Sonication-induced scission of molecular bottlebrushes: Implications of the “hairy” architecture


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1. Introduction

Molecular bottlebrushes are a unique class of graft copolymers exhibiting extended comb-like conformation due to steric repulsion of densely grafted side chains [1,2]. The special spatial dimensions and tunable architecture of bottlebrush macromolecules lead to potential applications including supr...
side-chain effect depends on the sonication-induced flow rate, which may result in solvent draining through the bottlebrush corona producing an additional drag force and leading to amplification of the scission process. As a result, the contribution of polymer architecture to sonication induced chain fracture is expected to be much richer than has been observed, for example, in three-arm star polymers [29]. Molecular bottlebrushes prepared from the same backbone with different side chain DPs were subjected to pulsed ultrasound to cause backbone scission. The scission kinetics was followed by monitoring the average contour length of the bottlebrushes via molecular imaging with the use of atomic force microscopy (AFM). We have analyzed the data and shown the dependence of the limiting contour length of the bottlebrush backbone and the scission rate on the side chain DP.

2. Experimental section

2.1. Materials

n-Butyl acrylate (nBA, 99%, Acros) and (2-trimethylsiloxylethyl methacrylate (HEMA-TMS, Scientific Polymer Products) were purified by passing the monomer through a column filled with basic alumina to remove the inhibitor; 2,2′-azobisis(2-methylpropionitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol and dried under vacuum prior use. Sulfacic acid (20% fuming) was purchased from Alfa Aesar. All other reagents: 2-cyano-2-propyl 4-cyanobenzidithioate (98%), copper(I) bromide (CuBr, 99.999%), copper(II) bromide (CuBr₂, 99.999%), 4,4′-diphenyl-2,2′-dipyridyl (dNbpy, 97%), potassium fluoride (KF, 99%), tetrahydrofuranmonium fluoride (TFBF, 1.0 M in THF), α-bromoisobutyryl bromide (98%), 2,5-di-tert-butylphenol (DTBP, 99%), triethylamine (TEA, <99%), 1-butanol (ACS reagent, >99.4%) and solvents were purchased from Aldrich and used as received without further purification.

2.2. Synthesis and characterization

The conversion of nBA was determined from 1H NMR spectra recorded in CDCl₃ as a solvent using Bruker 300 MHz spectrometer. Molecular weight distributions of the polymers were characterized by gel permeation chromatography (GPC) using Polymer Standards Services (PSS) columns (guard, 70,105, and 102 Å), with THF eluent at 35 °C, flow rate 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410). The apparent number-average molecular weights (Mn) and molecular weight dispersities (Mw/Mn) were determined with a calibration based on linear poly(methyl methacrylate) (PMMA) standards and diphenyl ether as an internal standard, using WinGPC 6.0 software from PSS. In addition to the conventional GPC technique, we used a combination of molecular imaging by AFM and preparation of monolayers at a controlled surface concentration. The solutions were deposited onto the surface of water (Milli-Q double-distilled, 18.2 MΩ·cm) and passivated with the column filled with basic alumina. The polymer was re-precipitated three times in hexanes and dried overnight under vacuum. Apparent molecular weight determined by THF GPC: \( M_{n, GPC} = 3.16 \times 10^2 \) and \( M_{n, Mn} = 1.31 \).

2.2.2. Synthesis of \( \text{PBiBEM}_{2000} \) (macroinitiator)

A 100 mL round-bottom flask was charged with \( \text{P(HEMA-TMS)}_{2000} \) (3.60 g, 17.8 mmol), KF (1.16 g, 19.6 mmol), DTBP (0.37 g, 1.78 mmol), and then dry THF (50 mL) was added under nitrogen. The reaction mixture was cooled down in an ice bath, followed by the injection of tetrabutylammonium fluoride (0.18 mL, 1.0 M in THF, 0.18 mmol) and subsequent dropwise addition of α-bromoisobutyryl bromide (4.50 g, 2.4 mL 19.6 mmol) over the course of 20 min. Upon addition, the reaction mixture was allowed to reach room temperature and was stirred for another 16 h. Afterwards solids were filtered and the mixture was precipitated into methanol/water (70/30), re-dissolved in chloroform (50 mL) and passed through the column filled with basic alumina. The product was re-precipitated three times in hexanes and dried overnight under vacuum. Apparent molecular weight determined by THF GPC: \( M_{n, GPC} = 3.15 \times 10^3 \), and \( M_{n, Mn}^\ast = 1.30 \).

2.2.3. Synthesis of polymer bottlebrushes

Four bottlebrush polymers were synthesized by ATRP from the same macroinitiator (PBiBEM₂₀₀₀) and varying in DP of poly (n-butyl acrylate) (PBA) side chains (Table 1). A typical procedure for the preparation of Brush-1 is described here: A 10 mL Schlenk flask equipped with a stir bar was charged with macroinitiator PBiBEM₂₀₀₀ (0.196 g, 0.703 mmol of BiBEM groups), nBA (10.0 mL, 70.2 mmol), dNbpy (0.155 g, 0.379 mmol), CuBr₂ (4.7 mg, 0.0210 mmol), and anisole (1.1 mL). The solution was degassed by three freeze–pump–thaw cycles. During the final cycle CuBr (24.6 mg, 0.1684 mmol) was quickly added to the frozen reaction mixture under nitrogen atmosphere. The flask was sealed, evacuated, back-filled with nitrogen five times, and then immersed in an oil bath thermostated at 70 °C. The polymerization was stopped after 18 h, and the monomer conversion was determined by 1H NMR (2.6%), resulting in the brush polymer with DP=26 of side chains. The polymer was purified by three precipitations from cold methanol, and dried under vacuum at room temperature, to a constant mass. Apparent molecular weight was determined using THF GPC: \( M_{n, GPC} = 1.35 \times 10^3 \), and \( M_{n, Mn}^\ast = 1.30 \).

2.3. Sonication experiments

Each sonication was performed in a three–armed Süsslich reaction vessel of -15 mL of molecular bottlebrush solution in chloroform at a concentration of 0.1 mg/mL. The solutions were deoxygenated by bubbling N₂ for 30 min prior to sonication. The temperature was kept between 6 and 9 °C in an ice-water bath, and the sonication pulse sequence was set to 1 s ON/1 s OFF, with a power of 6.8 W/cm² working at 20 kHz. Aliquots were removed from the vessel at various sonication time intervals for AFM analysis.

2.4. Langmuir–Blodgett monolayers

At different sonication times, solutions of the molecular bottlebrushes were extracted from the reactor, and 100 μL was deposited onto the surface of water (Milli-Q double-distilled, 18.2 MΩ·cm)/2-propanol (Sigma–Aldrich, HPLC grade) mixture (0.5 wt. % of propanol) in a Langmuir–Blodgett trough (KSV-5000 instrument equipped with a Wilhelmy plate balance) at room temperature. Propanol was added to reduce the surface energy to prevent backbone scission due to adsorption [16]. The monolayer
films were transferred from the air/aqueous interface to freshly cleaved mica substrates at a constant pressure of 0.5 mN/m for AFM studies.

2.5. AFM imaging and analysis

Height images of individual molecules were collected using a multimode Atomic Force Microscopy (Bruker) with a NanoScope V controller in the PeakForce QNM mode. We used silicon cantilevers with a resonance frequency of 50–90 kHz and a spring constant of about 0.4 N/m. Digital images of individual molecules were analyzed using a custom software program developed in-house. The contour length of the bottlebrush was measured directly by AFM due to the height contrast from the desorbed side chains segregated around the backbone. More than 600 molecules were counted to obtain the length distributions of the bottlebrushes, ensuring representative statistics.

3. Results and discussion

3.1. Molecular imaging of degradation products

Fig. 1a displays images of individual molecules of Brush-3 captured at different stages of the sonication process. Apparently, long bottlebrushes undergo progressive fragmentation to smaller species. Fig. 1b depicts the time evolution of the bottlebrush length distribution during the sonication process. For example, the average contour length of Brush-3 was \( L_0 = 369 \pm 8 \text{ nm} \) before sonication and then decreased to a limiting length of \( L_{\text{lim}} = 27 \pm 4 \text{ nm} \) within a total sonication time of 4 h. The length dispersity of the fractured bottlebrushes initially increased at the beginning of sonication and then followed by a decrease with time, as shown in Fig. 1c. This is consistent with previously reported results on ultrasonic degradation of poly(methyl methacrylate) that the dispersity of the fractured bottlebrush side chains determined by GPC of cleaved side chains, \( D = 1.2 - \text{dispersity of bottlebrush side chains determined by GPC} \), is substantially smaller than that for linear polymers under similar experimental conditions [34,35]. For Brush-4 with side chain DP of 222, the average molecular weight of two PBA side chains is about 57 kDa, which may cause their rupture. However, the probability of bond scission along any given side-chain to side-chain path is significantly lower than along the backbone. Due to multiple side chains coupled to a bottlebrush backbone, the drag force along the backbone is larger than along a side-chain path. It is also necessary to point out that recombination of daughter fragments can be neglected due to steric repulsion of densely-grafted side chains. Once the backbone is cleaved, the generated radicals will be spontaneously shielded by the side chains, which form a hemispherical cap at the bottlebrush ends hindering the recombination.

3.2. Degradation kinetics of molecular bottlebrushes

The scission rate and the limiting molecular weight for linear polymers can be determined by using the equation derived by Madras et al. [36,37]. This equation is based on the assumption that sonication-induced cleavage of polymers occurs at the mid-point of the chain and is a first-order reaction:

\[
\ln \left( \frac{L_{\text{lim}}^t - L_{\text{lim}}^0}{L_{\text{lim}}^0 - L_{\text{lim}}^0} \right) = -kd_{\text{lim}} t
\]

(1)

where \( L_{\text{lim}} \), \( L_0 \) and \( L_t \) are the limiting number average contour length, the initial number average contour length and the number average contour length of the backbone at time \( t \) respectively, and \( k \) is the rate constant that is independent of \( L_0 \). Note that Eq. (1) is expressed in terms of bottlebrush contour length, which is linearly proportional to the corresponding molecular weight \( \left( M_{\text{L}} - M_{\text{f}} \right) \) typically used in the kinetics analysis [28,29]. We use Eq. (1) to fit the experimental data with \( L_{\text{lim}} \) and \( k \) as the fitting parameters for all four bottlebrush samples. As shown in Fig. 2a, the fitted decay profiles (solid curves) are in good agreement with the experimental data (points). The fitting results are summarized in Table 2. The extrapolated \( L_{\text{lim}} \) values in Table 2 are verified by molecular imaging of bottlebrushes after long-time sonication for 4 h (Fig. 2b).

As shown in Table 2, the scission rate increases with increasing side chain DP, while the limiting contour length \( (L_{\text{lim}}) \) of the molecular bottlebrush decreases with increasing side chain DP. Both observations are consistent with previously reported results of sonication-induced scission of poly (alkyl methacrylate) that the scission rate increases and the limiting chain length decreases with increasing bulk size of the alkyl substituent [34,35]. This may be explained by larger drag force generated along the bottlebrush backbone with longer side chains during bubble collapse. Note that the limiting contour lengths for all four bottlebrushes are substantially smaller than that for linear polymers under similar

Table 1

<table>
<thead>
<tr>
<th>Characterization of the molecular bottlebrushes.</th>
<th>GPC</th>
<th>AFM-LB</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_m^a )</td>
<td>( n_m^b )</td>
<td>( M_0^c )</td>
</tr>
<tr>
<td>Brush-1 2000</td>
<td>26</td>
<td>1.35 \times 10^6</td>
</tr>
<tr>
<td>Brush-2 2000</td>
<td>60</td>
<td>1.63 \times 10^6</td>
</tr>
<tr>
<td>Brush-3 2000</td>
<td>100</td>
<td>1.75 \times 10^6</td>
</tr>
<tr>
<td>Brush-4 2000</td>
<td>130</td>
<td>2.14 \times 10^6</td>
</tr>
</tbody>
</table>

| a | Number average DP of the bottlebrush backbone estimated from its apparent molecular weight by GPC. |
| b | Apparent number average DP of side chains estimated from monomer conversion. |
| c | Apparent number average molecular weight measured by GPC. |
| d | Dispersity determined by GPC. |
| e | Contour length of bottlebrushes adsorbed to a mica substrate prior to sonication prepared by the LB technique. |
| f | Width of the bottlebrush adsorbed on a mica substrate determined by AFM. |
| g | Number average DP of the bottlebrush backbone calculated as \( n_m = L_0/L_b \), where \( L_b = 0.25 \text{ nm} \) — monomer contour length. |
| h | Number average DP of the side chains calculated as \( n_m = 9W/2D_kB \), where \( D_k = 1.2 - \text{dispersity of bottlebrush side chains determined by GPC} \). |
| i | Number average molecular weight measured by GPC. |
| j | Side chain DP of 222, the average molecular weight of two PBA side chains is about 57 kDa, which may cause their rupture. |
| k | \( r_T \) is the rate constant that is independent of \( L_0 \). \( k = 1.75 \) is the average number of repeat units of the backbone between neighboring side chains measured previously [6]. |
sonication conditions. Typical limiting molecular weight for poly(alkyl methacrylates) is about 40 kg/mol [35], corresponding to a contour length of ~100 nm, which is about 4 times larger than that for the bottlebrushes with the longest side chains (Brush-4). On the other hand, the densely grafted bottlebrush samples approach their limiting contour length within ~60 min, while it takes hours for linear poly(alkyl methacrylates) to reach their limiting molecular weights under similar conditions (or at even higher sonication powers) [34].

3.3. Data analysis

For scaling analysis of the dependence of the limiting contour length on the side chain DP, we will consider two different models to calculate the drag force at the center of a bottlebrush backbone. In the first model, solvent is assumed to be freely draining through the side chains as they move (Rouse model); while in the other model, we assume that the side chain drags the solvent in their pervaded volume as they move (Zimm model) [38].
3.3.1. Rouse model

We first consider the force at the center of a chain (maximum force $f_m$) for linear polymers with $n$ monomers in the elongational flow generated by sonication. Assuming that the chain is fully extended, we can write [39],

$$f_m \sim \zeta_m L^2$$

where $L = n$ is the contour length, $\zeta_m$ is the monomeric friction coefficient.

In this model, it is assumed that solvent can be freely drained through the volume occupied by the side chains as they move. The friction coefficient of each Kuhn monomer is evaluated as $\zeta = n b \eta$, where $b = 1.8$ nm is the Kuhn length of PBA side chains and $\eta$ is the viscosity of the solvent. Therefore the total friction coefficient of the whole side chain is the sum of the contributions of each monomer:

$$\zeta_R = N_{sc} \zeta_m = N_{sc} b \eta$$

where $N_{sc}$ is the number of Kuhn monomers of a side chain. Considering each side chain is an effective monomeric unit of bottlebrush molecules, we can obtain the maximum drag force at the center of the bottlebrush backbone as

$$f_m \sim \zeta_R L^2 \sim N_{sc} L^2$$

As the force along the bottlebrush backbone increases, the rate of backbone scission increases. It is known that the intrinsic tension in the bottlebrush backbone (prior to sonication) is on the order of 10 pN [15], while it requires $nN$ forces to break covalent bonds on the –μs time scale of a bubble collapse in the sonication experiment [40]. Therefore, the intrinsic tension can be neglected, and the external critical force ($f_c$) to break the C–C bonds in the backbone can be considered as the same for the four bottlebrushes regardless of the side chain DP. This differs from the case of solid filaments that exhibit an increase of the critical force with increasing filament diameter. The backbone will effectively stop breaking once $f_c$ becomes smaller than $f_c$, and therefore we can obtain the following relation between the limiting contour length ($L_{lim}$) and the number of Kuhn monomers in the side chain ($N_{sc}$):

$$f_c \sim N_{sc} L_{lim}^2$$

$$L_{lim} \sim (1/N_{sc})^{1/2}$$

To verify this prediction, we plot the experimentally determined limiting contour lengths as a function $1/N_{sc}$ (Fig. 3). The number of Kuhn monomers can be estimated as $N_{sc} \approx (n_{sc}/n_0) b$, where the number average DP of the side chains was determined from the brush width by the AFM-LB method (Table 1) [9,15,31]. For our bottlebrush macromolecules, $N_{sc}$ ranges from 3 to 18. The slope of 0.57 ± 0.06 is slightly larger than 0.5 - the scaling exponent predicted by the Rouse model (Eq. (6)). This deviation may be attributed to incomplete extension of the bottlebrush backbone in the elongational flow created by bubble collapse.

3.3.2. Zimm model

Assuming that the side chains drag solvent confined within a bottlebrush macromolecule, we consider molecular bottlebrushes as solid spherocylinders with radius $R = b N_{sc}^{1/2}$ (unperturbed side chains that are smaller than the thermal blob). The aspect ratio of the cylindrical brushes is given as

$$p = L'/2R = (L + 2R)/2R = L'/\left(2bN_{sc}^{1/2}\right) + 1$$

where $L' = L + 2R$ is the total length of molecular bottlebrushes including the end caps formed by side chains in solution. The aspect ratios for the four molecular bottlebrushes at limiting backbone contour length $L_{lim}$ are in the range of 2.4–9.7. Taking this into consideration, we can express the friction coefficient parallel to the backbone using the equation with numerical correction proposed by Aragon and Flamik for $1 \leq p < \infty$ [41]:

$$\zeta_z = 4 \pi \eta L'/[2 \ln(p) + C]$$

where

$$C = -0.113192 - 1.30429 \cdot 10^{-0.25} + 1.19032 \cdot 10^{-0.5} + 3.12756 \cdot p^{-1} - 1.56699 \cdot p^{-2} - 0.930791 \cdot p^{-3}$$

is the numerical correction.

To derive the forces in the bottlebrush backbone caused by velocity gradient along the backbone, we express the relative velocity ($V$) as a function of the distance ($x$) from the middle of the backbone by $V(x) = \dot{\varepsilon} \cdot x$, where $\dot{\varepsilon}$ is the strain rate. The force per unit length along the backbone is given by

$$f(x) = \zeta_z V(x)/L' = 4 \pi \eta \dot{\varepsilon} / [2 \ln(p) + C]$$

To calculate the maximum drag force at the backbone center $f_m$, we need to integrate the absolute value of $f(x)$ from 0 to $L'/2$ and obtain

$$f_m = \int_0^{L'/2} f(x) dx = \frac{1}{2} \pi \eta L^2 / [2 \ln(p) + C]$$

Similarly, we can obtain the following scaling relations:

**Table 2**

Results from fitting analysis in Fig. 2.

<table>
<thead>
<tr>
<th>$L_0$ (nm)$^a$</th>
<th>$L_{lim}$ (nm)$^b$</th>
<th>$K \cdot 10^3 (\text{min}^{-1} \text{nm}^{-1})^c$</th>
<th>$R^2_{fit}$ $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brush-1 371 ± 10</td>
<td>56 ± 6</td>
<td>4.3 ± 0.8</td>
<td>0.94</td>
</tr>
<tr>
<td>Brush-2 354 ± 8</td>
<td>36 ± 4</td>
<td>7.8 ± 1.5</td>
<td>0.95</td>
</tr>
<tr>
<td>Brush-3 369 ± 8</td>
<td>27 ± 4</td>
<td>8.2 ± 1.3</td>
<td>0.96</td>
</tr>
<tr>
<td>Brush-4 366 ± 9</td>
<td>21 ± 2</td>
<td>13.6 ± 1.3</td>
<td>0.98</td>
</tr>
</tbody>
</table>

$a$ Initial contour length of the bottlebrushes before sonication.

$b$ Limiting contour length of fractured bottlebrushes.

$c$ Rate constant of the sonication-induced fracture of bottlebrushes obtained by fitting the experimental data points in Fig. 2a with Eq. (1).

$d$ The adjusted $R^2$ values close to unity demonstrate the goodness of the fit.

Fig. 3. Experimentally determined scaling relation between the limiting contour length ($L_{lim}$) and the number of Kuhn monomers in the side chain ($N_{sc}$). The solid line represents the power-law fit to the data points.
\[ f_c \sim L_{\text{lim}}^2 / [2 \ln(p_{\text{lim}}) + C_{\text{lim}}] \]  
(11)

\[ L_{\text{lim}}' \sim [2 \ln(p_{\text{lim}}) + C_{\text{lim}}]^{1/2} \]  
(12)

where \( p_{\text{lim}} \) and \( C_{\text{lim}} \) are the corresponding aspect ratio (Eq. (7)) and numerical correction as a function of the limiting contour length (Eq. (8)), respectively. Fig. 4 shows a log–log plot of \( L_{\text{lim}}' \) as a function \( 2 \ln(p_{\text{lim}}) + C_{\text{lim}} \) with a slope of 0.83 \( \pm \) 0.05, which is markedly larger than the predicted value of 0.5 from Eq. (12).

4. Discussion

Scaling analysis of the bottlebrush backbone scission dynamics has been performed to quantify the effect of side chain DP on the limiting contour length using Rouse and Zimm models. The former model shows a better agreement between model predictions and experimental results. This indicates that the solvent molecules drain through the bottlebrush corona producing a larger drag force. The solvent draining can be rationalized by comparing the characteristic relaxation time of the side chains and the shear strain rate generated upon bubble collapse. For the solvent to move through the side chains its flow should be faster than the side chain Zimm relaxation time \( \tau_Z (\dot{\varepsilon} > \tau_Z^{-1}) \). We can estimate the Zimm relaxation time for the side chains with size \( R \approx \ln N_c^{1/2} \) as

\[ \tau_Z = \tau_0 N_c^{3/2} \]  
(13)

where \( \tau_0 = \eta_b k_b T \approx 1.0 \text{ ns} \) is the relaxation time of Kuhn monomer (\( b = 1.8 \text{ nm} \)) in chloroform with viscosity \( \eta \approx 0.64 \text{ mPa} \text{s} \) at the median temperature (6–9 °C) of \( T = 281 K \) and \( k_b \) is the Boltzmann constant. From Eq. (13), we can estimate the Zimm relaxation time to change between 6 ns (Brush-1) and 74 ns (Brush-4). It is known that the strain rate and, hence, drag force decrease with the distance from an imploding microbubble [18]. Yet, it may be strong enough to induce bond scission, provided that the bottlebrushes are sufficiently long. At the initial contour length \( L_0 \approx 370 \text{ nm} \) (Table 2), the maximum drag force \( f_m \sim \dot{\varepsilon} \tau_Z \) can reach the critical force \( f_c \) at a lower strain rate, e.g., \( 2 \times 10^5 \text{ s}^{-1} \) for Brush-1 and \( 3 \times 10^6 \text{ s}^{-1} \) for Brush-4. This is slower than the Zimm relaxation \( (\dot{\varepsilon} < \tau_Z^{-1}) \), indicating that the bottlebrush dynamics corresponds to non-draining regime described by the Zimm model. However, at a limiting contour length (analyzed in this paper), the bottlebrushes need to reach the vicinity of an imploding microbubble where the strain rate is the highest \( (\dot{\varepsilon} \approx 10^9 \text{ s}^{-1}) \) [18,19,42] to achieve the greatest force at the backbone center. In this case, the strain rate is larger than the Zimm relaxation time \( (\dot{\varepsilon} > \tau_Z^{-1}) \), suggesting that the bottlebrush dynamics corresponds to draining regime described by the Rouse model. In other words, the bottlebrush dynamics undergoes a transition from non-draining (Zimm) to draining (Rouse) regime as the bottlebrushes become shorter. At the initial stages of sonication, long bottlebrushes \( (\dot{\varepsilon} < \tau_Z^{-1}) \) may behave like solid cylindrically shaped objects, similar to carbon nanotubes, nanowires, polymeric fibrils [18,19,25,27,28]; while at the later stages, the backbone scission is controlled by solvent draining, which differentiates short bottlebrushes \( (\dot{\varepsilon} > \tau_Z^{-1}) \) from solid cylindrical objects. Besides, the critical force for cleavage for solid cylindrically shaped objects depends on their cross-sectional area, in contrast to its independence on diameter (DP of side chains) for bottlebrushes and that it is determined by the strength of backbone bonds.

5. Conclusions

We have studied the effect of the side chain DP on the sonication-induced scission of molecular bottlebrushes. The scission rate has been shown to increase with increasing side chain DP, while the limiting contour length decreases as side chain DP increases. This decrease of the limiting contour length is attributed to higher drag force exerted on the backbone with longer side chains by the solvent flow generated by bubble collapse. To quantify the effect of side chain DP on the limiting contour length, we have performed scaling analysis of the bottlebrush backbone scission dynamics using Rouse and Zimm models. The Rouse model shows a better agreement between model predictions and experimental results, which indicates that flexible and hairy molecular bottlebrushes behave differently from solid cylindrically shaped objects with respect to their interaction with solvent in the sonication process when the bottlebrushes are cut short enough \( (\dot{\varepsilon} > \tau_Z^{-1}) \); solvent drains through the bottlebrush corona formed by side chains, while it cannot penetrate through solid objects.

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References


Fig. 4. Dependence of the limiting total length of cylindrical bottlebrushes \( L_{\text{lim}}' \) as a function of parameter \( 2\ln(p_{\text{lim}}) + C_{\text{lim}} \).