; Patel, K.; Guironnet, D.; Sing, C. E.; Diao, Y. Concentration-Driven Self-Assembly of PS-b-PLA Bottlebrush Diblock Copolymers in Solution. *ACS Polym. Au* **2022**, *2* (4), 232–244. https://doi.org/10.1021/acspolymersau.1c00057.

(68) Song, D.-P.; Zhao, T. H.; Guidetti, G.; Vignolini, S.; Parker, R. M. Hierarchical Photonic Pigments via the Confined Self-Assembly of Bottlebrush Block Copolymers. *ACS Nano* **2019**, *13* (2), 1764–1771. https://doi.org/10.1021/acsnano.8b07845.

(69) Patel, B. B.; Walsh, D. J.; Kim, D. H.; Kwok, J.; Lee, B.; Guironnet, D.; Diao, Y. Tunable Structural Color of Bottlebrush Block Copolymers through Direct-Write 3D Printing from Solution. *Sci. Adv.* **2020**, *6* (24), eaaz7202. https://doi.org/10.1126/sciadv.aaz7202.

(70) Gu, W.; Huh, J.; Hong, S. W.; Sveinbjornsson, B. R.; Park, C.; Grubbs, R. H.; Russell, T. P. Self-Assembly of Symmetric Brush Diblock Copolymers. *ACS Nano* **2013**, *7* (3), 2551–2558. https://doi.org/10.1021/nn305867d.

(71) B. Patel, B.; J. Walsh, D.; Patel, K.; Hoon Kim, D.; J. Kwok, J.; Guironnet, D.; Diao, Y. Rapid, Interface-Driven Domain Orientation in Bottlebrush Diblock Copolymer Films during Thermal Annealing. *Soft Matter* **2022**, *18* (8), 1666–1677. https://doi.org/10.1039/D1SM01634B.
(72) Fei, H.-F.; Yavitt, B. M.; Hu, X.; Kopanati, G.; Ribbe, A.; Watkins, J. J. Influence of Molecular Architecture and Chain Flexibility on the Phase Map of Polystyrene-Block-Poly(Dimethylsiloxane) Brush Block Copolymers. *Macromolecules* **2019**, *52* (17), 6449–6457. https://doi.org/10.1021/acs.macromol.9b00843.
(73) Kawamoto, K.; Zhong, M.; Gadelrab, K. R.; Cheng, L.-C.; Ross, C. A.; Alexander-Katz, A.; Johnson, J. A. Graft-through Synthesis and Assembly of Janus Bottlebrush Polymers from A-Branch-B Diblock Macromonomers. *J. Am. Chem. Soc.* **2016**, *138* (36), 11501–11504. https://doi.org/10.1021/jacs.6b07670.
(74) Liberman-Martin, A. L.; Chu, C. K.; Grubbs, R. H. Application of Bottlebrush Block Copolymers as Photonic Crystals. *Macromol. Rapid Commun.* **2017**, *38* (13), 1700058. https://doi.org/10.1002/marc.201700058.
(75) Lee, D.; Charpota, N.; Mei, H.; Terlier, T.; Pietrzak, D.; Stein, G. E.; Verduzco, R. Impact of Processing Effects on Surface Segregation of Bottlebrush Polymer Additives. *Macromolecules* **2022**, *55* (19), 8909–8917. https://doi.org/10.1021/acs.macromol.2c01418.
(76) Miyagi, K.; Mei, H.; Terlier, T.; Stein, G. E.; Verduzco, R. Analysis of Surface Segregation of Bottlebrush Polymer Additives in Thin Film Blends with Attractive Intermolecular Interactions. *Macromolecules* **2020**, *53* (15), 6720–6730. https://doi.org/10.1021/acs.macromol.0c00744.
(77) Mei, H.; Laws, T. S.; Mahalik, J. P.; Li, J.; Mah, A. H.; Terlier, T.; Bonnesen, P.; Uhrig, D.; Kumar, R.; Stein, G. E.; Verduzco, R. Entropy and Enthalpy Mediated Segregation of Bottlebrush Copolymers to Interfaces. *Macromolecules* **2019**, *52* (22), 8910–8922. https://doi.org/10.1021/acs.macromol.9b01801.
(78) Mah, A. H.; Laws, T.; Li, W.; Mei, H.; Brown, C. C.; Ievlev, A.; Kumar, R.; Verduzco, R.; Stein, G. E. Entropic and Enthalpic Effects in Thin Film Blends of Homopolymers and Bottlebrush Polymers. *Macromolecules* **2019**, *52* (4), 1526–1535. https://doi.org/10.1021/acs.macromol.8b02242.
(79) Mitra, I.; Li, X.; Pesek, S. L.; Makarenko, B.; Lokitz, B. S.; Uhrig, D.; Ankner, J. F.; Verduzco, R.; Stein, G. E. Thin Film Phase Behavior of Bottlebrush/Linear Polymer Blends. *Macromolecules* **2014**, *47* (15), 5269–5276. https://doi.org/10.1021/ma501070w.
(80) Bates, C. M.; Maher, M. J.; Janes, D. W.; Ellison, C. J.; Willson, C. G. Block Copolymer Lithography. *Macromolecules* **2014**, *47* (1), 2–12. https://doi.org/10.1021/ma401762n.
(81) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. Controlling Polymer-Surface Interactions with Random Copolymer Brushes. *Science* **1997**, *275* (5305), 1458–1460. https://doi.org/10.1126/science.275.5305.1458.
(82) Bates, C. M.; Seshimo, T.; Maher, M. J.; Durand, W. J.; Cushen, J. D.; Dean, L. M.; Blachut, G.; Ellison, C. J.; Willson, C. G. Polarity-Switching Top Coats Enable Orientation of Sub–10-Nm Block Copolymer Domains. *Science* **2012**, *338* (6108), 775–779. https://doi.org/10.1126/science.1226046.
(83) Yamauchi, Y.; Samitsu, S.; Goto, K.; Takeuchi, M. Bottlebrush Polymer-Reinforced Transparent Multiphase Plastics with Enhanced Thermal Stability. *Chem. Commun.* **2020**, *56* (93), 14641–14644. https://doi.org/10.1039/D0CC06769E.

(84) Banquy, X.; Burdyńska, J.; Lee, D. W.; Matyjaszewski, K.; Israelachvili, J. Bioinspired Bottle-Brush Polymer Exhibits Low Friction and Amontons-like Behavior. *J. Am. Chem. Soc.* **2014**, *136* (17), 6199–6202. https://doi.org/10.1021/ja501770y.
(85) Seror, J.; Merkher, Y.; Kampf, N.; Collinson, L.; Day, A. J.; Maroudas, A.; Klein, J. Articular Cartilage Proteoglycans As Boundary Lubricants: Structure and Frictional Interaction of Surface-Attached Hyaluronan and Hyaluronan–Aggrecan Complexes. *Biomacromolecules* **2011**, *12* (10), 3432–3443. https://doi.org/10.1021/bm2004912.
(86) Andresen Eguiluz, R. C.; Cook, S. G.; Tan, M.; Brown, C. N.; Pacifici, N. J.; Samak, M. S.; Bonassar, L. J.; Putnam, D.; Gourdon, D. Synergistic Interactions of a Synthetic Lubricin-Mimetic with Fibronectin for Enhanced Wear Protection. *Front. Bioeng. Biotechnol.* **2017**, *5*.
(87) Faivre, J.; Shrestha, B. R.; Xie, G.; Olszewski, M.; Adibnia, V.; Moldovan, F.; Montembault, A.; Sudre, G.; Delair, T.; David, L.; Matyjaszewski, K.; Banquy, X. Intermolecular Interactions between Bottlebrush Polymers Boost the Protection of Surfaces against Frictional Wear. *Chem. Mater.* **2018**, *30* (12), 4140–4149. https://doi.org/10.1021/acs.chemmater.8b01676.
(88) *Influence of Block Length on Articular Cartilage Lubrication with a Diblock Bottle-Brush Copolymer | ACS Applied Materials & Interfaces*. https://pubs.acs.org/doi/full/10.1021/acsami.9b18933 (accessed 2023-07-05).
(89) Liu, X.; Thormann, E.; Dedinaite, A.; Rutland, M.; Visnevskij, C.; Makuska, R.; M. Claesson, P. Low Friction and High Load Bearing Capacity Layers Formed by Cationic-Block -Non-Ionic Bottle-Brush Copolymers in Aqueous Media. *Soft Matter* **2013**, *9* (22), 5361–5371. https://doi.org/10.1039/C3SM27862J.
(90) Moon, H. H.; Choi, E. J.; Yun, S. H.; Kim, Y. C.; Premkumar, T.; Song, C. Aqueous Lubrication and Wear Properties of Nonionic Bottle-Brush Polymers. *RSC Adv.* **2022**, *12* (28), 17740–17746. https://doi.org/10.1039/D2RA02711A.
(91) Olszewski, M.; Pham, D. A.; González Bolívar, S.; Rabanel, J.-M.; Martinez, M.; Matyjaszewski, K.; Banquy, X. Synthesis and Characterization of Biocompatible Sulfoxide-Containing Molecular Bottlebrushes. *ACS Appl. Polym. Mater.* **2022**, *4* (11), 8564–8573. https://doi.org/10.1021/acsapm.2c01468.
(92) Adibnia, V.; Olszewski, M.; De Crescenzo, G.; Matyjaszewski, K.; Banquy, X. Superlubricity of Zwitterionic Bottlebrush Polymers in the Presence of Multivalent Ions. *J. Am. Chem. Soc.* **2020**, *142* (35), 14843–14847. https://doi.org/10.1021/jacs.0c07215.
(93) Zhulina, E. B.; Borisov, O. V. Bottlebrush Polymer Gels: Architectural Control over Swelling and Osmotic Bulk Modulus. *Soft Matter* **2022**, *18* (6), 1239–1246. https://doi.org/10.1039/D1SM01575C.
(94) Wu, B.; Feng, E.; Liao, Y.; Liu, H.; Tang, R.; Tan, Y. Brush-Modified Hydrogels: Preparations, Properties, and Applications. *Chem. Mater.* **2022**, *34* (14), 6210–6231. https://doi.org/10.1021/acs.chemmater.2c01666.
(95) Vashahi, F.; Martinez, M. R.; Dashtimoghadam, E.; Fahimipour, F.; Keith, A. N.; Bersenev, E. A.; Ivanov, D. A.; Zhulina, E. B.; Popryadukhin, P.; Matyjaszewski, K.; Vatankhah-Varnosfaderani, M.; Sheiko, S. S. Injectable Bottlebrush Hydrogels with Tissue-Mimetic Mechanical Properties. *Sci. Adv.* **2022**, *8* (3), eabm2469. https://doi.org/10.1126/sciadv.abm2469.
(96) Vohidov, F.; Milling, L. E.; Chen, Q.; Zhang, W.; Bhagchandani, S.; Nguyen, H. V.-T.; Irvine, D. J.; Johnson, J. A. ABC Triblock Bottlebrush Copolymer-Based Injectable Hydrogels: Design, Synthesis, and Application to Expanding the Therapeutic Index of Cancer

Immunochemotherapy. *Chem. Sci.* **2020**, *11* (23), 5974–5986. https://doi.org/10.1039/D0SC02611E.