The Impact of Polymerization Chemistry on the Mechanical Properties of Poly(dimethylsiloxane) Bottlebrush Elastomers

Brandon R. Clarke,§ Hyemin Kim,§ Mark Ilton,* James J. Watkins,* Alfred J. Crosby,* and Gregory N. Tew*

ABSTRACT: We compare the low-strain mechanical properties of bottlebrush elastomers (BBEs) synthesized using ring-opening metathesis and free radical polymerization. Through comparison of experimentally measured elastic moduli and those predicted by an ideal, affine model, we evaluate the efficiency of our networks in forming stress-supporting strands. This comparison allowed us to develop a structural efficiency ratio that facilitates the prediction of mechanical properties relative to polymerization chemistry (e.g., softer BBEs when polymerizing under dilute conditions). This work highlights the impact that polymerization chemistry has on the structural efficiency ratio and the resultant mechanical properties of BBEs with identical side chains, providing another “knob” by which to control polymer network properties.

INTRODUCTION

Bottlebrush networks are receiving increased attention due to the unique architectural possibilities afforded by the side chains densely grafted upon strands of the network.1−14 The high local density of side chains extends the backbone and produces networks where the strands are rigid cylinders that are less likely to form physical entanglements, resulting in supersonic materials with moduli similar to biological tissue without the need for solvent swelling.4,7 Major architectural parameters of bottlebrush networks are $n_g$, $n_{sc}$, and $n_x$—the degree of polymerization between side chains, of side chains, and between crosslinks, respectively (Figure 1). This diversity of parameters allows for bottlebrush elastomers (BBEs) to have a wide degree of tunability, enabling the design of solvent-free materials with moduli ranging from $10^2$ to $10^6$ Pa.7,15,16

It is highly desirable to “map” the architectural parameters of BBEs such that materials of tunable elasticity, modulus, adhesion, and failure behavior can be designed.17−20 Modern advances in network theory allow for increasingly accurate predictions of network bulk properties (e.g., modulus, adhesion, fracture).5,10,20−29 These predictions are anchored by an evolving 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.30−37 This approach typically entails developing more accurate ways to estimate the number and type of molecular defects within the network.25,38−41 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(dimethylsiloxane)—but different backbones—poly(norbornene) and poly(methyl methacrylate)—are compared to evaluate the impact of network formation chemistry on the mechanical properties of polymerized elastomers. These

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backbones were chosen because ring-opening metathesis polymerization (ROMP) and free radical polymerization (FRP) are two of the most common methods to produce bottlebrush polymers. The two chemistries differ significantly with respect to chain growth mechanisms, backbone dispersities ($D$), propagation rates ($k_p$), growing chain lifetime, as well as the extent and type of chain transfer reactions (Figure 2). These different chemistries are expected to produce BBEs with different molecular topologies, including defects, that affect their mechanical properties.

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<tr>
<th>Ring-Opening Metathesis Polymerization</th>
<th>Free Radical Polymerization</th>
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<td>Living Polymerization</td>
<td>Chain Polymerization</td>
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<td>$D = 1.1-1.5$</td>
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<td>$k_p = 10^3$</td>
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<td>Relatively Long Chain Lifetime</td>
<td>Short Chain Lifetime</td>
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<td>Limited Chain Transfer</td>
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Figure 2. Comparison of the ring-opening metathesis polymerization (ROMP) and free radical polymerization (FRP) chemistries. The two chemistries differ significantly in mechanism, thermodynamics, and kinetics.

We applied Dobrynin and co-workers’ predictive model for BBE modulus to introduce the structural efficiency ratio (\(\rho_s^*/\rho_s^{SER}\)), a comparison of the number density of stress-supporting strands in an experimentally prepared BBE (\(\rho_s^*\)) to the number density of stress-supporting strands in an affine model BBE (\(\rho_s\)). Through this SER, the degree to which imperfections alter the molecular structure of our elastomers was evaluated. This analysis illustrated that (1) the ROMP chemistry produces stress-supporting strands less efficiently than the FRP chemistry, (2) the use of solvent during FRP leads to the production of samples with a lower SER, and (3) ROMP samples have lower density of stress-supporting strands than FRP samples due to their lower SER. Demonstrating that the chemistry used to grow the BBE significantly impacts the resulting mechanical properties expands the materials’ design opportunities.

**EXPERIMENTAL SECTION**

ROMP Bottlebrush Elastomer Synthesis. ROMP BBEs were synthesized by polymerizing norbornene-functionalized macromonomers (250 mg) with varied amounts of crosslinker (Scheme S.1). The ROMP BBEs were all polymerized using Grubbs’ second-generation catalyst (Sigma) at an $M:I$ ratio of 1000. For a typical reaction, the macromonomer and crosslinker were first dissolved in 1 mL of dried dichloromethane (DCM) in a 20 mL vial before adding 1 mL of catalyst/DCM solution. The reaction was allowed to run overnight before being quenched with three drops of ethyl vinyl ether (EVE, Sigma). An analogous bottlebrush polymerization was performed in a round-bottom flask in 20 mL of dried DCM with no crosslinker added to the reaction (Scheme S.2). The synthesized bottlebrush polymer was characterized by multi-angle light scattering (MALD).

FRP Bottlebrush Elastomer Synthesis. Monomethacryloxypropyl-terminated poly(dimethylsiloxane) (macromonomer; MCR-M11, Gelest) and methacryloxypropyl terminated poly-

![Scheme 1. General Polymerization Schemes for (Top) the Ring-Opening Metathesis Polymerization of Norbornene-Functionalized Macromonomers Using Grubbs’ Second-Generation Catalyst and (Bottom) the Free Radical Polymerization of Methacrylate-Functionalized Macromonomers Using Photopolymerization](image)

“\(n_e = (2 \times \text{mol} \% \text{XL})^{-1}\). The network schematics on the right are designed to scale, considering the length of the side chains ($<R_{sc}>$), the length of network strands ($<R_{nd}>$), monomer volume, and the effective Kuhn length. Refer to the SI for details on these calculations. Our ROMP systems have less extended side chains (2.38 nm) than our FRP systems (2.69 nm) due to the different bottlebrush regimes they belong to (SBB and SSC, respectively).
(dimethylsiloxane) (crosslinker; DMS-R18, and DMS-R22, Gelest) were passed through basic alumina to remove any inhibitor present. FRP BBEs were all polymerized with 1.1 mol % photo-initiator (2-hydroxy-2-methylpropophenone, Darocur 1173, BASF), and varied amounts of crosslinker. For a typical reaction, macromonomer and crosslinker were stirred with 1.1 mol % Darocur before being injected into a 40 mm diameter circular mold. Reaction mixtures were UV-cured for 6 h under N\textsubscript{2} with a high-pressure ultraviolet lamp (USH5085A, Ushio, 6.1 mW/cm\textsuperscript{2} at 365 nm). An analogous bottlebrush polymerization was performed with no crosslinker added to the reaction (Scheme S.2). The synthesized bottlebrush polymer was characterized by multi-angle light scattering (MALS).

**Proton Nuclear Magnetic Resonance (\textsuperscript{1}H-NMR).** \textsuperscript{1}H-NMR was used to determine the successful synthesis of macromonomer materials (Figures S.2 and S.3). \textsuperscript{1}H-NMR spectroscopy was performed using a Bruker Advance 500 MHz NMR spectrometer with CDCl\textsubscript{3} as a solvent.

**GPC and MALS.** GPC was performed using an Agilent Technologies 1260 Infinity series system with two \( 5 \) \( \mu \)m mixed-D columns, a \( 5 \) \( \mu \)m guard column, a PL Gel \( 5 \) \( \mu \)m analytical Mixed-D column, and an RI detector (HP1047A); dried tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 mL/min; polystyrene standards were used for the calibration. The dispersities (\( D \)) and molecular weights (\( M_n \)) of each macromonomer and crosslinker were measured using THF-GPC (Figures S.1 and S.4). MALS was performed in THF + 1 vol \% triethylamine (TEA) using two Polymer Laboratories 10 \( \mu \)m mixed-B LS columns connected in series with a Wyatt Technologies DAWN EOS MALLS detector and an RI detector at a flow rate of 1.0 mL/min. MALS was used to determine the \( M_n \)s of synthesized bottlebrushes, with an eluent of THF and 1\% TEA.

**Indentation with a Texture Analyzer.** Force/displacement data were collected using a TA.XT Plus Texture Analyzer from Texture Technologies. Networks were indented with a 2 mm diameter probe at a loading rate of 0.01 mm/s to a force of 20 mN, whereupon the probe was retracted at an unloading rate of 0.01 mm/s. The probe was cleaned with acetone between runs. Force/displacement data were analyzed using eq 1

\[
E_o = \frac{3}{8a} \frac{\Delta P}{\Delta \delta}\left( 1 + 1.33 \frac{a}{h} + 1.33 \left( \frac{a}{h} \right)^2 \right)^{-1}
\]

where \( E_o \) is the apparent elastic modulus, \( P \) is the load applied, \( a \) is the radius of the indentation probe, \( \delta \) is the displacement of the probe, and \( h \) is the thickness of the sample. An example force/displacement curve is available as Figure S.5. A Poisson’s ratio of 0.5 is assumed for these calculations.

**Dynamic Mechanical Analysis (DMA).** Networks were cut into either 8 or 13 mm circles with a circular punch and placed within the compression clamps of a Discovery DMA 850 from TA Instruments. Samples were tested at room temperature, sweeping a frequency range of 0.1–100 Hz at an amplitude of 1% with a preload force of 0.1 N. The sample stage was cleaned with isopropyl alcohol between samples.

**RESULTS AND DISCUSSION**

**Bottlebrush Elastomer Synthesis.** Norbornene-functionalized PDMS macromonomers were polymerized using ROMP utilizing Grubb’s second-generation catalyst, while methacrylate-functionalized PDMS macromonomers were polymerized using photo-initiated FRP (Scheme 1). The length of the side chains in both cases was \( n_s = 14 \), similar to the side chains used in a number of previous publications.\textsuperscript{4,6,7,12,15,46,47} The degree of polymerization between crosslinks (\( n_c \)) was altered to produce BBEs of varied modulus with gel fractions greater than 85% (Figure S.6). While the length of the PDMS crosslinker was varied for FRP samples, indentation showed that the length of the crosslinker had no effect on network modulus (Figure S.7). The BBE schematics in Scheme 1 are drawn to scale for representative \( n_c = 10 \) elastomers formed from ROMP and FRP. Special care was taken to consider the end-to-end distance of the side chains (<\( R_{sc} \)), the end-to-end distance of network strands (<\( R_{sc} \)), differences in monomer volume, and the effective Kuhn length of each system. Details on the calculation of these parameters can be found in the SI. Consideration of <\( R_{sc} \)> is especially interesting, as it provides information beyond “\( n_s = 10 \)” to conceptualize the physical differences between our ROMP and FRP networks (3.06 nm and 2.78 nm, respectively) and has not been reported elsewhere.

**Bottlebrush Elastomer Modulus.** Following extraction of unretracted macromonomer, the quasi-elastic apparent modulus (\( E_o \)) of the ROMP and FRP samples was determined via indentation using a texture analyzer (Figure 3). As expected of elastomeric materials, both ROMP and FRP samples displayed a direct, linear relationship between \( n_s^{-1} \) and \( E_o \).\textsuperscript{4,5,10,48} Samples produced via FRP were stiffer at low \( n_s \) values than analogous ROMP samples but also declined in \( E_o \) more sharply than ROMP samples as \( n_s \) increased. Notably, ROMP samples were able to access a region of high-\( n_s \) materials that FRP samples were not, with an \( n_s \) of 333 achieved for ROMP samples, while FRP samples were unable to reach an \( n_s \) of 50.

While previous studies by Sheiko and co-workers indicated that FRP samples should be capable of reaching \( n_s \) values of 600, we found that our samples became too weak to manipulate after \( n_s = 34 \).\textsuperscript{4,47} Furthermore, our FRP samples were able to achieve an \( E_o \) ~ 30 kPa at \( n_s = 34 \), a value not reached until \( n_s = 67 \) in Sheiko and co-workers’ studies.\textsuperscript{4,47} It should be noted that Sheiko and co-workers’ BBEs were polymerized using solvent while our FRP was performed solventless. For ROMP, our \( n_s = 333 \) sample had an \( E_o \) of 4.4 kPa, comparable to an \( n_s = 400 \) sample produced by Sheiko and co-workers (2.9 kPa), illustrating the potential of ROMP samples to become even softer than FRP samples at higher \( n_s \) values (ROMP BBEs can be made at \( n_s = 1000 \) with an \( E_o \) ~ 1 kPa, not shown here).
Modeling Elastic Modulus. To effectively compare the quasi-elastic modulus ($E_o$) of our BBEs to that of ideal BBEs, it was first essential to prepare a graft-copolymer phase diagram and determine whether our materials belonged to the comb, rodlike side chain (RSC), stretched backbone (SBB), or stretched side chain (SSC) regimes. While we use the nomenclature described by Dobrynin et al. in this study, it should be noted that other nomenclatures do exist. The regime that graft-copolymers belong to dictates how the crowding of side chains along the backbone affects the rigidity of the polymer, specifically the Kuhn length. The largest factors contributing to which regime bottlebrushes belong to are grafting density ($n_g$), side chain length ($n_{sc}$), and backbone/side-chain monomer volumes ($v_b$ and $v_s$). Table 1 collects all of the necessary values to form graft-copolymer phase diagrams for our systems.

Using these parameters, two graft-copolymer phase diagrams were constructed for PNB-g-PDMS and PMMA-g-PDMS (Figure S.8), indicating that our ROMP and FRP samples belong to the SBB and SSC regimes, respectively. Given that norbornene has a larger $v_b$ than methyl methacrylate ($0.20$ vs $0.15 \text{ nm}^3$), it is unsurprising that PNB-g-PDMS bottlebrushes belong to a less extended regime than PMMA-g-PDMS bottlebrushes. The flexibility of these systems is reflected in their effective Kuhn lengths of $b_k = 2.15$ and $2.80 \text{ nm}$ for PNB-g-PDMS and PMMA-g-PDMS graft-copolymer bottlebrushes, respectively.

Following the SBB and SSC regime classifications, the elastic modulus ($E_o$) of the ROMP and FRP systems were modeled using Dobrynin and co-workers’ adaptation of the affine model for the elasticity of BBEs:

$$E_o = 3\kappa_b T \beta \alpha^{-1} \rho_s$$

(2)

where $\kappa_b$ is the Boltzmann constant, $T$ is the absolute temperature, $\beta$ is the strand-extension ratio, $\alpha$ is the strand stiffness, $\rho_s$ is the number density of stress-supporting strands, and the scaling constant $C = 1$. For an affine bottlebrush network, the theoretical number density of stress-supporting strands is:

$$\rho_s = \rho \Phi (n_{bb}^{-1} - 2n_{bb}^{-1})$$

(3)

where $\rho$ is the monomer number density, $n_{bb}$ is the degree of polymerization of the bottlebrush backbone, and $\Phi$ is the volume fraction of backbone monomers. Though we required an affine model to model ideal BBEs, it should be noted that the elastic moduli of BBEs are better described by a phantom network model (Figure S.10).

Structural Efficiency Ratio. Analysis of eq 2 and 3 indicates that we can compare the measured elastic modulus to the physical and chemical properties of the network.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Plots of $n_s^{-1}$ against $E_o\alpha(3/\rho_{\Phi} \kappa_b T)^{-1}$ for our (a) ROMP and (b) FRP samples (refer to Figure S.11 for a plot of Sheiko et al.’s FRP samples), the slope of each line providing the value for the SER. (c) Collection of the SERs for our ROMP and FRP systems as well as Sheiko and co-workers’ samples from ref 4. Note that our FRP was solventless and Sheiko and co-workers’ FRP was performed in $p$-xylene. The $E_o$ values used for Sheiko et al.’s FRP samples were obtained using eq S.1 and are tabulated in Table S.1.
components. The experimentally determined number density of stress-supporting strands ($\rho_s^*$) will be lower than that predicted by the affine model ($\rho_s$) because not all monomers are part of stress-supporting strands, a typical scenario for viscoelastic systems. To estimate the degree of network defects, we introduce the concept of the structural efficiency ratio (SER = $\rho_s^*/\rho_s$), a comparison between the number density of stress-supporting strands in an experimental network ($\rho_s^*$) to that of an affine model network ($\rho_s$).

Due to the presence of molecular defects in our BBEs (or any network), it stands to reason that values of $\rho_s^*$ for our systems will be lower than the values of $\rho_s$ for the most perfect, ideal cases. To quantify the differences between $\rho_s^*$ and $\rho_s$, we divide both sides of eq 2 by $\rho_s$ and plot the known parameters of our network against one another as defined in eq 4:

$$\frac{\alpha E_0}{3\beta \rho_s^* k_B T} = \frac{\rho_s^*}{\rho_s} \frac{1}{n_B} - B_0$$

where $B_0$ is a numerical constant defined by the line's y-intercept. To calculate the normalized y-axis, we use the monomer number density calculated by inverting the volume of a monomer, e.g., norbornene carboxylic acid, with a monomer volume of 0.20 nm$^3$ and a monomer number density of 1/0.20 nm$^3 = 5.00$ nm$^{-3}$. The calculation of $\alpha$, $\beta$, and $\gamma$ are detailed by eqs S.6–S.12.

The slopes of the lines within Figure 4a,b represent the ratio $\rho_s^*/\rho_s$ for our ROMP and FRP samples and are tabulated in Figure 4c along with the corresponding value for Sheiko, et al.'s FRP samples. The SER provides insight into the efficiency of a given chemistry at forming stress-supporting strands, namely, the percentage of strands within a cubic nanometer that are stress-supporting (relative to the affine case). A physical interpretation of $\rho_s^*/\rho_s$ is illustrated in Figure 5, where red strands represent stress-supporting strands and black strands represent strands that should be stress-supporting but are not due to molecular defects introduced to the network by the chemistry.

This ratio is useful when comparing the efficiency of BBEs polymerized under different conditions. For example, we would predict that Sheiko and co-workers' low-SER FRP samples ($\rho_s^*/\rho_s \approx 0.26$) have fewer stress-supporting strands, more network defects, and lower $E_o$ than our higher-SER FRP samples ($\rho_s^*/\rho_s \approx 0.57$). Recalling that Sheiko and co-workers' system was polymerized in solvent, this observation is particularly interesting because it suggests that the presence of solvent has a large effect on the number of stress-supporting strands formed within the FRP networks. Indeed, experimentation with the conditions of our FRP led to samples that decreased in $E_o$ as the weight percent of p-xylene increased (Figure 6). For example, the addition of solvent to the polymerization of an $n_c = 14$ BBE decreased $E_o$ from $\sim$114 kPa to $\sim$45 kPa.

These results led us to conclude that the use of solvent in FRP allows for a lower SER and therefore fewer stress-supporting strands within each cubic nanometer of the BBEs. Furthermore, both Sheiko et al.'s BBEs and our ROMP BBEs were polymerized with solvent and are also capable of producing samples with much lower crosslink densities than our solventless FRP system ($n_c > 333$ vs $n_c < 40$). This further implies that when the concentration of crosslinker is low, the presence of solvent is advantageous, allowing for crosslinkers to be used “more efficiently” than within a solventless system.

Additionally, based on the values of $\rho_s^*/\rho_s$ extracted from the model (Figure 4c), the efficiency of the ROMP chemistry ($\rho_s^*/\rho_s \approx 0.14$) at producing stress-supporting strands is considerably lower than that of our FRP system ($\rho_s^*/\rho_s \approx 0.57$). This implies that the large differences in elastic moduli seen at lower $n_c$ values (higher crosslink densities) in Figure 3 are a result of the crosslinking becoming less efficient as the concentration of crosslinker is increased relative to the macromonomer. It is likely that the probability of successive crosslinkers being added to the “living” chain increases as the amount of crosslinker increases, resulting in networks where the number of stress-supporting strands is lower due to the increased number of ineffective crosslinks distributed throughout the network of the ROMP samples.

With this insight into network topology, it follows that the ROMP samples would have a larger number of molecular defects than the FRP samples and therefore would likely have a greater viscous component to their moduli (at low frequencies). Through dynamic mechanical analysis (DMA) of our systems (Figure 7), we show that this observation is true, with ROMP samples always having higher loss moduli (Figure 7a,b) and loss tangents (Figure 7c) than similarly crosslinked FRP samples at low frequencies. The magnitude of the complex moduli (Figure 7d) for each of the BBEs follows the same trends depicted in Figure 3, showing how the ROMP samples are softer than FRP samples with
analogous amounts of crosslinker due to the increased number of molecular defects.

**CONCLUSIONS**

Herein, the efficiencies of the ROMP and FRP chemistries at producing stress-supporting strands are evaluated through the use of Dobrynin et al.’s affine model for BBE modulus. To facilitate this comparison, we introduce the concept of the structural efficiency ratio (SER = \( \rho_s^*/\rho_s \)), a comparison of the number density of stress-supporting strands in a real BBE (\( \rho_s^* \)) to the expected number density of stress-supporting strands for an affine system (\( \rho_s \)). This SER provides a quantitative measure of the relative number of molecular defects within each sample set, revealing that the ROMP chemistry produces stress-supporting strands much less efficiently than the FRP chemistry. The SER was additionally demonstrated to correctly predict (1) that the addition of solvent to FRP results in samples with lower \( E_o \) and (2) that ROMP samples had both higher loss moduli and loss tangents than similarly crosslinked FRP samples. This analysis using \( \rho_s^*/\rho_s \) provides a unique and simple method by which it is possible to use chemistry as another “knob” to design materials using only theoretical information and knowledge of the elastic modulus.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01332.

Synthesis, Mechanical Characterization, and Model (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Mark Ilton — Department of Physics, Harvey Mudd College, Claremont, California 91711, United States; Email: milton@g.hmc.edu

James J. Watkins — Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States; orcid.org/0000-0001-8302-825X; Email: watkins@polysci.umass.edu

Alfred J. Crosby — Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States; Email: crosby@mail.pse.umass.edu

Gregory N. Tew — Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States; orcid.org/0000-0003-3277-7925; Email: tew@mail.pse.umass.edu

Figure 7. Dynamic mechanical analysis (DMA) of several ROMP and FRP samples. \( E^* \) and \( \tan(\delta) \) refer to the complex modulus and loss tangent respectively. The storage and loss moduli (\( E' \) and \( E'' \), respectively) of the ROMP (a) and FRP (b) samples illustrate how the magnitude of the loss moduli for ROMP samples is higher than that of similarly crosslinked FRP samples in the low-frequency regime (0.1 – 1 Hz). The loss tangents of the ROMP samples (c) are greater than that of the FRP samples within the low-frequency regime (as outlined by the blue box), indicating that the loss modulus has a higher contribution to the \( E^* \) in ROMP samples. This contribution can be seen in (d) a direct comparison between the \( E^* \) of the ROMP and FRP samples, where the ROMP samples always have lower \( E^* \) than analogously crosslinked FRP samples.
Authors
Brandon R. Clarke — Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States
Hyemin Kim — Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.2c01332

Author Contributions
$B.R.C.$ and H.K. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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