# Swelling of Graft Polymer Networks

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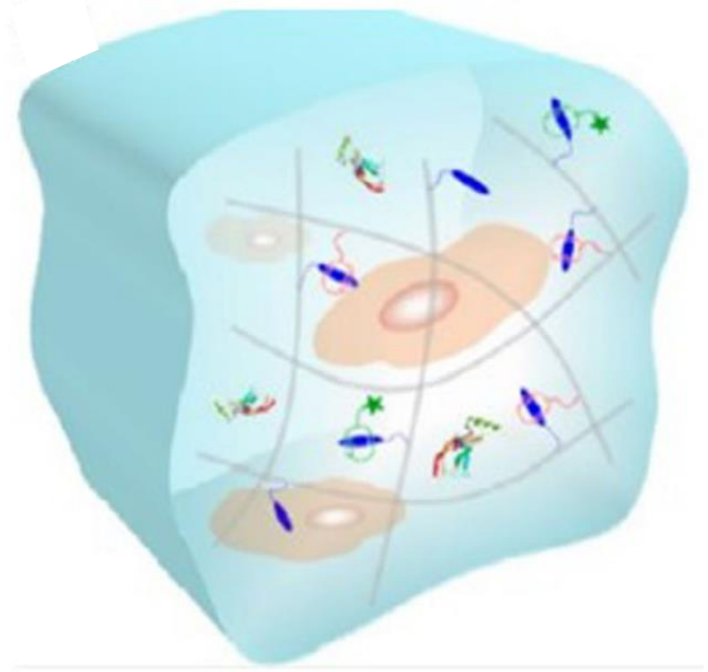
## Abstract

We use a combination of analytical calculations, coarse-grained molecular dynamics simulations and experiments to elucidate the effect of branched architecture on swelling of comb-like and bottlebrush networks. The equilibrium swelling ratio of such networks is shown to be larger than that of conventional linear chain networks. For networks of brush-like strands with poly(dimethyl siloxane) side chains in toluene, we achieve a swelling ratio of $Q = 30$, which is larger than that of linear chain networks with the same strand length. All of the studied systems, including linear chain, comb, and bottlebrush networks, follow a universal relationship, $G(Q) \propto Q^{-8/3}$, between the shear modulus $G(Q)$ and the swelling ratio $Q$.

## Motivation



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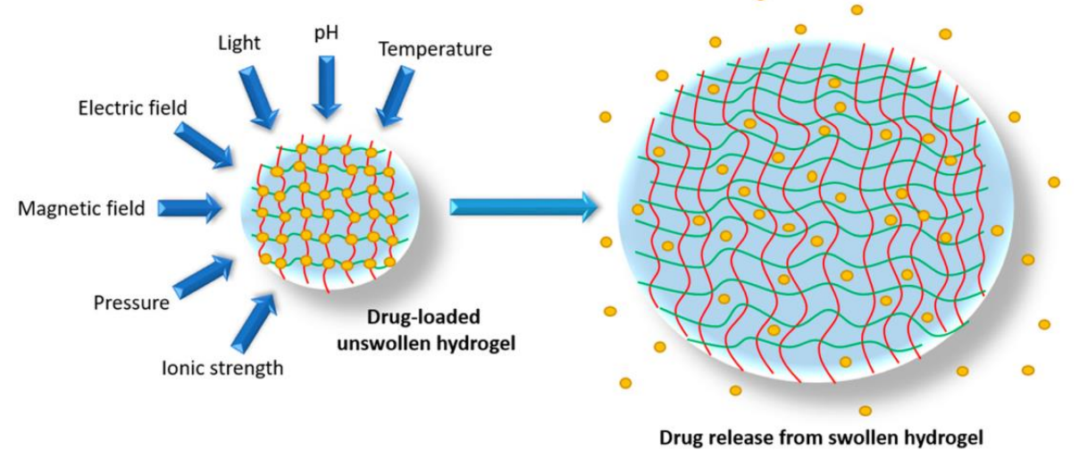
**Extracellular Matrix**

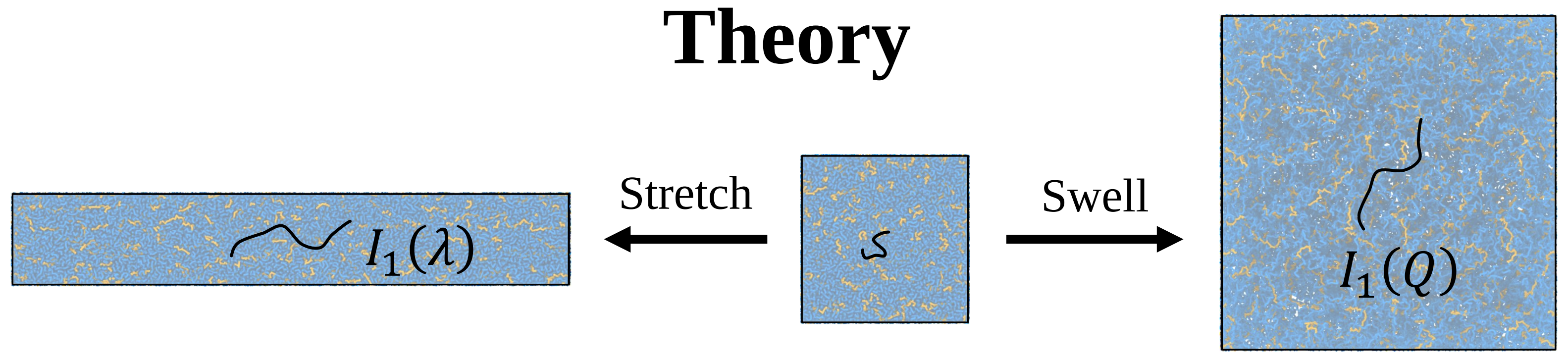


*Pharmaceutics* **2018**, *10*(2), 71

**Drug Delivery**

**Baby Diapers**

## Theory



When stretched or swollen, the deformation of a network's strands is described by the first invariant $I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2$.

$$F_{elast}(Q) = G_{dr} V_0 \left( \frac{I_1(Q)}{6} + \beta^{-1} \left( 1 - \frac{\beta I_1(Q)}{3} \right)^{-1} \right)$$

$$F_{osm}(Q) = k_B T \frac{V}{v} \left( \tau \frac{Q^{-2}}{2} + \frac{Q^{-3}}{6} \right)$$

Here, $\beta = \langle R_{in}^2 \rangle / R_{max}^2$ is the strand extensibility in the dry state, $G_{dr}$ is the structural shear modulus, $v$ is the monomer excluded volume, and $\tau = 1 - \Theta/T$ is the effective temperature. The equilibrium swelling condition is set by

$$\frac{\partial F_{elast}(Q)}{\partial V} + \frac{\partial F_{osm}(Q)}{\partial V} = 0$$

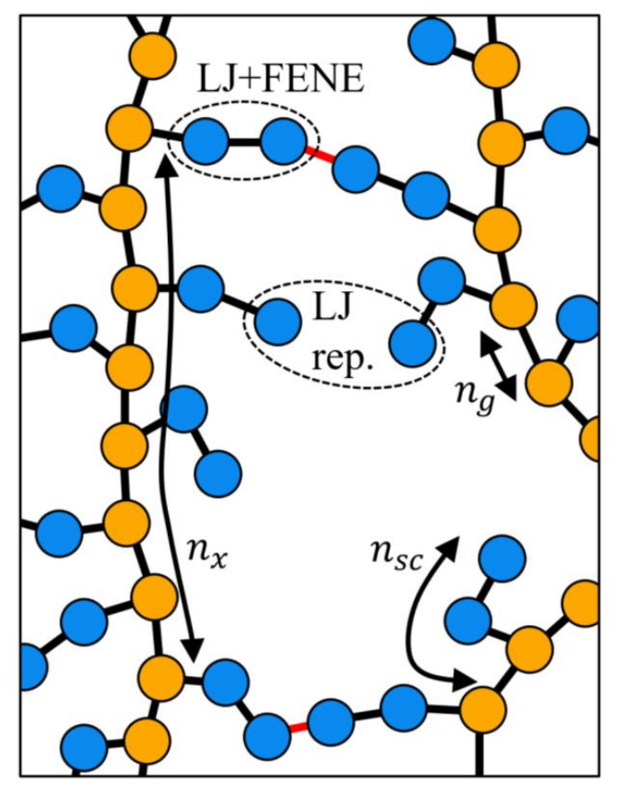
$$\frac{\partial F_{elast}(Q)}{\partial V} = Q^{-1/3} G(Q) = Q^{-1/3} \frac{G_{dr}}{3} \left( 1 + 2 \left( 1 - \frac{\beta I_1(Q)}{3} \right)^{-2} \right)$$

$$-\frac{\partial F_{osm}(Q)}{\partial V} = \pi(Q) = \frac{k_B T}{v} \left( \tau \frac{Q^{-2}}{2} + \frac{Q^{-3}}{3} \right)$$

In a $\Theta$-solvent, $\tau = 0$ and

$$\boxed{G(Q) = \frac{k_B T}{3v} Q^{-8/3} \propto Q^{-8/3}}$$

## Simulation Details



### General

- Lennard-Jones bead-spring model
- LJ truncated-shifted potential with repulsive parameters
- FENE bonds

### Stretching

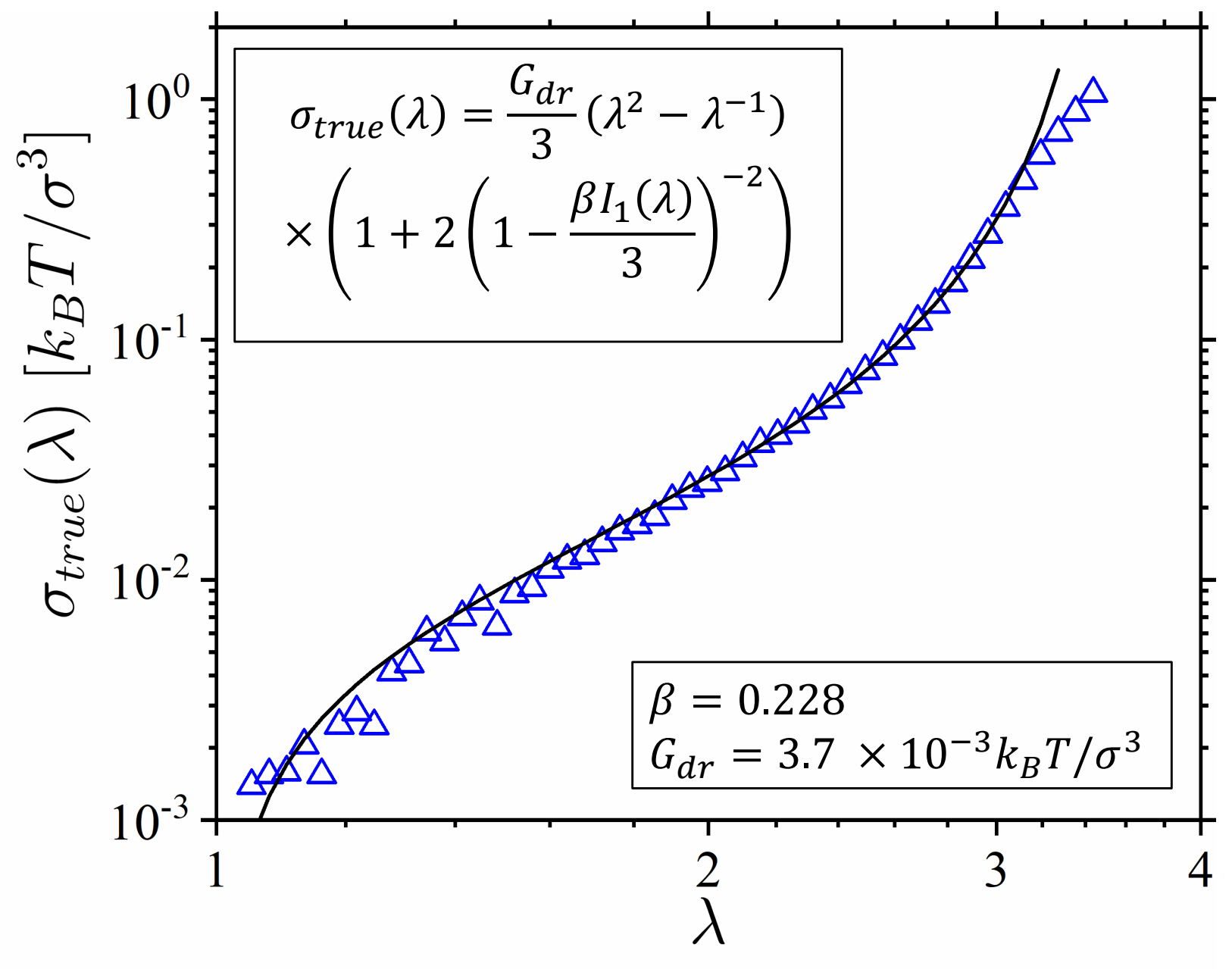
- Incremental step-wise uniaxial deformation
- NVT with Langevin thermostat

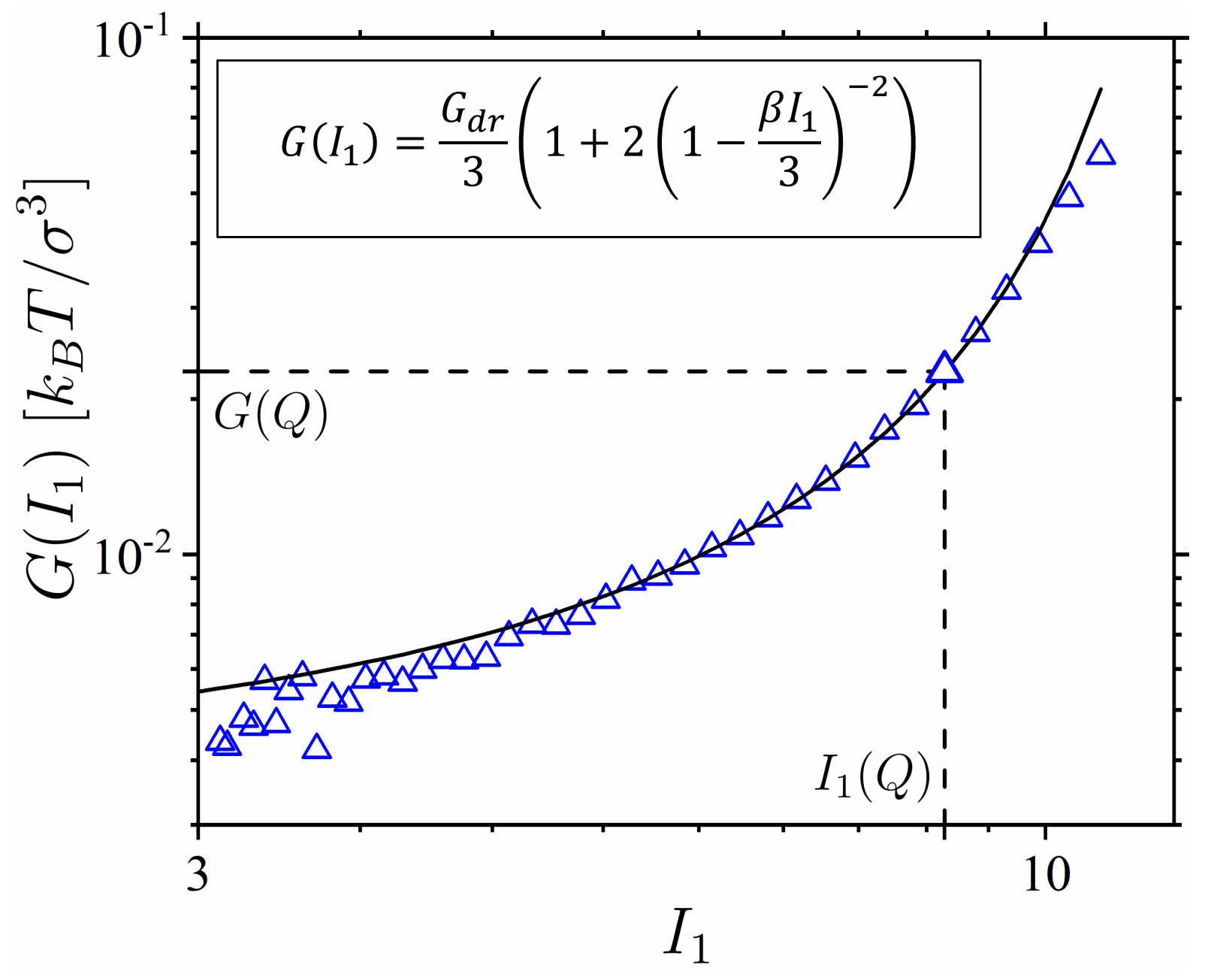
### Swelling

- NPT with Nose-Hoover thermostat
- $P = 0.0\ k_B T/\sigma^3$

## Nonlinear Shear Modulus $G(Q)$

1. Stretch the sample to obtain the stress-strain curve. Translate this data to the nonlinear shear modulus using $G(I_1) = \frac{\sigma_{true}(\lambda)}{\lambda^2 - \lambda^{-1}}$.
2. Swell the sample to obtain an equilibrium swelling ratio $Q$. Translate this to the first invariant using $I_1(Q) = 3Q^{2/3}$.
3. Either fit the stress-strain data or interpolate the data to find $G(Q)$.

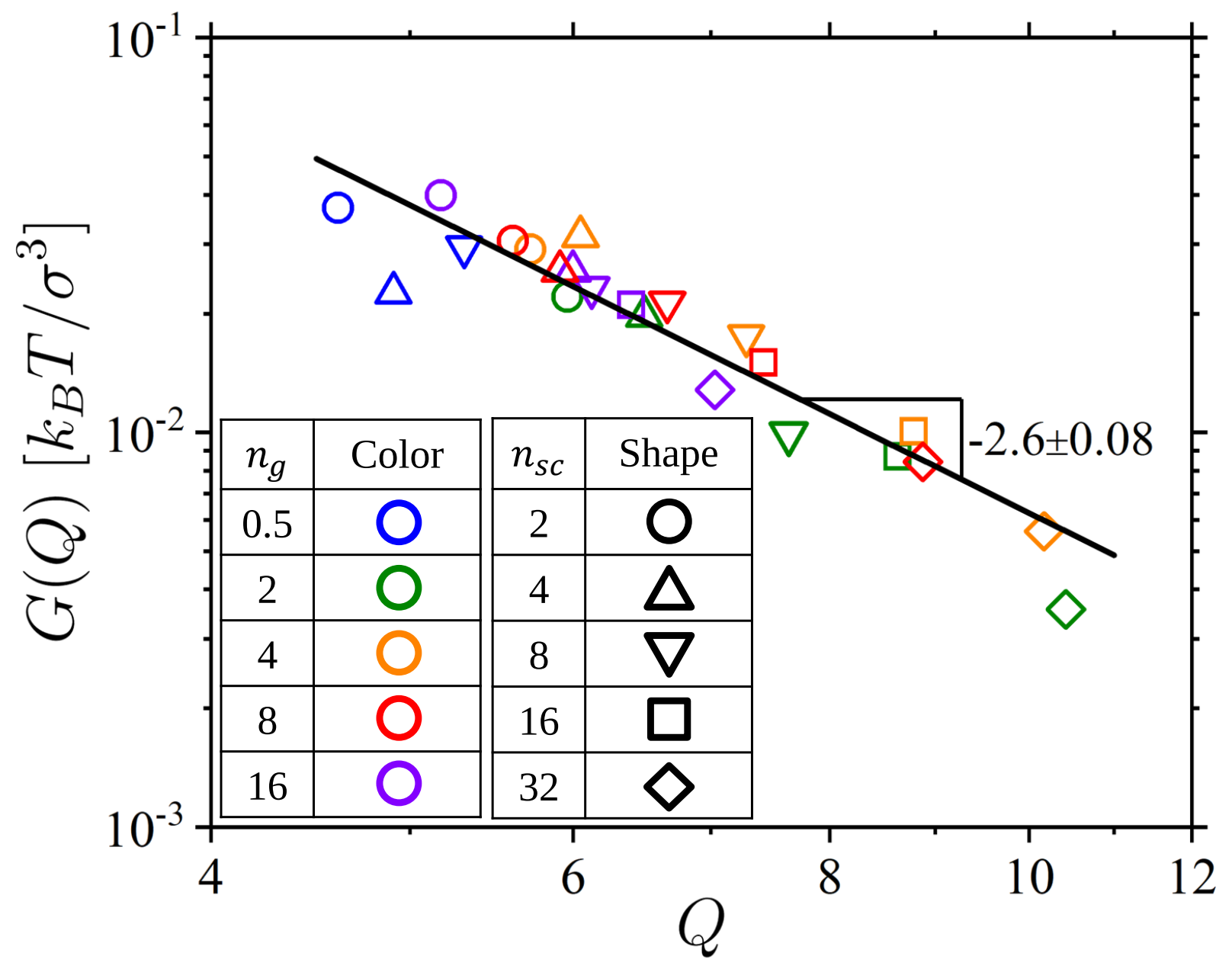




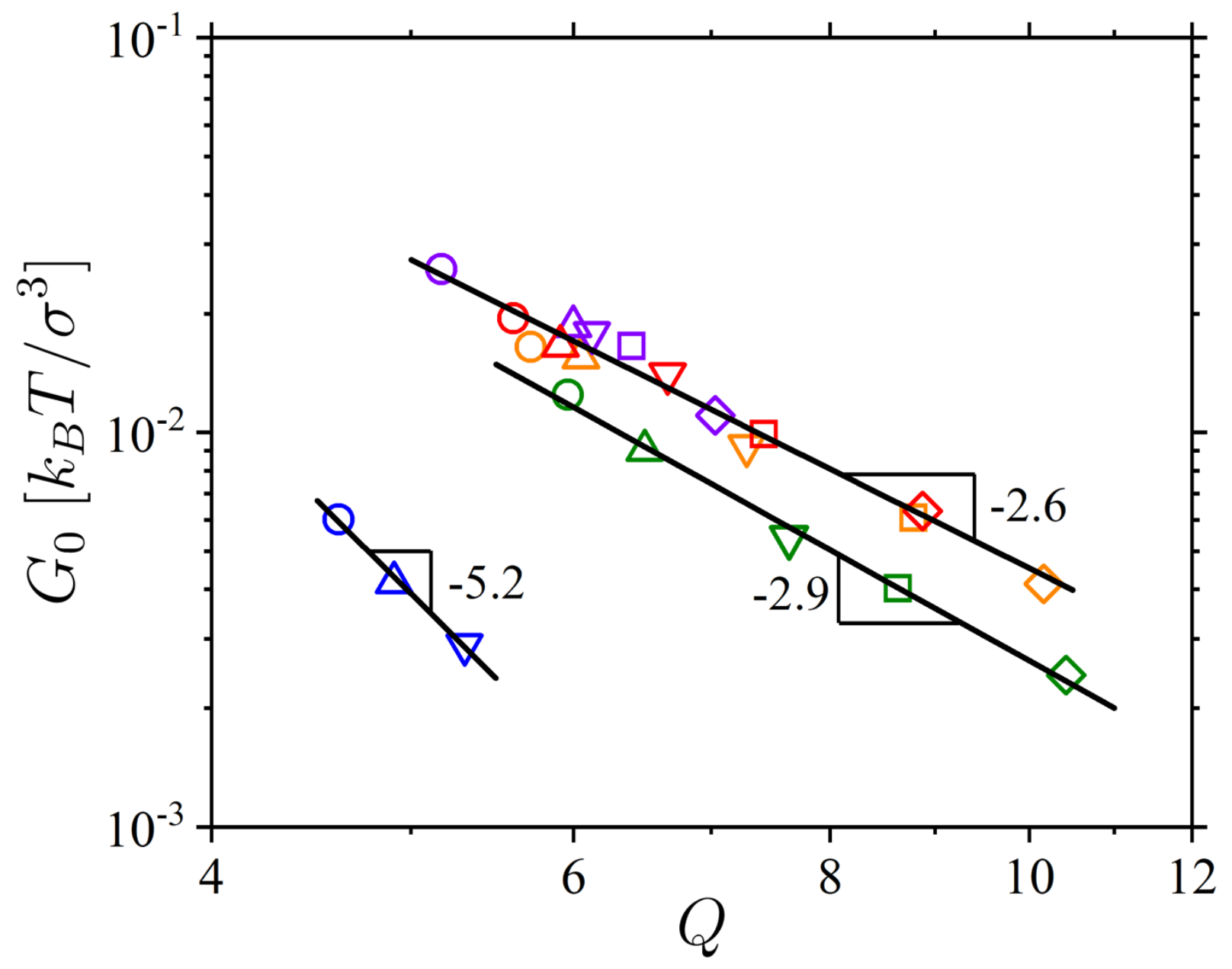
## Network Swelling Results

In both simulations and experiments, we see that the scaling relations $G(Q) \propto Q^{-2.6 \pm 0.08}$ and $G(Q) \propto Q^{-2.6 \pm 0.12}$, respectively, are driven by three-body repulsion for which $G(Q) \propto Q^{-8/3}$. It is important to point out that experimental data for network swelling are usually presented as the shear modulus at small deformations $G_0$ versus swelling ratio $Q$. However, this does not capture the nonlinear increase of shear modulus during swelling and therefore results in a broad range of power laws. Here we plotted the zero-strain shear modulus

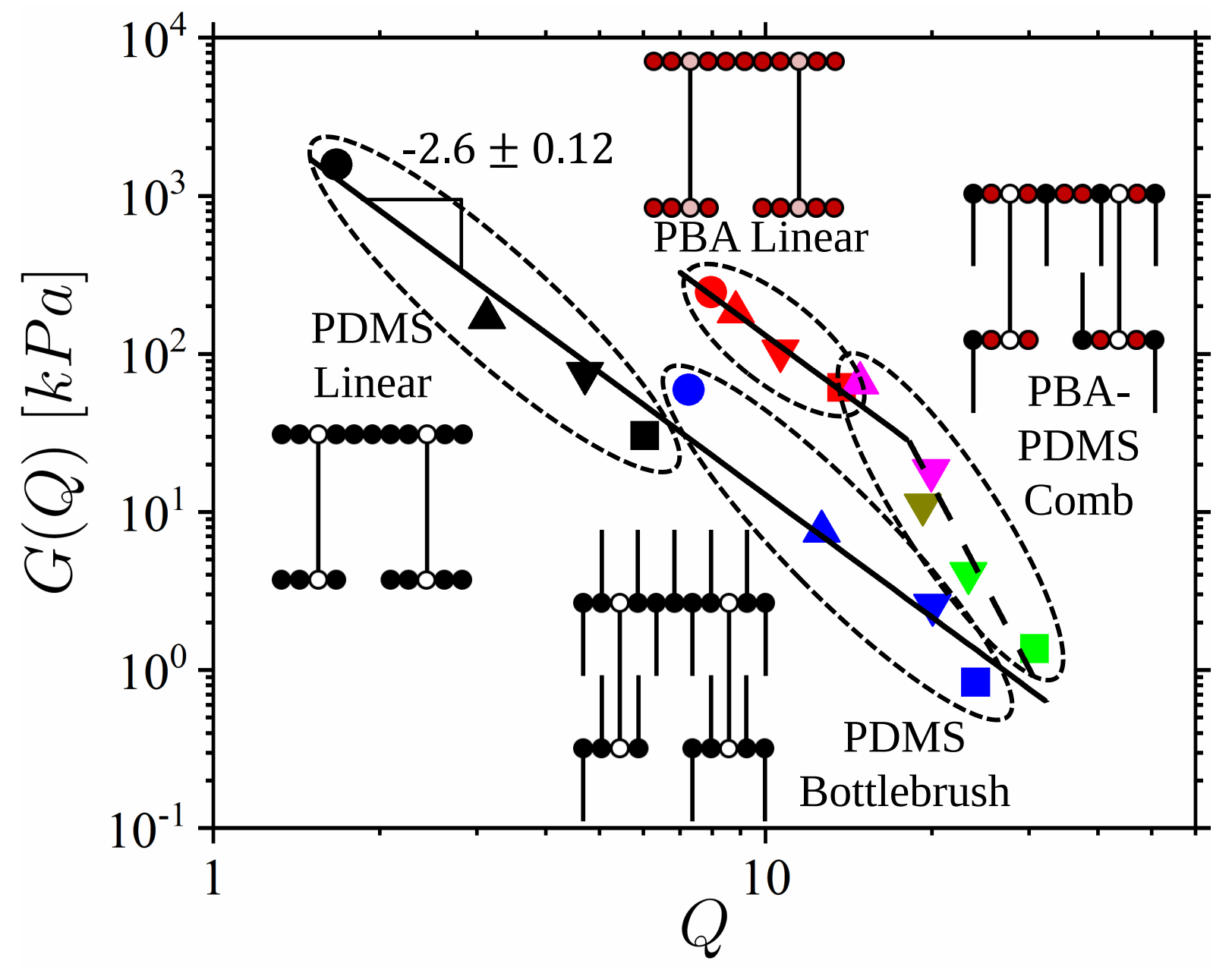
$$G_0 = G_{dr}(1 + 2(1 - \beta)^{-2})/3$$

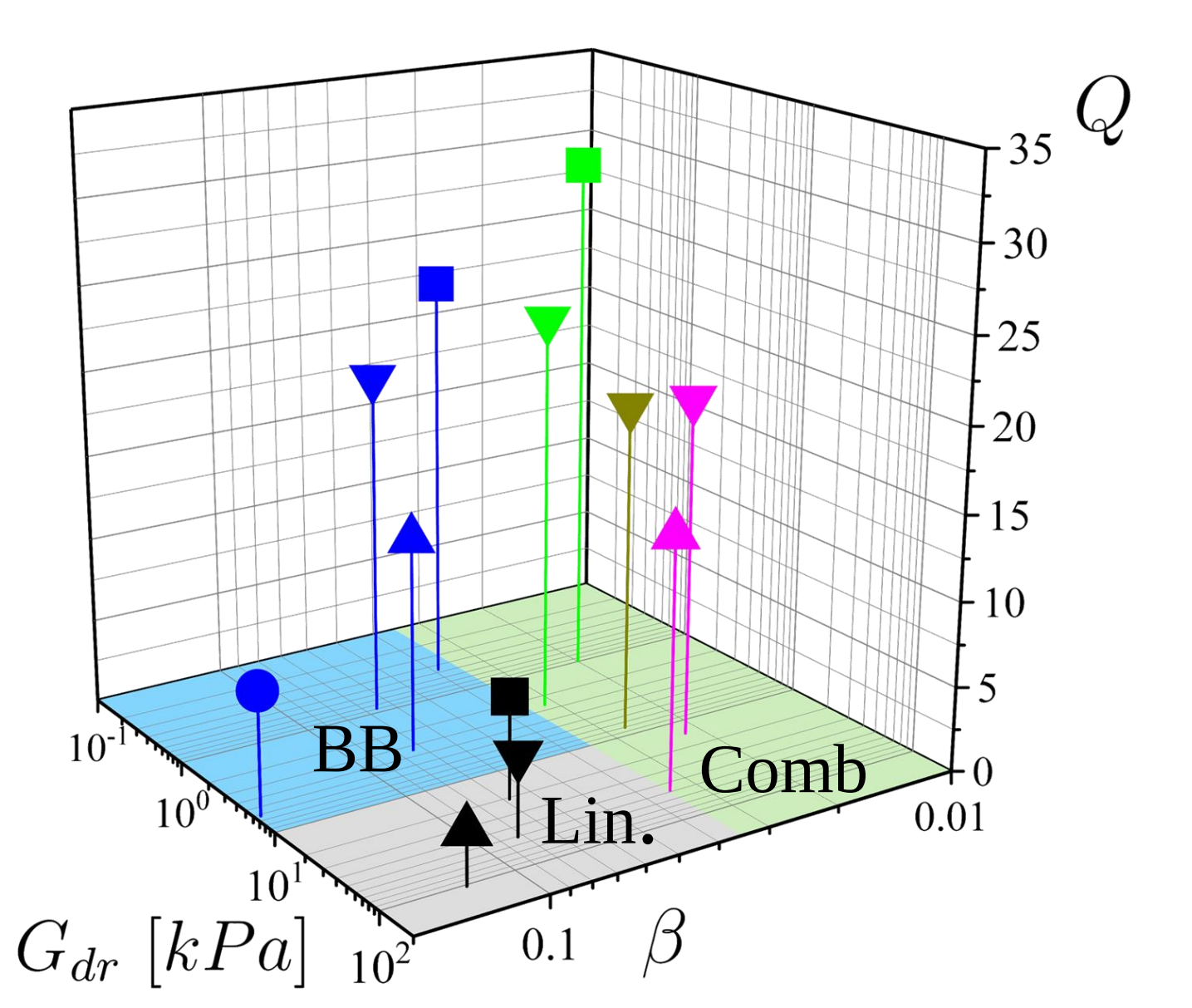


| $n_g$ | Color | $n_{sc}$ | Shape |
|---|---|---|---|
| 0.5 | 🔵 | 2 | ○ |
| 2 | 🟢 | 4 | △ |
| 4 | 🟠 | 8 | ▽ |
| 8 | 🔴 | 16 | □ |
| 16 | 🟣 | 32 | ◇ |



## Network Swelling Experiments





## Predicting Network Swelling

To demonstrate the swelling capacity of networks with entangled brush-like strands, we use results for the entanglement plateau modulus of melts of graft polymers

$$G_{e,gr} \approx G_{e,lin}(\varphi b_K/b)^3$$

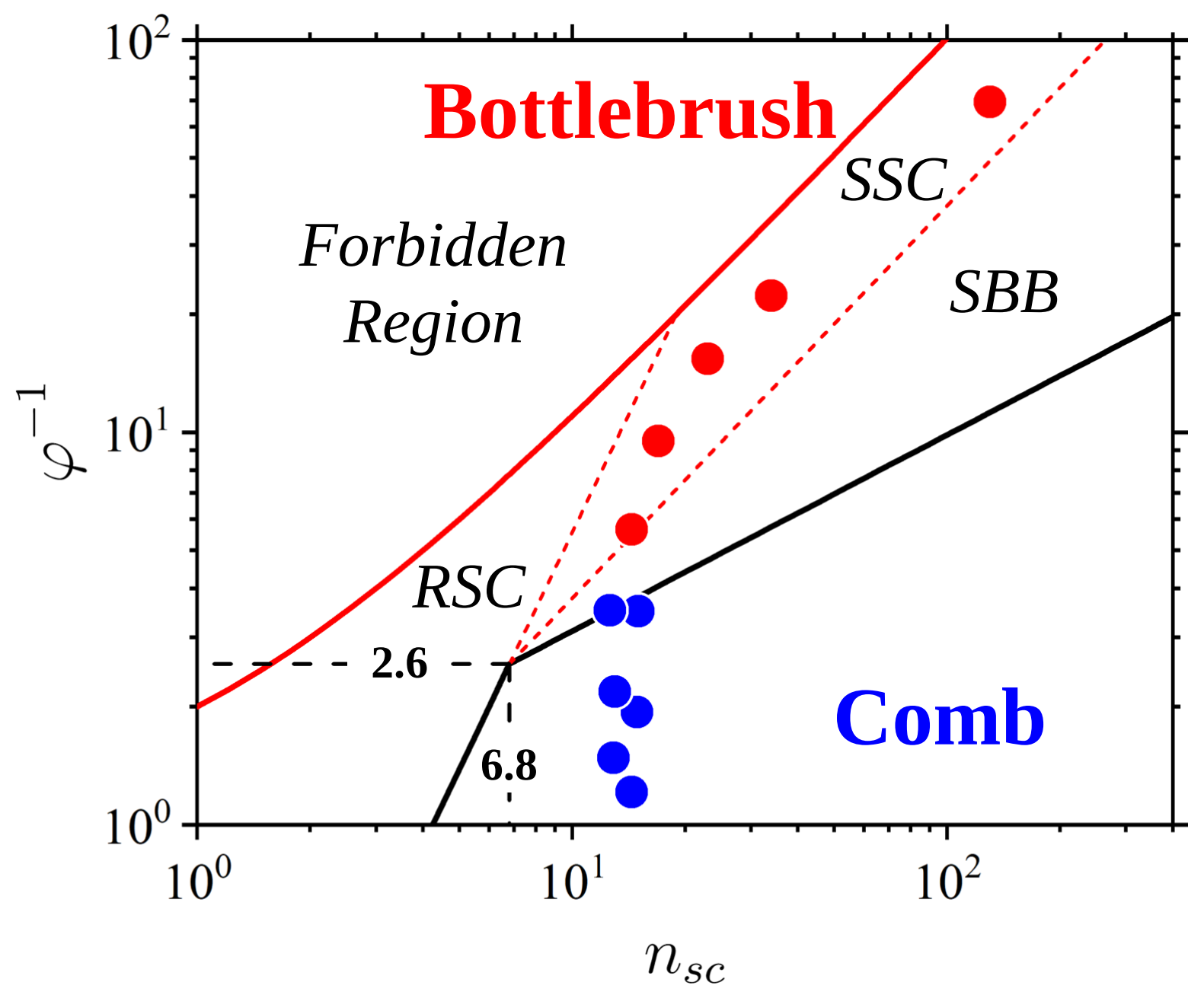
where $\varphi \equiv n_g/(n_g + n_{sc})$ is the architectural parameter, $G_{e,lin}$ is the entanglement modulus of a linear chain melt, $b_K$ is the effective Kuhn length of a graft polymer chain, and $b$ is the backbone Kuhn length. In the case of networks with comb-like strands swollen in a $\Theta$-solvent,

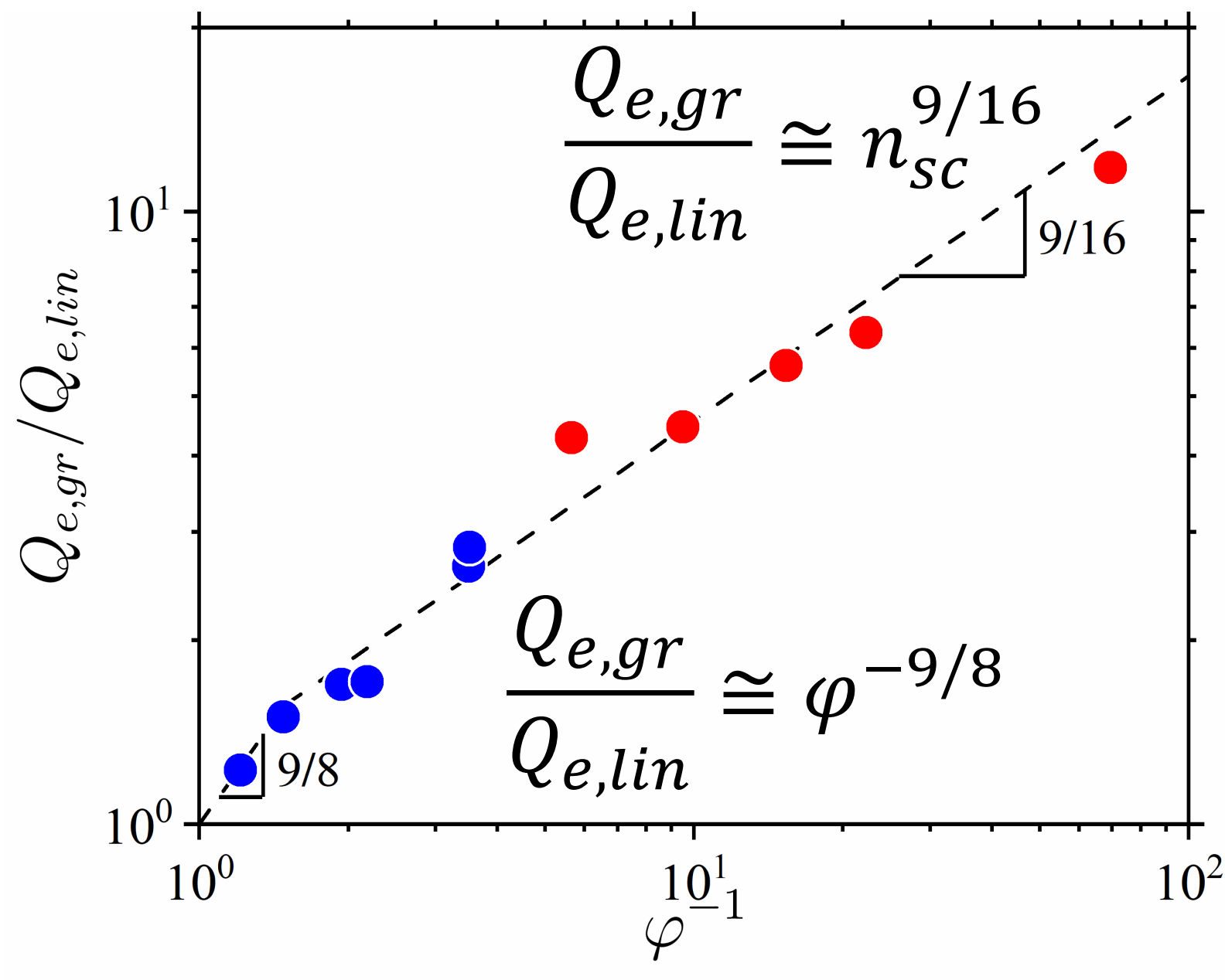
$$Q_{e,gr} \approx Q_{e,lin}(\varphi b_K/b)^{-9/8} \approx Q_{e,lin}\varphi^{-9/8}$$

and in the case of bottlebrush networks,

$$Q_{e,gr} \approx Q_{e,lin}(\varphi b_K/b)^{-9/8} \approx Q_{e,lin} n_{sc}^{9/16}$$

Below we show the normalized network swelling ratio expected for networks of entangled PBA comb and bottlebrush strands in a $\Theta$-solvent as a function of $\varphi^{-1}$.





## Conclusion

We have developed a network swelling model showing a universal scaling relation of $G(Q) \propto Q^{-8/3}$, which is supported by both computer simulations and experimental data. Furthermore, this indicates that it is necessary to use stress-strain data, obtained in the network's dry state, to properly analyze the network's swelling properties.

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### References

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*Macromolecules* **2018**, 51, 10028-10039