

New Chemistry Generates Novel Networks and Ultra-soft Solids

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Recent advances in polymer chemistry are revolutionizing tailor-made soft materials. One area experiencing significant advancement is polymeric networks with precise control over the molecular chains that constitute the network.¹⁻¹² Polymer networks are ubiquitous as the basis of a wide range of products including structural materials, adhesives, membranes, and biomaterials.¹⁻³ The next generation of materials are expected to exhibit a broader range of properties and be multifunctional.^{2,4-6} We will outline several contributions our laboratory has been in the area of novel networks and advanced soft materials. In all cases, an effort has been made to connect the molecular design with bulk mechanic properties.

Bio-inspired, perfectly elastic networks: Elastic proteins such as elastin and resilin are both water swollen (40-60%), yet have the remarkable ability to undergo significant reversible deformation with no energy loss, also known as having high resilience. Resilin, which is even more resilient than elastin, hence its name, serves a variety of purposes, from being involved in the jumping mechanism in fleas, to the flight system of dragonflies and the sound producing organs of the locust. First investigated by Weis-Fogh in the 1960s in the form of the dragonfly tendon, it was shown to be 92% resilient, which is greater than perhaps the most prototypical synthetic elastomer, polybutadiene rubber (80%). Studies of resilin have shown that the cross-linking chemistry is highly specific, occurring only through the tyrosine units, with approximately 40 to 60 amino acid residues (~4 to 7 kDa) between junctions. In addition, resilin is an amorphous material, with no stable secondary structures in the cross-linked primary chains. It is this uniform network (narrowly-defined MW between cross-links as well as robust cross-linking chemistry), low cross-link density, and the absence of secondary structure for the primary chains that are responsible for the remarkable elastomeric properties of resilin.

Inspired by these design criteria, a synthetic platform capable of reproducing the essential features responsible for the impressive elastic properties of resilin was pursued. We proposed that the combination of telechelic polymer chains coupled with high efficiency cross-linking chemistry would enable the creation of networks with high water content, low cross-link density, and uniformly spaced cross-links. These new highly swollen networks, reported here for the first time, demonstrate the ability to undergo large deformations both in compression and extension with remarkable resilience.

The networks described herein are based on the fast, photoinitiated cross-linking of norbornene functionalized poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) with a tetra-functional thiol cross-linker. This method is exceptionally simple, involving only the mixing of all of the components before photoinitiated network formation. The networks

are cross-linked in organic solvent, so the PEG and PDMS are homogeneously mixed in the precursor solution during network formation. The gels are then swollen to equilibrium in deionized water. By simply varying the ratio of PEG to PDMS, the water content and mechanical properties of the hydrogels are significantly altered, while the resilience remains constant. Robust mechanical analysis demonstrates that these are a new class of materials with exquisitely tunable mechanical properties and water contents, while remaining highly resilient across all strains (up to 170%) examined to date.

A series of hydrogels were prepared with molar ratios of PEG to PDMS ranging from 100 : 0 to 30 : 70, as shown in Figure 1. As the PDMS content increases, the water content decreases, going from over 95% water in the 100% PEG hydrogel to 80% water in the 30 : 70 hydrogel. This difference in swelling is visible in the representative photographs of the 100% PEG hydrogel and the 30 : 70 hydrogel (Figure 1). Although both samples started with the same initial polymer content, the equilibrium-swollen states are noticeably different. Hydrogels with Young's moduli ranging from 25 to 50 kPa were achieved by controlling the PDMS content.

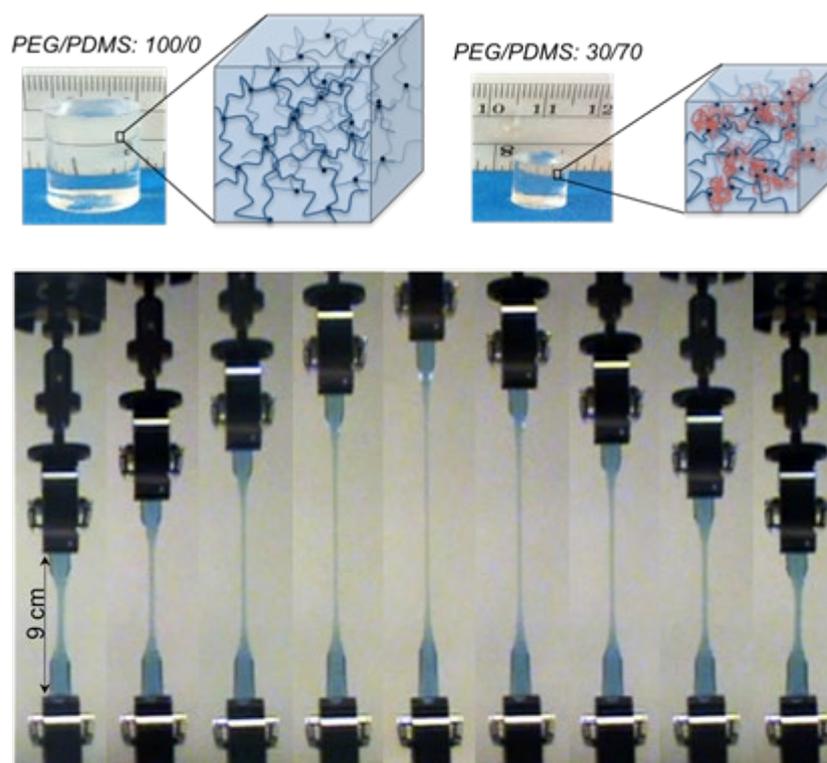


Figure 1. Photographs of a 100% PEG hydrogel and a 30:70 PEG/PDMS hydrogel, both cross-linked with the same initial total polymer content and swollen to equilibrium in water, along with the corresponding schematics illustrating the PEG (blue) and PDMS (red) polymer chains that constitute the networks. Representative photographs of a 100% PEG hydrogel during tensile testing over one strain cycle, reaching a maximum strain of 150%.

To investigate the resilience of these hydrogels, tensile measurements were carried out with a cyclic loading profile. Resilience, defined as energy recovered after removal of the stress divided by the total energy of deformation, measures the ability of a material to deform reversibly (elastically) without loss of energy. As shown in Figure 2, both the PEG and PEG/PDMS hydrogels showed negligible hysteresis across the entire measured range of strains. In addition, during consecutive loading cycles for each strain, the loading and unloading stress-strain curves were identical, demonstrating the remarkable properties of

these highly swollen, synthetic materials. This data also suggests that the Mullins effect did not occur, which was commonly observed but difficult to prevent in filled rubber and the double network hydrogels. For comparison, two commonly used prototypical hydrogels were characterized under identical conditions. One synthetic material, polyacrylamide, and one protein-based material, gelatin, were selected. For both hydrogels, the water content was circa 90% and the Young's modulus measured in tension was approximately 20 kPa, which was in the range of the moduli of the PEG/PDMS hydrogels. Resilience was measured with the same cyclic loading profile as the PEG and PEG/PDMS hydrogels. At low strains (<20%), a high resilience was observed for all samples, as expected, as resilience is typically high for all materials at small deformation. However, as the strain increased, the resilience of the polyacrylamide hydrogel remained constant, while the resilience of gelatin decreased. Fracture occurred at small strains (~30%) for both hydrogels, demonstrating their known relatively weak and brittle mechanical performance. Therefore, these two hydrogels cannot be resilient at high strains due to premature fracture.

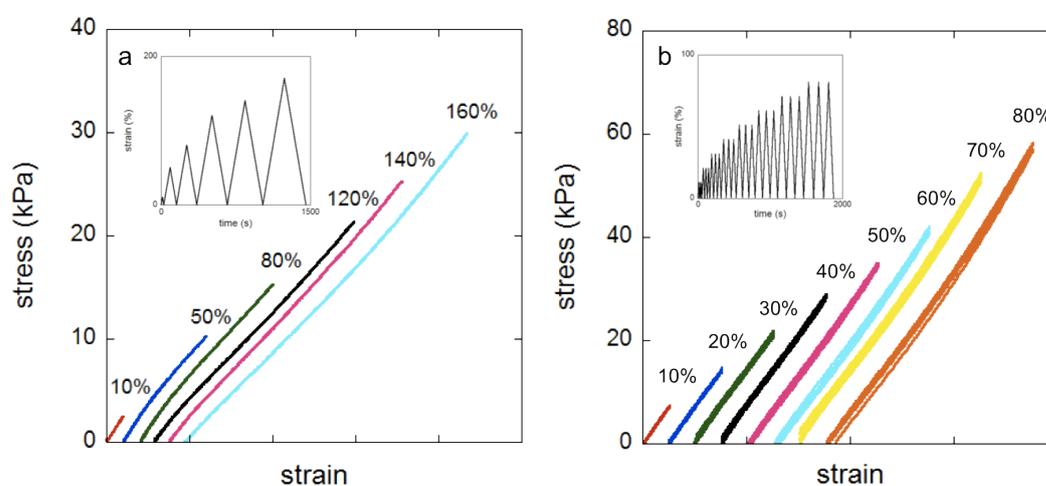


Figure 2. Curves from cyclic loading in tension. a and b. Representative stress-strain curves for the PEG hydrogel and the PEG/PDMS (with the molar ratio of 30:70) hydrogel, respectively. For clarity, the curves are shifted on the strain axis, and the final strains are given on the plots. The insets show the corresponding strain profiles as a function of time. Note in b that each strain % shows three cycles, demonstrating the reversibility of the stress-strain curves of these hydrogels.

Toward Ultra-Soft, yet Tough Elastomers: Bottlebrush networks have recently received a great deal of attention due to the unique architectural possibilities afforded by the side chains densely grafted upon strands of the network.⁷⁻¹⁸ The high local density of side chains extend the bottlebrush backbone and produce networks where the strands are rigid cylinders that are less likely to form physical entanglements, resulting in super-soft materials with moduli similar to biological tissue.^{10,11}

It is highly desirable to ‘map’ the architectural parameters of BBEs such that materials of tunable elasticity, modulus, and adhesion can be designed.¹⁹⁻²² Modern advances in network theory allow for increasingly accurate predictions of network bulk properties (e.g. modulus, adhesion, fracture).^{3,13,14,22-30} These predictions are anchored by an increasingly deep understanding of the underlying molecular parameters associated with network materials. Models developed this way are often improved through correlation of molecular structure and bulk mechanical properties.³¹⁻³⁸ This typically entails developing more accurate ways to estimate the number of molecular defects (e.g. loops, dangling ends, entanglements) within materials.^{27,39-42} Despite these recent advancements, it remains difficult to predict the

mechanical properties of BBEs specifically due to their unique molecular structure.

Herein BBEs with identical side chains— $n_{sc} = 14$ poly(dimethyl siloxane)—but different backbones—poly(norbornene) and poly(methyl methacrylate)—are compared to evaluate the impact that chemistry has on the mechanical properties of polymerized elastomers. These backbones were chosen because ring-opening metathesis polymerization (ROMP) and free radical polymerization (FRP) are two of the most common methods to produce BBEs. The two chemistries differ significantly, with completely different propagation rates (k_p), backbone dispersities (\mathcal{D}), polymerization mechanisms, and driving forces of reaction (**Figure 3**).^{43,44} These different chemistries produce BBEs with different molecular defects that affect their bulk properties.

We further apply Dobrynin and coworkers' predictive model for BBE modulus to extract and define a new parameter: ρ^* , the number density of monomers participating in stress-supporting strands.¹⁰ Through comparison of ρ^* to the case of a perfectly affine network, we evaluate the degree to which imperfections alter the molecular structure of our elastomers. This analysis allowed us to accurately predict that (1) the use of solvent during FRP leads to the production of samples with lower elastic modulus and that (2) our ROMP samples have loss moduli and loss tangents of greater magnitude than our FRP samples.

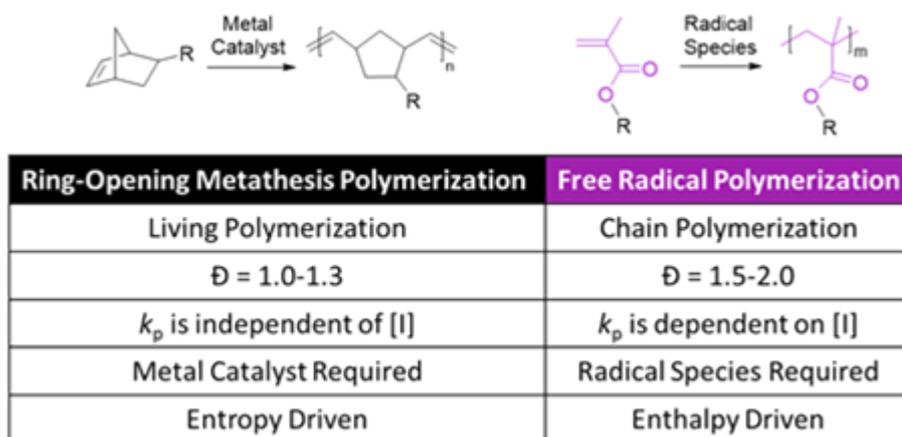


Figure 3. Comparison of the ring-opening metathesis polymerization (ROMP) and free radical polymerization (FRP) chemistries. The two chemistries differ significantly in mechanism, thermodynamics, and kinetics.

While previous studies by Sheiko, *et al.* indicate that FRP samples should be capable of reaching n_x values of 600, we found that our samples became too weak to manipulate after $n_x = 34$.^{10,45} Furthermore, our FRP samples were able to achieve an $E \sim 20$ kPa at $n_x = 34$, a value not reached until $n_x = 100$ in Sheiko, *et al.*'s studies.^{10,45} For ROMP, our $n_x = 333$ sample had an E of 4.4 kPa, comparable to an $n_x = 400$ sample produced by Sheiko, *et al.* (3.3 kPa), illustrating the potential of ROMP samples to become even softer than FRP samples at higher n_x values.

Following the SBB and SSC regime classifications, the elastic modulus (E) of the ROMP and FRP systems were predicted using Dobrynin and coworkers' adaptation of the affine model for the elasticity of bottlebrush elastomers¹⁰:

$$E = 3k_b T \beta \alpha^{-1} \rho_s \quad (2)$$

where k_b is the Boltzmann constant, T is the absolute temperature, β is the strand-extension ratio, α is the strand stiffness, and ρ_s is the number density of stress-supporting strands. ρ_s is

further defined as¹⁰:

$$\rho_s = \rho \varphi_m (n_x^{-1} - 2n_{bb}^{-1}) \quad (3)$$

where ρ is the monomer number density, n_{bb} is the degree of polymerization of the bottlebrush backbone, and φ_m is the molar fraction of backbone monomers (not to be confused with ϕ , the *volume* fraction of backbone monomers). The values used for ρ were taken from the literature values for the monomer volumes of norbornene and methyl methacrylate, 2.86 nm^{-3} and 6.67 nm^{-3} respectively.

Analysis of **eq 2-3** indicates that the only variable we do not have a way of accurately estimating is ρ , the monomer number density. The value of this parameter is typically determined by inverting the volume of a monomer, *e.g.* PDMS, with a monomer volume of 0.13 nm^3 and a monomer number density of $1/0.13 \text{ nm}^3 = 7.7 \text{ nm}^{-3}$. Using values determined in this manner for ρ in **eq 2** leads to error because it carries the implicit assumption that all monomers are part of stress-supporting strands that are perfectly elastic with no defects, an assumption that is invalid for viscoelastic systems. To estimate the degree to which the viscous response of materials effects network E , we introduce the concept of ρ^* , the number density of monomers participating in stress-supporting strands. Due to the presence of molecular defects in our BBEs (*e.g.* dangling ends or loops), it stands to reason that values of ρ^* for our systems will be lower than the values of ρ for the most perfect, ideal cases (2.86 nm^{-3} and 6.67 nm^{-3} for ROMP and FRP respectively). A physical interpretation of ρ^* is illustrated in **Figure 4**, where red strands represent stress-supporting strands and black strands represent strands that *should* be stress-supporting but *are not* due to molecular defects within the BBE. It is important to understand that while ρ^* is constant within each sample set, the effective number of stress-supporting strands (ρ_{s^*}) decreases as n_x increases:

$$\rho_{s^*} = \frac{\rho_s}{n_x} \quad (4)$$

The ratio ρ^*/ρ provides insight into the structure of the network's molecular structure, namely the percentage of monomers within a cubic nanometer that are participating in stress-supporting strands. This ratio is useful when comparing the molecular structure of BBEs polymerized under different conditions.

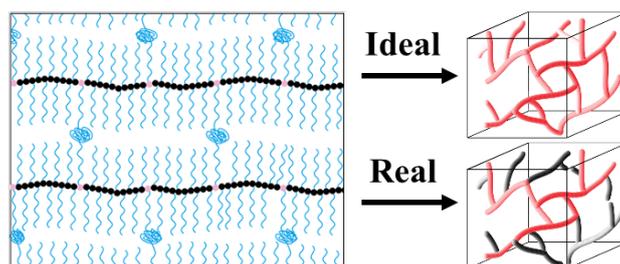


Figure 4. Representative depiction of 1 nm^3 sections of ROMP samples with (*left*) perfectly affine strands and (*right*) real strands with defects that alter the molecular structure of the samples. The red strands represent stress-supporting strands while the black strands represent strands that should be stress-supporting but are not due to molecular defects introduced to the network by the ROMP chemistry.

Two very different chemistry approaches to new elastomers is discussed. In both cases, connects were made between molecular structure and bulk mechanic properties. One

case yielded highly elastic, bio-inspired materials. Although not discussed specifically in this paper, these networks are ideal models and have yielded new insight into soft material fracture theories.²⁹ We further introduce the concept of the number density of monomers participating in stress-supporting strands (ρ^*) for new bottlebrush-based elastomers. The ratio of ρ^*/ρ provides a measure of how many monomers are participating in stress-supporting strands relative to the most ideal, perfect case ($\rho^*/\rho = 1.00$).

References:

- (1) Fan, H.; Gong, J. P. *Macromolecules* **2020**.
- (2) Patrickios, C. S. *Amphiphilic Polymer Co-networks*; 2020.
- (3) Creton, C.; Ciccotti, M. *Reports Prog. Phys.* **2016**, *79* (4), 46601.
- (4) Erdodi, G.; Kennedy, J. P. *Prog. Polym. Sci.* **2006**, *31* (1), 1.
- (5) Mespouille, L.; Hedrick, J. L.; Dubois, P. *Soft Matter* **2009**, *5* (24), 4878.
- (6) Patrickios, C. S.; Matyjaszewski, K. *Polym. Int.* **2021**, *70* (1), 10.
- (7) Xie, R.; Mukherjee, S.; Levi, A. E.; Reynolds, V. G.; Wang, H.; Chabinye, M. L.; Bates, C. M. *Sci. Adv.* **2020**, *6* (46), 1.
- (8) Clarke, B. R.; Tew, G. N. *J. Polym. Sci.* **2022**, 1.
- (9) Xie, G.; Martinez, M. R.; Olszewski, M.; Sheiko, S. S.; Matyjaszewski, K. *Biomacromolecules* **2019**, *20* (1), 27.
- (10) Vatankhah-Varnosfaderani, M.; Daniel, W. F. M.; Everhart, M. H.; Pandya, A. A.; Liang, H.; Matyjaszewski, K.; Dobrynin, A. V.; Sheiko, S. S. *Nature* **2017**, *549* (7673), 497.
- (11) Daniel, W. F. M.; Burdyńska, J.; Vatankhah-Varnoosfaderani, M.; Matyjaszewski, K.; Paturej, J.; Rubinstein, M.; Dobrynin, A. V.; Sheiko, S. S. *Nat. Mater.* **2016**, *15* (2), 183.
- (12) Mukherjee, S.; Xie, R.; Reynolds, V. G.; Uchiyama, T.; Levi, A. E.; Valois, E.; Wang, H.; Chabinye, M. L.; Bates, C. M. *Macromolecules* **2020**, *53* (3), 1090.
- (13) Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2019**, *52* (20), 7531.
- (14) Sarapas, J. M.; Chan, E. P.; Rettner, E. M.; Beers, K. L. *Macromolecules* **2018**, *51* (6), 2359.
- (15) Cao, Z.; Daniel, W. F. M.; Vatankhah-Varnosfaderani, M.; Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2016**, *49* (20), 8009.
- (16) Cushman, K.; Keith, A.; Tanaka, J.; Sheiko, S. S.; You, W. *Macromolecules* **2021**, *54* (18), 8365.
- (17) Li, Z.; Tang, M.; Liang, S.; Zhang, M.; Biesold, G. M.; He, Y.; Hao, S. M.; Choi, W.; Liu, Y.; Peng, J.; Lin, Z. *Progress in Polymer Science.* 2021,.
- (18) Weaver, J. A.; Morelly, S. L.; Alvarez, N. J.; Magenau, A. J. D. *Polym. Chem.* **2018**, *9* (42), 5173.
- (19) Liang, H.; Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2018**, *51* (2), 638.
- (20) Aoyama, T.; Yamada, N.; Urayama, K. *Macromolecules* **2021**, *54* (5), 2353.
- (21) Jacobs, M.; Liang, H.; Dashtimoghadam, E.; Morgan, B. J.; Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2019**, *52* (14), 5095.
- (22) Tian, Y.; Ina, M.; Cao, Z.; Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2018**, *51* (11), 4059.
- (23) Kim, J.; Zhang, G.; Shi, M.; Suo, Z. *Science* **2021**, *374* (6564), 212.
- (24) Panyukov, S. *Polymers (Basel)*. **2020**, *12* (4).
- (25) Barney, C. W.; Dougan, C. E.; McLeod, K. R.; Kazemi-Moridani, A.; Zheng, Y.; Ye, Z.; Tiwari, S.; Sacligil, I.; Riggleman, R. A.; Cai, S.; Lee, J.-H.; Peyton, S. R.; Tew, G. N.; Crosby, A. J. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117* (17), 9157.

- (26) Barney, C. W.; Zheng, Y.; Wu, S.; Cai, S.; Crosby, A. J. *Soft Matter* **2019**, *15* (37), 7390.
- (27) Zhong, M.; Wang, R.; Kawamoto, K.; Olsen, B. D.; Johnson, J. A. *Science* **2016**, *353* (6305), 1264.
- (28) Akagi, Y.; Gong, J. P.; Chung, U. Il; Sakai, T. *Macromolecules* **2013**, *46* (3), 1035.
- (29) Barney, C. W.; Ye, Z.; Sacligil, I.; McLeod, K. R.; Zhang, H.; Tew, G. N.; Riggleman, R. A.; Crosby, A. J. *Proc. Natl. Acad. Sci. U. S. A.* **2022**, *119* (7).
- (30) Tiwari, S.; Kazemi-Moridani, A.; Zheng, Y.; Barney, C. W.; McLeod, K. R.; Dougan, C. E.; Crosby, A. J.; Tew, G. N.; Peyton, S. R.; Cai, S.; Lee, J. H. *Soft Matter* **2020**, *16* (39), 9006.
- (31) Cao, Z.; Carrillo, J. M. Y.; Sheiko, S. S.; Dobrynin, A. V. *Macromolecules* **2015**, *48* (14), 5006.
- (32) Hatami-Marbini, H. *Phys. Rev. E* **2018**, *97* (2), 1.
- (33) Golitsyn, Y.; Pulst, M.; Samiullah, M. H.; Busse, K.; Kressler, J.; Reichert, D. *Polymer (Guildf)*. **2019**, *165* (January), 72.
- (34) Kawamoto, K.; Zhong, M.; Wang, R.; Olsen, B. D.; Johnson, J. A. *Macromolecules* **2015**, *48* (24), 8980.
- (35) Sorichetti, V.; Ninarello, A.; Ruiz-Franco, J. M.; Hugouvieux, V.; Kob, W.; Zaccarelli, E.; Rovigatti, L. *Macromolecules* **2021**, *54* (8), 3769.
- (36) Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27* (9), 2454.
- (37) Fujiyabu, T.; Yoshikawa, Y.; Chung, U. il; Sakai, T. *Sci. Technol. Adv. Mater.* **2019**, *20* (1), 608.
- (38) Chan, D.; Ding, Y.; Dauskardt, R. H.; Appel, E. A. *ACS Appl. Mater. Interfaces* **2017**, *9* (48), 42217.
- (39) Lin, T. S.; Wang, R.; Johnson, J. A.; Olsen, B. D. *Macromolecules* **2019**, *52* (4), 1685.
- (40) Lang, M. *ACS Macro Lett.* **2018**, *7* (5), 536.
- (41) Lin, T. S.; Wang, R.; Johnson, J. A.; Olsen, B. D. *Macromol. Symp.* **2019**, *385* (1), 1.
- (42) Fu, L.; Li, H. *Macromolecules* **2020**.
- (43) Walsh, D. J.; Lau, S. H.; Hyatt, M. G.; Guironnet, D. *J. Am. Chem. Soc.* **2017**, *139* (39), 13644.
- (44) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Ltd: Hoboken, NJ, 2004.
- (45) 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. *Adv. Mater.* **2017**, *29* (2).

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