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Super-soft and super-elastic dry gels

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Molecular Design of Super-Soft, Super-Elastic Dry Gels

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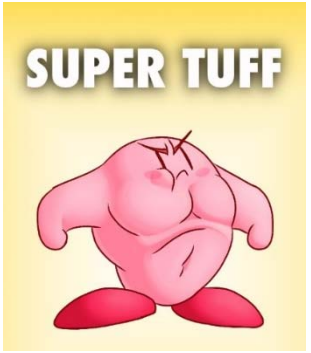
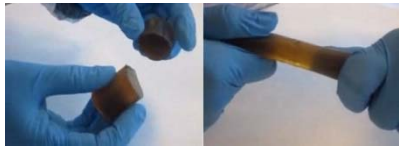
Liheng Cai & David Weitz



Nature Materials 15, 283, 2016

Science Advances 2016

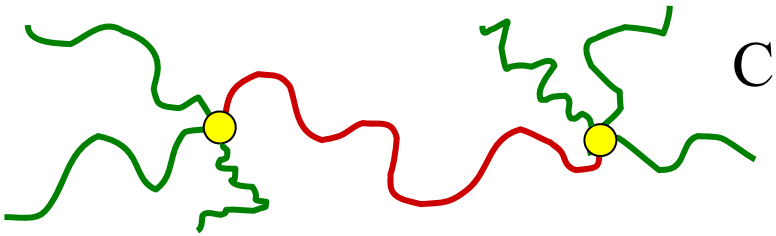
Advanced Materials 27, 5132–5140, 2015



Network Modulus

P. Flory

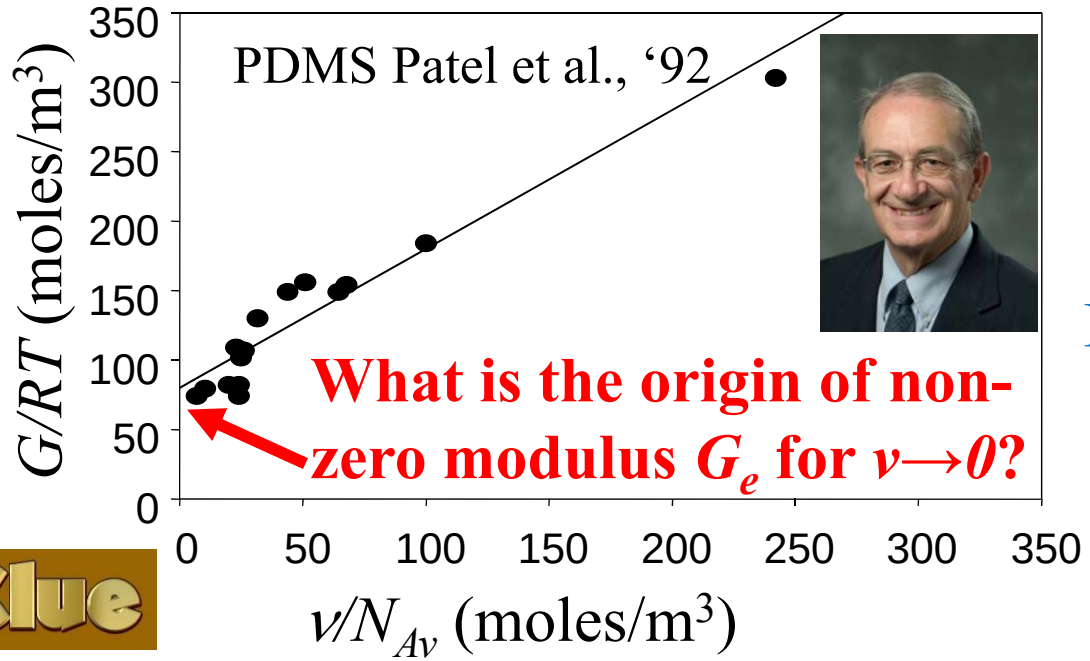
Entropic elasticity of polymer networks is due to the **suppression** of chain **fluctuations** by **cross-links.**



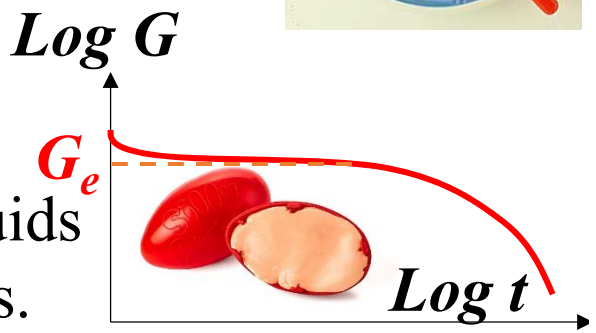
Classical elasticity theory:

network modulus $G \approx \nu kT$

ν – number density of network strands



Entanglements!



High molecular weight uncrosslinked polymer liquids behave as crosslinked networks at short time scales.

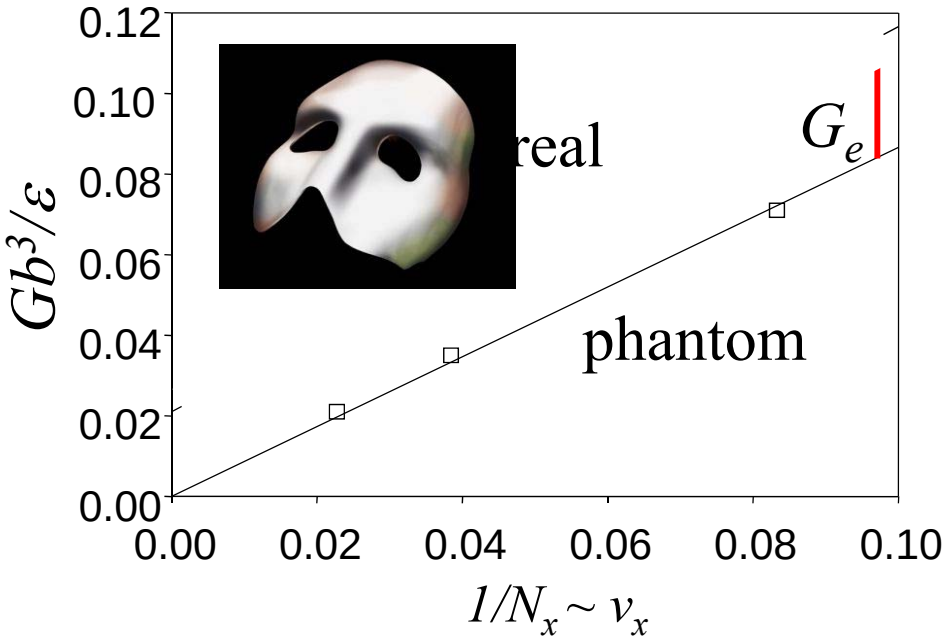
Modulus of Phantom and Entangled Networks

Contains contributions from crosslinks and entanglements

$$G \approx G_x + G_e$$

$G_x = kTv_x$ - modulus due to chemical crosslinks

$G_e = kTv_e$ - modulus due to entanglements



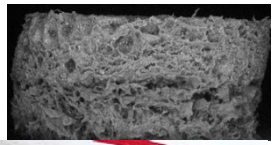
Computer simulations – Everaers
New J. Phys. **1**, 12.1 (1998)

Typical value of entanglement modulus in undiluted polymers

$$G_e = 0.1 - 1\ MPa$$

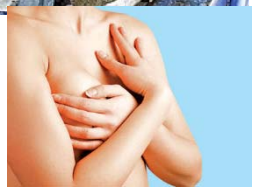
Can one make super-soft dry solids with 10^3 lower modulus?

Tissue growth scaffolds

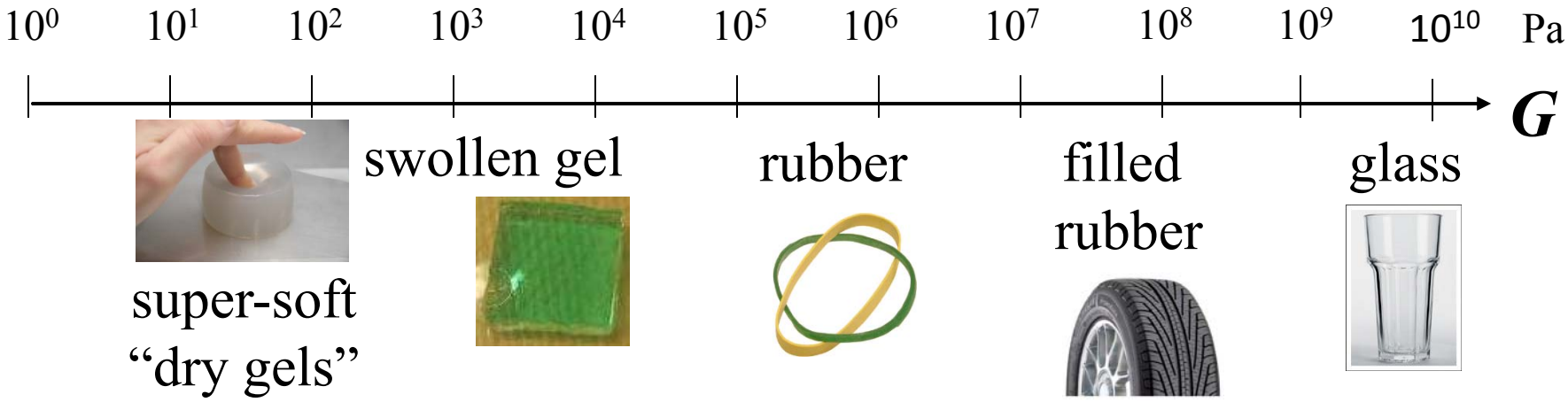


Antibacterial & antifouling surfaces

Solvent-free implants for reconstructive surgeries



How Soft is Super-Soft?



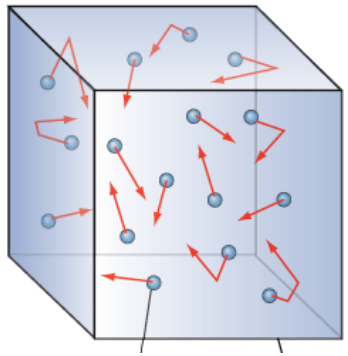
Swollen gels are soft, but contain solvent that can evaporate or diffuse out.

Can one make super-soft elastomers – solvent-free networks with $G \ll$ kPa?

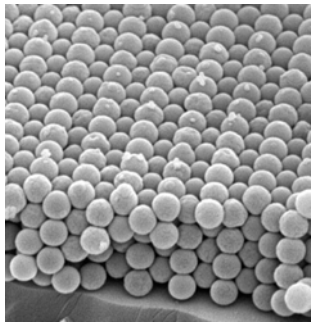
Need to lower plateau modulus G_e by 3 orders of magnitude.

From Soft Matter to Super-Soft Matter

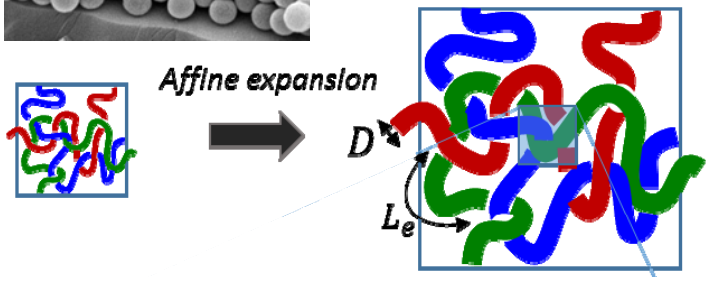
Increasing distance between molecules of gas from 3.5 nm to 35 nm lowers gas pressure and bulk modulus at T=300°K from 10^5 Pa to 100 Pa



Increasing size of crystallizing objects from atoms to colloids lowers modulus from GPa to Pa.

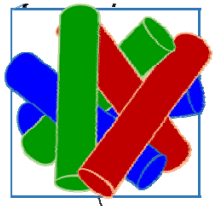


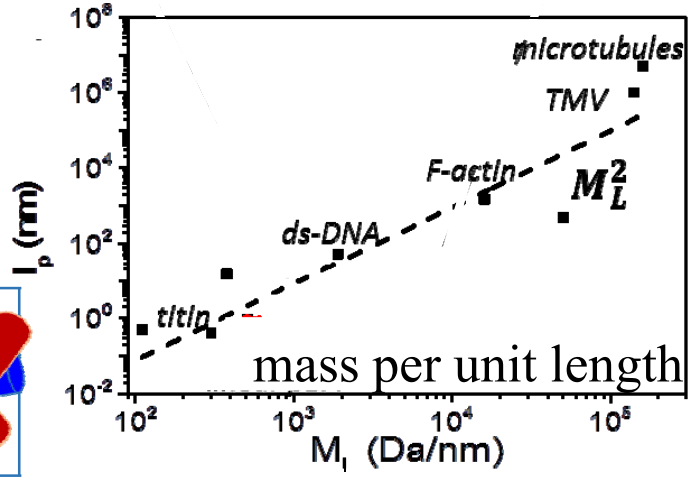
Similarly would like to perform affine expansion of length scales from "thin" linear chains to "thick" filaments.



Problem with solid filaments is that they strongly stiffen with increasing thickness D. Persistence length $l_p \sim D^4 \sim M_L^2$

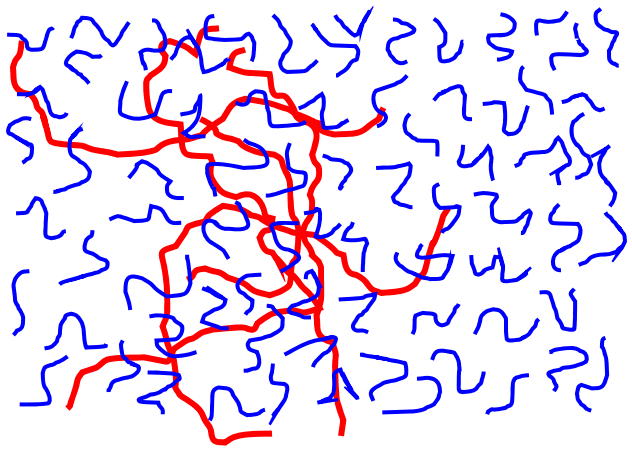
Entanglement modulus $\boldsymbol{G_e \sim l_p^3/D^6}$ increases as D^6





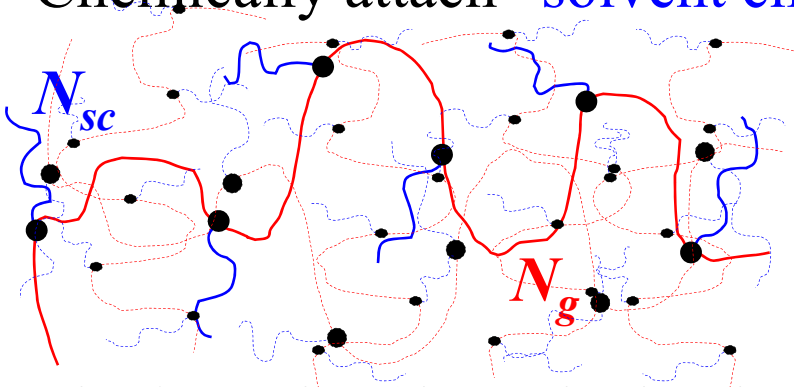
Toward Low-Plateau-Modulus Melts

Dilution of polymer by short unentangled chains reduces the number of entanglements between long polymer chains.



Short solvent chains are not long enough to be entangled. Gel swollen in oligomers, but we need solvent-free "gel".

Chemically attach "solvent chains" to polymer backbone.

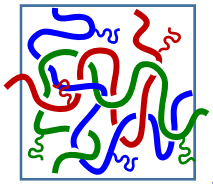


N_{sc}-monomer side chains are grafted to backbone with N_g monomers between grafting points

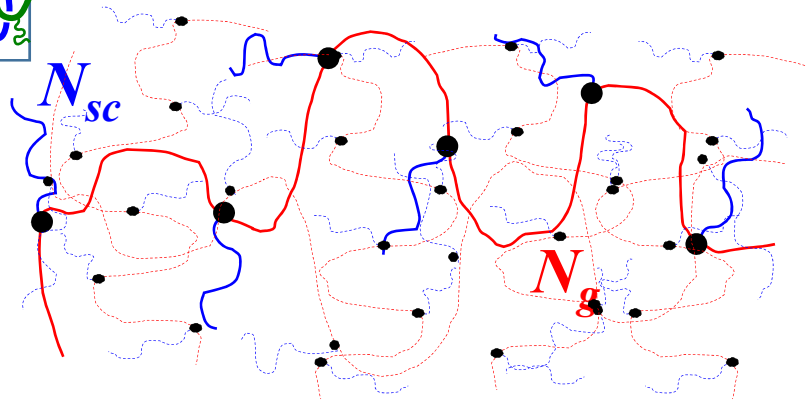
N_{bb} – backbone degree of polymerization

Obtain melt of branched polymers (combs or bottlebrushes) with low entanglement density dependent on volume fraction of backbone chains

$$\phi_{bb} = \frac{N_g}{N_g + N_{sc}}$$



Loosely Grafted Combs $N_{sc} < N_g$



Most of the melt volume is occupied by backbones.

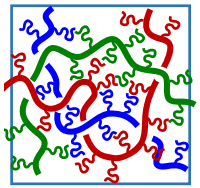
$$\phi_{bb} = \frac{N_g}{N_g + N_{sc}} \sim 1$$

Relatively dilute side chains do not significantly affect properties of backbone-dominated melt.

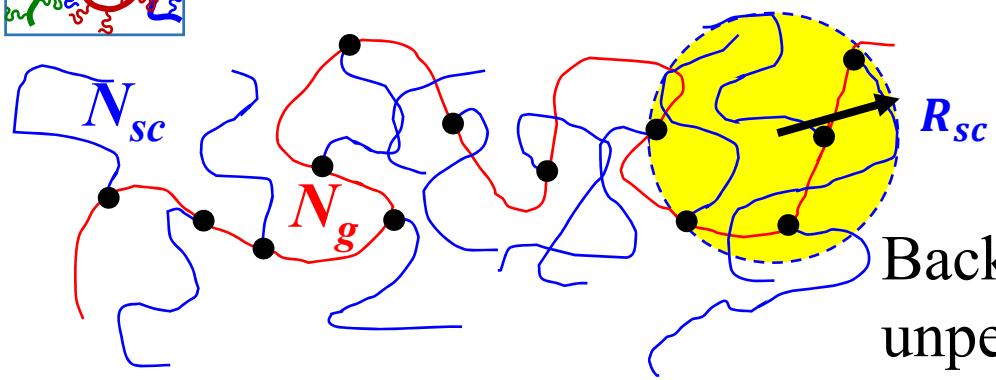
Backbones and side chains are in almost unperturbed Gaussian conformations.

Plateau modulus G_e due to entanglements between backbones is similar to modulus $G_{e,linear}$ of linear polymer melts.

To lower plateau modulus - need to increase the density of teeth of a comb – decrease backbone volume fraction $\phi_{bb} << 1$.



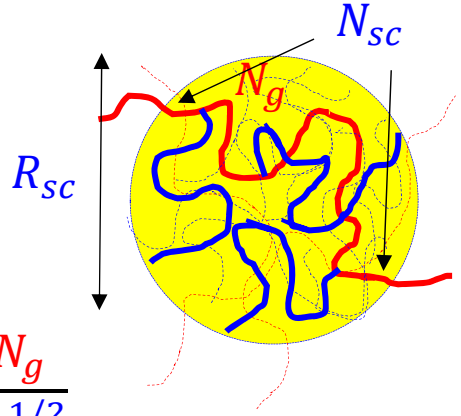
Densely Grafted Combs $N_{sc}^{1/2} < N_g < N_{sc}$



Most of the melt volume is occupied by side chains $\phi_{bb} << 1$.

Backbones and side chains are in almost unperturbed Gaussian conformations.

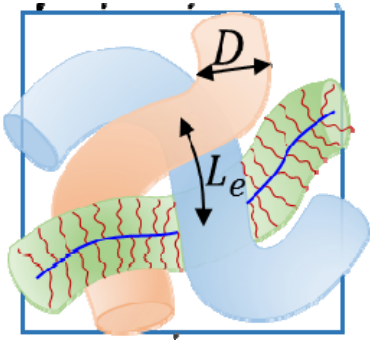
Side chains overlap parameter O_{sc}: # of side chains within the pervaded volume R_{sc}^3 of a side chain $O_{sc} \approx N_{sc}^{1/2}$

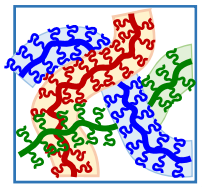


# of side chains out of this number O_{sc} within volume R_{sc}^3 belonging to the same comb is N_{sc}/N_g.

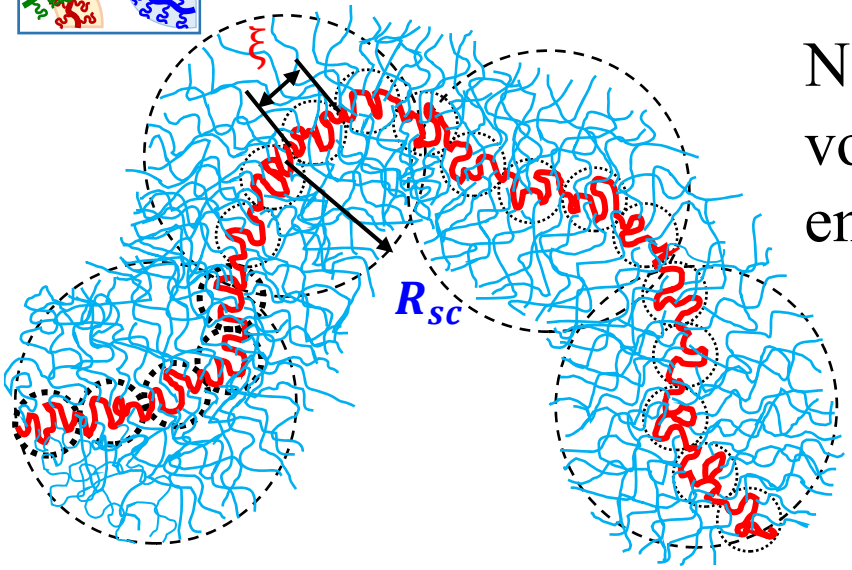
Number of overlapping comb sections $\frac{O_{sc}}{N_{sc}/N_g} \approx \frac{N_g}{N_{sc}^{1/2}}$

decreases with increasing grafting density $1/N_g$ and reaches unity at $N_g \approx N_{sc}^{1/2}$ for $\phi_{bb} \approx 1/N_{sc}^{1/2}$ - combs disinterpenetrate forming flexible filaments.





Loosely Grafted Bottlebrushes $N_g < N_{sc}^{1/2}$



Not enough room within the pervaded volume R_{sc}^3 of a side chain for side chains emanating from an unperturbed backbone.

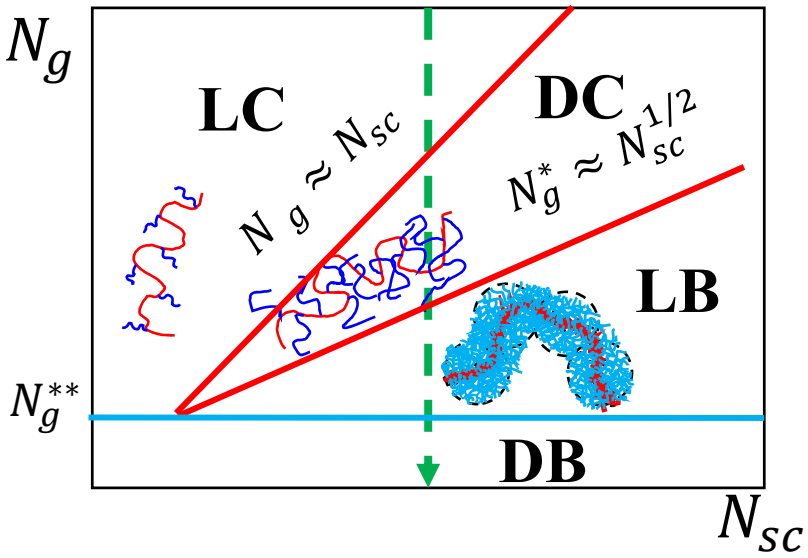
Backbone stretches on length scale of side chain R_{sc} to assure that only $O_{sc} \approx N_{sc}^{1/2}$ side chains are grafted to it on this length scale.

Backbone is almost unperturbed on length scales shorter than tension blob $\xi \approx bN_g$, extended at intermediate length scales $\xi < r < R_{sc}$, and is Gaussian on scale larger than R_{sc}.

Conformation analogous to polyelectrolytes in semidilute solution with long-range repulsion between backbone monomers induced by side chains.

Bottlebrush behaves as a thick sausage – polymer with effective monomers of size R_{sc}.

Diagram of States of Combs & Bottlebrushes



LC – Loosely-grafted Comb regime with ideal backbone & side chains and fully interpenetrating molecules

- similar to melts and concentrated solutions of backbones with $\phi_{bb} \sim 1$.

DC – Densely-grafted Comb regime with ideal backbone & side chains and partially interpenetrating molecules

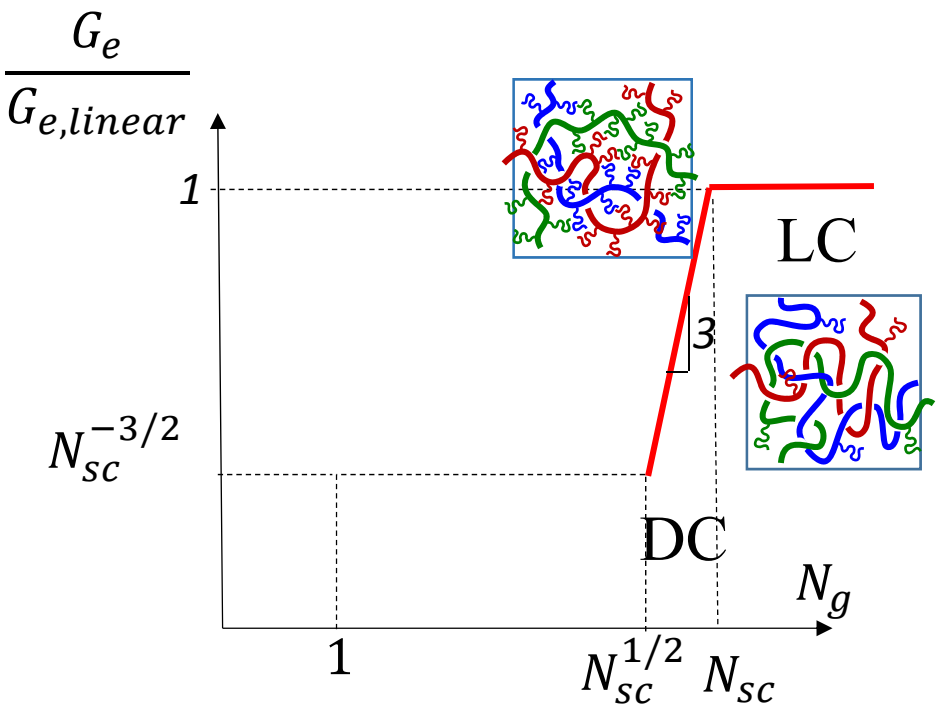
- similar to semidilute solutions of backbones in solvent of its own side chains with $\phi_{bb} << 1$.

LB – Loosely-grafted Bottlebrush regime with partially extended backbone & ideal side chains

- similar to melt of thick flexible filaments.

DB – Densely-grafted Bottlebrush regime with extended backbones and partially extended side chains

Plateau Modulus of Comb Melts



Kavassalis-Noolandi conjecture – plateau modulus decreases upon dilution of backbone as

$$G_e \sim \phi_{bb}^{\,3}$$

$$\phi_{bb} = N_g/(N_g + N_{sc})$$

$$G_e = G_{e,linear}\left(\frac{N_g}{N_g + N_{sc}}\right)^3$$

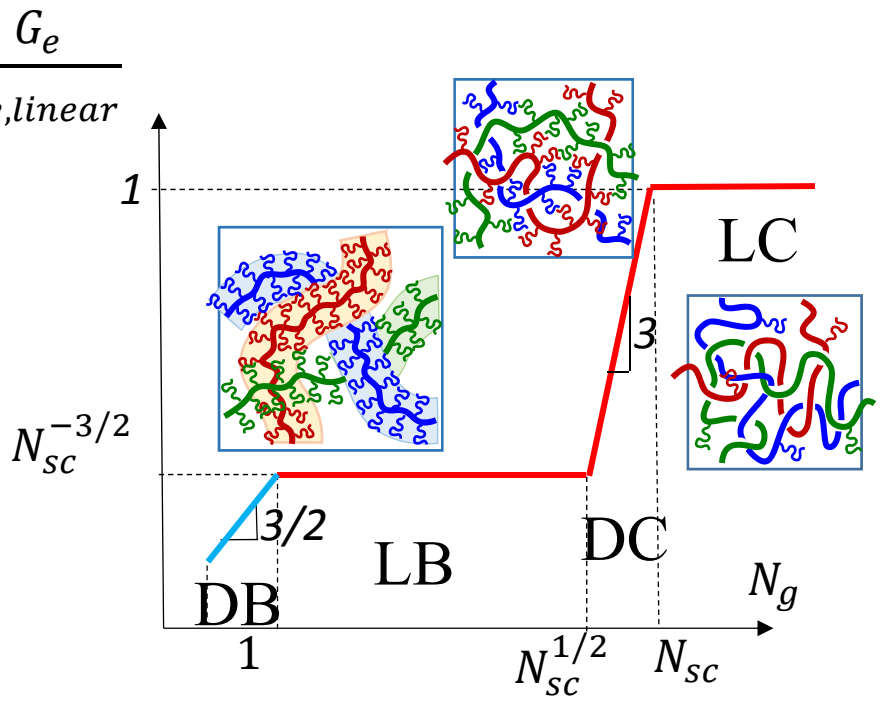
In loosely-grafted comb melts LC with $N_{sc} < N_g$ plateau modulus is similar to linear melt

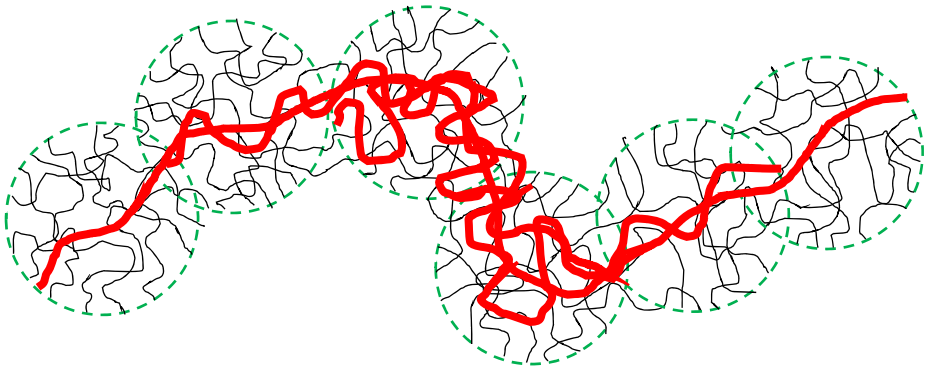
$$G_e \approx G_{e,linear}$$

In densely-grafted comb melts DC with $N_{sc}^{1/2} < N_g < N_{sc}$ plateau modulus sharply decreases with N_g/N_{sc}

$$G_e \approx G_{e,linear}\left(\frac{N_g}{N_{sc}}\right)^3$$

Plateau Modulus of Bottlebrush Melts





Contour length of loosely-grafted (LB) bottlebrushes with $N_g < N_{sc}^{1/2}$ grows with increasing grafting density $1/N_g$.

Effective monomer size $R_{sc} \approx bN_{sc}^{1/2}$, persistence length, and entanglement length do not depend on grafting density $1/N_g$ as long as side chain length N_{sc} is kept constant.

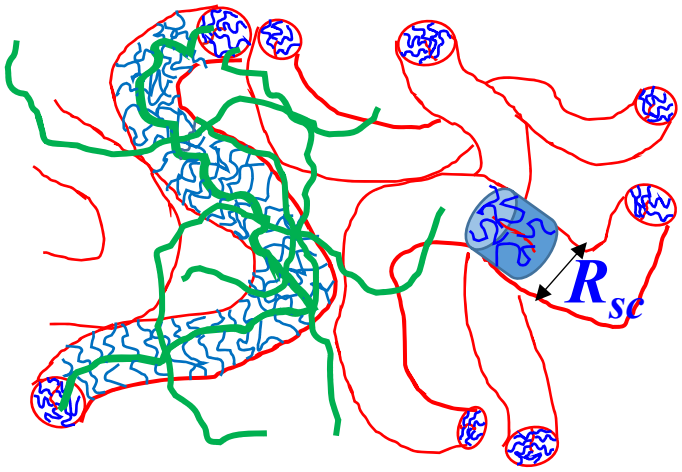
Plateau modulus G_e is independent of N_g in loosely-grafted bottlebrush regime.

$$G_e \approx \frac{G_{e,linear}}{N_{sc}^{3/2}}$$

Stretching of a backbone compensates increasing grafting density $1/N_g$ leaving G_e unchanged.

Bottlebrush Melts with Super-Low Rubbery Plateau

Bottlebrush molecules with N_{sc}-monomer side chains grafted to backbone reduce molecular overlap and entanglement density.

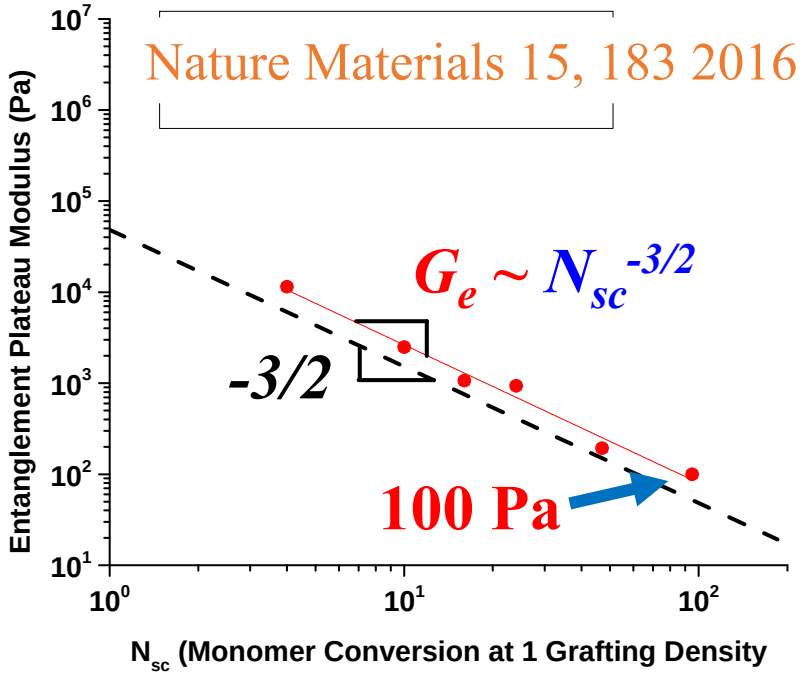


$R_{sc} \sim N_{sc}^{1/2}$ - size of effective monomers

persistence length $l_p \sim R_{sc}$

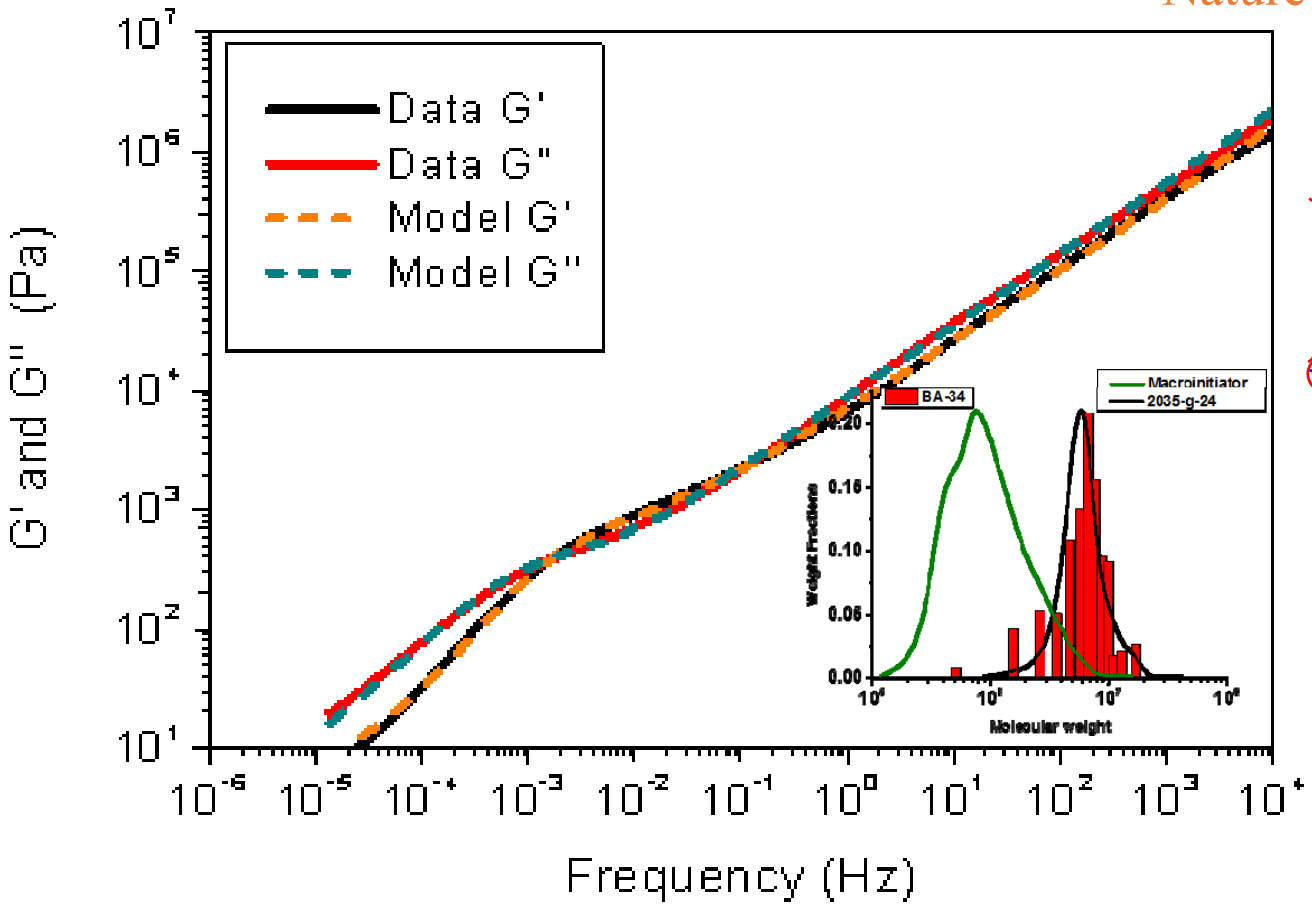
Plateau modulus

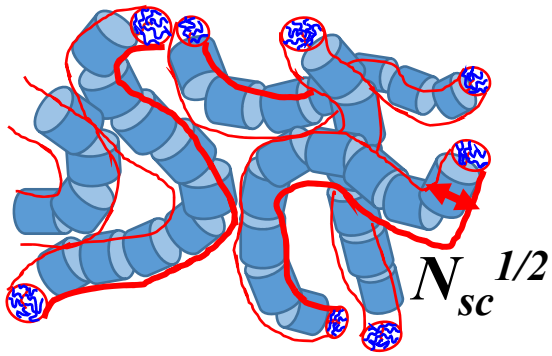
$$G_e \sim l_p^3 / R_{sc}^6 \sim R_{sc}^{-3} \sim N_{sc}^{-3/2}$$



Bottle-Brush Melt Rheology: Chain of Effective Monomers

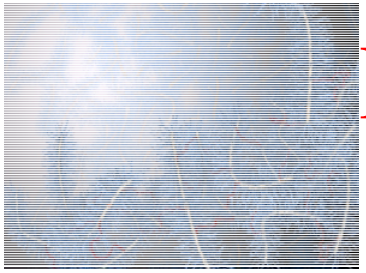
Nature Materials 15, 183 2016





Fit by power law + double-reptation model of known distribution of brush lengths w_i .

$$G(t) = G_1\left(\frac{t}{\tau_1}\right)^{-0.6} + \frac{\rho RT}{M_e}\left(\sum_{i=1}^{i=k} w_i e^{-t/\tau_e\left(\frac{m_i}{M_e}\right)^{3.4}}\right)^2$$



Networks of Bottle-Brushes

Super-Soft Dry Gels

A melt of bottle brushes is cross-linked into a network

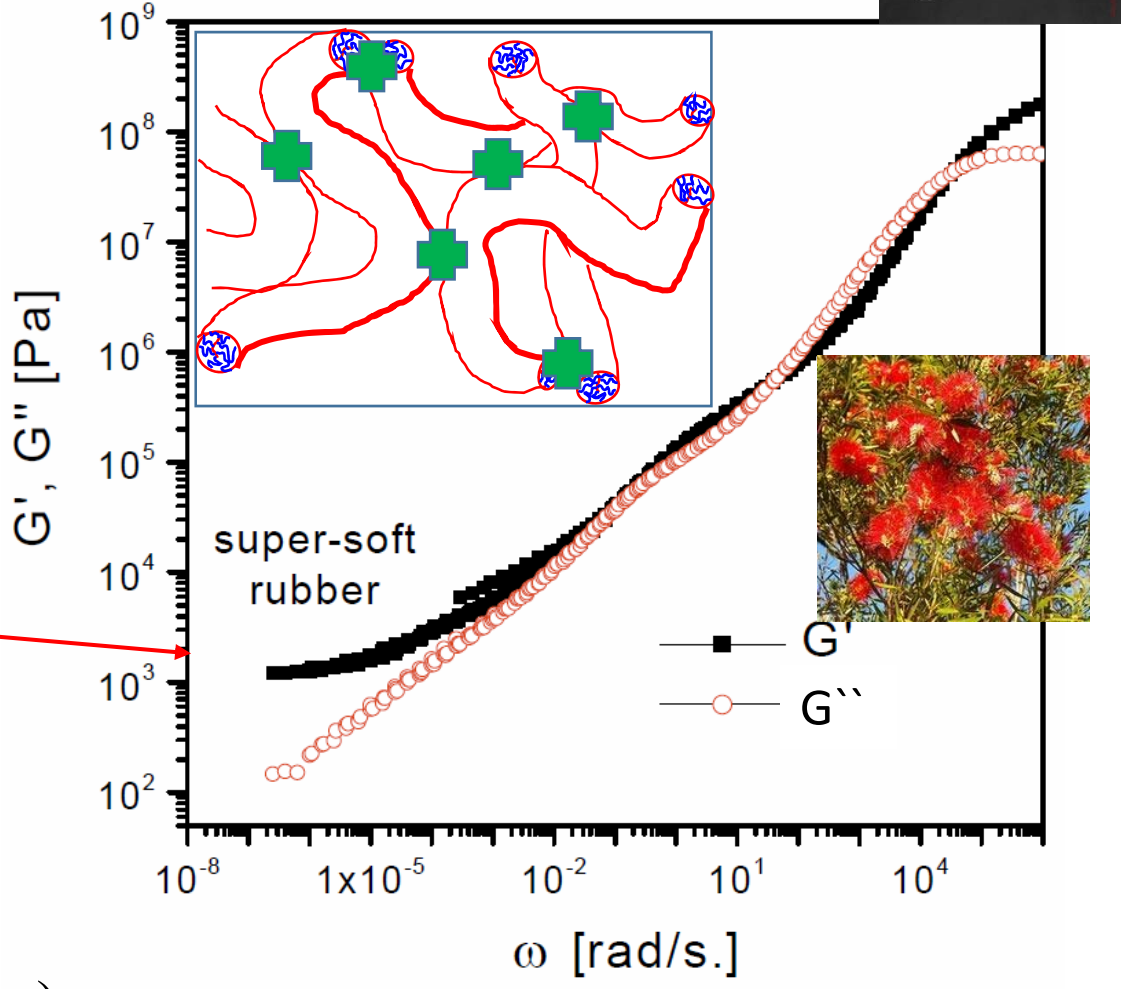
Network modulus for $M_x < M_e$

$G_x \approx \rho RT/M_x$

e.g. $M_x \approx 1.6 \times 10^6 g/mol$,
$G_x \approx 1.3\ kPa$

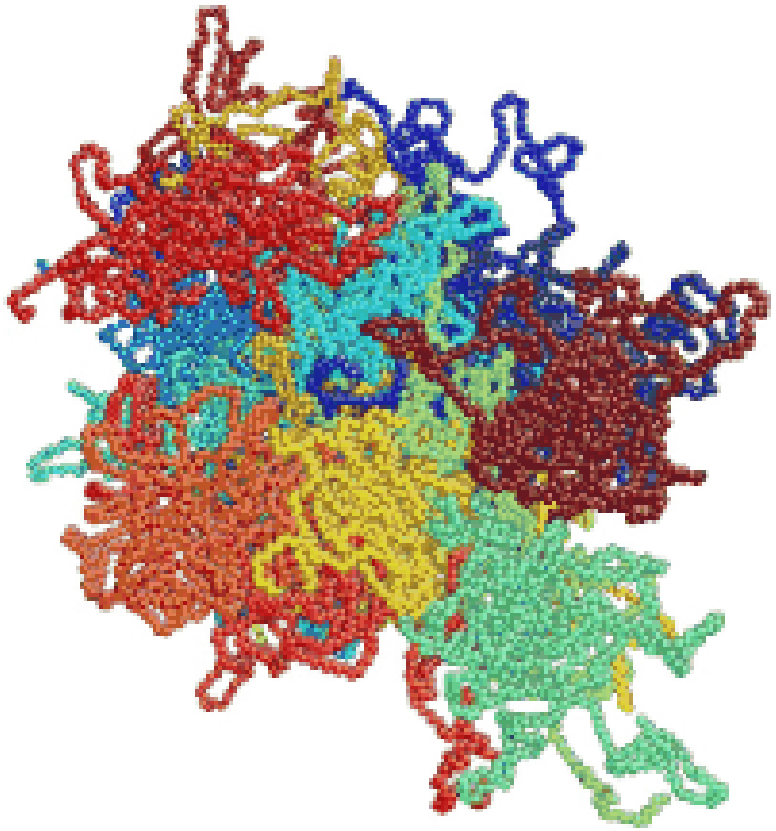
Side chains could be functionalized with ionic or H-bonds to form reversible associations for specific applications (e.g. self-healing).

Unique stress-strain properties

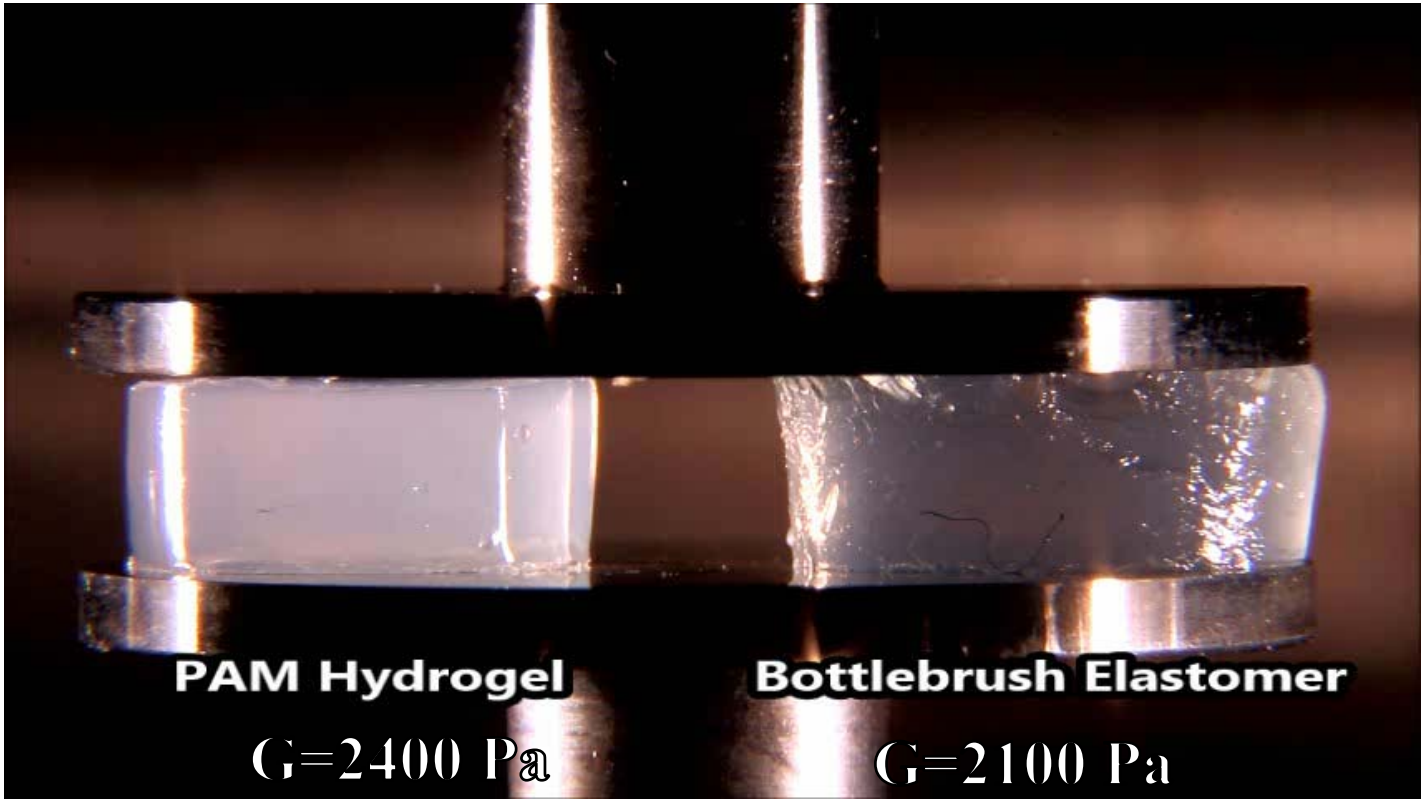


Pakula et al, Polymer 47, 7198 (2006)

DEFORMATION OF NETWORKS

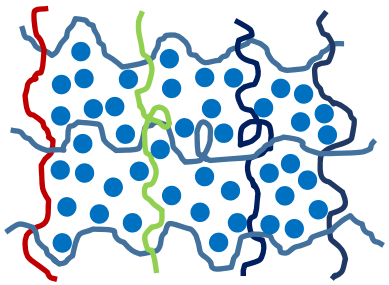


Super-Soft and Super-Elastic



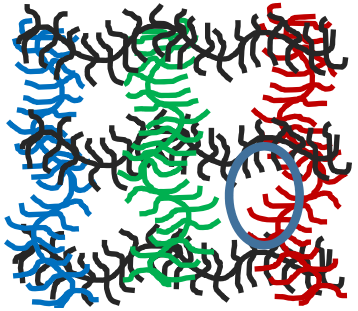
10% polymer

Solvent-swelled



8% backbone

Solvent-free



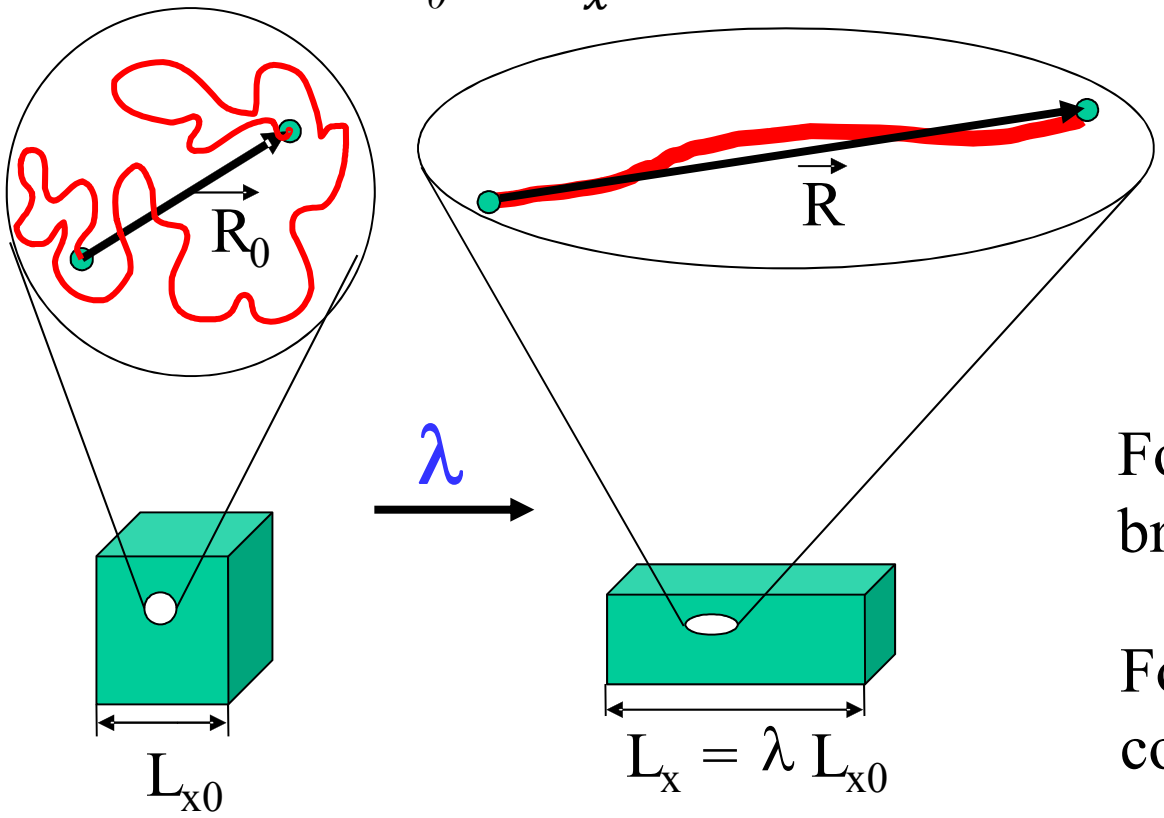
Elasticity – Elongation at Break

Elongation at break of most hard materials is << 100%

Soft materials (e.g. rubber) extend >100% before breaking.

Chain size before deformation $R_0 \approx bN_x^{1/2}$

Chain size after deformation $R = \lambda R_0$



Maximum elongation

$R_{max} = bN_x$

$\lambda_{max} \approx R_{max}/R_0 \approx N_x^{1/2}$

For larger elongation at break – increase N_x

For $N_x >> N_e$ entanglements control elongation at break

Super-soft Networks can also be Super-elastic

Maximum extension of elastomers with long backbone strands between cross-links $N_x > N_e$ is controlled by entanglements.

Typical $N_{e,linear} \sim 10 - 100 \rightarrow \lambda_{max,linear} \approx \sqrt{N_{e,linear}} \sim 3 - 10$

Soft materials (e.g. networks) are elastic $\lambda_{max} > 100\%$

For combs with $N_{sc}^{1/2} < N_g$ $N_{bb,e} \sim N_{e,linear}/\varphi_{bb}^2$

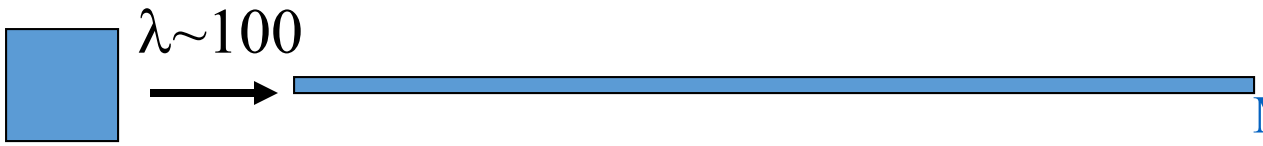
$\lambda_{max} \sim \lambda_{max,linear}/\varphi_{bb}$

For $N_g \approx N_{sc}^{1/2}$ $\lambda_{max}/\lambda_{max,linear} \approx N_{sc}/N_g \approx N_{sc}^{1/2}$

E. g. combs with $N_{sc}=100$ and $N_g=10$ are ~ ***10X*** **more extendable than linear chains** $\lambda_{max} \sim 30 - 100$.

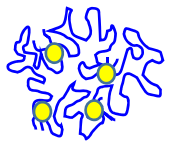
Is there another way of making soft super-elastic networks?

Deswollen Gels are Superelastic!



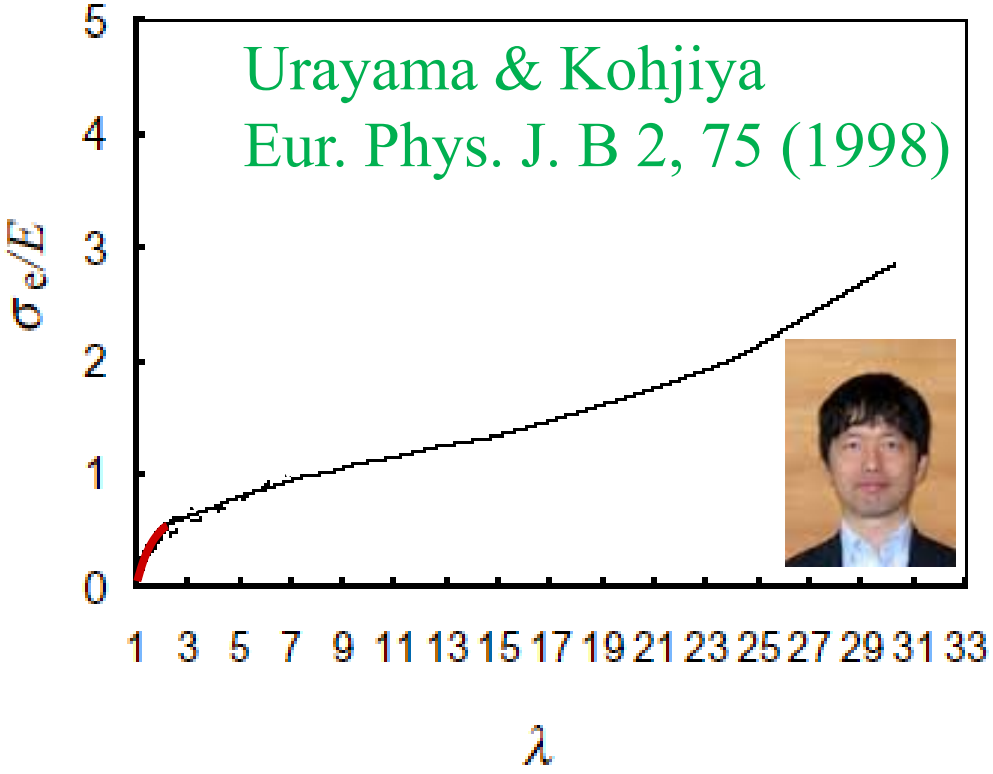
Obukhov, MR, Colby
Macromol. 27, 3184 (1994)

Deswollen gels can elongate much more than networks prepared from melt due to length stored in smaller loops.



Maximum extension of entangled networks cross-linked from melt

$$\lambda_{max} \sim N_e^{1/2}$$



For deswollen networks

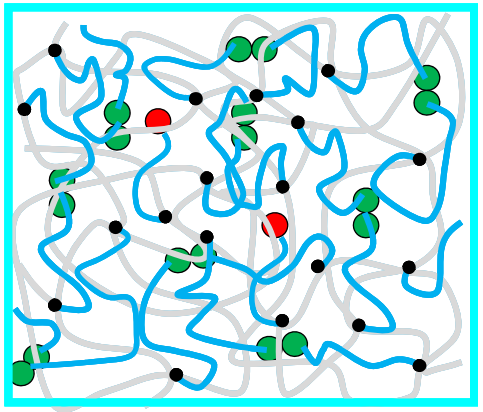
$$\lambda_{max} \sim N_e^{1/2} \phi_0^{-1}$$

— Network cross-linked from 10^5 Da PDMS melt

— Deswollen PDMS gels prepared at $\phi_0 = 0.1$ from 10^5 Da PDMS elongate up to $\lambda = 30$!

Hybrid Networks from Combs & Brushes

Chemical network of backbones with sticky monomers at the ends of side chains which can form pairwise reversible associations with other stickers



e.g. hydrogen bonds, ionic bonds, reversible metal–ligand bonds

open sticker

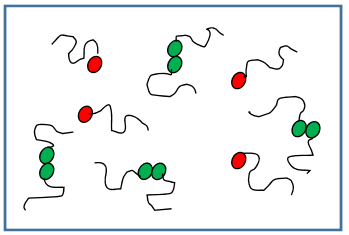
reversible (sacrificial) bond between a pair of closed stickers

Sacrificial bonds are designed to fail under stress, protecting irreversible bonds and dissipating energy.

Reversible groups re-associate upon stress relaxation, rebuilding the strength of the network.

Leash wagging the dog

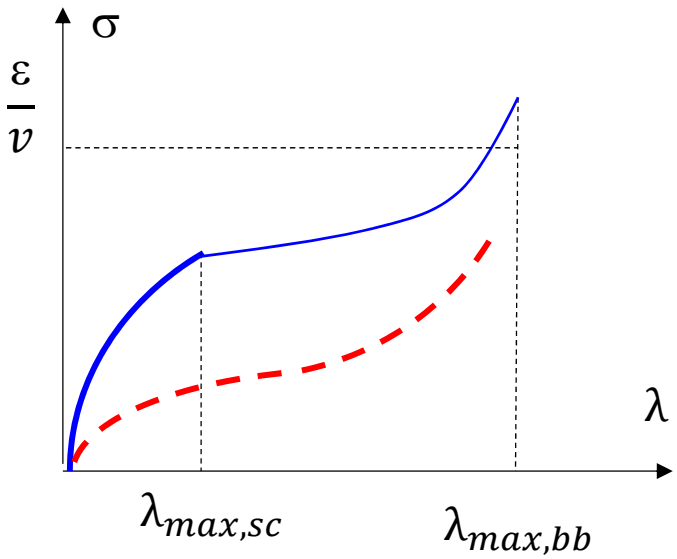
Mobility of reactive groups is restricted because they are attached to polymer chains (stickers on a leash).

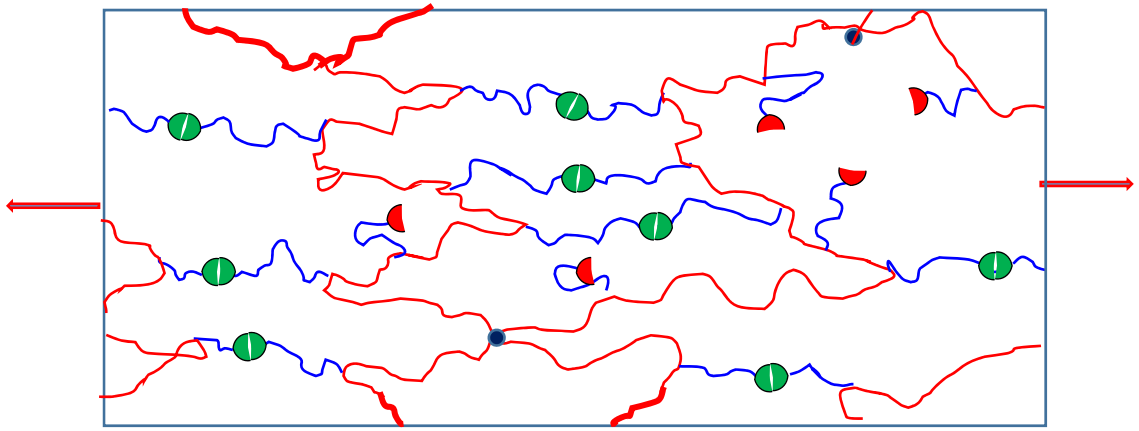


Super-Tough Hybrid Networks

Both permanent and reversible components of hybrid networks contribute to stress.

Reversible part contributes more due to higher volume fraction.



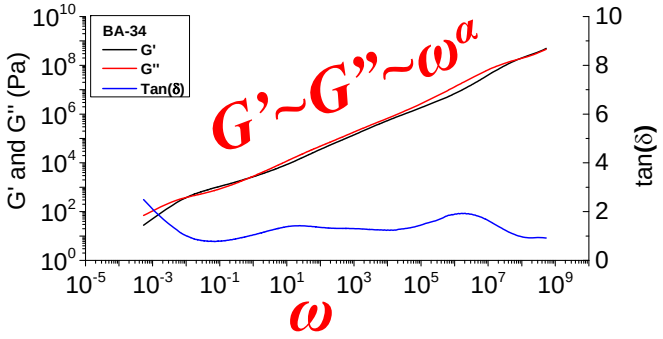


Reversible bonds in hybrid networks are broken and formed again $\lambda_{max,bb}/\lambda_{max,sc} \sim \sqrt{N_{e,linear}}$ times before permanent bonds break and network fails resulting in large strain at break.

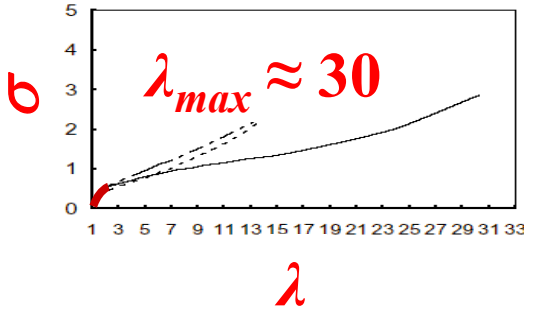
Large strain & stress at break → high toughness of hybrid networks

Molecular Design of Materials

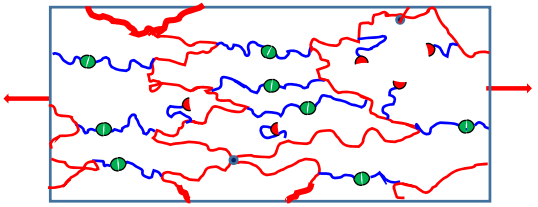
(i) Super-soft "dry gels":
Power law dynamic moduli & dramatic decrease of "plateau" $G_e \sim \varphi_{bb}^3$ by diluting backbones with side chains in molecular combs



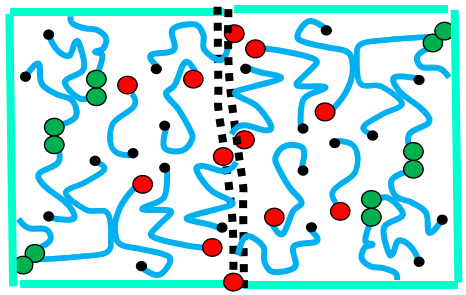
(ii) Super-elastic networks:
Maximum extension λ_{max} in comb regime increases with degree of polymerization of backbone strands between entanglements $N_{bb,e} \sim \varphi_{bb}^{-2}$ as $\lambda_{max} \sim \varphi_{bb}^{-1}$



(iii) Super-tough elastomers:
Reversible associations between chains of hybrid networks increase both strain & stress at break.

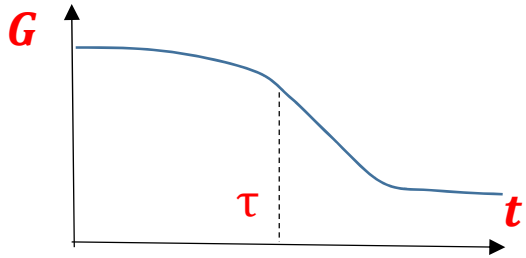


(iv) Self-healing elastomers:
High concentration of "broken" bonds – open "stickers on a leash" at the fractured surface results in fast interface strength recovery – **self-healing**

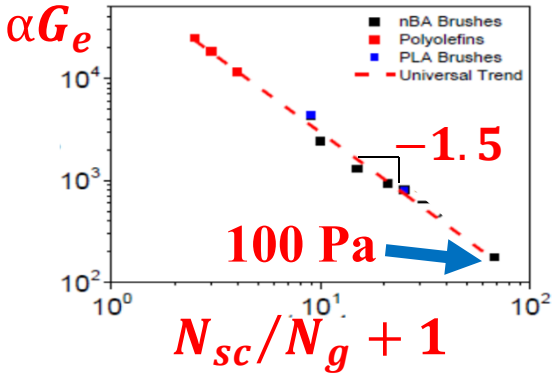


Future Directions

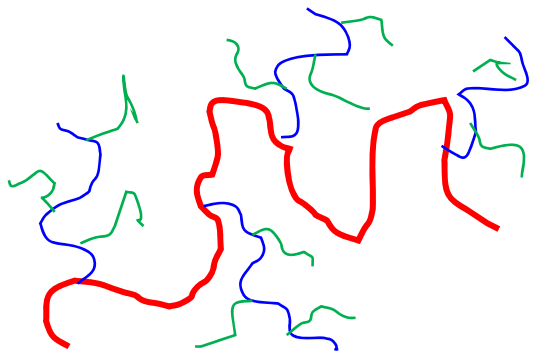
In addition to (or instead of) reversible associations one can introduce temporary entanglements between side chains if $N_{sc}>N_{e,0}$.



To avoid strong entanglements of side chains N_{sc}~100 → G_e decrease by $N_{sc}^{3/2}$ – 3 decades from 100kPa to 100Pa

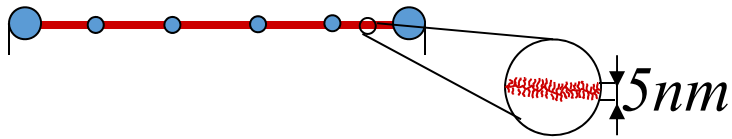


Further decrease of plateau modulus without side chain entanglements can be achieved by hierarchical branching structure: comb of combs or brush of brushes.



This requires synthesizing GIANT molecules with super-high molecular weight > 100MDa

e.g. bottle-brush mucin macromolecules



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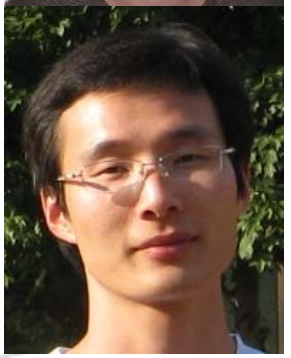

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