Comb and Bottlebrush Polymers with Superior Rheological and Mechanical Properties

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Comb and bottlebrush polymers present a wide range of rheological and mechanical properties that can be controlled through their molecular characteristics, such as the backbone and side chain lengths as well as the number of branches per molecule or the grafting density. This review investigates the impact of these characteristics specifically on the zero shear viscosity, strain hardening behavior, and plateau shear modulus. It is shown that for a comb polymer with an entangled backbone and entangled side chains, a maximum in the strain hardening factor and minimum in the zero shear viscosity $\eta_0$ can be achieved through selection of an optimum number of branches $q$. Bottlebrush polymers with flexible filaments and extremely low plateau shear moduli relative to linear polymers open the door for a new class of solvent-free supersoft elastomers, where their network modulus can be controlled through both the degree of polymerization between crosslinks, $n_s$, and the length of the side chains, $n_{sc}$, with $G_{\infty} = pkn_s^2(n_{sc} + 1)^{-1}$.

1. Introduction

Comb polymers are a class of branched polymers consisting of a linear backbone with a low grafting density of side chains,[1] while bottlebrushes are formally also combs but with a significantly higher grafting density of the side chains.[2,3] These classes of polymers can be synthesized via different polymerization techniques, e.g., anionic polymerization,[1,4,5] ring-opening metathesis polymerization (ROMP),[6] atom transfer radical polymerization (ATRP),[7] and reversible addition–fragmentation chain transfer (RAFT).[8] Combined with a grafting method: grafting-from, grafting-to, and grafting-through,[1,3,9] Systematic investigation of different relaxation times and plateau modulus of these polymers ideally requires monodisperse systems with well-entangled backbone and side chains as well as well-defined number of branches per backbone (or grafting density) with equal branching point spacing. The anionic polymerization guarantees the presence of one side chain per repeating unit on the backbone. Bottlebrushes with more than one branch per backbone repeating unit can also be synthesized using ROMP and macromonomers with more bulky groups referred as wedge polymers.[13] These bottlebrushes are similar to that of the dendronized polymer with only one layer of grafting. Loosely grafted bottlebrushes with longer distance between the branching points can be achieved using ROMP technique through copolymerization of macromonomer and a diluent molecule, e.g., racemic endo,exo-norbornenyl diesters, with different ratios. However, different reactivity of macromonomer and diluent leads to a gradient of branching point spacing along the backbone,[14] where the conformations of side chains along the backbone are affected by this gradient.[15] It should be mentioned that the bottlebrushes synthesized with ROMP technique have different repeating units in the backbone than the side chains which might cause microphase separation. However this issue could be ignorable in dense bottlebrushes where the volume fraction of backbone is less than 1 wt%. In order to avoid any microphase separation, Sheiko and co-workers[16] synthesized a series of dense comb and loose bottlebrushes homo poly(n-butyl acrylates) (PBA) with similar side chains and systematically varied grafting density through copolymerization of nonfunctional n-butyl acrylates with trimethylsilyl-protected acrylates by ATRP. However, in order to achieve high degree of polymerization (DP) of backbone (entangled system) for dense bottlebrushes, they had to use slightly different backbones, i.e., poly(n-butyl methacrylate). An organometallic coordinative insertion polymerization of α-olefins results in entangled densely grafted bottlebrushes with rod-like side chains where both backbone and side chains have alkane groups. However the dispersity index of such homopolymer bottlebrushes would

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be around $D \approx 2$.\textsuperscript{17–19} In addition, the glass transition temperature of the comb and bottlebrush topologies depends on the length of branches as well as their polarity.\textsuperscript{18,20,21} All of these synthetic constraints and inherent properties should be considered in generic conclusions for rheological data linked to the polymer physics.

Viscoelastic characteristics as described by the rheological and mechanical properties of comb and bottlebrush polymers strongly depend on the formation of entanglements as well as the backbone and side chain conformations.\textsuperscript{1,3,10,22–28} A comb structure can be quantified through three independent molecular characteristics: the molecular weight of the backbone, $M_{bb}$, the molecular weight of the side chains, $M_{sc}$, and the number of side chains per backbone, $q$. However, $M_{bb}$ and $M_{sc}$ of the comb structures mostly are normalized to the molecular weight between physical entanglements, $M_e$, which are referred to as the number of entanglements in the backbone, $Z_{gb} = M_{bb}/M_e$, and the number of entanglements in the side chain, $Z_{sc} = M_{sc}/M_e$, respectively. It should be mentioned that here $M_e$ is a constant for a given chemical composition and for simplicity is defined as an entanglement strand of a linear polymer of the same chemical composition as its comb (or bottlebrush) counterpart. Another dependent molecular characteristic for comb topologies is the average number of entanglements between the branching points, $Z_q = Z_{gb}/(q + 1)$. The molecular weight of backbone, $M_{bb}$, and side chains, $M_{sc}$, of bottlebrush structures are normalized to the monomer molecular weight, $M_0$, as the DP of the backbone, $n_{bb} = M_{bb}/M_0$, and DP of the side chain, $n_{sc} = M_{sc}/M_0$. Nevertheless, the average DP between two neighbor branching points, $n_q = M_q/M_0$, or the grafting density, $n_q^{-1}$, together with the DP of the side chains, $n_{sc}$, are often used for bottlebrush polymers (see Figure 1). In the current paper, we investigate the transitions from comb to bottlebrush behavior; therefore, all of these variables are used for both topologies especially in the transition from comb to bottlebrush conformations. Figure 1 shows the correlation between these variables.

Substantial experimental\textsuperscript{11,29–31} and coarse-grained simulation works along with scaling analysis\textsuperscript{24,25,32–35} have been done to classify graft polymers into comb and bottlebrush classes with distinct rheological and mechanical properties. The differences observed between comb and bottlebrush structures were related to the Gaussian and stretched conformations of the backbone and side chains.\textsuperscript{24,25} Comb topologies have a backbone and side chains with an unperturbed random Gaussian conformation, while a densely grafted bottlebrush has a stretched backbone and side chains. The side chains of the comb topologies can easily overlap physically with each other, while densely grafted bottlebrush molecules are segregated and weakly penetrated.

Side chains were introduced on comb polymers to mainly control the rheological properties of polymers melt and solutions, especially the extensional viscosity and strain hardening behavior under extensional deformations, through variation of $Z_{gb}$, $Z_{sc}$, and $q$.\textsuperscript{10,11,21,36–43} While bottlebrushes generally were designed to control the elastic properties of polymers, e.g., the shear and extensional moduli, through independent variation of the DP of side chain, $n_{sc}$, and their grafting density, $n_q^{-1}$,\textsuperscript{3,24,25,32,44} Side chains in comb polymers increase the friction of the backbone chain with neighboring molecules in the melt or solution state, which enhances the strain hardening (see below) of the polymer melt under processing conditions. Consequently, entangled side chains induce substantially higher strain hardening than unentangled branches in comb polymers due to their higher topological constraint. However, both the shear and extensional viscosity increase exponentially\textsuperscript{22,35,38,45} with the length of the entangled branches, which results in ultrahigh viscous materials with poor processing properties. Therefore, an optimum length of entangled branches is assumed to exist for comb polymers to improve the practically

$$\begin{align*}
Z_{gb} = M_{bb}/M_e \\
n_{bb} &= M_{bb}/M_0 \\
n_{sc} &= M_{sc}/M_0 \\
Z_q &= Z_{gb}/(q + 1) \\
Z_{sc} &= M_{sc}/M_e \\
Z_q &= Z_{sc}/(q + 1)
\end{align*}$$

Figure 1. Molecular characteristics of comb and bottlebrush polymers.

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very important strain hardening properties. According to the experimental and theoretical results on comb polymers with entangled branches, the strain hardening properties exponentially increase with side chain length, while glassy modulus and arm relaxation plateau modulus are weakly affected by the well-entangled side chains. However, rubbery plateau modulus related to the backbone relaxation time reduces (dilutes) by decreasing of volume fraction of backbone, \( G'_{\infty} = G'_{\infty}^{\phi_{bb}} \). The self-dilution effect of side chains in comb polymer melts is different than the dilution concept in polymer solution due to the simultaneous strong frictional role of side chains in comb polymer melts compared to the frictional effect of unentangled solvent molecules in polymer solutions. In the current progress report, we investigate the behavior of the comb and bottlebrush topologies only in the melt state.

Side chains in bottlebrushes suppress the entanglement threshold of polymer strands, which reduces the rubber plateau modulus from typically 1 MPa for an entangled linear polymer down to 100 Pa for a densely grafted bottlebrush polymer. This substantial reduction in both entanglements and modulus creates the possibility to design supersons and at the same time supercial elastomers which have a tensile strain at break up to 800% in the solvent-free networks.[24] Densely grafted bottlebrushes are supposed to be thick (compared to linear polymer), flexible, cylindrically shaped filaments with both stretched side chains and backbone due to the steric repulsion between densely grafted side chains. Therefore, the side chains of a given bottlebrush molecule cannot interpenetrate the pervaded volume of side chains of neighboring molecules. This means that longer side chains in bottlebrushes theoretically result in a bigger diameter for a given polymer strand and, therefore, a lower modulus, \( G'_{\infty} \approx M'^{-1} \). However, increasing the length of a side chain above the entanglement length of a linear polymer increases the pervaded volume of the end of the side chains where they can penetrate among the side chains of neighboring molecules and possibly make more entanglements. Therefore, the relaxation time of loosely grafted bottlebrushes with entangled side chains drastically increases, which results in ultrahigh zero shear viscosity.[11]

**Figure 2** shows the difference between the comb and bottlebrush structures according to their main applications. Figure 2a–c shows that branched polymers which have mainly comb topology are mostly used in extensional, e.g., electropinning and foaming, processes where their strain hardening properties under uniaxial and biaxial extensional deformations are of great importance, respectively. Electropinning of three different comb polystyrene solutions with the same backbone, \( M_{n,bb} = 90 \text{ kg mol}^{-1} \), and similar volume fraction of side chains \( \phi_{sc} = 0.64 \), showed that transition in morphology of electropun fibers from bead to fiber structure occurred at substantially lower polymer concentrations for combs with fewer, but longer side chains.[28] The current research in our group on a series of comb PS with the same backbone, \( M_{n,bb} = 290 \text{ kg mol}^{-1} \), and similar side chains, \( M_{n,sc} = 44 \text{ kg mol}^{-1} \), but different number of side chains per backbone showed that a comb with 120 side chains, PS290-120-44, shows the maximum strain hardening and minimum zero shear viscosity in this series.[11] The scanning electron microscopy image in Figure 2a is related to the foam of this comb PS with a cell density of \( 10^9 \text{ cells cm}^{-3} \), volume expansion ratio around 40, and an average wall thickness of the cells around 250 nm. In the other word, the lower zero shear viscosity of a comb structure facilitates the bubble growing at the early stage of foaming, while the higher strain hardening property of comb PS stabilizes the ripened cells at the end of foaming process. To the best of our knowledge, there is no available biaxial extensional data for well-defined comb or bottlebrush polymers; however, commercial branched polymers showed strain hardening under biaxial extension.[49,50] In Section 2, we investigate the effect of different molecular characteristics, \( Z_{bb}, Z_{sc}, \) and \( q \), on the shear and extensional viscosity as well as strain hardening behavior. The impact of each characteristic specifically on the zero shear viscosity behavior, \( \eta_0 \), and the strain hardening factor (SHF), \( \text{SHF} = \frac{\eta_{\text{eff}}}{\eta_0} \), will be clarified by reviewing the literature on experimental and modified reptation-based models for comb topologies.

Matyjaszewski and co-workers recently reviewed the correlations between bottlebrush architectures and their properties as novel materials with various potential applications such as templates of well-defined nanostructures, drug carriers, surfactants, lubricants, stimuli-responsive materials, and super-soft elastomers. Figure 2d–f shows the advantages of using bottlebrush elastomers as solvent-free, supersons, and super-elastic materials compared with hydrogels and conventional elastomers.[24,44] One example is that a poly(dimethylsiloxane) (PDMS) bottlebrush elastomer exhibits a considerably higher fracture energy than its poly(acrylamide) (PAM) hydrogel counterpart with a similar backbone volume fraction (Figure 2d,e), even though both materials show a similar modulus. Moreover, bottlebrush elastomers exhibit substantially higher compression ratios at break, \( \approx 10 \), relative to hydrogels, \( \approx 3 \). Comparison of true stress as a function of areal expansion (\( \sigma_{\text{true}} - \lambda^{-1} \)) for a conventional elastomer and a bottlebrush elastomer (Figure 2f) shows that a conventional elastomer (line 1) with coiled network strands exhibits linear elasticity over a wide range of areal expansion without strain-stiffening (increase in modulus during deformation) properties. Prestretching and then bracing these conventional elastomers with either physical (e.g., lamination) or chemical (swelling in a solvent) methods results in materials with better strain-stiffening properties (line 2), which is necessary for the use of dielectric elastomers in an actuator application. However, these kinds of modifications to dielectric elastomers increase the size of the total actuator assembly leading to a significant reduction in efficiency.[44] Bottlebrush elastomers (line 3) with an inherently prestrained structure have inherent strain-stiffening properties as a single component. Furthermore, polymer chains in bottlebrush elastomers are disentangled, which results in high extensibility. In Section 3, the effect of the different molecular characteristics of bottlebrush elastomers, \( n_{sc} \) and \( n_{bb} \), as well as degree of polymerization of backbone between crosslinks, \( n_s \), on the plateau modulus are presented. Transitions from a comb topology with unperturbed backbone and side chain conformations to a loosely grafted bottlebrush with a stretched backbone conformation and finally to a densely grafted bottlebrush with both stretched backbone and side chains will be discussed in more detail.
2. Rheological Properties

2.1. Zero Shear Viscosity

Comb and bottlebrush polymer melts present a wide range of longest relaxation times, $\tau$, plateau moduli, $G_0$, and zero shear viscosities, $\eta_0 = \tau G_0$, relative to either their linear counterparts with the same total molecular weight or a linear polymer with a similar backbone length. Extensional properties of these combs and bottlebrushes, specifically their extensional viscosity, $\eta_E$, maximum polymer chain extensibility, $\lambda_{\text{max}}$, and strain hardening factor, $\text{SHF} = \eta_{\text{SHF}} / 3\eta_0$, strongly depend on their molecular characteristics. Tube (reptation) theory developed for comb polymers considers the effects of both entangled side chains and entangled backbone on the longest relaxation time and plateau modulus of the polymer.\[22,38\] For combs with entangled side chains, branching points are sluggish and therefore retard the reptation of backbone segments between the branching points until all of the side chains can relax. This means that side chains increase the longest relaxation time of the polymer via their strong frictional effect on the backbone. On the other hand, the tips of the arms (chain ends) in a molecule are highly mobile and relax faster than the other parts of the molecule via primitive path fluctuations (PPF) or contour length fluctuation (CLF) mechanisms. Increasing the chain ends (number of side chains, $q$) in a comb architecture accelerates this mechanism because the relaxed tips of the side chains dilute the tube of the backbone and reduce the longest relaxation time. Therefore, depending on the length and the number of entangled side chains, comb polymers have either

Figure 2. Classification of comb and bottlebrush structures according to their applications. Comb polymers are mainly used in processes which are based on the extensional deformation of polymers with pronounced strain hardening compared to the linear polymers (b). c) Transition from bead to fiber morphology as a function of concentration of electrospun solutions (12, 16, 24 wt%) of three different comb PS, abbreviated $\text{PS}_{M_n,bb,q-M_n,sc}$, which have the same backbone, $M_{n,bb} = 90 \text{ kg mol}^{-1}$, and similar volume fraction of side chains $\phi_{sc} = 0.64$, but different number, $q = 13, 5, 4$, and molecular weight, $M_{n,sc} = 12, 30, 42 \text{ kg mol}^{-1}$, of side chains. Reproduced with permission.\[28\] Copyright 2016, Elsevier. a) Foam out of a comb $\text{PS}_{290-120-44}$ which results in a foam structure with cell density of $10^9 \text{ cells cm}^{-3}$, volume expansion ratio around 40, and an average wall thickness of the cells around 250 nm. Bottlebrush polymers (d–f) are used as bottlebrush elastomers with solvent-free, supersoft, and superelastic properties. d) Compression test and e) the true stress versus compression ratio of poly(dimethylsiloxane) (PDMS) bottlebrush elastomers, with a poly(acrylamide) (PAM) hydrogel. Reproduced with permission.\[24\] Copyright 2016, Springer Nature. e) The tensile behavior of PDMS bottlebrush elastomers with a conventional elastomer with and without a prestrained structure, reproduced with permission.\[44\]
a longer or shorter relaxation time relative to their linear counterpart. Inkson et al.\[38\] considered all of these mechanisms in the reptation theory and presented the following relation for the longest relaxation time of a comb polymer with entangled backbone and side chains

\[
\tau_{\text{rep}} \propto Z_{\text{sc}}^{1/2} \phi_{\text{bb}} q \tau_{\text{sc}}
\]  

(1)

where \(1 < \alpha < 4/3\) is the dilution exponent, and \(\phi_{\text{bb}}\) is the volume fraction of the backbone (see Figure 1). The exact value of dilution exponent \(\alpha\) for branched polymers depends on the mathematical definition of relaxation mechanisms and moduli considered in the tube theory[22,38,45,52,53] as well as the experimental method to define this value.[54] It should be mentioned that Equation (1) considers combs with a limited number of side chains, \(6 \leq q \leq Z_{\text{bb}}\). The upper limit of \(q\) in this model is equal to the number of entanglements of the backbone, \(Z_{\text{bb}}\), where the branching point spacing is almost equal to one entanglement, \(Z_{\text{e}} = 1\). The longest relaxation time of a side chain, \(\tau_{\text{sc}}\), is related to the innermost segments of the arms attached to the backbone, which exponentially depends on the length of the side chains

\[
\tau_{\text{sc}} \propto Z_{\text{sc}}^{1/2} \phi_{\text{sc}} q \tau_{\text{sc}}
\]  

(2)

where \(\phi_{\text{sc}} = 1 - \phi_{\text{bb}}\) is the volume fraction of the side chains and \(\tau_{\text{sc}}\) is the Rouse relaxation time of one entanglement. Considering the relaxed side chains formally as a solvent for the backbone segments[45] the effective backbone modulus of a comb with entangled side chains reduces to \(G_{b,s}^\text{eff} = G_{b}^{\text{eff}}\phi_{\text{bb}}\), where \(G_{b}^{\text{eff}}\) is the plateau modulus of the linear entangled polymer. The zero shear viscosity of a polymer melt can be approximately calculated from the product of the plateau modulus and the terminal relaxation time, \(\eta_0 \propto \tau_{\text{rep}} G_{b,s}^{\text{eff}}\). For simplicity, \(\alpha\) in Equations (1) and (2) was taken to equal 1, the volume fraction of side chains, \(\phi_{\text{sc}}\), was substituted with \(1 - \phi_{\text{bb}}\), and \(qZ_{\text{sc}}\) was replaced with \(Z_{\text{bb}} (1 - \phi_{\text{bb}})/\phi_{\text{bb}}\) to give

\[
\eta_0 \propto \tau_{\text{rep}} G_{b,s}^{\text{eff}} Z_{\text{sc}}^{1/2} \phi_{\text{bb}} (1 - \phi_{\text{bb}}) Z_{\text{sc}}^{1/2} \exp \left[ \frac{5Z_{\text{sc}} (1 + 2\phi_{\text{bb}})}{8} \right]
\]  

(3)

It is worth mentioning that the right side of Equation (3) includes the term \(\eta_0 \propto \tau_{\text{rep}} G_{b,s}^{\text{eff}} Z_{ \text{sc}}^{1/2} \phi_{\text{bb}} (1 - \phi_{\text{bb}}) Z_{\text{sc}}^{1/2}\), which is almost equal to the zero shear viscosity of the linear polymer (backbone in the absence of side chains). The middle part of Equation (3) contains a pure dilution term, \(\phi_{\text{bb}} (1 - \phi_{\text{bb}})\), which has the potential to reduce the \(\eta_0\) of a comb below that of the linear backbone. However, the last term in Equation (3), \(Z_{\text{sc}}^{1/2} \exp[5Z_{\text{sc}} (1 + 2\phi_{\text{bb}})/8]\), which is basically related to the strong frictional effect of the side chains on the backbone, increases the \(\eta_0\) of a comb to a value that is not only above the zero shear viscosity of the linear backbone, \(\eta_{0,\text{bb}} = \tau_{\text{rep}} G_{b,s}^{\text{eff}} Z_{\text{sc}}^{1/2}\) but also, for long enough side arms, \(Z_{\text{sc}} \gtrsim 1\), raises \(\eta_0\) above linear counterparts with the same total molecular weight. It should be mentioned that this friction term, \(Z_{\text{sc}}^{1/2} \exp[5Z_{\text{sc}} (1 + 2\phi_{\text{bb}})/8]\), also contains a dilution term, \((1 + 2\phi_{\text{bb}})\), which is related to the dynamic dilution effect of side chains on their own relaxation.[52,53,55]

Figure 3 shows the calculated zero shear viscosity of comb polyethylene (PE) versus the total molecular weight of the polymer, \(M = M_{\text{bb}} + q M_{\text{sc}}\), using the same method presented in Equations (1)–(3) with a dilution exponent \(\alpha = 4/3\), \(g = 9.5 \times 10^{-8}\) s, and \(M_{\text{sc}} = 1150\) g mol\(^{-1}\) for linear PE at 190 °C.[38] The drawn power law line, \(\eta_0 = 5.8 \times 10^{-14} M_{\text{bb}}^4\) (with \(\eta_0\) in Pa·s and \(M_{\text{sc}}\) in g mol\(^{-1}\)) is the zero shear viscosity of linear reference PEs at 190 °C.[56] Figure 3a was plotted for combs with \(6 \leq Z_{\text{bb}} \leq 100\), \(2 \leq Z_{\text{sc}} \leq 10\), and \(6 \leq q \leq Z_{\text{bb}}\) as well as three-arm star PEs. It can be seen that there are upper and lower boundaries for \(\eta_0\), which are related to three-arm stars and combs with a maximum number of branches, \(q = Z_{\text{bb}}\), respectively. It can be concluded that the region above the linear reference encompasses the comb topologies whose side chains have a strong frictional effect on the backbone. In contrast, the region below the linear reference is composed of combs where the frictional effect of their side chains on \(\eta_0\) is overcompensated by their strong dilution effect on the backbone, \(\phi_{\text{bb}} \ll 1\).

Figure 3b shows that for certain backbone and side chain lengths, the zero shear viscosity follows an almost power–law function decrease with increasing number of side chains on the backbone, \(q\), or total molecular weight (for instance, see the trend line for combs with \(Z_{\text{bb}} = 100\) and \(Z_{\text{sc}} = 10\)). Our analysis

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**Figure 3.** Zero shear viscosity of comb polyethylene as a function of total molecular weight for a) combs with different backbone lengths, \(6 \leq Z_{\text{bb}} \leq 100\), side chain lengths, \(2 \leq Z_{\text{sc}} \leq 10\), and number of side chains per backbone, \(6 \leq q \leq Z_{\text{bb}}\), as well as the three-arm star polymers, and b) only four different series of combs with \(Z_{\text{bb}} = 10, 20, 50,\) and 100, where the length of side chains are \(Z_{\text{sc}} = 2, 4, 6, 8,\) and 10, and the number of side chains per backbone varied between the 6 and \(Z_{\text{bb}}\). All panels reproduced with permission.[38] Copyright 2006, American Chemical Society.
of \(\eta_0\) of comb series with well-entangled backbone, \(Z_{bb} > 20\), in Figure 3b shows that \(\eta_0\) of comb with branching point spacing \(Z_g = 2–2.5\) are above that of the linear reference, while \(\eta_0\) of combs with \(1 < Z_g < 2–2.5\) are below the linear counterparts. However, what is missing in Figure 3 is the zero shear viscosity of combs with higher number of side chains, i.e., \(g > Z_{bb}\) or \(Z_g < 1\). Experimental data for a series of nearly monodisperse comb polystyrenes (nomenclature: \(PS_{n,bb-q-M_{n,sc}}\)) with similar backbone \(M_{n,bb} = 290\) kg mol\(^{-1}\) \((Z_{bb} = 20)\), and side chains \(M_{n,sc} = 44\) kg mol\(^{-1}\) \((Z_{sc} = 3)\), but a different number of branches per molecules, \(0 < q < 190\), shown in Figure 4, demonstrate that \(\eta_0\) increases exponentially with total molecular weight, \(M_w = M_{n,bb} + qM_{n,sc}\), to a level that is even above their linear counterparts (solid line \(\eta_0 = 3.31 \times 10^{-14} M_w^{1.4}\)) for combs with \(Z_g > Z_{sc}\). A relative maximum in \(\eta_0\) seems to be related to a comb with approximately \(Z_g = Z_{sc}\) (or equivalently a comb with \(q = Z_{bb} / Z_{sc} - 1 \approx 6\) for this specific backbone and side chains). A further increase in \(q\) results in a reduction in the zero shear viscosity below the linear counterparts with an almost a power–law behavior, \(\eta_0 \propto M_w^{1.4}\), which is in agreement with the predictions shown in Figure 3b and Equation (3). The limited range of scaling laws for \(\eta_0\) of these comb series (1–2 decades in \(\eta_0\)) is related to the limited number of entanglements in the backbone and side chains of these comb series, i.e., \(Z_{bb} = 20\) and \(Z_{sc} = 3\), respectively, which results in a limited range for the variation of longest relaxation times for this comb series. However, these scaling laws are in agreement with the predictions of reptation theory in Figure 3b and Equation (3) for the comb topologies with \(q < Z_{bb}\). It should be mentioned that increase of \(Z_{bb}\) or \(Z_{sc}\) for such comb PS series might cause a very high \(\eta_0\) above the linear counterparts for the loosely grafted combs, which might not be achieved easily within the reasonable experimental temperature–frequency window, e.g., \(130–240°C\) for PS. Further reduction in \(\eta_0\) as a function of \(M_w\) with increasing \(q\) was achieved for combs with \(g > Z_{sc}\). In this highly branched region, the comb polymers have an unentangled branching point spacing, \(Z_g < 1\), and \(\eta_0\) reduces with a power of around 1 as a function of \(q\). This means that the backbone of a comb-PS with an entangled branching point spacing, \(1 < Z_g < Z_{sc}\), relaxes with a reptation mechanism, while the backbone of a comb with an unentangled branching point spacing relaxes with a Rouse mechanism. Figure 4 shows results for such a comb-PS series where a relative minimum in \(\eta_0\) was observed for a comb-PS with \(Z_g = 0.2\) which is almost equal to the \(\eta_0\) of its linear polymer equivalent with the same backbone.\(^{[11]}\) Further increases in the number of branches on the same backbone to \(q = 190\) significantly increased \(\eta_0\). Investigation of a series of densely grafted combs with longer backbone, \(20 < Z_{bb}\), which most probably have lower \(\eta_0\) than the linear counterpart, is needed for accurate analysis of these transitional regions toward the dense bottlebrush regime.

Abbasi et al.\(^{[11]}\) used the scaling analysis criteria of Sheiko and co-workers\(^{[24–25]}\) (see details in Section 3) for this series of grafted PS to classify them into comb and bottlebrush conformations. According to the length of the backbone and side chains (i.e., \(Z_{bb} = 20\) and \(Z_{sc} = 3\)), grafted polymers with \(142 < q < 951\), which is equivalent to \(3 < n_g < 20\), have a loose bottlebrush topology and grafted polymers with lower values were classified as densely comb topology. Figure 4 shows that the plateau modulus almost reduces with the same scaling, \(G_0 = G_{0,bb}\phi_{bb}\) for the entire series of comb-PS. Now the question arises why the loose bottlebrush PS290-190-44 has a significantly higher \(\eta_0\) than dense comb PS290-120-44 even though its diluted modulus is lower. This behavior might be related to difference between the frictional coefficient of comb and bottlebrushes. In comb polymers, the frictional effect of side chains exponentially increases with the length of side chains (see Equations (2) and (3)). While López-Barrón et al.\(^{[18–19]}\) showed that in a series of densely grafted bottlebrushes with short side chains \((n_{sc} \leq 16)\), the monomeric friction coefficient, \(\xi\), decreases upon increasing the side chain length, due to the lower flexibility combined with the higher distance (free volume) between adjacent bottlebrush backbones and consequently lower glass transition temperature, \(T_g\). Transition from the dense comb to loose bottlebrush regimes (see Section 3) results in a complex behavior where the ends of the entangled side chains of loose bottlebrush topologies might be able to penetrate between the side chains of neighboring molecules during deformation. Due to the very tight spacing between the branching points, the diffusion coefficient \((D = kT\xi)\), where \(\xi\) is the total friction coefficient of side chains) of the trapped part of the side chains significantly decreases, which results in longer arm relaxation times. This transition in rheological behaviors depends on
grafting density and most probably the DP of side chains. However, to the best of our knowledge, this behavior has not been systematically studied yet.

Several studies investigated the zero shear viscosity \( \eta_0 \) as a function of total molecular weight for different series of loose and dense bottlebrushes with either short chain branches (SCB)\(^{13,18,19,24,29–31,57} \) or long chain branches (LCB)\(^{11,30} \). Within these bottlebrush series, two characteristics out of \( n_{sc} \), \( n_g \), and \( n_{bb} \) are fixed and one of them is varied in the series. Figure 5a presents the reduced \( \eta_0 \) for five bottlebrush series and a linear series at a reference temperature \( T_{ref} = T_g + 34 \) °C. All of the bottlebrush series are poly-(norbornene)-graft-poly(\( z \)-lactide) with a fixed length of SCB polyolactide (PLA, \( M_n = 3.5 \text{ kg mol}^{-1} \), \( M_n/\rho_{PLA} = 0.4 \)). These bottlebrushes were synthesized via ROMP of \( \omega \)-norbornenyl polyolactide macromonomers. Norbornene dimethyl ester (DME) as comonomer was used to vary the grafting density in the range of 0 < \( z < 1 \), where \( \eta_0 = 2.68/z \). Each series has a fixed grafting density and \( n_{sc} \), but the degree of polymerization of the backbone, \( n_{bb} \), was varied. It was shown that \( \eta_0 \) versus \( M_n \) has two different scaling regimes 1 and 3, which could be related to Rouse and reptation dynamics, respectively. This demonstrates that grafting density strongly impacts the apparent entanglement molar mass of bottlebrushes. Figure 5b shows these data as a function of the number of entanglements in the bottlebrush strands. The entanglement molecular weight, \( M_e \), of these bottlebrushes was calculated from the diluted modulus, \( M_e = \rho RT/\Gamma n^* \), which was defined from the van Gurp-Palmen plots as the value of \( G^s \) or \( G^* \) at the minimum value of \( \tan \delta \) within the entanglement regime.\(^{38} \) It can be seen in Figure 5b that the Rouse and reptation relaxation mechanisms have a sharp transition at \( M_e/M_n = 1 \). This means that in principle similar to linear polymers, the number of entanglements in the bottlebrush strands with SCB structure plays the most important role in the increase of \( \eta_0 \) for bottlebrushes. The main difference between the linear and SCB-bottlebrushes is related to the friction coefficient, where in the linear polymers is due to the monomers on the backbone but in SCB-bottlebrushes is caused by monomers on the surface of the bottlebrush cylinders. It is also clear that vertical shift of the \( \eta_0 \) data in entangled region in Figure 5b is related to the increase in the diluted modulus of densely grafted bottlebrushes with branching point spacing.\(^{24} \) It was shown that \( G_{c,b} \approx (\eta_0/n_{bb})^{1.2} \).

Grubbs and co-workers\(^ {13} \) showed that the scaling exponent of the zero shear viscosity–molecular weight dependence of a series of entangled wedge polymers (very dense bottlebrushes with three branches per repeating unit of backbone, i.e., \( n_g = 0.3 \)) with SCB structure might be even above the 3 power law with an exponent of around 4.2. However, there were only four samples available for this series.

The zero shear viscosity for two series of bottlebrushes with \( n_g = 1 \) are shown in Figure 5c. The first series, aPP-NB-SCB, had short chain branches that were unentangled side chains of atactic polypropylene (aPP, \( M_n = 2.05 \text{ kg mol}^{-1} \), \( M_n/\rho_{aPP} = 0.5 \)),\(^ {29} \) while the second series, PEP-NB-LCB, had long chain branches of entangled side chains of poly-ethylene-alt-propylene (PEP, \( M_n = 6.7 \text{ kg mol}^{-1} \), \( M_n/\rho_{PEP} = 3.5 \)).\(^ {30} \) Both prepared from norbornene-terminated macromonomers. In both series, the DP of the backbone was below the entanglement length, \( n_{bb} < n_{c,b} \), and both series show almost a Rouse relaxation mechanism for \( \eta_0 \). This means that for densely grafted bottlebrushes, \( n_g = 1 \), even side chains long enough to have originally 3.5 entanglements are fully stretched and cannot penetrate into neighboring side chains or flexible bottlebrush cylinders to respond like an entangled system.
It can be concluded that \( \eta_0 \) of the bottlebrushes strongly depends on the number of entanglements in the bottlebrush filament as well as the DP of the side chains (Figure 5); however, the dependency of \( \eta_0 \) for loose bottlebrush systems with entangled side chains on the DP of the side chains is stronger due to penetration of side chains into neighboring molecules, which results in entangled systems (Figure 4).

### 2.2. Strain Hardening Factor

The preceding analyses in Figure 4 revealed that the number of branches in a comb polymer with a given backbone and side chain length can be optimized to achieve a minimum in the shear viscosity, which is important for the processability of polymers under shear deformations. However, optimization of the molecular structure of branched polymers for extensional processes, e.g., film blowing, should take into account both shear and extensional behaviors and especially the strain hardening property. The original pom-pom model for sufficiently high extensional rates predicts the strain hardening factor to be:

\[
\text{SHF} = \frac{\eta_0^{\text{bulk}}}{3\eta_0} \approx \frac{\lambda_{\text{max}}^3}{\sigma} / \tau_b \quad (4)
\]

where \( \tau_c = qZ_{lb}\sigma_c \) and \( \tau_b = 4/\pi^2 qZ_{lb}\phi_b\sigma_c \) are the stretch and orientation relaxation times of the backbone, respectively, and the maximum limiting stretch of the backbone, \( \lambda_{\text{max}} \), is equal to \( q \) when there are \( q \) dangling arms on each side for a total of \( 2q \) side chains per molecule, \( \lambda_{\text{max}} = q \). Equation (4) can be simplified to \( \text{SHF} = qZ_{lb}\phi_b^3 \), which shows that for a given backbone and side chain length, SHF scales with \( q^3 \) or \( M^3 \). This scaling is a bit stronger than the experimentally observed scaling for SHF at \( \dot{\varepsilon} = 1 \text{ s}^{-1} \) for the comb series shown in Figure 4 (right y-axis), which was SHF \( \propto q^{1.7} \propto M^{1.7} \). The concept of a constitutive equation for the pom-pom model was extended for more complicated branched topologies, e.g., Cayley trees, randomly branched polymers, as well as comb structures. For comb polymers with multiple branching points, equivalent to a pom-pom molecule with \( 2q \), the maximum limiting stretch of the backbone segments hierarchically increases from 1 for the outermost segments of the backbone to almost \( q \) for the innermost ones located in the middle of the backbone. Therefore, the average maximum stretching of a backbone within a comb should be lower than that of a pom-pom with the same amount of branches. Liu et al. showed that a comb PS with well-entangled branching point spacing \( (Z_c = 10) \) has a maximum in the engineering stress that emerges at a stretching ratio of \( \lambda_{\text{max}} \approx 4\sqrt{Z_{lb}/C} \), rather than \( \lambda_{\text{max}} = q \) for the pom-pom model. Consequently, the strain hardening for comb polymers in Equation (4) is a weaker function of the number of branches (or molecular weight for a certain backbone), \( \text{SHF} \propto \phi_b^3 \propto M \propto q \), than the original pom-pom equation, \( \text{SHF} = qZ_{lb}\phi_b^3 \propto M^3 \propto q^3 \). Figure 4 shows that the SHF levels off or even decreases with further increase in \( q \) or decrease in \( Z_{g} \) for this series of combs with similar backbone and side chains. This means that stretchability of segments between the branch points reduces as soon as the conformation of backbone shift to a loose bottlebrush conformation with inherently stretched segments. The maximum SHF almost matches the minimum observed for \( \eta_0 \) in this comb series, where a transition from the comb to bottlebrush regimes occurred, \( Z_{g} \approx 0.2 \). From a processing point of view, a polymer with minimum shear viscosity and a maximum in SHF is an ideal structure for extensional process, e.g., film blowing and foaming. We showed that these properties in a comb structure can be achieved through an optimum number of branches or branching point spacing. The branching point spacing \( Z_{g} \approx 0.2 \) might not be a universal number for other backbones; however, it seems that \( Z_{g} \) should be at least smaller than 1 to achieve the minimum in \( \eta_0 \). In order to find a more accurate and universal equation, a detailed scaling analysis for relaxation time and plateau modulus, especially for the transition from comb to bottlebrush, is needed to define a general equation for this proposed optimum number of branches. In the next section, this analysis was done for plateau modulus.

### 3. Diluted Plateau Shear Modulus

Entangled linear polymer melts typically possess a plateau modulus \( \text{G}_0^0 \approx 10^5 \text{ to } 10^6 \text{ Pa} \) that is consistent with their entanglement molecular weights, \( M_e = \rho R T / \text{G}_0^0 \approx 10^6 \text{ to } 10^9 \text{ g mol}^{-1} \). The presence of low molecular weight components (e.g., solvents or oligomers) in a melt of entangled polymers increases \( M_e \) as \( M_e = M_\phi^{-\alpha} \) and consequently decreases the plateau modulus of the concentrated entangled system, \( \text{G}_0^0 \approx \text{G}_0^0 \phi^{1-\alpha} \) with \( 1 < \alpha < 4/3 \). The side chains of comb and bottlebrush polymers, which relax faster than their backbones, dilute the tube diameter of the backbone and consequently also behave like a solvent. Fetters et al.\(^{[36,66]}\) obtained two empirical relationships for the plateau modulus of poly(\( \alpha \)-olefins):

\[
\text{G}_0^0 = 24820 m_b^{-1.49} \quad m_b = 14 - 28 \text{ g mol}^{-1} \quad (5a)
\]

\[
\text{G}_0^0 = 41.84 m_b^{-1.58} \quad m_b = 35 - 56 \text{ g mol}^{-1} \quad (5b)
\]

where \( \text{G}_0^0 \) is given in MPA, \( m_b \) is the average molecular weight per backbone bond and, analogous to bottlebrush structures, is proportional to the inverse of the volume fraction of the backbone bonds, \( \phi_b \). López-Barrón et al.\(^{[18]}\) reported the rheological data of a series of ultrahigh molecular weight poly(\( \alpha \)-olefins) with bottlebrush architectures, ranging from poly(1-hexene) to poly(1-octadecene). The rubbery plateau modulus was clearly achieved

\[
\text{G}_0^0 = 1.05n_{sc}^{1.47} = 1.05 \left( \frac{1}{7} m_b - 2 \right)^{-1.47} \quad m_b = 42 - 126 \text{ g mol}^{-1} \quad (5c)
\]

where \( m_b = 14 + 7n_{sc} \). These empirical equations, Equations (5a)–(5c), are consistent with the scaling analysis of Sheiko and co-workers for bottlebrush polymers with rod-like side chains.\(^{[12]}\) Sheiko and co-workers investigated the effect of side chain spacing on the conformations of the backbone and side chains as well as the plateau modulus for comb and bottlebrush polymers. It was shown that the molecular conformation of a comb topology in the melt phase depends on the DP of the side chains, \( n_{sc} \), and DP of the backbone spacer between grafting points, \( n_{bp} \). Using a scaling analysis, they distinguished between four different conformational regimes:
loosely grafted comb (LC), densely grafted comb (DC), loosely
grafted bottlebrush (LB), and densely grafted bottlebrush (DB), to
the $n_{sc}$ and $n_{c}$ of the polymers. In their recent
work,[12] they divided the bottlebrush regime into three different
subregions including stretched backbone (SBB), stretched side
chain (SSC), and rod-like side chain (RSC) according to the
volume fraction of the backbone, $\phi_{bb}$, equals $n_{bb}/(n_{bb} + n_{sc})$ and $n_{sc}$. However, the LB and DB regions are basically consistent with
the SBB and SSC regimes, respectively, and the RSC region
describes a class of bottlebrushes with very short side chain
lengths. Figure 6 shows these conformational regimes in the
framework of $\phi_{bb}$ versus $n_{sc}$ for these systems. In the right side
of Figure 6, the corresponding equations for the moduli of
these regions are shown.

Both the backbone and side chains in LC and DC polymers have almost unperturbed random Gaussian conformation;
however, DC polymers have shorter side chains than the branching point spacer, $n_{s} < n_{c}$. The total number of monomers between the entanglements, $n_{e}$, as well as the plateau modulus of entangled comb and bottlebrush systems, $G_{0,cc} = kT/V_{c}$, were
defined based on the Kavassalis–Noolandi conjecture,[67] which
states that there is an almost fixed, $P_{c} = 20.8 \pm 0.8$, number of sections of different chains within the volume of an entanglement
strand, $V_{c} = V_{n_{e}}$ (v is monomeric volume).

This concept results in a relation for the modulus
$G_{0,cc} = G_{0,cc} \phi_{cc}$ for both LC and DC polymers,[24,25] where
$G_{0,cc}$ is the plateau modulus of an entangled linear polymer. However, this scaling is different compared to previous find-

ings for comb polymers with entangled side chains. Further
reduction in the branching point spacing, $n_{s}$, at constant $n_{c}$
(or increasing $\phi_{cc} = n_{bb}/n_{c} + 1$) toward SBB bottlebrush structures results in the segregation of molecules and reduces the
overlap of side chains belonging to neighboring bottlebrushes. The backbone in an SBB is stretched due to side
chain crowding, while the side chains still maintain their
flexibility. This concept results in a relation for the modulus
$G_{0,cc} = G_{0,cc} \phi_{cc}$ for both LC and DC polymers, where
$G_{0,cc} = G_{0,cc} \phi_{cc}$ is the Kuhn length of the polymer.

For the SBB regime, the rubber plateau modulus, $G_{0,SSC} = G_{0,SSC} b^{-3/2} \sigma_{b}^{1/2} \phi_{bb}^{2}$, scales with $\phi_{bb}^{2}$, however $\phi_{bb}$ is very close to 1 and no longer has a
strong effect on the modulus. It is interesting to note that,
for both SSC and SBB regimes, the rubber plateau modulus has a similar scaling as Equation (5b) for poly($\alpha$-olefins) with $m_{b} = 35 - 56$ g mol$^{-1}$. In other words, dense bottlebrush topologies behave like poly($\alpha$-olefins) with $m_{b} = 35 - 56$ g mol$^{-1}$.

Further reduction in $n_{sc}$ and the Kuhn length of the polymer.

Further reduction in $n_{sc}$ at constant $n_{s}$ (or increasing $\phi_{cc} = n_{bb}/n_{c} + 1$) toward SBB bottlebrush structures results in the segregation of molecules and reduces the
overlap of side chains belonging to neighboring bottlebrushes. The backbone in an SBB is stretched due to side
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$G_{0,cc} = G_{0,cc} \phi_{cc}$ is the Kuhn length of the polymer.

For the SBB regime, the rubber plateau modulus, $G_{0,SSC} = G_{0,SSC} b^{-3/2} \sigma_{b}^{1/2} \phi_{bb}^{2}$, scales with $\phi_{bb}^{2}$, however $\phi_{bb}$ is very close to 1 and no longer has a
strong effect on the modulus. It is interesting to note that,
for both SSC and SBB regimes, the rubber plateau modulus has a similar scaling as Equation (5b) for poly($\alpha$-olefins) with $m_{b} = 35 - 56$ g mol$^{-1}$. In other words, dense bottlebrush topologies behave like poly($\alpha$-olefins) with $m_{b} = 35 - 56$ g mol$^{-1}$.

Figure 6 shows another regime for bottlebrushes with fully
stretched side chains and backbone, called the RSC regime.
The side chains in the RSC regime are below a certain limit so
that $b^{-3/2} \sigma_{b}^{1/2} \phi_{bb}^{2} < \phi_{bb}^{2}$. The modulus in this regime scales with
$G_{0,bb} = G_{0,bb} \phi_{bb}^{3/2}$, which is also similar to the scaling for poly($\alpha$-olefins) with $m_{b} = 14 - 28$ g mol$^{-1}$ shown in Equation (5a).

It should be mentioned that the scaling analysis for all three regimes of bottlebrushes, SBB, SSC, and RSC, was only
investigated experimentally for bottlebrushes with unentan-
gled side chains. Dalsin et al.[18] investigated the modulus and rheological properties of a series of bottlebrushes with entangled side chains; however, the whole bottlebrush strand was not entangled, and still acted as a Rouse molecule. Increasing the length of side chains of a bottlebrush to above a certain limit (e.g., longer than one entanglement) might facilitate the penetration of side chains into neighboring molecules as the side chain ends might be located outside the backbone tube.

One of the breakthrough applications of bottlebrushes with
a substantially lower plateau modulus is bottlebrush elastomers with a permanent network structure. These elastomers have intrinsic supersons and superelastic properties without additional solvents and are promising candidates for synthetic substitutes of biological tissues.[68] Therefore, another important parameter affecting the network shear modulus is the crosslink density,[24,33,34,69] or the DP of the bottlebrush backbone between crosslinks, $n_{c}$. It was shown that for dense bottlebrush networks with $n_{b} = 1$ and fully stretched strands between crosslinks (= $n_{b} b$) that were longer than the bottlebrush Kuhn length, $b_{s} = 1/2^{1/2} n_{b} b_{s}$, i.e., $n_{b} b > n_{b} b_{s}$, the

![Figure 6](https://www.advmat.de)
bottlebrush network behaved in a similar way to a flexible filament with a network shear modulus given by \[ G^{\theta}_{bb} = \frac{p k T n_c^2 (n_g + 1)^{-1}}{\eta_0} \] (6)

Equation (6) shows that the modulus of such a bottlebrush elastomer is, by a factor of \((n_g + 1)^{-1}\), smaller than that of conventional elastomers. In other words, the modulus of these bottlebrushes can simply be adjusted by the DP of the side chains. However, bottlebrushes with strands shorter than the bottlebrush Kuhn length behave as semiflexible filaments with a weaker dependence of the shear modulus on the side chain length, \(G^{\theta}_{bb} \propto n_c^{-0.5}\).

4. Conclusions and Outlook

This paper discussed the effect of the molecular structure of combs and bottlebrushes on the most important rheological and mechanical properties in both shear and elongation. Comb topologies with entangled side chains are interesting due to their pronounced strain hardening behavior under extensional flows. The SHF increases with an increase in the number of side chains for a given backbone and levels off when the minimum zero shear viscosity, \(\eta_0\), was reached. The origin of strain hardening in comb polymers is the stretchability of branching point spacing in a diluted environment. This means that an enough flexible backbone diluted with enough side chain results in a maximum SHF and minimum zero shear viscosity. The transition from a dense comb to a loose bottlebrush topology for entangled systems drastically increases \(\eta_0\) and reduces SHF for a given backbone and side chain length. The origin of this transition for \(\eta_0\) could be related to the different monomeric frictions in comb and bottlebrush structures. Penetration of entangled side chains of comb topologies into neighboring molecules results in higher frictional coefficient for combs with longer side chains, while intermolecular penetration is diminished for dense bottlebrush topologies which results in lower frictional effect in bottlebrushes with longer side chains. However, this phenomenon should be quantified using scaling analysis of relaxation times. This means that the frictional mechanisms for dense comb and loose bottlebrushes should be revisited according to the penetration of side chains of neighboring molecules. For a better understanding of these frictional coefficients, the extensional experiments should be performed. To the best of our knowledge, there are wide range of experimental data for linear rheological behavior of densely grafted comb and loosely grafted bottlebrushes; however, the lack of both uniaxial and biaxial extensional properties of such systems is obvious. Performing these extensional experiments in the melt state might help to quantify and understand the frictional mechanisms in transitional region from comb to bottlebrush topology. The plateau modulus of both comb and bottlebrushes were investigated based on the scaling analysis. Different conformations of backbone and side chains in comb and bottlebrushes were investigated according to the degree of polymerization of the side chains, \(n_{sc}\), branching point spacing, \(n_g\), and the volume fraction of the backbone, \(\phi_{bb}\). The shear plateau modulus of all conformational regimes was presented and correlated to \(n_{sc}\), \(n_g\), and \(\phi_{bb}\), as well as to the average monomeric volume and length. The volume fraction of the backbone, as well as the length of the side chains in dense bottlebrush topologies, plays the most important roles in the resulting rubber plateau shear modulus of the bottlebrush melts. Bottlebrush elastomers (networks) present solvent-free, super-soft, and superelastic behavior via a controlled network shear modulus through the length of the side chains and crosslink density.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bottlebrush, comb, extensional rheology, linear rheology, strain hardening, zero shear viscosity

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[1] J. Roovers, Polymer 1979, 20, 843.
[2] M. Winterrmantel, M. Gerle, K. Fischer, M. Schmidt, I. Wataoka, H. Urakawa, K. Kajiwara, Y. Tsukahara, Macromolecules 1996, 29, 978.
[3] S. S. Sheiko, B. S. Sumerlin, K. Matyjaszewski, Prog. Polym. Sci. 2008, 33, 759.
[4] J. Li, M. Gautier, Macromolecules 2001, 34, 8918.
[5] D. Pantazis, I. Chalari, N. Hadjichristidis, Macromolecules 2003, 36, 3783.
[6] Y. Xia, J. A. Kornfield, R. H. Grubbs, Macromolecules 2009, 42, 3761.
[7] K. Matyjaszewski, Adv. Mater. 2018, 30, 1706441.
[8] K. Huang, J. Rzayev, J. Am. Chem. Soc. 2009, 131, 6880.
[9] R. Verduzco, X. Li, S. L. Pesek, E. G. Stein, Chem. Soc. Rev. 2015, 44, 2405.
[10] J. Roovers, W. W. Graessley, Macromolecules 1981, 14, 766.
[11] M. Abbasi, L. Faust, K. Riazzi, M. Wilhelm, Macromolecules 2017, 50, 5964.
[12] G. Liu, H. Ma, H. Lee, H. Xu, S. Cheng, H. Sun, T. Chang, R. P. Quirk, S.-Q. Wang, Polymer 2013, 54, 6608.
[13] M. Hu, Y. Xia, C. S. Daefller, J. Wang, C. B. McKenna, J. A. Kornfield, R. H. Grubbs, J. Polym. Sci., Part B: Polym. Phys. 2015, 53, 899.
[14] T.-P. Lin, A. B. Chang, H.-Y. Chen, A. L. Liberman-Martin, C. M. Bates, M. J. Voegtle, C. A. Bauer, R. H. Grubbs, J. Am. Chem. Soc. 2017, 139, 3896.
[15] A. B. Chang, T.-P. Lin, N. B. Thompson, S.-X. Luo, A. L. Liberman-Martin, H.-Y. Chen, B. Lee, R. H. Grubbs, J. Am. Chem. Soc. 2017, 139, 17683.
