



**HAL**  
open science

# Bottlebrush polymer gels: architectural control over swelling and osmotic bulk modulus

Ekaterina Zhulina, Oleg Borisov

► **To cite this version:**

Ekaterina Zhulina, Oleg Borisov. Bottlebrush polymer gels: architectural control over swelling and osmotic bulk modulus. *Soft Matter*, 2022, 18 (6), pp.1239-1246. 10.1039/D1SM01575C . hal-03867860

**HAL Id: hal-03867860**

**<https://hal.science/hal-03867860v1>**

Submitted on 24 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Bottlebrush polymer gels: architectural control over swelling and osmotic bulk modulus.

Ekaterina B.Zhulina<sup>1</sup> and Oleg V.Borisov<sup>1,2</sup>

<sup>1</sup>Institute of Macromolecular Compounds  
of the Russian Academy of Sciences,  
St.Petersburg, Russia

<sup>2</sup>Institut des Sciences Analytiques et de Physico-Chimie pour  
l'Environnement et les Matériaux, UMR 5254 CNRS UPPA,  
Pau, France

January 1, 2022

## Abstract

Swelling behaviour and bulk moduli of polymer gels comprising of crosslinked bottlebrush subchains enables fine tuning by varying polymerization degrees of the main and side chains of the bottlebrush strands as well as their grafting densities. By using scaling approach we predic power law dependences of structural and elastic properties of swollen bottlebrush gels on the set of relevant architectural parameters and construct phase diagrams consisting of regions corresponding to different power law asymptotics for these dependences. In particular, our theory predict that bulk elastic modulus of the gel exhibits non-monotonous dependence on the degree of polymerization of side chains of the bottlebrush strands.

# 1 Introduction

Architectural control of the performance polymer material properties by varying topology of the macromolecules without changing their chemical nature is a popular paradigm in contemporary material science.

Comb-shape polymers and molecular brushes comprising of long main chain with multiple side chains tethered to it at regular intervals present one of the most popular class of branched macromolecules used for fabricating more complex, including supramolecular architectures.<sup>1-6</sup> Macromolecules with even more complex topology based on the bottlebrush motive, e.g. barb-wire macromolecules<sup>7-9</sup> or dendronized polymers<sup>10,11</sup> have recently become available as well. Progress in chemical synthesis allowed for a wide variety polymers and copolymers with elaborately controlled branched architectures<sup>12-15</sup> that can, in turn, serve as precursors for more complex constructs, e.g., swelling networks with branched strands that could mimic elements of natural systems.<sup>16</sup>

Covalent cross-linking of comb-shaped polymers or molecular brushes gives rise to solvent-free elastomeric networks<sup>17,18</sup> or polymer gels with novel unusual mechanical properties that can be tuned by proper variation in the architectural codon of the constituent strands (polymerization degrees of the main chains, i.e., cross-linking density, and side chains as well as grafting density). Such materials exhibit very unusual mechanical properties, and allow for independent tuning of elastic moduli in different regimes and in a wide deformation range.<sup>19</sup> Remarkably, living nature amply employes bottlebrush structure for adjusting mechanical properties of different tissues<sup>20-22</sup>

Recently we examined the swelling behavior of networks formed by barb-wire molecular brushes with multiple short side chains emanating from each branching point in the loosely crosslinked network subchains.<sup>23</sup> The aim of the present work is to extend the scaling analysis for bottlebrush networks to the cases of arbitrary cross-linking density and degrees of polymerization (DPs) of the side chains, and to predict the power law dependences for the degree of gel swelling and its bulk elastic modulus as a function of relevant architectural parameters.

## 2 The bottlebrush gel model

Consider a network formed by bottlebrush macromolecules crosslinked by the end segments of the main chains in the network nodes and immersed into a good (athermal) solvent. Each subchain of the network consists of the backbone (main chain) comprising  $M \gg 1$  monomer units and multiple side

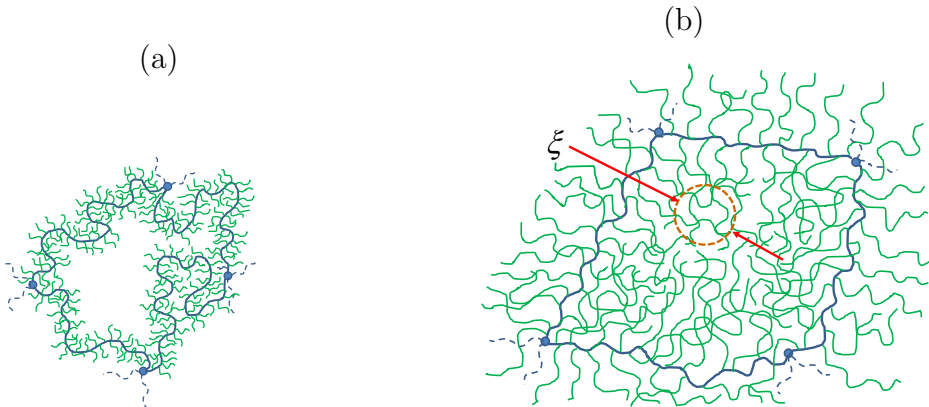


Figure 1: Schematics of a swollen bottlebrush gel in semi-dilute,  $C^*$  (a) and concentrated,  $C^{**}$ , (b) regimes. The number of monomer units in the main chain is  $M$ . The numbers of monomer units in a side chain is  $n$ , the number of monomer units in a segment of the main chain separating neighbouring side chains (spacer) is  $m$ .

chains each comprising  $n$  monomer units that are attached by one end to each  $m$ -th monomer unit of the main chain. Total number of monomer units in one strand of the network is  $N = M(1 + n/m)$ . The main chain and side chains are assumed to be chemically identical, with Kuhn segment length on the order of monomer size  $a$  taken below as a unit of length.

Below we address the case  $n \gg m$  which corresponds specifically to the bottlebrush limit. Repulsive (in athermal solvent) interactions between densely grafted side chains lead to stretching of both side chains and spacers in the network strands and swelling of the gel. Two regimes of the bottlebrush gel swelling are distinguished below depending on the set of architectural parameters  $\{M, m, n\}$ .

### 3 The semi-dilute $C^*$ -regime

In this regime the characteristic mesh size  $R$  (the average end-to-end distance of the main chain of a bottlebrush network strand) in the swollen gel exceeds by far thickness  $D$  of the individual bottlebrush, which is controlled by extension of the side chains, **Figure 1a**. The swollen gel can be treated as a gel formed by cross-linked linear chain strands with renormalized contour length and thickness (or, equivalently, effective excluded volume parameter). The equilibrium degree of gel swelling,  $Q = V/V_{dr} \simeq R^3/N$ , which is the

ratio of volumes,  $V \simeq R^3$ , and  $V_{dr} \simeq N$  in the swollen and dry states of the network, respectively, can be found by applying the  $c^*$ -theorem,<sup>24</sup> according to which the equilibrium mesh size  $R$  of the gel is on the order of the size  $R_{eq}$  of a single strand.

The individual bottlebrush strand can be assimilated<sup>23,25-30</sup> to a self-avoiding wormlike chain with thickness  $D$  determined by extension of the side chains, and the effective contour length  $L \cong (M/m)h$ , where  $h$  is the average extension (end-to-end distance) of a spacer (segment of the main chain connecting neighboring branching points). Equivalently, the bottlebrush can be presented as a flexible chain composed of  $L/D$  impermeable superblobs each of size  $D$ . Repulsive (under good solvent conditions) interactions between densely grafted to the backbone side chains impose stretching of both side and main chains and impermeability of the superblobs. Hence, the characteristic size of a swollen network strand is

$$R \simeq R_{eq} \cong L^\nu D^{1-\nu} = \left(\frac{M}{m}\right)^\nu h^\nu D^{1-\nu} \quad (1)$$

where<sup>25,30</sup>

$$h \cong \begin{cases} m^\nu (n/m)^{\nu(1-\nu)/2}, & m \geq n^{\nu/(2+\nu)}, \left(C_a^*\right) \\ m, & m \leq n^{\nu/(2+\nu)}, \left(C_b^*\right) \end{cases} \quad (2)$$

$$D \cong \begin{cases} n^\nu (n/m)^{\nu(1-\nu)/2}, & m \geq n^{\nu/(2+\nu)} \\ n^{2\nu/(1+\nu)} m^{-(1-\nu)/(1+\nu)}, & m \leq n^{\nu/(2+\nu)} \end{cases} \quad (3)$$

and  $\nu \approx 0.6$  is the Flory exponent. The first and the second lines in eqs 2 and 3 correspond to partial and full (up to the contour length,  $m$ ) stretching of spacers of the main chain, respectively. Below we refer, respectively, to subregime  $C_a^*$  (corresponding to  $m \geq n^{\nu/(2+\nu)}$ , partial spacer stretching) and subregime  $C_b^*$ , (corresponding to  $m \leq n^{\nu/(2+\nu)}$ , full spacer stretching).

Scaling expressions, eqs 2 and 3, were derived in ref,<sup>25</sup> based on the representation of a cylindrical brush of side chains with average axial distance  $h$  per chain as an array of densely packed concentration blobs of size  $\xi(\rho) \cong (\rho h)^{1/2}$ , where  $\rho$  is radial distance from the main chain, and volume fraction of monomer units of the side chains

$$\phi(\rho) \cong \xi^{-(3\nu-1)/\nu}(\rho) \quad (4)$$

The condition of conservation of the number of monomer units in the side chain

$$h \int_0^D \phi(\rho) \rho d\rho = n \quad (5)$$

provides scaling relation for the brush thickness  $D \cong n^{2\nu/(1+\nu)}h^{-(1-\nu)/(1+\nu)}$ . When the spacers of the main chain do not reach limit of their extensibility, i.e.,  $h \leq m$ , the equilibrium extension  $h$  of the spacers is found by balancing the elastic free energy of the extended spacer<sup>24</sup>

$$\frac{F_{elastic}}{k_B T} \cong \frac{h^{1/(1-\nu)}}{m^{\nu/(1-\nu)}} \quad (6)$$

with the free energy (in  $k_B T$  units) evaluated as a number of concentration blobs per side chain

$$\frac{F_{conc}}{k_B T} \cong h \int_0^D \frac{\rho d\rho}{\xi^3(\rho)} \cong (D/h)^{1/2} \quad (7)$$

Using eqs 1, 2 and 3 we can express the equilibrium dimensions of one network strand (the gel mesh size) as

$$R_{eq} \cong \begin{cases} N^\nu (n/m)^{\nu(1-3\nu)/2} \cong M^\nu \left(\frac{n}{m}\right)^{3\nu(1-\nu)/2}, & \begin{pmatrix} C_a^* \\ C_b^* \end{pmatrix} \\ N^\nu (n^\nu/m)^{(1-3\nu)/(1+\nu)} \cong M^\nu n^{2\nu(1-\nu)/(1+\nu)} m^{-(1-\nu)^2/(1+\nu)}, & \end{cases} \quad (8)$$

As seen from eq 8, replacing of linear network strands by bottlebrushes with the same total degree of polymerization  $N$  leads to weaker swelling of the gel. The mesh size decreases as a function of  $n/m$  or  $n^\nu/m$  in regimes  $C_a^*$  and  $C_b^*$ , respectively.

At the same time, attaching of side chains to the linear network strands with constant polymerization degree  $M$  leads to stronger swelling of the gel, i.e. larger  $R_{eq}$ . Remarkably, as long as spacers of the main chains are only partially stretched (subregime  $C_a^*$ ), dimensions of the swollen gel depend only on the ratio  $n/m$ , whereas in the regime of full stretching of spacers (subregime  $C_b^*$ ) this universality breaks down.

The osmotic modulus  $G$  of the swollen gel can be evaluated as<sup>24</sup>

$$\frac{G}{k_B T} \cong R_{eq}^{-3} \cong \begin{cases} N^{-3\nu} (n/m)^{3\nu(3\nu-1)/2} \cong M^{-3\nu} (n/m)^{-9\nu(1-\nu)/2}, & \begin{pmatrix} C_a^* \\ C_b^* \end{pmatrix} \\ N^{-3\nu} (n/m)^{3(3\nu-1)/(1+\nu)} \cong M^{-3\nu} n^{-6\nu(1-\nu)/(1+\nu)} m^{3(1-\nu)^2/(1+\nu)}, & \end{cases} \quad (9)$$

This result can be obtained also from the condition  $G_{osm} \cong \pi$  where  $\pi$  is osmotic pressure which can be evaluated as

$$\pi/k_B T \cong (\phi_D^*)^{3\nu/(3\nu-1)} D^{-3} \quad (10)$$

and

$$\phi_D^* \cong \frac{LD^2}{R_{eq}^3} \quad (11)$$

is volume fraction of  $D$ -superblobs in the swollen gel.

## 4 Concentrated regime (regime $C^{**}$ )

The  $C^*$  regime applies as long as the volume fraction  $\phi_D^*$  of  $D$ -superblobs in the swollen gel is smaller than unity, i.e.,  $D \leq L$ . Alternatively, the boundary of the  $C_a^*$  and  $C_b^*$  regimes can be evaluated as equality of the average concentrations of the monomer units in the gel,  $c^*$ , with

$$c^* \cong \frac{N}{R_{eq}^3} \cong \quad (12)$$

$$\begin{cases} N^{1-3\nu}(n/m)^{3\nu(3\nu-1)/2} = M^{1-3\nu}(n/m)^{(3\nu-2)(3\nu-1)/2}, & \left( C_a^* \right) \\ N^{1-3\nu}(n^\nu/m)^{3(3\nu-1)/(1+\nu)} = M^{1-3\nu} n^{(2\nu-1)(3\nu-1)/(1+\nu)} m^{-(2-\nu)(3\nu-1)/(1+\nu)}, & \left( C_b^* \right) \end{cases} \quad (13)$$

and the concentration  $c^{**}$  of monomer units within distance  $D$  from the main chains of the bottlebrush strands,

$$c^{**} \cong \frac{n+m}{D^2 h} \cong \frac{n}{D^2 h} \cong \begin{cases} n^{1-3\nu}(n/m)^{\nu(3\nu-1)/2}, & \left( C_a^* \right) \\ (nm)^{(1-3\nu)/(1+\nu)}, & \left( C_b^* \right) \end{cases} \quad (14)$$

with  $h$  and  $D$  specified by eqs 2 and 3, respectively, and the last equality implying  $n \gg m$ .

Hence,  $C_a^*$  and  $C_b^*$  regimes apply as long as  $c^* \leq c^{**}$ , that is

$$M \geq \begin{cases} m(n/m)^\nu, & m \geq n^{\nu/(2+\nu)}, \left( C_a^* \right) \\ n^{2\nu/(1+\nu)} m^{-(1-\nu)/(1+\nu)}, & m \leq n^{\nu/(2+\nu)}, \left( C_b^* \right) \end{cases} \quad (15)$$

or

$$N \geq \begin{cases} n(n/m)^\nu, & m \geq n^{\nu/(2+\nu)}, \left( C_a^* \right) \\ n^{(3\nu+1)/(1+\nu)} m^{-2/(1+\nu)}, & m \leq n^{\nu/(2+\nu)}, \left( C_b^* \right) \end{cases} \quad (16)$$

#### 4.1 Subregime $C_a^{**}$

For shorter main chain or longer side chains of the network strands the  $c^*$ -theorem is not applicable anymore. In the case when the main chains of the stands remain not fully stretched (subregime  $(C_a^{**})$ ) we can estimate the mesh size (i.e. the extent of the gel swelling) from the minimization of the free energy (per strand or per mesh volume)

$$F = F_{elastic} + F_{vol} \quad (17)$$

with the elastic free energy of the main chain<sup>24</sup>

$$F_{elastic}/k_B T \cong \frac{R^{1/(1-\nu)}}{M^{\nu/(1-\nu)}} \quad (18)$$

and the excluded volume contribution

$$F_{vol}/k_B T \cong \frac{\pi}{k_B T} R^3 \quad (19)$$

The osmotic pressure in the gel is given by  $\pi/k_B T \cong c^{3\nu/(3\nu-1)}$ , and the concentration of monomer units in the gel is

$$c \cong N/R^3 \quad (20)$$

The result of minimization of the free energy given by eqs 17, 18, 19 with respect to  $c$  gives equilibrium concentration of monomer units in the swollen gel

$$c \cong N^{1-3\nu} (n/m)^{3\nu(3\nu-1)/2} = M^{1-3\nu} (n/m)^{(3\nu-2)(3\nu-1)/2} \quad (21)$$

that coincides in terms of scaling dependences with eq 13 at  $m \geq n^{\nu/(2+\nu)}$  (regime  $C_a^*$ ).

The dimensions  $R \cong (N/c)^{1/3}$  of an individual network strand in this regime are given by the first line in eq 8 which grows as a function of  $n/m$  and reaches the limit of extensibility,  $R \cong M$ , at  $n/m \cong M^{2/3\nu}$ .

The gel osmotic modulus in this regime  $C_a^{**}$  is given by

$$\frac{G}{k_B T} \cong \frac{\pi}{k_B T} \cong c^{3\nu/(3\nu-1)} \cong N^{-3\nu} (n/m)^{9\nu^2/2} = M^{-3\nu} (n/m)^{3\nu(3\nu-2)/2} \quad (22)$$

which weakly decreases as a function of  $n/m$  at constant  $M$ .



## 4.2 Subregime $C_b^{**}$

In the regime  $C_b^{**}$  the main chains of the bottlebrush strands are fully stretched,  $R \cong M$ , the concentration of monomer units in the gel is

$$c \cong \frac{N}{M^3} \cong M^{-2} \frac{n}{m} \cong N^{-2} \left(\frac{n}{m}\right)^3 \quad (23)$$

and the bulk osmotic modulus of the gel in the regime  $C_b^{**}$  is given by

$$\frac{G}{k_B T} \cong \frac{\pi}{k_B T} \cong c^{3\nu/(3\nu-1)} \cong N^{-6\nu/(3\nu-1)} (n/m)^{9\nu/(3\nu-1)} = M^{-6\nu/(3\nu-1)} (n/m)^{3\nu/(3\nu-1)} \quad (24)$$

## 4.3 Diagram of states

In Figures 2a,b,c the diagrams of states of the bottlebrush gel are presented in  $M, n$  (Figure 2a),  $M, m$  (Figure 2b) and  $m, n$  (Figure 2c) coordinates, respectively. Regimes  $C_a^*$  and  $C_b^*$  correspond to loose networks,  $D \ll R_{eq}$ , where the main chains of the bottlebrush strands are not fully stretched ( $C_a^*$ ) or are fully stretched ( $C_b^*$ ), respectively (see Figure 1a). Regimes  $C_a^{**}$  and  $C_b^{**}$  correspond to dense networks where the main chains of the bottlebrush strands are not fully stretched ( $C_a^{**}$ ) or fully stretched ( $C_b^{**}$ ), respectively, (see Figure 1b). At the boundaries between the regimes smooth crossover of the gel mesh size,  $R \simeq R_{eq}$ , occurs. As for the bulk osmotic modulus, the smooth crossover occurs at the boundary between regimes  $C_a^*$  and  $C_b^*$ , as given by eq 9, and between regimes  $C_a^{**}$  and  $C_b^{**}$ , as given by eqs 22 and 24.

However, there is no smooth crossover for the osmotic modulus between regimes  $C_a^*$  and  $C_a^{**}$ , as well as between regimes  $C_b^*$  and  $C_b^{**}$ . Indeed, in regimes  $C_a^*$  and  $C_b^*$  the modulus at the boundary  $C_a^*/C_a^{**}$  and  $C_b^*/C_b^{**}$  is proportional to  $D^{-3}$ , whereas in regimes  $C_a^{**}$  and  $C_b^{**}$  at the same boundary it is proportional to the inverse volume of the concentration blob  $\sim (c^{-\nu/(3\nu-1)})^{-3}$ . Therefore,

$$G|_{C_a^{**}}/G|_{C_a^*} \cong (n/m)^{3\nu/2} \quad (25)$$

and

$$G|_{C_b^{**}}/G|_{C_b^*} \cong (n^\nu/m)^{3/(1+\nu)} \quad (26)$$

In Figures 3a and 3b we present the dependences of the gel mesh size  $R$  and the gel osmotic modulus  $G$  on the DP of side chains  $n$  for the case  $m \geq M^{1/3}$ . Similar dependences for the case  $m \leq M^{1/3}$  are presented in Figures 4a and 4b, respectively. These dependences correspond to cross-sections of the diagram in Figure 2c indicated by dash-dotted arrows.

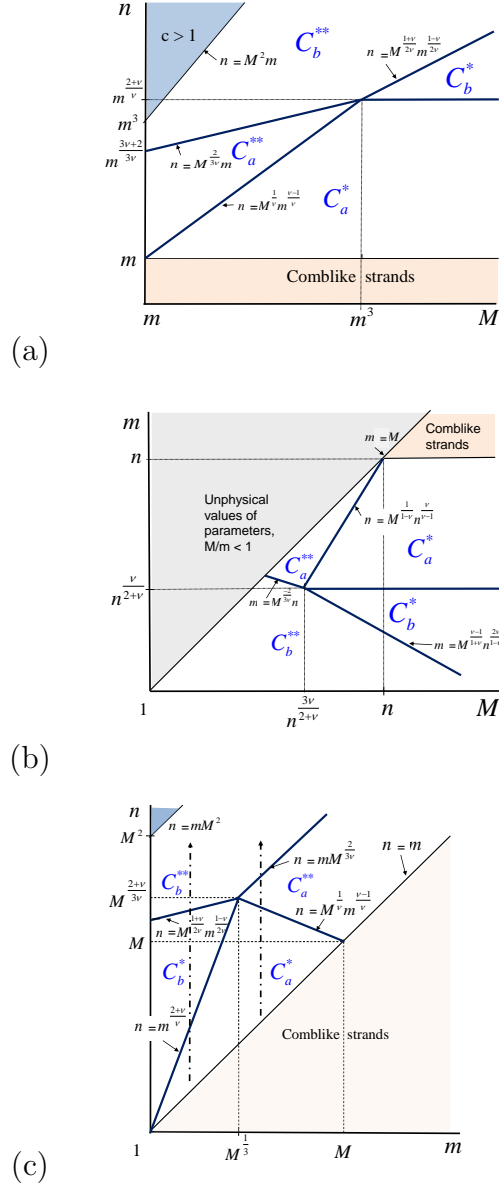


Figure 2: Scaling diagrams of state of a swollen bottlebrush gel in  $M, n$  (a),  $M, m$  (b) and  $m, n$  (c) coordinates. Equation for boundaries between regimes are indicated. The region  $m \geq M$  in panel (a) is unphysical. The regions  $n \leq m$  in panels (b) and (c) correspond to comb-shaped network strands with loosely grafted side chains not considered here. The regions shaded in blue correspond to polymer volume fraction larger than unity, that is, are unphysical.

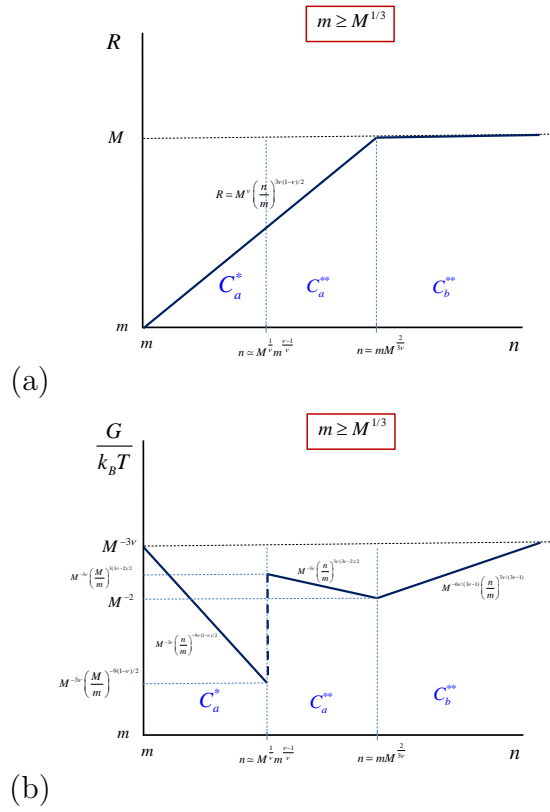


Figure 3: Gel meshsize  $R$  (a) and the gel modulus (b) as a function of DP of side chains  $n$  for the case  $m \geq M^{1/3}$

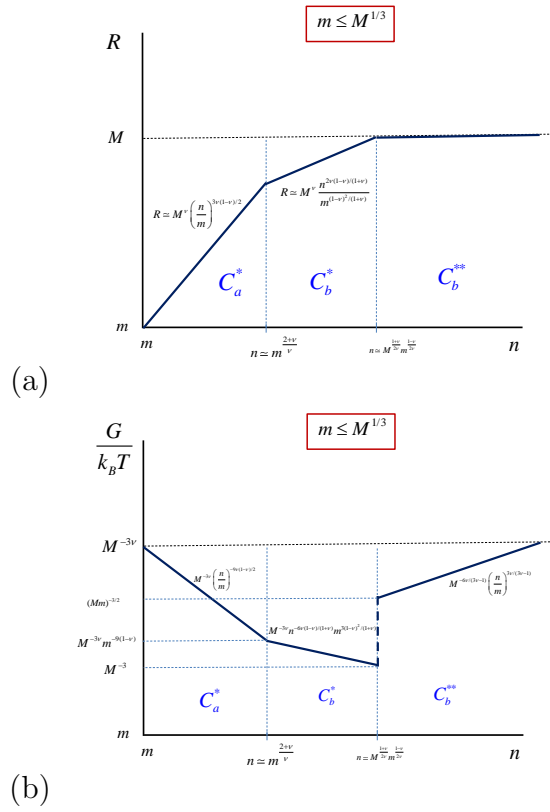


Figure 4: Gel meshsize  $R$  (a) and the gel modulus (b) as a function of DP of side chains  $n$  for the case  $m \leq M^{1/3}$

## 5 Discussion and conclusions

In the present paper we have studied conformational and elastic properties, that is, the swelling behavior and bulk osmotic modulus of the gels formed by crosslinked bottlebrushes. The scaling approach is suitable for polymer networks formed by densely grafted bottlebrush strands immersed in low molecular weight solvent with varying thermodynamic quality. This approach properly accounts for correlation in fluctuations in polymer density arising due to the gel hierarchical connectivity with explicit account of the network topology and goes beyond the mean-field models. Two major gel regimes were established: with non-overlapping (subregimes  $C_a^*$ ,  $C_b^*$ ) and overlapping side chains belonging to different network strands within a mesh (subregimes  $C_a^{**}$ ,  $C_b^{**}$ ). The results are summarized in the scaling-type diagrams of states (figures 2) with boundaries indicated in the plots. The power law dependences for the equilibrium gel parameters in different regimes are collected in Table 1.

**Table 1.** *Equilibrium parameters of swollen gels with bottlebrush strands in various regimes of the diagram of states*

	$R_{eq}$	$Q = V/V_{dr} \simeq R_{eq}^3/N$	$G \simeq \pi$
$C_a^*$	$M^\nu \left(\frac{n}{m}\right)^{\frac{3\nu(1-\nu)}{2}}$	$M^{3\nu-1} \left(\frac{n}{m}\right)^{-\frac{(3\nu-2)(3\nu-1)}{2}}$	$M^{-3\nu} \left(\frac{n}{m}\right)^{-\frac{9\nu(1-\nu)}{2}}$
$C_a^{**}$	$M^\nu \left(\frac{n}{m}\right)^{\frac{3\nu(1-\nu)}{2}}$	$M^{3\nu-1} \left(\frac{n}{m}\right)^{\frac{9\nu(1-\nu)}{2}}$	$M^{-3\nu} \left(\frac{n}{m}\right)^{\frac{3\nu(3\nu-2)}{2}}$
$C_b^*$	$M^\nu n^{\frac{2\nu(1-\nu)}{(1+\nu)}} m^{-\frac{(1-\nu)^2}{(1+\nu)}}$	$M^{3\nu-1} \left(\frac{n}{m}\right)^{(6\nu-1)}$	$M^{-3\nu} n^{-\frac{6\nu(1-\nu)}{(1+\nu)}} m^{\frac{3(1-\nu)^2}{(1+\nu)}}$
$C_b^{**}$	$M$	$M^2 \left(\frac{n}{m}\right)^{-1}$	$M^{-6\nu/(3\nu-1)} \left(\frac{n}{m}\right)^{\frac{3\nu}{(3\nu-1)}}$

The theory predicts that the gel mesh size,  $R$ , either increases upon increasing DP  $n$  of the side chains, or remains constant upon the approach to the limit of the backbone extensibility. A more complex behavior is predicted for the bulk osmotic modulus,  $G$ , which is expected to vary non-monotonously (i.e., exhibit the local minimum) as a function of DP of the side chains and undergo abrupt changes at the boundaries between the regimes.

The power law dependences in Table 1 were derived based on the asymptotic behavior of bottlebrush strands with long side chains and backbones. That is, the side chains in the bottlebrush strands were presumed to be long enough to swell and stretch due to the intermolecular repulsions under good and theta solvent conditions. However in the majority of experimental systems the side chains and backbones of the strands are still relatively short that makes the behavior of these polymers closer to that of linear chains. The DPs of grafts in currently simulated bottlebrush networks<sup>33</sup> remain also  $\sim 10 - 30$  monomers, which makes it difficult to compare the predictions of

the presented scaling model (dealing with asymptotically long side chains and backbones) with the results of available experiments and simulations. Notably, a similar situation took place upon publication of the first scaling models of polymer brushes formed by linear chains,<sup>3637</sup> for which the theoretical predictions preceded the experimental realizations.

However, in some cases the comparison between our predictions and the experimental results is possible. As it follows from Table 1, in the sub-regimes  $C_a^*$ ,  $C_b^*$ , and  $C_a^{**}$ , at fixed strand architecture,  $n/m = const$ , swelling ratio  $V/V_{dr}$  is predicted to vary with the strand backbone length  $M$  as  $V/V_{dr} \sim M^{3\nu-1}$ . Recent experiments on chemically crosslinked gels<sup>35</sup> implementing mononorborene macromonomer for ROMP polymerization and dinorborene cross-linker (both composed of poly(n-butyl acrylate)) demonstrated the increase in  $V/V_{dr}$  upon increasing macromonomer to cross-linker ratio,  $[MM]/[XL]$ . The latter correlates with the density of gel cross-linking<sup>35</sup> to approximate the average DP of the strand backbone as  $M \sim [MM]/[XL]$ . Each macromonomer contained approximately 30 n-butyl acrylate monomer units, and according to the scaling estimates, sizes of the peripheral concentration blob in the bottlebrush strand (modelled as cylindrical brush) and of the thermal blob are close. That is, the side chains in bottlebrush strands were (presumably) close to theta-solvent conditions, and we used the value of exponent  $\nu = 1/2$  in comparing the experimental data to the theoretical estimate,  $V/V_{dr} \sim M^{3\nu-1} \sim M^{1/2} \sim ([MM]/[XL])^{1/2}$ . **Figure 5** the experimental swelling ratio  $Q = V/V_{dr}$  in toluene at  $37C^\circ$  (Table 1 in ref<sup>35</sup>) is presented as a function of  $[MM]/[XL]$  in the logarithmic coordinates. The slope 1/2 indicated by the solid line clearly fits the experimental data better than the slope 4/5, corresponding to athermal solvent conditions with  $\nu = 3/5$ .

Another set of experimental data on physically cross-linked (self-assembled) networks formed by micro phase segregated triblock copolymer PNIPAM-PEO-PNIPAM with PEO bottlebrush block in toluene allows us to compare the theoretical and experimental swelling ratios,  $Q = V/V_{dr}$ , more accurately. In contrast to a small number of strands emanating from each cross-link, and structural heterogeneity of chemically cross-linked gels, micro phase segregated *ABA* triblock copolymers give rise to networks with well defined domains (cross-links) and numerous bridges (strands) connecting neighboring domains. At low contents of condensing blocks *A*, the spherical domains surrounded by swollen bottlebrush blocks *B* can be assimilated to starlike micelles with aggregation number  $P \gg 1$ , and the corona thickness  $H$  much larger than the core radius. Scaling model of starlike micelle with bottlebrush

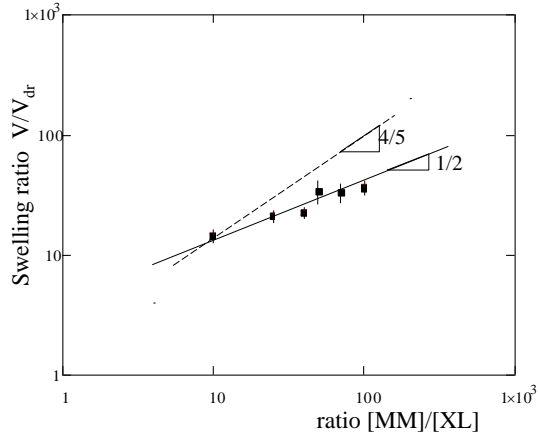


Figure 5: Equilibrium gel swelling ratio  $V/V_{dr}$  versus macromonomer,  $[MM]$ , to cross-linker,  $[XL]$ , ratio in chemically cross-linked gel with bottlebrush spacers (norbornene backbone and n-butyl acrylate side chains,) [Data from Table 1 in ref<sup>35</sup>], in log-log coordinates. Assuming  $[MM]/[XL]$  to be proportional to the average backbone polymerization degree,  $M$ , the slope  $(3\nu - 1)$  predicted by eqs (8),  $V/V_{dr} \sim R_{eq}^3/N \sim M^{3\nu-1}$ , is indicated by solid line for  $\nu = 1/2$  (theta solvent conditions) and dashed line for  $\nu = 3/5$  (athermal solvent conditions).

corona<sup>34</sup> allows us to express the network swelling ratio  $V/V_{dr}$  as

$$Q_{theor} = \left( \frac{V}{V_{dr}} \right)_{theor} = \phi_L \left( \frac{4\pi}{3} \frac{H^3}{Pn_L} + 1 \right) = \phi_L \left( \frac{4\pi}{3} k \frac{(M/2)^{9/5}}{n_L^{33/25}} + 1 \right) \quad (27)$$

Here, the first term in brackets is ratio of volumes of block  $B$  in the swollen corona of micelle and of the condensed block  $A$ , the corona thickness  $H \sim (M/2)^{3/5} P^{1/5}$  with  $M$  as DP of the backbone in block  $B$ , the aggregation number  $P \sim n_L^{4/5}$  with  $n_L$  being DP of block  $A$  (regime ST in ref<sup>34</sup>). Prefactor  $k$  incorporates thickness  $D_B$  of the bottlebrush, while

$$\phi_L = \frac{n_L}{n_L + M(n/m + 1)/2}$$

is volume fraction of  $A$  in  $ABA$  triblock copolymer, and monomer units  $A$  and  $B$  are assumed to have equal sizes.

In **Figure 6** we plot the experimentally measured swelling ratio  $Q = V/V_{dr}$  for series of samples in Table S8 in ref.<sup>16</sup> versus  $Q_{theor}$  calculated according to eq 27 with prefactor  $k = 1$ , and values of  $\phi_L$ ,  $n_L$ , and  $M/2$  from Table S8. (Note that in Table S8 DP of the bottlebrush block,  $M$ , is denoted as  $n_{bb}$ ). As it is seen in Figure 6, the experimental and theoretical values of  $Q$  are consistent (follow the straight line with slope 1 in log-log coordinates, and (as expected) the numerical difference between them is on the order of unity.

Overall, the correspondence between the theoretical predictions and the experimental data is reasonable taking into account the number of approximations involved. Our theoretical predictions could be therefore used for rationalizing the experimental data on samples with systematically varied parameters and might promote experimental and computational studies of structural and elastic properties of bottlebrush gels. The developed scaling model provides guidelines for rational control of structural and mechanical properties of polymer gels by tuning architecture of the subchains, and thus might contribute to the design concept of new materials with programmed properties.

## Acknowledgements

This work was supported by Russian Science Foundation grant 20-13-00270



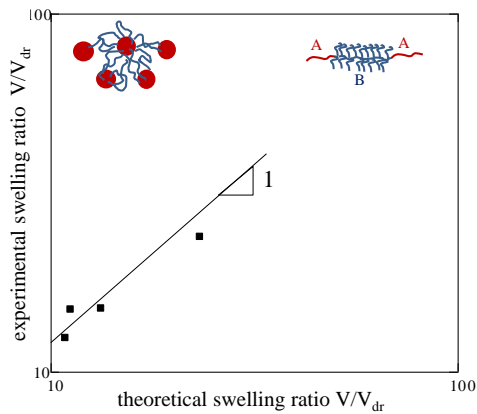


Figure 6: Equilibrium swelling ratio  $V/V_{dr}$  of physically crosslinked gel<sup>16</sup> formed by microsegregated triblock copolymer PNIPAM-PEO-PNIPAM with PEO bottlebrush block in toluene at  $37C^o$  (data for samples in Table S8 in ref<sup>16</sup> with varied block copolymer composition  $\phi_L = n_L/[M(n+1)/2 + n_L]$  with DP of the side chains  $n = 9$ , DP  $n_L$  of linear PNIPAM block, DP  $M$  of the PEO bottlebrush backbone) versus theoretical dependence  $V/V_{dr} = [(4\pi/3)H^3/Pn_L + 1]\phi_L$  predicted in ref<sup>34</sup> for spherical starlike micelles with aggregation number  $P \sim n_L^{4/5}$  and corona thickness  $H \sim M^{3/5}P^{1/5}$  (regime ST, all other prefactors are assigned unity). Slope 1 is indicated by solid line.

## References

- [1] Sheiko, S.S.; Sumerlin, B.S.; Matyjaszewski, K. Cylindrical molecular brushes: Synthesis, characterization and properties. *Progress in Polymer Science* **2008**, *33*, 759-785
- [2] Verduzco, R.; Li, X.; Pesek, S.L.; Stein, G.E. Structure, function, self-assembly of bottlebrush copolymers. *Chem.Soc.Rev.* **2015**, *44*, 2405-2420
- [3] Müllner, M.; Müller, A.H.E. Cylindrical polymer brushes - anisotropic building blocks, unimolecular templates and particulate nanocarriers. *Polymer* **2016**, *98*, 389-401
- [4] Rzaev, J. Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication. *ACS Macro Lett.* **2012**, *1*, 1146-1149
- [5] Liang, H.; Sheiko, S.S.; Dobrynin, A.V.; Supersoft Polymer Networks with Brushlike Strands *Macromolecules* **2018**, *51*, 638-645
- [6] Yuan, J.; Müller, A.H.E.; Matyjaszewski, K.; Sheiko, S. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Möller, M., Eds.-in-Chief; Elsevier, Amsterdam, 2012.
- [7] X. Liang, Y. Liu, J. Huang, L. Wei, G. Wang. Synthesis and characterization of novel barbwire-like graft polymers poly(ethylene oxide)-g-poly( $\epsilon$ -caprolactone)<sub>4</sub> by the 'grafting from' strategy. *Polym. Chem.* **2015**, *6*, 466-475
- [8] D. Uhrig, J.W. Mays. Synthesis of Combs, Centipedes, and Barbwires: thinspace Poly(isoprene-graft-styrene) Regular Multigraft Copolymers with Trifunctional, Tetrafunctional, and Hexafunctional Branch Points. *Macromolecules* **2002**, *35* (19), 7182-7190
- [9] T. Pelras, C. S. Mahon, Nonappa, O. Ikkala, A. H. Gröschel, M. Müllner. Polymer Nanowires with Highly Precise Internal Morphology and Topography. *J. Am. Chem. Soc.* **2018**, *140* (40), 12736-12740
- [10] Rosen, B.M.; Wilson, C.J.; Wilson, D.A.; Peterca, M.; Imam, M.R.; Percec, V. Dendron-mediated self-assembly, disassembly, and self-organization of complex systems. *Chemical Reviews* **2009**, *109*, 6275-6540

- [11] S. Costanzo, L. F. Scherz, T. Schweizer, M. Kröger, G. Floudas, A. D. Schlüter, D. Vlassopoulos. Rheology and Packing of Dendronized Polymers. *Macromolecules*, **2016**, *49* (18), 7054–7068
- [12] M. Zamurovic, S. Christodoulou, A. Vazaios, E. Iatrou, M. Pitsikalis, N. Hadjichristidis. Micellization Behavior of Complex Comblike Block Copolymer Architectures. *Macromolecules* **2007**, *40*, 5835-5849.
- [13] Y. Wang, F. Shao, E.R. Sauve, C.M. Tonge, Z.M. Hudson. Self-assembly of giant bottlebrush block copolymer surfactants from luminescent organic electronic materials. *Soft Matter* **2019**, *15*, 5421-5430.
- [14] Z. Li, J. Ma, C. Xheng, K. Zhang, K.L. Wooley. Synthesis of Hetero-Grafted Amphiphilic Diblock Molecular Brushes and Their Self-Assembly in Aqueous Medium. *Macromolecules* **2010**, *43*, 1182-1184.
- [15] R. Fenyves, M. Schmutz, I.J. Horner, F.V. Bright, J. Rzaev. Aqueous Self-Assembly of Giant Bottlebrush Block Copolymer Sufactants as Shape-Tunable Building Blocks. *J. Am. Chem. Soc.* **2014**, *136*, 7762-7770.
- [16] F. Vashahi, M.R. Martinez, E. Dashtimoghadam, F. Fahimpour, A.N. Keith, E.A. Bersenev, D.A. Ivanov, E.B. Zhulina, K. Matyjaszewski, M. Vatankhah-Varnosfaderani and S.S. Sheiko. Injectable hydrogels with tissue-adaptive gelation and mechanical properties. *Sci. Adv.* **8**, eabm2469 (2022) 21 January 2022.
- [17] J.L. Self, C.S. Sample, A.E. Levi, K. Li, R. Xi, J.R. de Alaniz, C. M. Bates Dynamic Bottlebrush Polymer Networks: Self-Healing in Super-Soft Materials *J. Am. Chem. Soc.* **2020**, *142* (16), 75677573
- [18] R.Xie, S.Mukherjee, A. E.Levit, V. G.Reynolds, H.Wang, M.L.Chabinye, C. M.Bates Room temperature 3D printing of super-soft and solvent-free elastomers. *Science Advances* **2020**, *6* (46), eabc6900.
- [19] Daniel, W.F.M.; Burdynska, J.; Vatankhah-Varnoosfaderani, M.; Matyjaszewski, K.; Paturej, J.; Rubinstein, M.; Dobrynin, A.V.; Sheiko, S.S. Solvent-Free, Supersoft and Superelastic Bottlebrush Melts and Networks. *Nat. Mater.* **2016**, *15*, 183-189
- [20] Klein, J. Polymer in living systems:from biological lubrication to tissue engineering and biomedical devices *Polym. Adv. Technol.* **2012**, *23*, 729-735

- [21] C. Kiani, L. Cheng, Y.J. Wu, A.J. Yee, B.B. Yang. Structure and function of aggrecan. *Cell Research* **2002**, *12(1)*, 19-32
- [22] Button, B.; Cai, L.-H.; Ehre, C.; Kesimer, M.; Hill, D.B.; Sheehan, J.K.; Boucher, R.C.; Rubinstein, M. A periciliary brush promotes the lung health by separating the mucus layer from airway epithelia. *Science* **2012**, *337*, 937-941.
- [23] E.B. Zhulina, S.S. Sheiko, O.V. Borisov. Polymer Networks Formed by Molecular Brushes: Scaling Theory. *Polymer Science Ser. A* **2019**, *61*, 799-804
- [24] de Gennes, P.-G. Scaling Concepts in Polymer Physics. Cornell University Press, Ithaca and London, 1976
- [25] T. M. Birshtein, O. V. Borisov, Y. B. Zhulina, A. R. Khokhlov, T. A. Yurasova. Conformations of comb-like macromolecules. *Polym. Sci. USSR* **1987**, *29*, 1293–1300.
- [26] L. Feuz, F. A. M. Leermakers, M. Textor, O. Borisov, Bending rigidity and induced persistence length of molecular bottle brushes: A self-consistent-field theory. *Macromolecules* **2005**, *38*, 8891–8901.
- [27] P. E. Theodorakis, H.-P. Hsu, W. Paul, K. Binder, Computer simulation of bottle-brush polymers with flexible backbone: Good solvent versus theta solvent conditions. *J. Chem. Phys.* **2011**, *135*, 164903.
- [28] G. H. Fredrickson, Surfactant-induced lyotropic behavior of flexible polymer solutions. *Macromolecules* **1993**, *26*, 2825–2831.
- [29] Subbotin, A. V.; Semenov, A. N. Spatial Self-Organization of Comb Macromolecules. *Polym. Sci., Ser. A* **2007**, *49*, 1328-1357.
- [30] E.B. Zhulina, S.S. Sheiko, O.V. Borisov. Solution and Melts of Barbwire Bottlebrushes: Hierarchical Structure and Scale-Dependent Elasticity. *Macromolecules* **2019**, *52(4)*, 1671-1684
- [31] Daoud, M.; Cotton, J.-P. Star shaped polymers. *J.Phys.(France)*, **1982**, *43*, 531-538
- [32] T.M. Birshtein and E.B. Zhulina Conformations of Star-Branched Macromolecules *Polymer* **1984**, *25 (10)*, 1453 - 1461

- [33] M.Jacobs, H.Liang, E.Dashtimoghadam, B.J. Morgan, S.S. Sheiko, A.V. Dobrynin Nonlinear Elasticity and Swelling of Comb and Bottlebrush Networks. *Macromolecules* **2019**, 52(14), 5095-5101
- [34] E.B. Zhulina and O.V. Borisov. Micelles Formed by AB Copolymer with Bottlebrush blocks. Scaling Theory. *J. Phys. Chem. B* **2021**, 125 (45), 12603–12616
- [35] J.M. Sarapas, E.P. Chan, E.M. Rettner, K.L. Beers. Compressing and Swelling To Study the Structure of Extremely Soft Bottlebrush Networks Prepared by ROMP. *Macromolecules* **2018**, 51, 2359-2366
- [36] S. Alexander. Adsorption of chain molecules with a polar head a scaling description. *Journal de Physique*, **1977**, 38 (8), pp.983-987
- [37] P.G. de Gennes. Conformations of Polymers Attached to an Interface. *Macromolecules* **1980**, 13 (5), 1069–1075