Stretchable Figures of Merit in Deformable Electronics

Darren J. Lipomi

1. What Is Stretchable?

Readers of this Special Issue are well aware of the advantages of electronic materials and devices exhibiting the unusual property of "stretchability." For example, such devices can be bonded to substrates exhibiting complex topography without becoming wrinkled, they are, or should be, resilient and tough, and are enabling the next generation of semiconductor devices in fields as disparate as energy conversion and storage, digital imaging, and implantable biomedical devices. The proliferation of materials, device layouts, and applications in the burgeoning field of stretchable electronics, however, has produced fuzziness in the meaning of the word "stretchable." A rubber band is stretchable because it exhibits an elastic (reversible) mechanical response over a wide range of imposed strains. In a different sense of the word, no one would object to the classification of chewing gum as stretchable, but its deformation becomes plastic (irreversible) after only a few percent strain. Indeed, visitors to Italy's Museo della Tortura will find The Rack, along with a placard describing its operation and its special place in the depths of medieval sadism, which proved that the stretchability of *Homo sapiens* is not reversible. Stretchability is, nevertheless, a useful word for illustrating the distinction of materials and devices that can be deformed by more than a few percent (while retaining their function) from materials and devices that are only flexible due to the fact that they are thin. Stretchable materials and devices, however, can be made to accommodate strain using several different strategies, which are based on using either composite materials or electronic materials that are stretchable in the bulk.

2. Types of Stretchable Electronics

Stretchable electronics can be subdivided conveniently into two classes: stretchable composites[1] and intrinsically stretchable[2] electronic materials. Stretchable composites use high-performance functional components, which are usually not stretchable on their own, and pair them with an elastic matrix, into which the functional components are embedded, or onto which they sit. Stretchable composites can be further subdivided on the basis of whether the active materials are deterministically patterned or randomly incorporated. Deterministic composites (**Figure 1**a), exemplified by the work of Rogers, Wagner, Suo, and co-workers,[3] generally use wavy or serpentine structures that accommodate strain between rigid islands, which support the functional components, for example, individual solar cells,[4] light-emitting devices,[5] or sensors.[6] While semiconductors can be rendered stretchable as wavy nanoribbons,[7] complex integrated circuits are generally still rigid and the stretchable components are metallic interconnects. The mechanical properties of the device are generally dominated by the mechanical properties of the stretchable substrate or matrix. Sometimes, in the case of tunable antennae based on liquid metals embedded in microchannels,[8] the stretchable conductor is also the active component (and the strain changes the resonant frequency of the antennae). There is some flexibility in the choice of the substrate, which can be, for example, silicone elastomer, or silk fibroin (which has the additional advantage of bioresorbability).[9]

Random composites generally comprise high-aspect-ratio structures, for example, nanowires[10] or carbon nanotubes,[2a] dispersed in or atop a stretchable matrix.[11] Percolation of the nanostructures preserves the interconnectedness under global strain. Metallic nanowires,[10] carbon nanotubes,[2a] intentionally fractured thin films,[12] and nanowires of semiconducting polymers[13] have all been used in this way. Stretchable conductors formed by random compositing can also be used with rigid components, as demonstrated by Someya and co-workers in a stretchable organic light-emitting display, which used stretchable interconnects based on carbon nanotubes.[14] The matrix for either deterministic or random composites can be either elastomeric or, less often, thermoplastic.[2a] The principal advantage of stretchable composites is that the high performance of the active components is preserved. Challenges to this approach include the necessity for multistep microfabrication, including lithography, transfer printing, and vacuum deposition of metallic films, and the incorporation of relief structures by soft lithographic techniques.

The alternative, though substantially less developed, approach to compositing is to use electronic materials whose molecular structure or solid-state microstructure produces stretchability.[2c] Variously called intrinsically[2a] or molecularly[2c] stretchable electronics, such materials and devices have, in principle, the advantage of not requiring relief features or photolithography. Ideally, every component of a device, including the active components and interconnects, should exhibit similar elasticity and should be printed from the solution phase directly on an elastomeric substrate, which ideally would also serve as a barrier to water and oxygen. The disadvantage is that printed electronic materials, especially organics, have inferior electronic performance to metals and conventional semiconductors, and the additional constraint of making them also elastic and electronically invariant to stretching limits the choice of possible materials substantially. (To address these deficiencies, our laboratory and others have begun to discover and develop rules that might allow one to achieve the "best of both worlds" in printed

D. J. Lipomi
Department of NanoEngineering
University of California
San Diego 9500 Gilman Drive Mail Code 0448
La Jolla, CA 92093-0448, USA
E-mail: dlipomi@eng.ucsd.edu

DOI: 10.1002/adma.201504196

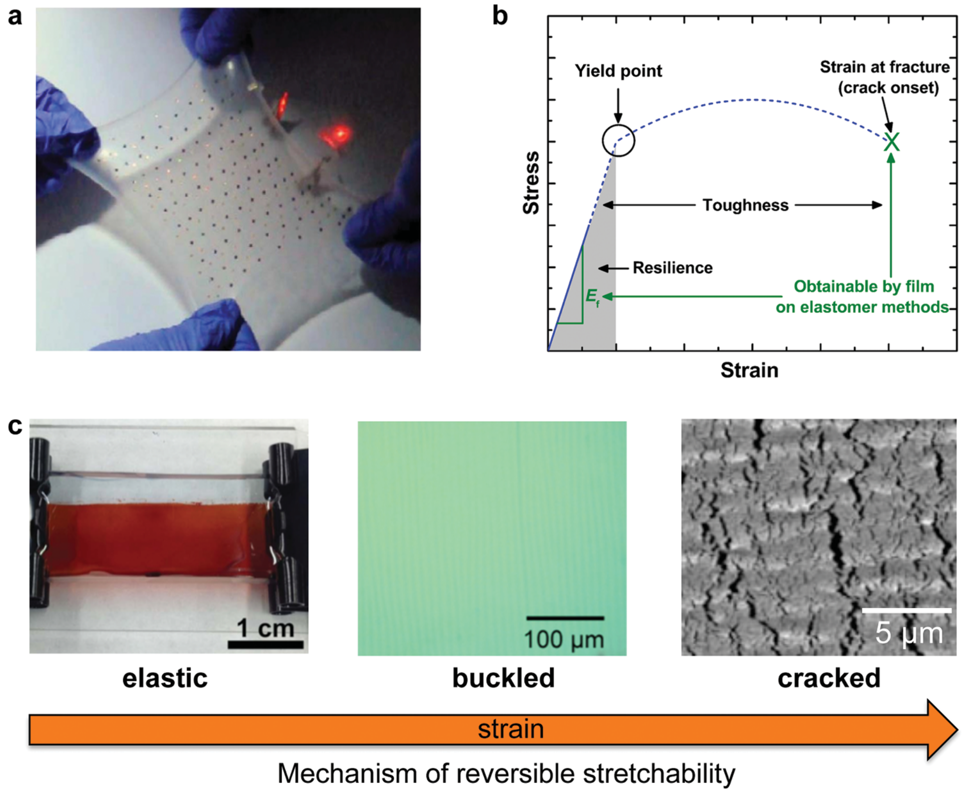

Figure 1. Images of stretchable electronic materials and devices and depictions of the terminology used here. a) A stretchable device comprising rigid active components and stretchable interconnects. Reproduced with permission.[3b] Copyright 2013, Nature Publishing Group. b) Simplified hypothetical stress–strain curve for a polymer under uniaxial deformation. The slope of the curve in the elastic regime, E_f, is the tensile modulus of the film. The tensile modulus, along with the crack-onset strain, can be determined readily from film-on-elastomer systems. The resilience can be calculated roughly from the yield point and the tensile modulus, and the toughness (the area under the curve) can be very crudely estimated with knowledge of the crack-onset strain, the yield point, and the tensile modulus. Reproduced with permission.[16] Copyright 2015, ACS. c) Mechanisms by which thin films exhibit reversible stretchability. Left, a polymer solar cell stretched to 10 percent elastically. Reproduced with permission.[17] Copyright 2014, Wiley-VCH. Center, an optical microscopy image of an organic semiconductor stretched beyond its yield point and then relaxed to the equilibrium dimensions of the substrate and exhibiting buckles. Reproduced with permission.[18] Copyright 2012, Elsevier. Right, a metallic film stretched beyond its crack onset strain on a polymeric substrate. Reproduced with permission.[19] Copyright 2009, American Institute of Physics. Each system is stretchable, though the active components accommodate strain by different mechanisms.

electronic materials that combine deformability with state-of-the-art electronic performance.[15]) It is likely that intrinsically stretchable electronics can only be used for relatively simple devices, such as light-emitting devices, solar cells, or circuits comprising only a few transistors, at least until the advent of high-performance semiconducting elastomers.

3. Modes of Deformation

Given the range of possible materials and device layouts (and the corresponding range of mechanical response), it is easy to see why notions of stretchability might differ between researchers whose training is in different fields. For stretchable systems comprising deterministic composites, in which the potential effects of cyclic loading and deformation are not expected to change the microstructure of the deformed components during the normal use of the device, stretchability simply means elasticity. Devices that are completely elastic can be used in all scenarios requiring stretchability, including integration with moving parts, soft and reconfigurable surfaces (as in the skin[6] and internal organs[20]), and one-time bonding to unchanging nonplanar surfaces (e.g., hemispheres, lenses, windshields, and architectural elements),[14] as long as they are restrained against returning to their equilibrium shape. For such devices, strains must be kept within a specified range, beyond which the interconnects fracture, components delaminate, or the elastomeric matrix ruptures.

Intrinsically stretchable electronic devices based on organic semiconductors exhibit a complex range of behavior, since all of the components deform simultaneously, and all have their own tensile moduli, yield point, and crack-onset strain. Generally, there is an elastic range in which the components can be stretched before they either plastically deform or crack. In this range, the form factors of intrinsically stretchable materials are interchangeable with those of stretchable composites. Beyond this range, however, one or more of the components may undergo plastic (irreversible) deformation. In the plastically deformed state, the device may still be bonded to nonplanar substrates. If the matrix is still in its elastic regime then the device may still be able to accommodate strain reversibly, but by a mechanism in which a film stretched beyond its yield point forms accordion-like buckles when the substrate is returned to its equilibrium shape. After reaching the yield point, the mechanism that accommodates reversible stretching is bending and unbending of the buckles, and thus a device that started out as "intrinsically" stretchable ends up exhibiting a mechanism that resembles the strain response of deterministic composites.[18] In fact, devices stretched to the point at which the active materials crack is not necessarily the point at which the device fails. Intentional cracking of metallic films has long been a useful strategy in creating stretchable conductors,[21] though the structure (and conductivity) evolves over many cycles of loading.[12] Chortos et al. even found that cracked semiconductor films in stretchable field-effect transistors retain function under cyclic loading.[22] Thus, intrinsically stretchable devices remain "stretchable" until catastrophic failure, which could include complete delamination of the layers (open circuit), complete bifurcation of the channel in a transistor (open circuit), or contact of the electrodes between the active layer in a solar cell (short circuit). It is interesting to note that in most studies of stretched semiconducting polymers, charge transport tends to improve along the strained axis because of the alignment of chains.[23] Thus, in devices such as OTFTs, some degree of stretching may actually improve the properties of devices, until they begin to fail by either adhesive or cohesive modes.

4. Figures of Merit

The ultimate goal of the science of stability of stretchable (and ultraflexible) electronics is to be able to mitigate the mechanical failure of such devices by the appropriate selection of materials or device layouts.[24] Since intrinsically stretchable electronic devices generally use thin films, which often have mechanical properties different from the same materials in bulk form, unconventional methods, in which the film is measured bonded to an elastomer in a composite system ("film-on-elastomer" (FOE), Figure 1b), are typically used to measure these properties.[25] For example, the tensile modulus can be obtained by the buckling methodology, the strain at fracture can be estimated by the crack-onset strain,[26] and the yield point can be estimated from the minimum tensile strain that produces buckles once the film is relaxed to its equilibrium dimensions.[16] Once the yield point is known, it is possible to calculate the modulus of resilience (the maximum energy stored in the elastic regime of a material per unit volume) and, combined with the crack-onset strain, one can estimate (very crudely) the modulus of toughness (the total amount of energy absorbed by a material prior to fracture, per unit volume). Once obtained, these values can be used in finite-element models of whole devices for the purpose of changing the device layout to place the greatest strains in the materials with the greatest elastic range (or to direct strain away from the most brittle components). Other issues, such as poor adhesion, can in principle be mitigated by matching the tensile moduli of the different layers. Since the active components in a stretchable device are not intended to be load bearing, and since the substrate generally comprises more than ninety percent of the mass of the device, deformation on the active materials is imposed by deformation of the stretchable substrate. Thus the quantities that are generally desirable in engineering plastics: tensile strength and toughness, are less important than the tensile modulus (which in most cases should be low), the elastic limit (which should be high for devices demanding reversible stretchability), and the ductility (i.e., a large crack-onset strain). We have found that these quantities are well correlated for many semiconducting polymers: a semiconducting elastomer like poly(3-heptylthiophene) (P3HpT) (tensile modulus $\approx$ 100 MPa) also has a relatively large elastic limit (ca. 10%)[16] and does not exhibit cracks until strains of over 50%.[15b]

5. Areas for Exploration

The research community has taken immense strides in engineering devices that are ordinarily regarded as rigid to reach extraordinary levels of elasticity (or ductility). There are, however, a few aspects related to device reliability against cyclic loading and extreme, perhaps accidental, deformation, that deserve attention. For example, the fatigue behavior of thin films, especially semiconducting polymers, is relatively unexplored. While it is now well known (largely due to the efforts of O'Connor and co-workers[23,27]) that conjugated polymers undergo strain-induced alignment of chains, enlargement of aggregated domains, and reorientation of texture under both uniaxial and biaxial strain, the microstructural consequences of repeated strains of lesser magnitude are less well known. In the case of stretchable electronics involving deformable metallic films (either deterministically patterned or intentionally fractured), the effect of the conditions of deposition and their known influence on the mechanical properties of these films are generally unexplored, but are bound to have an effect given extreme deformation or cyclic loading at more moderate strains.

There are some forms of damage that occur not from the intrinsic brittleness of the materials used, but rather from poor adhesion between layers. It is known, for example, that adhesion promotors suppress the formation of cracks in rigid films on stretchable substrates.[28] The effect arises because, in a poorly adhered film, a globally applied strain localizes to thin areas and defects (as it would in an unsupported film), whereas in a well-adhered film, the strain is distributed evenly (and thus the crack-onset strain of a film on an elastomer is generally equal to or greater than the strain at fracture of a free-standing film).[28] The effect of film thickness (for polymers) is also an interesting area for investigation. While it is known that several thermomechanical properties change below some critical thickness, for example, the tensile modulus[29] and the glass-transition temperature decrease while the elastic limit increases,[30] this knowledge has not been applied toward improving the properties of stretchable electronic devices. In cases where the performance of a device is relatively insensitive to its thickness (as in a stretchable OTFT), reducing the thickness of the channel for the sake of increasing the stretchability might be a useful strategy.

6. So, What Is Stretchable?

This essay began by asking the meaning of the word "stretchable" in stretchable electronics. The answer is that it is idiosyncratic, and this idiosyncrasy is the origin of the distress it causes some researchers, reviewers, and exam committees. As we have seen, "stretchable electronics" comprise materials and devices that accommodate strain, or do not accommodate strain, depending on your perspective, by a variety of mechanisms: elastic deformation, plastic deformation, strain-evolved formation of buckles, and even formation of cracks (Figure 1c). The most conservative definition involves a device that can be elastically deformed and then returned to its original shape in its original condition. The more inclusive definition is that a device can be returned to its original shape in whatever condition, as long as it still functions and can be stretched again. The most inclusive definition does not require the device to be returned to its equilibrium shape: such devices fulfill their purpose in their static, deformed state (like Parafilm). Such plastic, as opposed to elastic, electronic devices can be used for one-time bonding to non-planar surfaces. The definition is thus malleable, but the requirement common to all three definitions is that a device is stretchable if it still works after it is stretched. Eureka!

Acknowledgements

Our research group's support for the primary research that inspired this Essay was provided by the Air Force Office of Scientific Research (AFOSR) Young Investigator Program, grant number FA9550-13-1-0156. In addition, the author gratefully acknowledges Suchol Savagatrup and Adam Printz for kindly providing comments on this manuscript.

Received: August 27, 2015
Revised: September 11, 2015
Published online: November 25, 2015

[1] J. A. Fan, W. H. Yeo, Y. W. Su, Y. Hattori, W. Lee, S. Y. Jung, Y. H. Zhang, Z. J. Liu, H. Y. Cheng, L. Falgout, M. Bajema, T. Coleman, D. Gregoire, R. J. Larsen, Y. G. Huang, J. A. Rogers, *Nat. Commun.* **2014**, *5*, 3266.
[2] a) Z. B. Yu, X. F. Niu, Z. Liu, Q. B. Pei, *Adv. Mater.* **2011**, *23*, 3989; b) J. Liang, L. Li, D. Chen, T. Hajagos, Z. Ren, S.-Y. Chou, W. Hu, Q. B. Pei, *Nat. Commun.* **2015**, *6*, 7647; c) S. Savagatrup, A. D. Printz, T. F. O'Connor, A. V. Zaretski, D. J. Lipomi, *Chem. Mater.* **2014**, *26*, 3028.
[3] a) J. Jones, S. P. Lacour, S. Wagner, Z. G. Suo, *J. Vac. Sci. Technol., A* **2004**, *22*, 1723; b) S. Xu, Y. Zhang, J. H. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. W. Su, J. Su, H. Zhang, H. Cheng, B. Lu, C. J. Yu, C. Chuang, T.-I. Kim, T. Song, K. Shigeta, S. H. Kang, C. Dagdeviren, I. Petrov, P. V. Braun, Y. Huang, U. Paik, J. A. Rogers, *Nat. Commun.* **2013**, *4*, 1543.
[4] J. Lee, J. A. Wu, M. X. Shi, J. Yoon, S. I. Park, M. Li, Z. J. Liu, Y. G. Huang, J. A. Rogers, *Adv. Mater.* **2011**, *23*, 986.
[5] R. H. Kim, D. H. Kim, J. L. Xiao, B. H. Kim, S. I. Park, B. Panilaitis, R. Ghaffari, J. M. Yao, M. Li, Z. J. Liu, V. Malyarchuk, D. G. Kim, A. P. Le, R. G. Nuzzo, D. L. Kaplan, F. G. Omenetto, Y. G. Huang, Z. Kang, J. A. Rogers, *Nat. Mater.* **2010**, *9*, 929.
[6] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. H. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838.
[7] Y. G. Sun, W. M. Choi, H. Q. Jiang, Y. G. Y. Huang, J. A. Rogers, *Nat. Nanotechnol.* **2006**, *1*, 201.
[8] J. H. So, J. Thelen, A. Qusba, G. J. Hayes, G. Lazzi, M. D. Dickey, *Adv. Funct. Mater.* **2009**, *19*, 3632.
[9] D. H. Kim, J. Viventi, J. J. Amsden, J. L. Xiao, L. Vigeland, Y. S. Kim, J. A. Blanco, B. Panilaitis, E. S. Frechette, D. Contreras, D. L. Kaplan, F. G. Omenetto, Y. G. Huang, K. C. Hwang, M. R. Zakin, B. Litt, J. A. Rogers, *Nat. Mater.* **2010**, *9*, 511.
[10] J. Liang, L. Li, K. Tong, Z. Ren, W. Hu, X. F. Niu, Y. S. Chen, Q. B. Pei, *ACS Nano* **2014**, *8*, 1590.
[11] D. J. Lipomi, M. Vosgueritchian, B. C.-K. Tee, C. H. Fox, J. A. Lee, Z. N. Bao, *Nat. Nanotechnol.* **2011**, *6*, 788.
[12] S. P. Lacour, D. Chan, S. Wagner, T. Li, Z. Suo, *Appl. Phys. Lett.* **2006**, *88*, 204103.
[13] M. Shin, J. H. Song, G. H. Lim, B. Lim, J. J. Park, U. Jeong, *Adv. Mater.* **2014**, *26*, 3706.
[14] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nat. Mater.* **2009**, *8*, 494.
[15] a) S. Savagatrup, A. D. Printz, D. Rodriquez, D. J. Lipomi, *Macromolecules* **2014**, *47*, 1981; b) S. Savagatrup, A. D. Printz, H. S. Wu, K. M. Rajan, E. J. Sawyer, A. V. Zaretski, C. J. Bettinger, D. J. Lipomi, *Synth. Met.* **2015**, *203*, 208.
[16] A. D. Printz, A. V. Zaretski, S. Savagatrup, A. S.-C. Chiang, D. J. Lipomi, *ACS Appl. Mater. Interfaces* **2015**, *7*, 23257.
[17] S. Savagatrup, A. S. Makaram, D. J. Burke, D. J. Lipomi, *Adv. Funct. Mater.* **2014**, *24*, 1169.
[18] D. J. Lipomi, H. Chong, M. Vosgueritchian, J. G. Mei, Z. N. Bao, *Sol. Energy Mater. Sol. Cells* **2012**, *107*, 355.
[19] I. M. Graz, D. P. J. Cotton, S. P. Lacour, *Appl. Phys. Lett.* **2009**, *98*, 071902.
[20] J. Viventi, D. H. Kim, J. D. Moss, Y. S. Kim, J. A. Blanco, N. Annetta, A. Hicks, J. L. Xiao, Y. G. Huang, D. J. Callans, J. A. Rogers, B. Litt, *Sci. Transl. Med.* **2010**, *2*, 24.
[21] S. P. Lacour, S. Wagner, Z. Y. Huang, Z. Suo, *Appl. Phys. Lett.* **2003**, *82*, 2404.
[22] A. Chortos, J. Lim, J. W. F. To, M. Vosgueritchian, T. J. Dusseault, T. H. Kim, S. W. Hwang, Z. N. Bao, *Adv. Mater.* **2014**, *26*, 4253.
[23] B. O'Connor, R. J. Kline, B. R. Conrad, L. J. Richter, D. Gundlach, M. F. Toney, D. M. DeLongchamp, *Adv. Funct. Mater.* **2011**, *21*, 3697.
[24] S. Savagatrup, A. D. Printz, T. F. O'Connor, A. V. Zaretski, D. Rodriquez, E. J. Sawyer, K. M. Rajan, R. I. Acosta, S. E. Root, D. J. Lipomi, *Energy Environ. Sci.* **2015**, *8*, 55.
[25] a) N. Bowden, W. T. S. Huck, K. E. Paul, G. M. Whitesides, *Appl. Phys. Lett.* **1999**, *75*, 2557; b) J. Y. Chung, A. J. Nolte, C. M. Stafford, *Adv. Mater.* **2011**, *23*, 349; c) C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. Vanlandingham, H. C. Kim, W. Volksen, R. D. Miller, E. E. Simonyi, *Nat. Mater.* **2004**, *3*, 545.
[26] a) A. D. Printz, S. Savagatrup, D. Rodriquez, T. F. O'Connor, D. J. Lipomi, *Sol. Energy Mater. Sol. Cells* **2015**, *134*, 64; b) O. Awartani, B. Lemanski, H. W. Ro, L. J. Richter, D. M. DeLongchamp, B. T. O'Connor, *Adv. Energy Mater.* **2013**, *3*, 399.
[27] a) D. Gargi, R. J. Kline, D. M. DeLongchamp, D. A. Fischer, M. F. Toney, B. T. O'Connor, *J. Phys. Chem. C* **2013**, *117*, 17421; b) B. O'Connor, E. P. Chan, C. Chan, B. R. Conrad, L. J. Richter, R. J. Kline, M. Heeney, I. McCulloch, C. L. Soles, D. M. DeLongchamp, *ACS Nano* **2010**, *4*, 7538.
[28] N. S. Lu, X. Wang, Z. G. Suo, J. Vlassak, *Appl. Phys. Lett.* **2007**, *91*, 221909.
[29] C. M. Stafford, B. D. Vogt, C. Harrison, D. Julthongpiput, R. Huang, *Macromolecules* **2006**, *39*, 5095.
[30] a) B. J. Gurmessa, A. B. Croll, *Phys. Rev. Lett.* **2013**, *110*, 074301; b) B. J. Gurmessa, A. B. Croll, *Macromolecules* **2015**, DOI: 10.1021/acs.macromol.5b01240.