Dynamics of Bottlebrush Networks

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ABSTRACT: The deformation dynamics of bottlebrush networks in a melt state is studied using a combination of theoretical, computational, and experimental techniques. Three main molecular relaxation processes are identified in these systems: (i) relaxation of the side chains, (ii) relaxation of the bottlebrush backbone on length scales shorter than the bottlebrush Kuhn length \( b_\text{K} \), and (iii) relaxation of the bottlebrush network strands between cross-links. The relaxation of side chains having a degree of polymerization (DP) \( n_\text{sc} \) dominates the network dynamics on the time scales \( \tau_\text{sc} < t \leq \tau_\text{c} \), where \( \tau_\text{sc} \approx \tau_\text{K}(n_\text{sc} + 1)^{1/2} \) are the characteristic relaxation times of monomeric units and side chains, respectively. In this time interval, the shear modulus at small deformations decays with time as \( G_\text{BB}(t) \sim t^{-1/2} \). On time scales \( t > \tau_\text{c} \), bottlebrush elastomers behave as networks of filaments with a shear modulus \( G_\text{BB}(t) \sim (n_\text{sc} + 1)^{-1/2}t^{-1/2} \). Finally, the response of the bottlebrush networks becomes time independent at times scales longer than the Rouse time of the bottlebrush network strands, \( \tau_\text{R} \approx \tau_\text{K}n^2(n_\text{sc} + 1)^{3/2} \), where \( N \) is DP of the bottlebrush backbone between cross-links. In this time interval, the network shear modulus depends on the network molecular parameters as \( G_\text{BB}(t) \sim (n_\text{sc} + 1)^{-1}N^{-1} \). Analysis of the simulation data shows that the stress evolution in the bottlebrush networks during constant strain-rate deformation can be described by a universal function. The developed scaling model is consistent with the dynamic response of a series of poly(dimethylsiloxane) bottlebrush networks \( (n_\text{sc} = 14 \text{ and } N = 50, 70, 100, 200) \) measured experimentally.

INTRODUCTION

Bottlebrush macromolecules\(^1\)\textendash}\(^{12}\) can be viewed as filaments where polymer side chains play a dual role of diluent and rigidity mediator of the backbone.\(^1\)\textendash}\(^10\),\(^13\)\textendash}\(^20\) Their unique combination of large diameter and high flexibility results in disentanglement of bottlebrush melts manifested in a corresponding decrease of the entanglement plateau modulus.\(^1\)\textendash}\(^11\),\(^21\)\textendash}\(^24\) This intrinsic disentanglement allows for the synthesis of the superrigid, superelastic solvent-free elastomers with shear modulus down to \( \approx 100 \text{ Pa} \) and tensile strains at break up to 800% in a solvent free state.\(^1\)

Along with the degree of polymerization (DP) of the backbone between cross-links \( (N) \), mechanical properties of disentangled bottlebrush networks are determined by two independently controlled parameters: DP of side chains \( (n_\text{sc}) \) and DP of the spacer between the neighboring side chains \( (n_\text{ff}) \). The ratio of \( n_\text{sc}/n_\text{ff} \) controls the molar fraction of the backbone in the network (dilution of the backbone) and the rigidity (Kuhn length) of bottlebrush filaments with diameter \( D_\text{sc} \). For bottlebrush networks with \( n_\text{ff} = 1 \), when the strands between cross-links are longer than bottlebrush Kuhn length \( b_\text{K} \approx D_\text{sc} \approx n_\text{sc}/1, \), the bottlebrush network can be viewed as networks of flexible filaments.\(^26\)\textendash}\(^28\) In this so-called backbone dilution regime, the equilibrium shear modulus of a bottlebrush network at small deformations decreases with increasing the side chain and backbone DPs of a network strand as \( G_\text{BB} \approx [N(n_\text{ff} + 1)]^{-1} \).\(^25\) This scaling behavior continues until the contour length of a bottlebrush strand becomes smaller than its Kuhn length \( b_\text{K} \). For systems with shorter strands, the network’s elasticity is controlled by the bending modes of the bottlebrush macromolecules on the length scales smaller than \( b_\text{K} \). The properties of such networks are similar to those of semiflexible filaments\(^29\)\textendash}\(^32\) and demonstrate a weaker dependence of the shear modulus on the side chain DP as \( G_\text{BB} \sim n_\text{sc}^{-0.5} \).\(^25\) Therefore, by changing \( n_\text{sc} \) (at the same \( N \)), we can access different network deformation regimes in chemically identical polymeric networks.

Although the description of equilibrium properties of bottlebrush networks is relatively straightforward, the behavior at short and intermediate length and time scales remains unclear. In this regard, it is important to realize that bottlebrush macromolecules represent a hierarchical multiscale system capable of demonstrating both molecular and particulate (filament-like) features (Figure 1). On length scales of a single side chain, the system can be viewed as a melt of linear chains,\(^33\) while on the longer length scales, bottlebrushes behave as thick filaments. However, unlike the biological filaments,\(^29\) bottlebrush macromolecules in a melt are significantly more flexible with the effective Kuhn length being proportional to their diameter \( b_\text{K} \approx D_\text{sc} \). While our understanding of this dual nature...
of bottlebrushes is beginning to emerge\textsuperscript{1,11,21,22,34} its role in network dynamics and viscoelastic properties, which is vital for many applications including implants, membranes, and actuators, is still unclear. In this paper, we use a combination of the scaling analysis, computer simulations, and experimental studies to elucidate factors controlling the dynamic response of bottlebrush networks on different time and length scales. Particularly, we are interested in the crossover between the chain-like and filament-like regimes. We identify two Rouse-like relaxation regimes\textsuperscript{33,35} of bottlebrush network dynamics. In the first regime, at time scales shorter than the Rouse time of the side chains, the relaxation of the bottlebrush network is similar to the melt of side chains. At longer times confined between the Rouse times of the side chains and the bottlebrush strands between cross-links, the relaxation behavior of the bottlebrush network displays a second Rouse-like regime similar to relaxation of filaments with thicknesses determined by the bottlebrush diameter and with a transition zone in between. Finally, at time intervals longer than the Rouse time of bottlebrush strands between cross-links the network displays a purely elastic response. The rest of the paper is organized as follows: we first present a scaling analysis of the bottlebrush network dynamics, the scaling model predictions are compared with results of the molecular dynamics simulations of uniaxial deformation of bottlebrush networks at different deformation rates, and finally we present results of the experimental studies of the poly(dimethylsiloxane) (PDMS) bottlebrush networks to confirm the network relaxation picture observed in molecular dynamics simulations and predicted by the scaling approach.

\section*{RESULTS AND DISCUSSION}

\subsection*{Scaling Analysis of Network’s Dynamics. Linear Chain Networks.} We begin our discussion with a brief overview of the Rouse dynamics of linear chain networks\textsuperscript{33,36–39} cross-linked in a melt state. We consider a monodisperse polymeric networks with DP between cross-links, \(N_{t}<N_{c}\) shorter than the corresponding DP of entanglement strand\textsuperscript{33,40} \(N_{e}(N<N_{c})\). In the framework of the scaling model of polymeric networks, on the time scales \(t\) smaller than the strands’ Rouse time, \(t_{R}\approx\tau_{0}N^{2}\) (\(\tau_{0}\) is characteristic monomer relaxation time), the dynamics of the network strands is considered to be identical to those in a melt of polymer chains with the same DP.\textsuperscript{33,40} At such time scales, the chain’s dynamics is not influenced by cross-links and network relaxation occurs through relaxation of short sections of the network strands with the number of monomers, \(g(t)<N_{t}\), whose Rouse time, \(\tau_{g}(t)^{2}\), is on the order of time \(t\) (see Figure 2a). The number density of such strands in a melt with monomer number density \(\rho\) is equal to \(\rho / g(t)\approx \rho (\tau_{g}(t))/2\). Each strand contributes on the order of thermal energy \(k_{B}T\) (\(k_{B}\) is the Boltzmann constant and \(T\) is the absolute temperature) to the network modulus. Therefore, modulus at small deformations decays with time as

\begin{equation}
G_{0}(t)\approx \rho k_{B}T\left(\frac{\tau_{0}}{t}\right)^{1/2}, \quad \text{for } \tau_{0}<t<\tau_{R}
\end{equation}

However, at time scales longer than the Rouse time of polymeric strands, \(t>\tau_{R}\approx\tau_{0}N^{2}\), the network response is purely elastic with a constant shear modulus\textsuperscript{26}

\begin{equation}
G_{0}(t)\approx \rho k_{B}T/N_{t}, \quad \text{for } \tau_{R}<t
\end{equation}

In Figure 3, we summarized different relaxation regimes of networks of linear chains in accordance with eqs 1 and 2.

\subsection*{Bottlebrush Networks.} As mentioned in the Introduction, molecular bottlebrushes can be viewed as filaments with a brush interior structure (see Figures 2b,c).\textsuperscript{35} Therefore, assuming sufficient separation of the time scales and sufficiently large molecular dimensions, we consider three main relaxation processes in bottlebrush networks: (i) relaxation of the side chains (see Figure 2b), (ii) relaxation of the bottlebrush backbone on length scales shorter than the bottlebrush Kuhn length, \(b_{K}\), and (iii) relaxation of an entire bottlebrush filament between cross-links (see Figure 2c). Below we develop a scaling model incorporating these relaxation processes to describe dynamics of bottlebrush networks on different time and length scales. We will illustrate this approach on bottlebrush networks with \(Nb\gg b_{K}\), where \(b\) is the bond length assumed to be the same for backbone and side chains.

The side chains undergo the fastest relaxation. Here we consider a case when each bottlebrush backbone monomer has one side chain attached to it \((n_{e}=1)\). Assuming that the side chains relax as in an isotropic melt, the backbone dynamics is controlled by a small deformation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Simulation snapshots of hierarchical structure of bottlebrush macromolecules illustrating different length scales: bottlebrush network (a), single bottlebrush macromolecule with bottlebrush backbone shown in green and side chains colored in blue (b), and bottlebrush chain segment (c).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Schematic representation of different Rouse modes of network strand relaxation: (a) segments of linear chain made of blobs with number of monomers \(g(t)\), (b) side chain of a bottlebrush macromolecule considered as being made of blobs with \(g_{sc}(t)\) monomers, and (c) blob structure of the bottlebrush backbone with each blob having \(g_{BB}(t)\) backbone monomers. Cross-links are shown by green squares.}
\end{figure}
chains relax independently and are unaware of their connectivity to the backbone, we can write the following expression for the time-dependent modulus of the relaxation time of this longest bending mode as

\[ G(t) = \frac{\rho k_B T}{\xi^2 b \rho_n T} \left( \frac{\tau_0}{t} \right)^{1/2}, \]

where \( \tau_0 \approx (n_c + 1)^2 / 2 \) is the Rouse time of the side chain, and \( \xi \approx (n_c + 1)^2 / 2 \) is the Rouse time of the backbone monomer to which the side chain is attached. Note that at time scales \( t \approx \tau_0 \), the network modulus decreases by a factor of \( (n_c + 1)^{-1} \) (see Figure 3).

At longer time scales, \( \tau_0 \approx \tau_c \) the network modulus decreases by a factor of \( (n_c + 1)^{-1} \) (see Figure 3).

At time scales \( t \approx \tau_k \), we can consider bottlebrushes as linear chains made of Kuhn monomers with effective monomer relaxation time, \( \tau_k \). By applying the Rouse model to a melt of chains of Kuhn monomers \( g(t) \), we obtain

\[ G(t) \approx \frac{\rho k_B T}{\xi^2 b \rho_n T} \left( \frac{\tau_0}{t} \right)^{1/2}, \]

where \( \tau_k \approx \rho/(n_c + 1)^{-1/2} \) is the number density of the effective Kuhn monomers each containing \( (D/\rho)^{1/2} \) chemical monomeric units. Correspondingly, the characteristic Rouse relaxation time of the bottlebrush network strand can be written as

\[ \tau_k \approx \frac{N b}{b_k} \approx \frac{(n_c + 1)^{3/2}}{2} N^2. \]

It is interesting to point out that the expression for the modulus \( G(t) \) in this regime is identical to eq 5. Finally, for \( t \ll \tau_k \) the response of the bottlebrush networks is time independent with modulus

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dynamics simulations\textsuperscript{31,42} of bottlebrush networks undergoing uniaxial deformation\textsuperscript{43,44} at a constant strain rate, \(\dot{\varepsilon}\). Bottlebrush macromolecules are modeled as bead–spring chains composed of beads with diameter \(\sigma\) interacting through truncated shifted Lennard-Jones (LJ) potential.\textsuperscript{45} The connectivity of monomers into bottlebrush macromolecules is maintained by the combination of the FENE and truncated shifted LJ potentials. In our simulations, each monomer belonging to the bottlebrush backbone has a side chain attached to it. The number of monomers belonging to the side chains, \(n_{\text{sc}}\), is varied between 0 and 20. The bottlebrush macromolecules are randomly cross-linked by the same bonds as the ones connecting monomers into bottlebrush macromolecules (see ref 25 and Supporting Information for simulation details). The relaxed bottlebrush networks with monomer number density 0.8 \(\sigma^{-3}\) are uniaxially deformed at a constant volume and a strain rate \(\dot{\varepsilon}\) varying between \(10^{-7}\) and \(10^{-3}\) \(\tau_{\text{LJ}}^{-1}\), where \(\tau_{\text{LJ}}\) is the standard Lennard-Jones time. In the simulated bottlebrush networks, the number-average degree of polymerization between cross-links (\(N\)) is varied between 17.2 and 19.7 for a FENE potential spring constant equal to 30 \(k_B T/\sigma^2\), and 15.7 to 16.7 for a FENE potential spring constant equal to 50 \(k_B T/\sigma^2\) (see Supporting Information for details).

Figure 4 summarizes our results for true stress dependence on the strain at different strain rates varying between \(10^{-7}\) and \(10^{-3}\) \(\tau_{\text{LJ}}^{-1}\). According to the Boltzmann superposition principle,\textsuperscript{46,47} stress evolution in polymeric networks undergoing small uniaxial elongation at a constant strain rate \(\dot{\varepsilon}\) is

\[
\sigma_{\text{eq}}(t) = \int_0^t E_0(t - t') \, d\varepsilon(t') = \dot{\varepsilon} \int_0^t E_0(\Delta t) \, d\Delta t \quad (9)
\]

where \(E_0(t)\) is a time-dependent Young’s modulus measured at small deformations (\(\varepsilon \to 0\)). Note that \(E_0(t) = 3G_0(t)\) for incompressible networks with Poisson ratio equal to 0.5.\textsuperscript{47} Using the stress relaxation shear modulus for linear chains given by eqs 1 and 2, integration of eq 9 results in

\[
\sigma_{\text{eq}}(t) \approx 2E_0^L \dot{\varepsilon} R_1^{1/2} t^{1/2}, \quad \text{for } t < t_R \quad (10)
\]

where \(E_0^L = 3G_0^L \approx 3\rho k_B T/N\) is the Young’s modulus of network of linear chains at small deformations. For networks undergoing uniaxial deformation at a constant strain rate, we can substitute \(t = \varepsilon/\dot{\varepsilon}\) into eq 10 to express \(\sigma_{\text{eq}}(t)\) as a function of strain \(\varepsilon\)

\[
\sigma_{\text{eq}}(\varepsilon) \approx 2E_0^L \dot{\varepsilon} R_1^{1/2} \varepsilon^{1/2}, \quad \text{for } t < t_R \quad (11)
\]

In the opposite limit, \(t > t_R\)

\[
\sigma_{\text{eq}}(\varepsilon) \approx 2E_0^L \dot{\varepsilon} R_1 + E_0^L \dot{\varepsilon}(t - t_R) \approx E_0^L \dot{\varepsilon}, \quad \text{for } t \geq t_R \quad (12)
\]

Equation 11 suggests nonlinear behavior of the network shear modulus at high strain rates, which is verified by stress–strain curves of both linear chain (see Figure 4a) and bottlebrush networks (see Figure 4b–d). (The log–log version of this plot is shown in the Supporting Information to highlight curves overlap.) This indicates that such deformation rates probe chain dynamics at the time scales shorter than the Rouse time. Overlap of the stress–strain curves obtained at slow strain rates suggests that at such deformations the system response is both purely elastic and rate (time) independent in accordance with eq 12. Note that the stress–strain behaviors of the linear chain and bottlebrush systems are qualitatively similar, with the only difference being the crossover values of the strain rates and values of the equilibrium (rate independent) Young’s modulus. This similarity is consistent with Figure 3, which displays the relaxation moduli of linear and bottlebrush networks as shifted parallel lines both having a slope of −0.5. Since time dependent stress \(\sigma_{\text{eq}}(t)\) is an integral characteristic of the modulus (see eq 9), this shift is further smoothed by the integration.
where we introduce \( E_\text{m} = 3\rho k_BT \). Note that for monodisperse bottlebrush networks with \( Nb \gg b_K \) the value of the Young’s modulus at small deformations is \( E_\text{m}^{\text{BB}} \approx E_\text{m}/(N(n_{sc} + 1)) \).

However, real networks are polydisperse which results in a distribution of the Rouse times for individual network strands between cross-links such that crossover from the melt-like relaxation of strands to network relaxation regime depends on the number-average degree of polymerization between cross-links. In these networks, the Kuhn length of the bottlebrush strands is on the order of the distance between cross-links. Therefore, small deformations begin to deviate due to nonlinear deformation of the bottlebrush strands between cross-links. In these networks, the Kuhn length of the bottlebrush strands is on the order of the distance between cross-links. Therefore, small deformations begin to deviate due to nonlinear deformation of the network as a fitting parameter.

Thus, the stress evolution in a polydisperse network of linear chains undergoing uniaxial constant rate deformations depends on the Rouse relaxation time of an average strand between cross-links such that crossover from the melt-like relaxation of strands to network relaxation regime depends on the Kuhn length of the bottlebrush backbone by its average value \( \langle N \rangle \) in the corresponding expressions for the Young’s modulus and backbone Rouse time as \( E_\text{m}^{\text{BB}} \approx E_\text{m}/(N(n_{sc} + 1)) \) and \( \tilde{\tau}_\text{BB} \approx \tau_0(n_{sc} + 1)^{3/2}\langle N \rangle^2 \), respectively. Below we will apply eq 14 to analyze data shown in Figure 4 for linear chains and those for bottlebrush networks.

In Figure 5, we replot the stress–strain data from Figure 4 using universal coordinates in accordance with eq 14. For this plot, we have used data sets with \( 0.05 < \varepsilon < 0.8 \) and excluded data with \( \varepsilon < 0.05 \) that show large stress fluctuations. The solid lines in Figures 5 correspond to the best fit of the small deformation data with eq 14, using the Rouse time as a fitting parameter and the modulus obtained from equilibrium network deformation simulations.26 There is a very good agreement between simulation data and eq 14. For our longest side chains \( n_{sc} = 20 \), the simulation data first follow the universal line then begin to deviate due to nonlinear deformation of the bottlebrush backbone.

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Thus, the stress evolution in a polydisperse network of linear chains undergoing uniaxial constant rate deformations depends on the Kuhn length of the bottlebrush backbone by its average value \( \langle N \rangle \) in the corresponding expressions for the Young’s modulus and backbone Rouse time as \( E_\text{m}^{\text{BB}} \approx E_\text{m}/(N(n_{sc} + 1)) \) and \( \tilde{\tau}_\text{BB} \approx \tau_0(n_{sc} + 1)^{3/2}\langle N \rangle^2 \), respectively. Below we will apply eq 14 to analyze data shown in Figure 4 for linear chains and those for bottlebrush networks.

In Figure 5, we replot the stress–strain data from Figure 4 using universal coordinates in accordance with eq 14. For this plot, we have used data sets with \( 0.05 < \varepsilon < 0.8 \) and excluded data with \( \varepsilon < 0.05 \) that show large stress fluctuations. The solid lines in Figures 5 correspond to the best fit of the small deformation data with eq 14, using the Rouse time as a fitting parameter and the modulus obtained from equilibrium network deformation simulations.26 There is a very good agreement between simulation data and eq 14. For our longest side chains \( n_{sc} = 20 \), the simulation data first follow the universal line then begin to deviate due to nonlinear deformation of the bottlebrush backbone.
we use the values of the Rouse times obtained from fitting simulation data with eq 14 to collapse all our simulation curves in linear network deformation regime with $0.05 < \varepsilon < 0.3$ into one universal plot as shown in Figure 6.

The corresponding values of the Rouse time obtained from the fit of the deformation of different bottlebrush networks are shown in Figure 7 as a function of the parameter $\tau_0(n_c + 1)^{3/2}/N^2$. (The value $\tau_0$ for this plot was estimated from monomer mean-square displacement.) The linear scaling of the Rouse time with this parameter confirms the scaling relation given by eq 7 for the Rouse model of bottlebrush strand. Such bottlebrush networks can be considered as networks of flexible filaments. Deviation from the linear scaling is an indication of crossover into the regime when bottlebrush strands between cross-links behave as semiflexible filaments, i.e., $\langle N \rangle < \sqrt{(n_c + 1)}$. For such networks, the longest relaxation time scales with the system parameters as $\tau_{BB} \approx \tau_0(\langle N \rangle/n_c + 1)^{3/2}$. This behavior is in agreement with our simulations of the static properties of the bottlebrush network, which demonstrate two different dependencies of the network shear modulus.25

**Experimental Studies of Dynamics of Bottlebrush Networks.** The trends seen in Figures 3 and 6 are corroborated through a series of mechanical tests of covalently cross-linked poly(dimethylsiloxane) (PDMS) bottlebrush elastomers (see the Supporting Information for details on synthesis, characterization and mechanical measurements of bottlebrush networks). The first test was a series of uniaxial extensions at different strain rates of a PDMS bottlebrush elastomer ($n_c = 14, n_g = 1, N = 200$, Poisson’s ratio $\approx 0.5$), where $n_c$ is chemical DP of the side chain, $n_g$ is number of chemical backbone monomers per side chain, and $N$ is chemical DP of the backbone between cross-links as determined through stoichiometry.1 Figure 8 displays a normalized stress $\sigma_{ax}/\dot{\varepsilon}$ versus $\varepsilon/\dot{\varepsilon}$ master curve, which was constructed by combining the multiple sets of the stress/strain curves recorded at different strain rates. On time scales shorter than the Rouse time of the network, $\tau_{BB}$ (achieved at high strain rates), the normalized stress displays a characteristic slope of 0.5 with respect to time in accordance with eq 14. At lower rates, the sample is deformed on time scale longer than $\tau_{BB}$ and the time dependence of normalized stress increases to a power of 1. Both characteristic slopes are consistent with the computer simulation results shown in Figures 5 and 6. By fitting the experimental data with eq 14, we obtained a relaxation time of $\tau_{BB} = 0.046$ s and a bottlebrush network Young’s modulus of $E_{BB} = 6.6 \pm 0.1$ kPa. The Rouse time extracted from Figure 8 is conceptually the same as the Rouse time given by eq 7; however, eq 14 accounts for the inherent polydispersity of real networks using number-average values of $N$. 

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**Figure 6.** A master curve for bottlebrush networks undergoing uniaxial deformation at constant strain rates $\dot{\varepsilon}$. $E_0$ is the Young’s modulus at small deformations, and $\tau_R$ is the Rouse time. Simulations of the bottlebrush networks with different degrees of polymerizations of the side chains are shown by changing symbol colors: $n_c = 0$ (black), $n_c = 2$ (red), $n_c = 5$ (blue), $n_c = 10$ (purple), and $n_c = 20$ (wine); simulations with different FENE potential spring constants are shown by using different symbol shapes: 30 $k_B T/\sigma^2$ (squares) and 500 $k_B T/\sigma^2$ (circles); simulations at temperature 1.0 (filled symbols) and 3.0 (open symbols) in reduced LJ units. Dashed line is given by the equation $y = x^2/2(1 - \exp(-x))$. 

**Figure 7.** Dependence of the Rouse time of the bottlebrush network strands, $\tau_R$, obtained from fitting simulation data for time-dependent normalized true stress (see Figure 5) as a function of the estimated Rouse relaxation time of the bottlebrush network $\tau_0(n_c + 1)^{3/2}/N^2$ (eq 7) for systems with different FENE potential spring constants $k_w$ and temperatures (reduced LJ units): 30 $k_B T/\sigma^2$ and 1.0 (filled red squares); 30 $k_B T/\sigma^2$ and 3.0 (open red squares); 500 $k_B T/\sigma^2$ and 1.0 (filled blue circles); 500 $k_B T/\sigma^2$, and 3.0 (open blue circles).

**Figure 8.** Experimentally measured time dependence of the normalized tensile stress for a PDMS bottlebrush network ($N = 200$, $n_c = 14$, $n_g = 1$) subjected to uniaxial extension at constant strain rates: 0.0026 s$^{-1}$ (black squares), 0.0127 s$^{-1}$ (red circles), 0.0250 s$^{-1}$ (blue triangles), 0.1010 s$^{-1}$ (pink inverted triangles), 0.2392 s$^{-1}$ (yellow rhombus), 0.2907 s$^{-1}$ (wine left triangles), 0.6773 s$^{-1}$ (cyan right triangles), 1.1069 s$^{-1}$ (violet hexagons), 0.0127 s$^{-1}$ (orange stars), 0.0127 s$^{-1}$ (navy pentagons). Solid line corresponds to the best fit to eq 14 with $E_{BB} = 6.61$ kPa and $\tau_{BB} = 0.046$ s. Inset: schematical representation of bottlebrush network illustrating primary structural parameter ($N$, $n_{ax}$, and $n_c$) and cross-linking mechanism (black dots represent cross-linking separate backbones through mutual incorporation of short difunctional linear cross-linker).
In order to confirm the power law relaxations and transition regimes predicted in Figure 3, Figure 9 displays master curves of shear storage modulus, \( G_s \), versus the radial frequency, \( \omega \), which were measured for a series of covalently cross-linked PDMS bottlebrush elastomers with \( n_{sc} = 14 \) and \( N \) values of 200, 100, 70, and 50 estimated from stoichiometry (see Supporting Information for details). The modulus relaxation spectrum can be broken down into two distinct zones. Zone A (bottlebrush filaments) corresponds to the relaxation of filament-like strands and consists of two regimes (regime I and II). Regime I represents the time independent rubbery plateau due to chemical cross-links resulting in permanent rubbery behavior and linear chain behavior) displays a visible increase in the slope of \( G_s \) versus \( \omega \) with respect to the Rouse-like behavior (slope 0.5) of both bottlebrush filaments (regime II) and linear side chains (regime IV). This behavior is consistent with the scaling model predictions shown in Figure 3: namely, a side chain Rouse relaxation is followed by a drop in modulus and then Rouse relaxation of filamentous bottlebrush segments. However, due to the weak dependence of the drop in modulus \( (n_{sc} = 14) \) and the inherent dispersity \( (D = 1.01) \) of the side chains in the currently available bottlebrush elastomers, we are not able to resolve a clean transition between the two Rouse regimes. It would be desirable to synthesize a new set of bottlebrushes with significantly longer side chains \( (n_{sc} \approx 1000) \), but such materials would also require a simultaneous and nontrivial increase in backbone length, which represents a substantial synthetic challenge for future studies.

![Image](90x570 to 270x716)

Figure 9. Master curves of the storage modulus of PDMS bottlebrush networks \((n_{sc} = 14, N = 1)\) with four different degrees of polymerizations between cross-links \( N = 200 \) (green), 100 (red), 70 (blue), and 50 (black). The curves display five relaxation regimes: I, the elastic network plateau; II, the Rouse-like relaxation of bottlebrush segments and transition to elastic plateau. The Rouse-like zones are marked by the series of light blue lines with slopes of 0.5: III, the transition between filament-like (regime I and II) and linear chain (regimes IV and V) behaviors; IV, Rouse-like regime of linear side chains represented by the orange line in regime IV in Figure 9), followed by the glass transition zone universal to neat polymer materials (regime V). A shoulder-like feature can be seen in regime IV where the frequency dependence of modulus becomes weaker than the Rouse one, \( G_s \sim \omega^{0.5} \), and the storage modulus dominates over the loss modulus (Supporting Information Figure S3). Because the side chain molar mass \( (1000 \text{ g/mol}) \) is about 10 times below the entanglement molar mass, this feature cannot be attributed to the entanglement of side chains. Similar behavior has been observed in previous studies of bottlebrush polymers\(^\text{11}\) and was ascribed to orientation dynamics of bottlebrush molecules. Note that this behavior could also be explained by coupling in relaxation dynamics of neighboring side chains through bottlebrush backbone.

A closer look at regime III (transition between filament-like and linear chain behavior) displays a visible increase in the slope of \( G_s \) versus \( \omega \) with respect to the Rouse-like behavior (slope 0.5) of both bottlebrush filaments (regime II) and linear side chains (regime IV). This behavior is consistent with the scaling model predictions shown in Figure 3: namely, a side chain Rouse relaxation is followed by a drop in modulus and then Rouse relaxation of filamentous bottlebrush segments. However, due to the weak dependence of the drop in modulus \( (n_{sc} = 14) \) and the inherent dispersity \( (D = 1.01) \) of the side chains in the currently available bottlebrush elastomers, we are not able to resolve a clean transition between the two Rouse regimes. It would be desirable to synthesize a new set of bottlebrushes with significantly longer side chains \( (n_{sc} \approx 1000) \), but such materials would also require a simultaneous and nontrivial increase in backbone length, which represents a substantial synthetic challenge for future studies.

However, unlike the ambiguous behavior in regime III, the rubbery plateau in regime I demonstrate a clear effect of the cross-link density on the plateau modulus. The values of the shear modulus \( G_{BB} \) for the bottlebrush networks obtained from the plateau shear modulus are consistent with those obtained from tensile tests \( G_{BB} = 3G_{BB} \) (see Table 1).

In our scaling analysis of the plateau modulus of the bottlebrush networks, we consider two pure asymptotic regimes for shear modulus dependence on the bottlebrush molecular parameters. However, our bottlebrush systems are in a crossover; therefore, to take this fact into account, we have to use a general expression for the shear modulus at small deformations \( (\varepsilon \to 0) \)\(^\text{35,31}\).

<table>
<thead>
<tr>
<th>( N )</th>
<th>( n_{sc} )</th>
<th>( G_{BB} ) [kPa]</th>
<th>( G_{ff} ) [kPa]</th>
<th>( \beta' )</th>
<th>( \tau_{ff} ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>14</td>
<td>2.5</td>
<td>9.9 ± 0.3</td>
<td>2.8 ± 0.1</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>100</td>
<td>14</td>
<td>7.3</td>
<td>24.3 ± 0.3</td>
<td>6.2 ± 0.2</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>70</td>
<td>14</td>
<td>15.5</td>
<td>45.0 ± 0.6</td>
<td>10 ± 0.4</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>50</td>
<td>14</td>
<td>20.1</td>
<td>66.0 ± 0.9</td>
<td>13.5 ± 0.5</td>
<td>0.28 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\)Targeted DP of the backbone between cross-links calculated from the molar fraction of the difunctional cross-linker (see Supporting Information). 
\(^b\)Young's modulus obtained from uniaxial extension stress–strain curves at small strain \( (\varepsilon \to 0) \). 
\(^c\)Degree of polymerization of the side chains. 
\(^d\)Shear modulus of the bottlebrush samples at small deformations as obtained from the master curves. 
\(^e\)Rouse times of the bottlebrush networks.
\[ G_0^{BB} = G_0^{BB}(1 + 2(1 - \beta)^2)/3 \]  

(15)

where \( G_0^{BB} \) is the structural modulus of the network which is proportional to concentration of the stress supporting strands, and \( \beta = (R_n^3)/R_{max}^3 \) is the extension ratio of the network strands prior to deformation, \( \langle R_n^3 \rangle \), and the square of the end-to-end distance of the fully extended bottlebrush backbone strand, \( R_{max} = N b \). For networks made of flexible strands for which \( \langle R_n^3 \rangle \approx b_k n b \) and \( b n > b_k \) the values of the parameter \( \beta = b_k/n b \ll 1 \) the structural modulus \( G_0^{BB} \) and shear modulus \( G_0^{BB} \) at small deformations are the same, and both are determined by the concentration of the stress supporting strands (see for discussion in refs 25 and 31). However, for the finite values of the parameter \( \beta \) the shear modulus \( G_0^{BB} \) at small deformations is a function of the strand extension ratio.\(^{25,31}\) This additional contribution should be eliminated (see eq 15) to obtain system structural modulus \( G_0^{BB} \). This requires knowledge of the value of the parameter \( \beta \). These values for studied networks were obtained from fitting equilibrium stress/strain curves (see Supporting Information Figure S3). The inset in Figure 9 shows the structural network modulus \( G_0^{BB} \) as a function of \( N \). The data points for this plot were obtained from the corresponding values of the network shear modulus \( G_0^{BB} \) at small deformations using eq 15. The observed \( G_0^{BB} \sim N^{-1} \) trend is consistent with the scaling prediction for structural modulus \( G_0^{BB} \sim (N(1+n_b))^{-1.25} \).

The estimation of the Rouse time from the \( G_0'(\omega) \) curves is ambiguous since we do not observe a pure filament relaxation regime (filament Rouse regime) with a characteristic scaling dependence \( G_0'(\omega) \sim \omega^{\beta/2} \). Therefore, to estimate the Rouse time of the bottlebrush networks, we use a point where the ratio of the storage modulus \( G_0(\omega_{BB}) \) to its plateau value is the same as for sample with \( N = 200 \), for which we have independently obtained the Rouse time and is approximately equal to 1.45. This gives the estimated Rouse times \( \tau_{BB} \approx 2\pi/\omega_{BB} \) to be \( 5.2 \times 10^{-3}, 1.6 \times 10^{-3}, \) and \( 8.1 \times 10^{-4} \) s for bottlebrush networks with \( N = 100, 70, \) and \( 50, \) respectively.

### CONCLUSIONS

We have demonstrated the hierarchical nature of the bottlebrush network relaxation. This multiscale relaxation process is confirmed by using a combination of the scaling analysis as well as computational and experimental studies. In particular, our analysis shows that at time scales shorter than the Rouse time of the side chains, \( \tau_0 < t < \tau_0(n_b + 1)^2 \), the relaxation of the bottlebrush network is that of a melt of linear chains with the time-dependent shear modulus \( G_0^{BB}(t) \sim t^{-1/2} \).

At the time scale \( t \approx \tau_0(n_b + 1)^2 \), the relaxation process of bottlebrush backbone and side chains are coupled, resulting in a crossover to filament-like behavior. This filament-like relaxation process continues up to time scales \( t \sim \tau_0 N_b^2(n_b + 1)^{3/2} \). In this interval the time-dependent bottlebrush shear modulus has a weak dependence on the side chain degree of polymerization, \( G_0^{BB}(t) \sim (n_b + 1)^{-1/2}t^{-1/2} \). Finally, at the time scales longer than the Rouse time of the bottlebrush strand, \( t \sim \tau_k N_b^2(n_b + 1)^{3/2} \), the response of the bottlebrush networks is purely elastic with network shear modulus \( G_0^{BB}(t) \sim (n_b + 1)^{-1}t^{-1}N_b^{-1} \) for networks made of bottlebrush strands with \( b n > b_k \). When the opposite inequality holds, \( b n \leq b_k \), the bottlebrush strands between cross-links behave as semiflexible filaments with longest relaxation time being on the order of \( t \approx \tau_0 N_b^2(n_b + 1)^{1/2} \) and network plateau modulus \( G_0^{BB}(t) \sim (n_b + 1)^{-1/2}N_b^{-2} \).

These different modes of the bottlebrush network relaxation within a hierarchy of the time scales could have vital implications for the design of supersons and superelastic materials for applications such as adhesive surfaces, implants, and actuators.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01358.

Simulation details, dynamics of polydisperse networks, synthesis, characterization, and mechanical properties of PDMS bottlebrush networks (PDF)

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