DNA-Origami Applications in Polymer Model Materials

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- **Stuff we want to do:**

  - **Strengthen mixtures of plastics**

    - Incompatible plastics
    - Combine properties (strength, flexibility)

  - **Lubricate/protect surfaces**

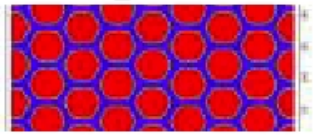
    

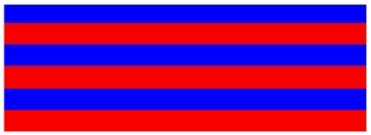
    - Prevent contact
    - Avoid damage

  - **Encapsulate drugs**

  - **Create patterns**

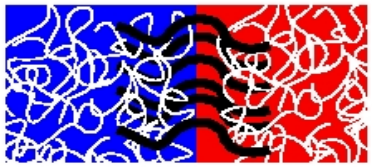
    

    - Symmetry, scale

- **Stuff that can do it.**

  - **Stitching polymers: reinforce mixtures**



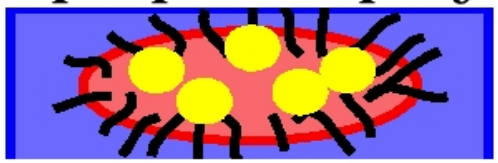
    - Half blue/half red reinforces interface.

  - **End-grafted polymers: lubrication**



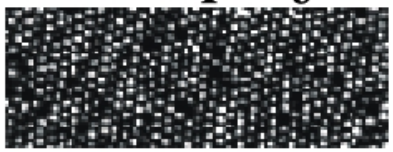
    - Trapped coating
    - "Osmotic" barrier

  - **Amphiphillic polymers: housing for droplets**



    - Polymer forms vesicles
    - Release contents, pH *e.g.*

  - **Block copolymers: templates for ordering**

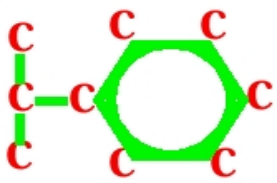




http://www.princeton.edu/~polymer/

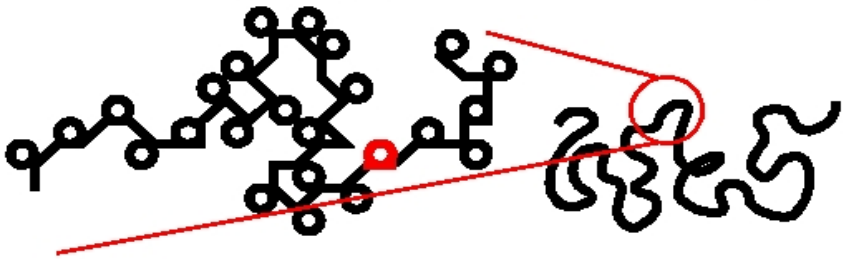
Polymers

- Are made of monomers...



Styrene
104AMU
1nm

- ... strung together into huge chains...



Polystyrene
1000 monomers:104,000AMU
$1000\,nm = 1\,\mu m$

- ... which mostly ignore h...

$$\Delta x \Delta p \approx (1\,nm)(10^5\,\mathrm{AMU}\,v) \approx 10^8 \frac{v}{m/s} h$$

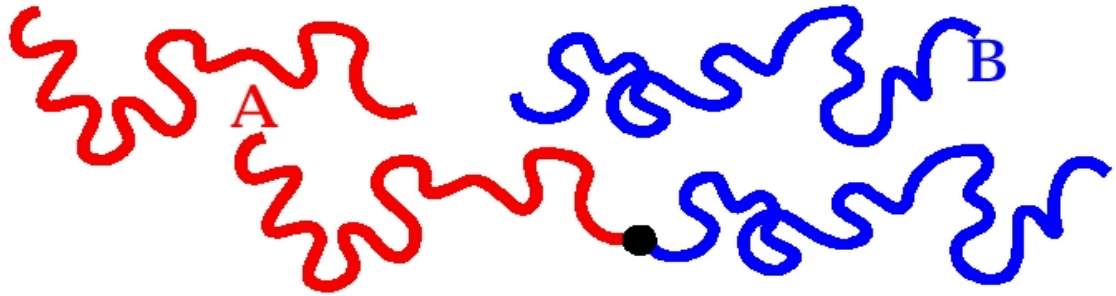
- ... and are all tangled up.



Entangling, knots

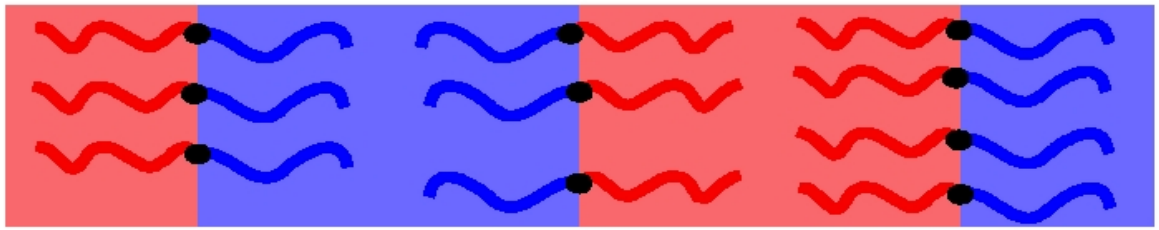
- **Block copolymers**

  - **Two kinds of monomers strung together.**



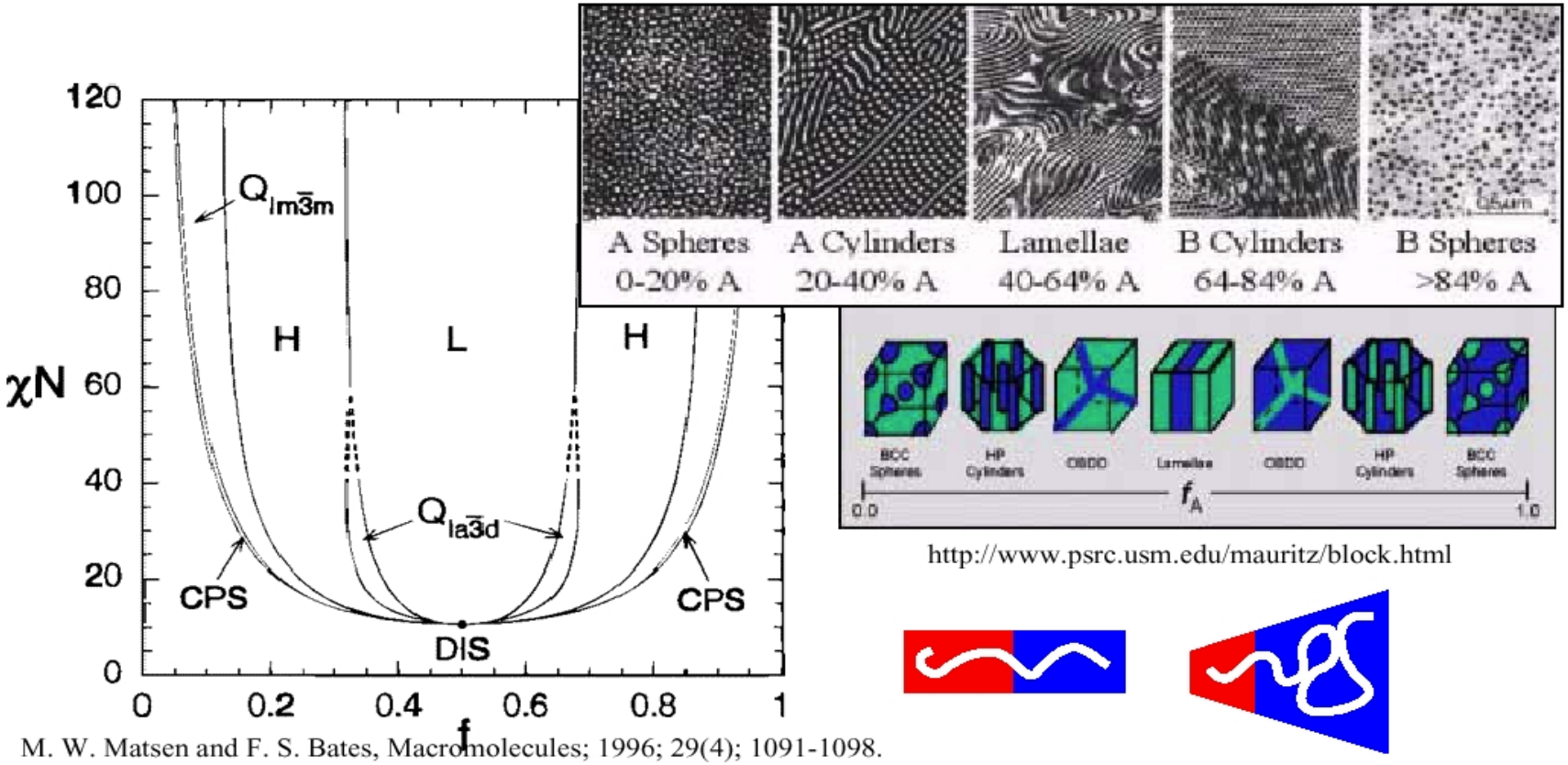
    - A-block and B-block: "diblock"

  - **Unless you break bonds, micro-scale texture happens.**



- **Asymmetric diblocks**

  - *f*= fraction of A on molecule, controls symmetry:



M. W. Matsen and F. S. Bates, Macromolecules; 1996; 29(4); 1091-1098.

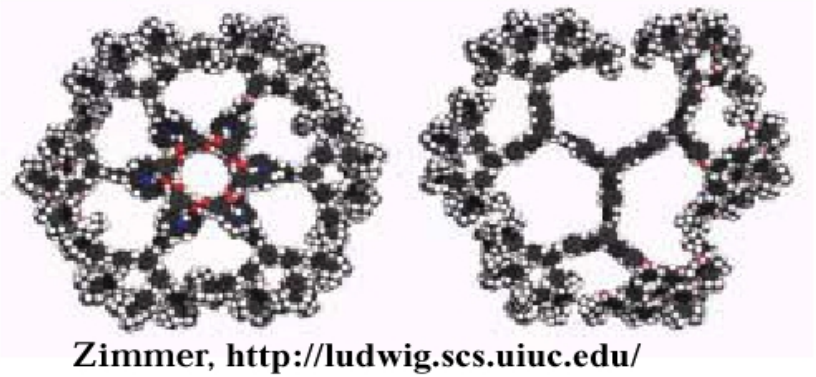
http://www.psrc.usm.edu/mauritz/block.html

- Architecture controls properties

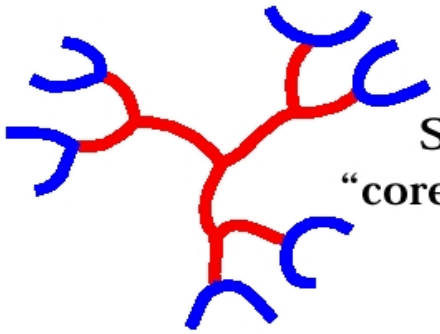
  - Diblocks, composition fraction is only control
  - Chain topology is also something to consider:



  - "Starburst" dendrimers



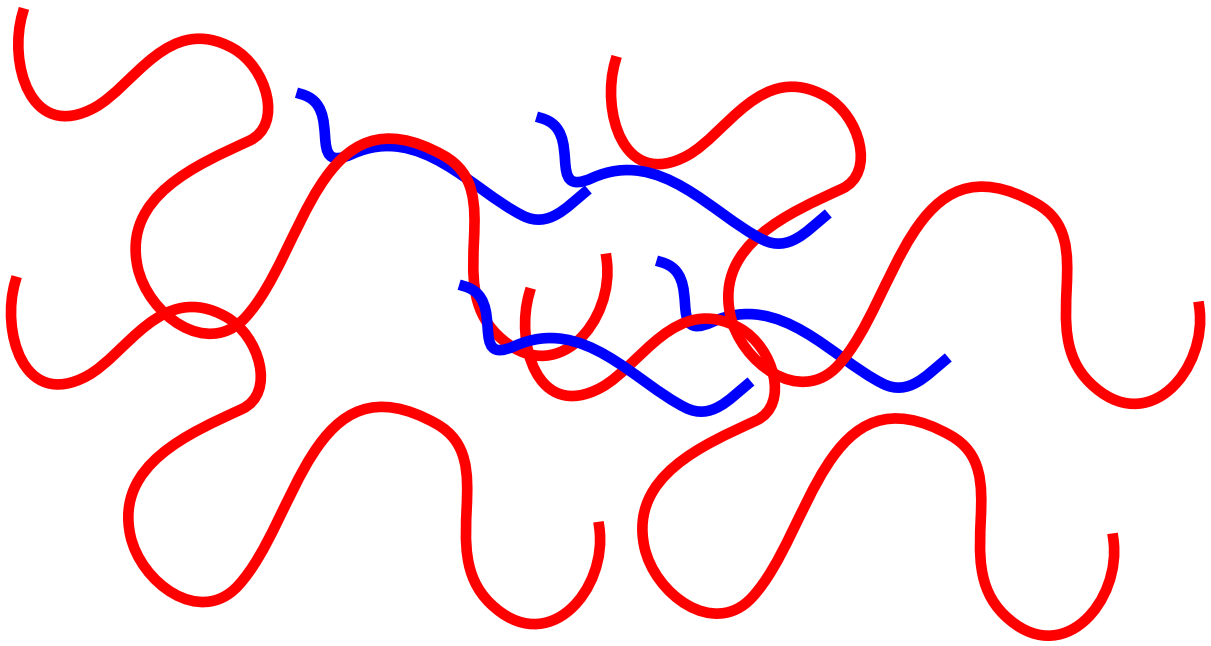
Zimmer, http://ludwig.scs.uiuc.edu/



Schematic, G3
"core-shell" copolymer

- **Monodispersity**

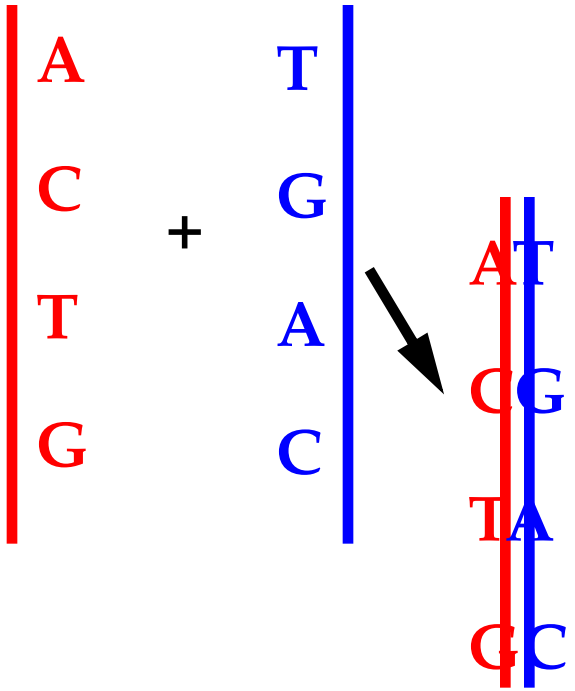
  - **Are all the chains the same?**



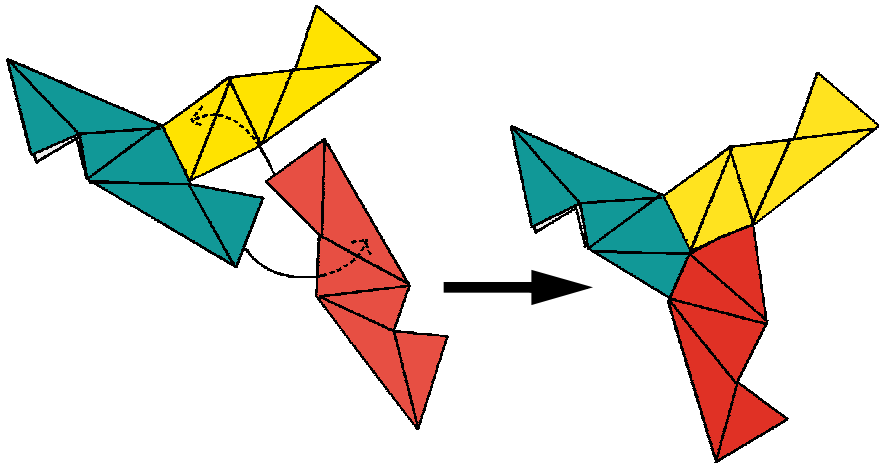
    - Short chains lubricate long chains
    - Short chains don’t entangle.

- **DNA-Origami**

  - **Base-pairing of complimentary DNA strands:**



Hull "Phizz" Units



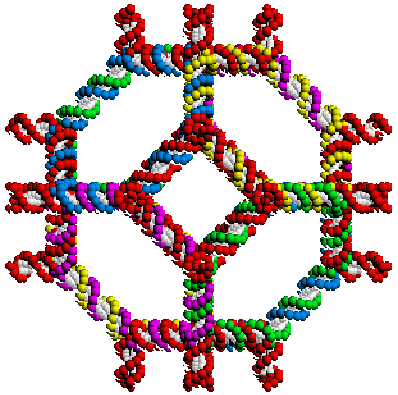
http://www.merrimack.edu/~thull/phzig/phzig.html

  - **"Modular" Origami, Self Assembled.**

DNA Origami

Examples

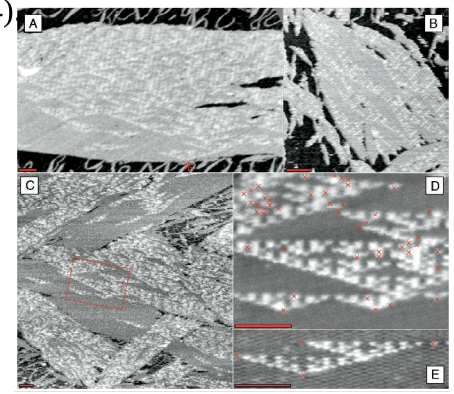
WILLIAM M. SHIH, JOEL D. QUISPE & GERALD F. JOYCE
Nature 427, 618- 621 (2004);



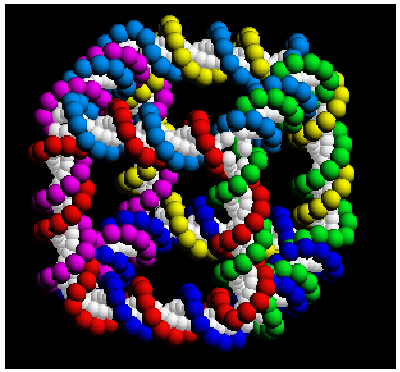
Paul Rothemund, Nature Physics, 2006



Paul W. K. Rothemund ,Nick Papadakis, Erik Winfree,
PLOS Biol. 2,e424 (2004).

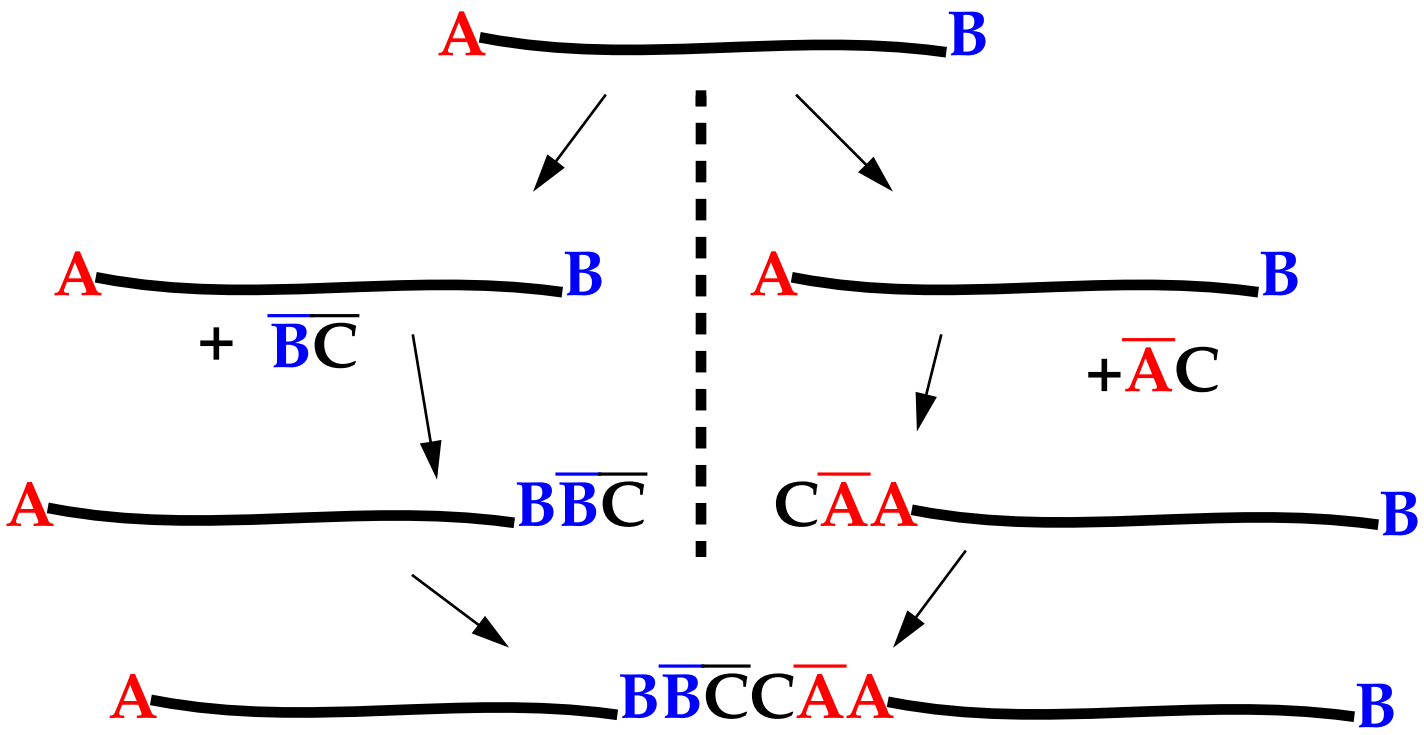


Junghuei Chen & Nadrian C. Seeman,
Nature 350, 631 (1991).



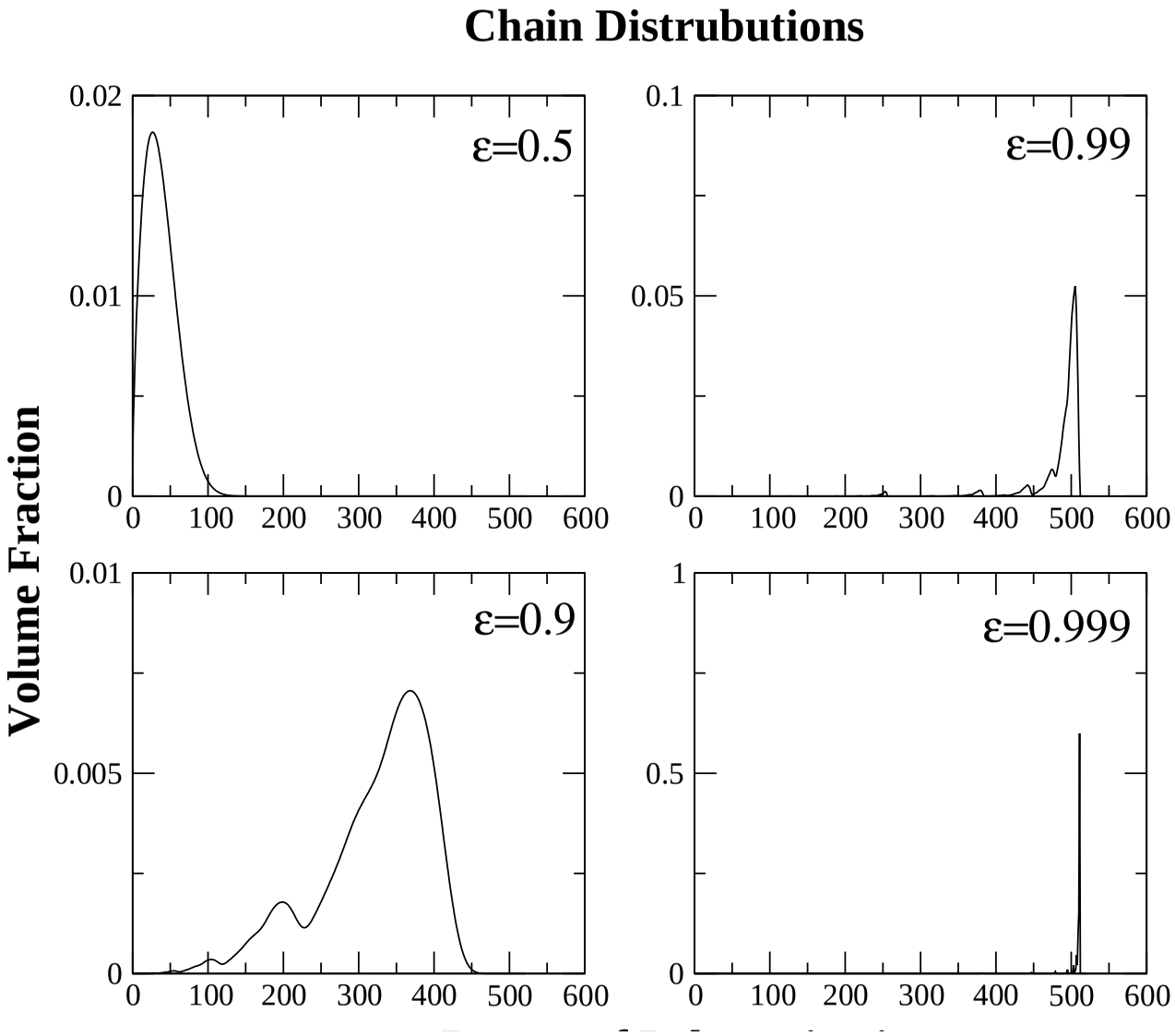
Chain Doubling Reaction

- End-labled chains:



- Pairs of chains joined, still end-labled A, B.

Chain Redoubling Reaction

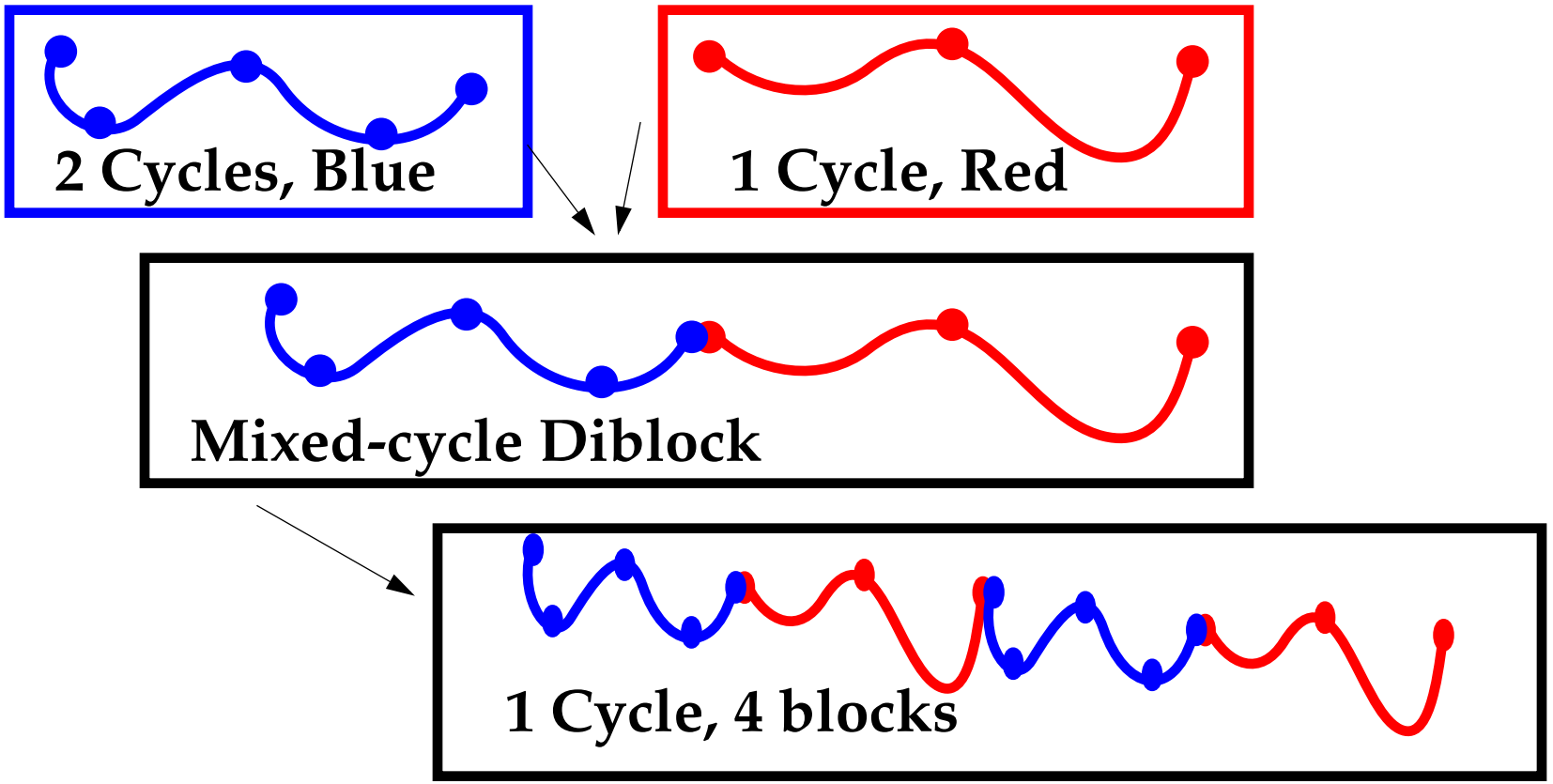


ε is fraction of chains reacted at each step

Syntheis is self-driven. Not micro-scopic.

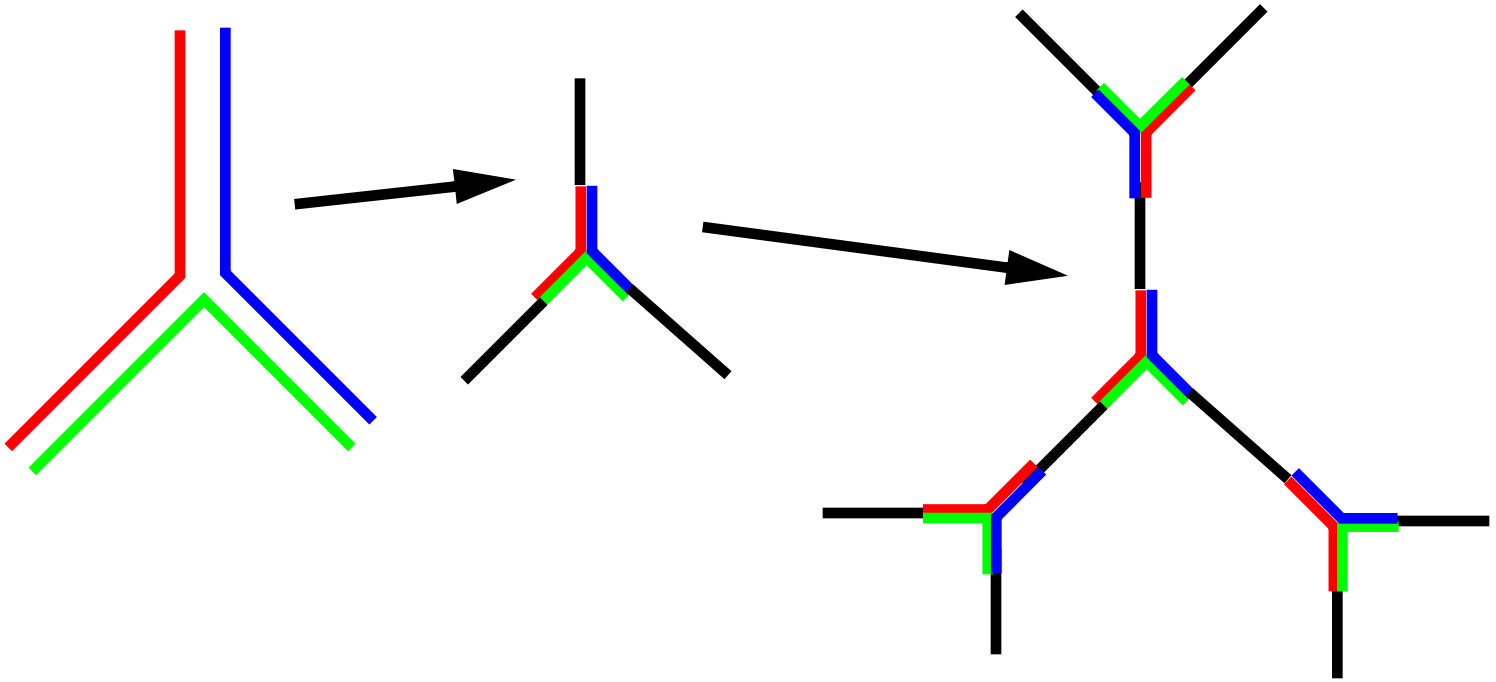
- **Multiblock Copolymers: Multiblocks**

  - **Combine vats with different backbone chains:**



- **Branches**

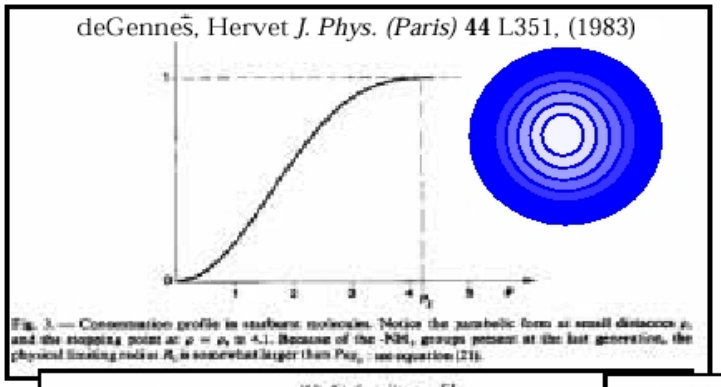
  - **3 strands -> Trifold junctions:**



  - **Regular Dendrimer Structures.**

- **Other theories, experiments support Filled core**

deGennes, Hervet *J. Phys. (Paris)* **44** L351, (1983)



Potschke, *et al. Macomolecules* **32** 4079 (1999)

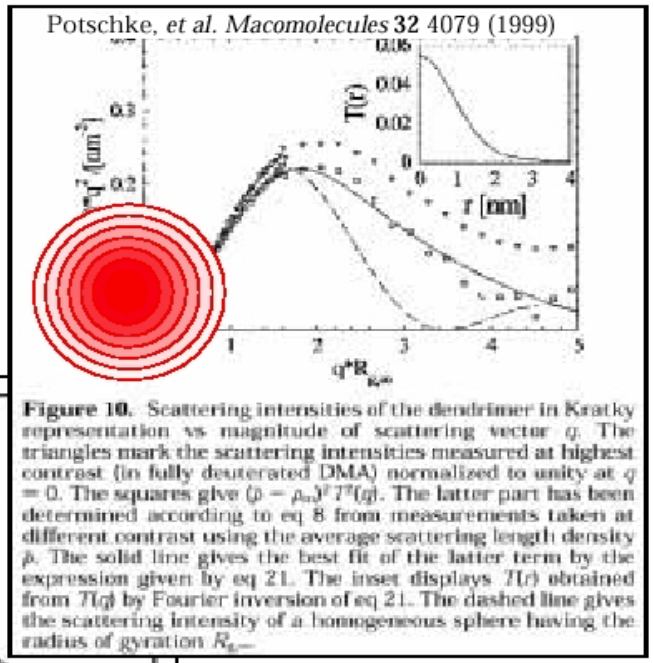


Figure 10. Scattering intensities of the dendrimer in Kratky representation vs magnitude of scattering vector q. The triangles mark the scattering intensities measured at highest contrast (in fully deuterated DMA) normalized to unity at $q = 0$. The squares give $(\rho - \rho_m)^2 T^2(q)$. The latter part has been determined according to eq 8 from measurements taken at different contrast using the average scattering length density ρ. The solid line gives the best fit of the latter term by the expression given by eq 21. The inset displays $T(r)$ obtained from $T(q)$ by Fourier inversion of eq 21. The dashed line gives the scattering intensity of a homogeneous sphere having the radius of gyration R_g.

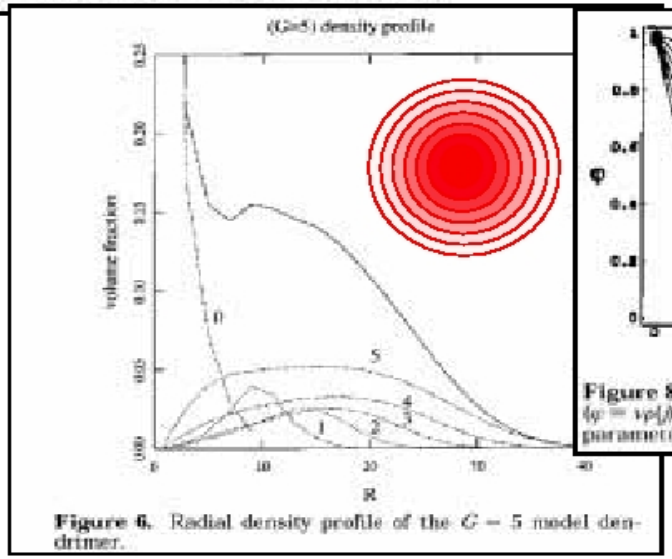


Figure 6. Radial density profile of the $G = 5$ model dendrimer.

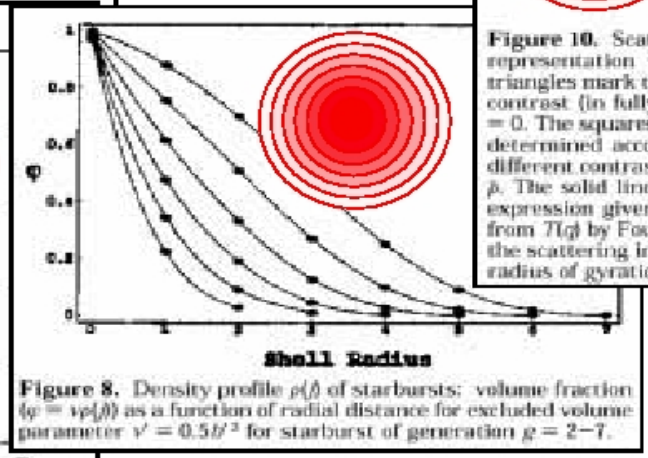


Figure 8. Density profile $\rho(i)$ of starbursts: volume fraction $(\varphi = v\rho(i))$ as a function of radial distance for excluded volume parameter $v' = 0.5b^3$ for starburst of generation $g = 2-7$.

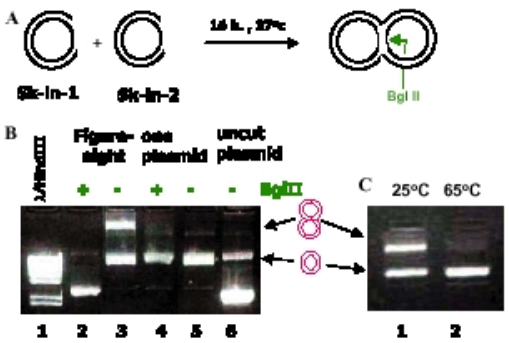
Boris, Rubinstein *Macromolecules* **29** 7251 (1996)

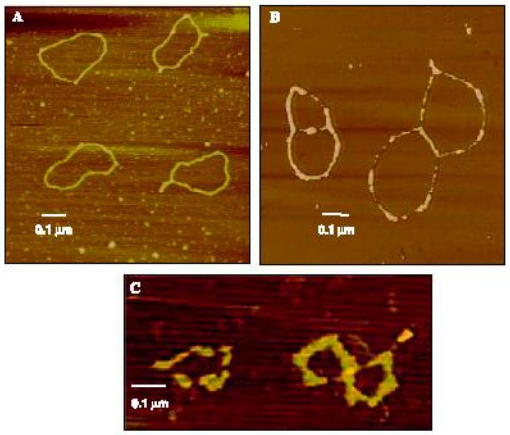
Mansfield, *Macromolecules* **33** 8043 (2000).

- **Look at hollow-core model again**

- **Connected Loops**

  - **Figure 8 loops -> chains**



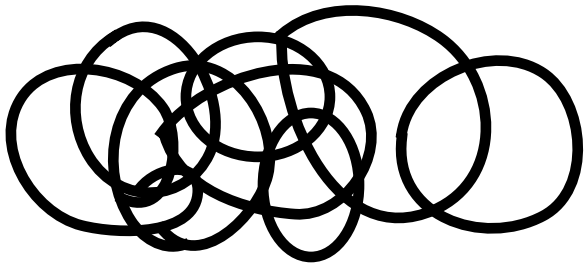


H.Nir, Y. Eichen, G. Schuster, Analytical Biochem, 344, (2005), 86.

  - **Melt of looped chains: "Olympipc gel"**

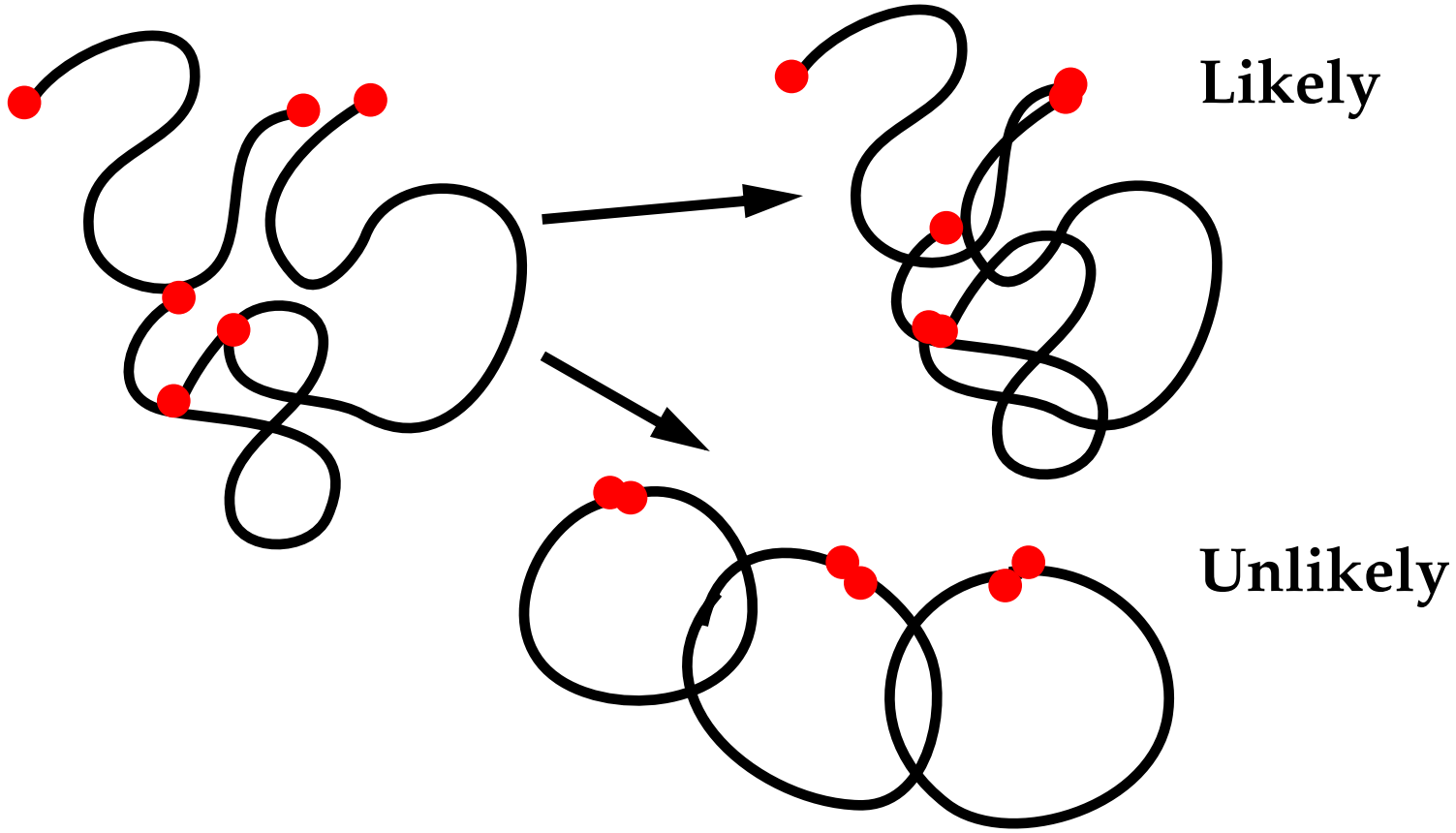
deGennes, *Scaling Concepts in Polymer Physics*, Cornell, 1979





- **"Olympic" Gels**

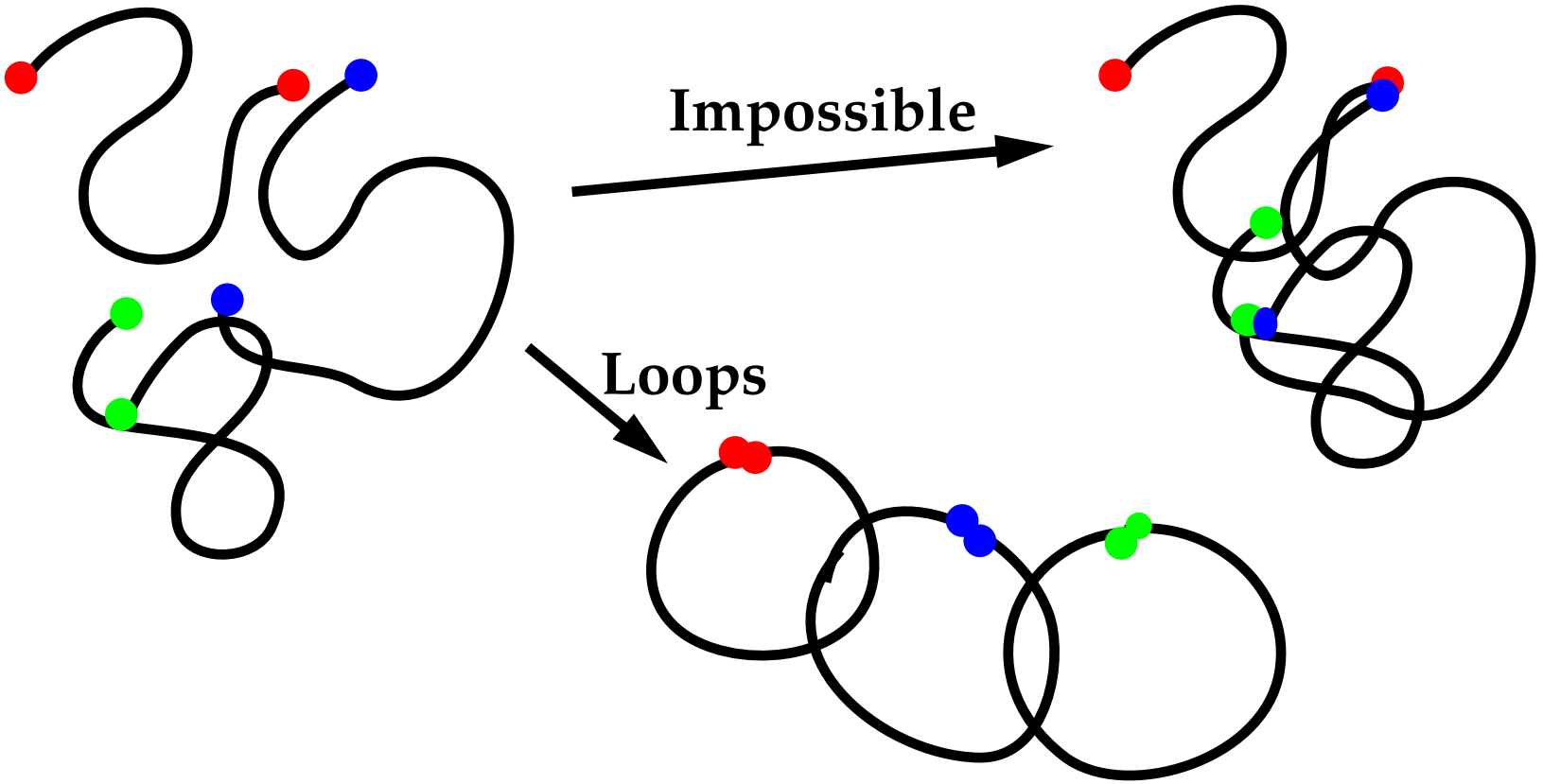
  - **Can't just connect end-labled chains:**



  - **Chains GROW ... don't loop.**

- **Use DNA-Origami ... Unique closures**

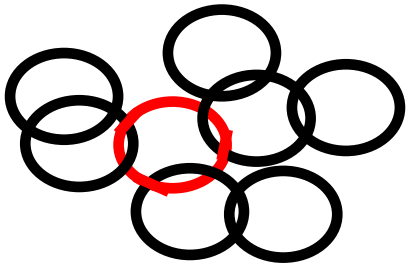
  - **Lots of end-groups ... p differnt types of pairs.**



  - **Random closings: loops are encouraged.**

- **Loop Fraction**

  - **Need each loop connected to 3 other loops**



Gels

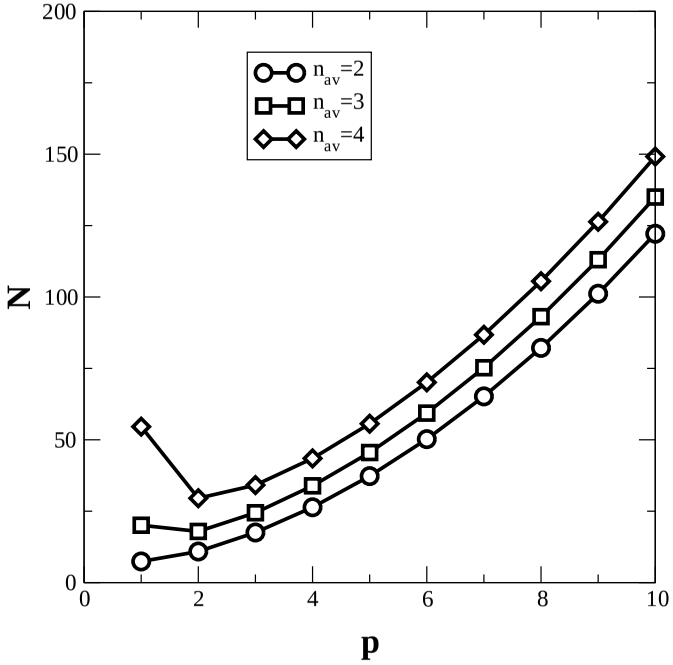
$N_{av} = 3$

Chains

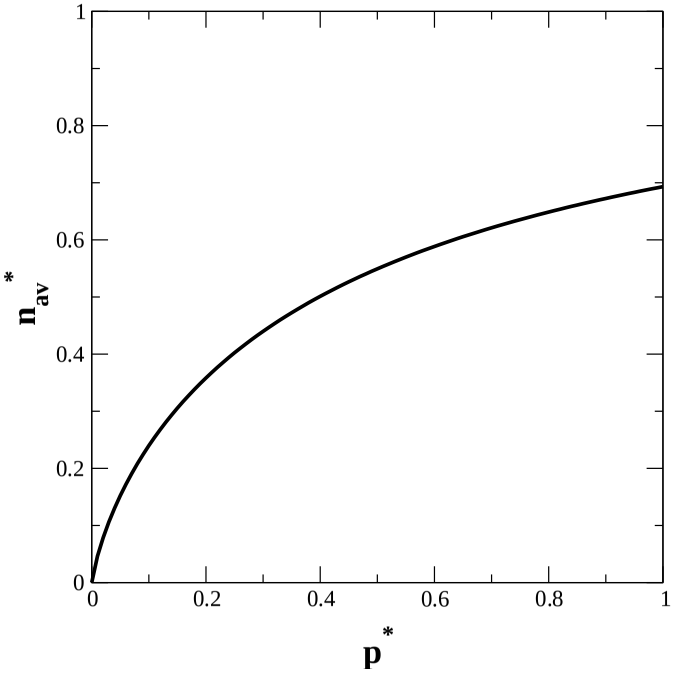
$N_{av} = 2$



N vs. p for various n_{av}



n_{av}^* vs. p^*



- **Olympic Membranes, Solids**

  - **Flexible, strong, designable:**





  - **These models "by hand"**
  - **DNA-Origami "self-assemble".**

- **Conclusion**

  - DNA-origami stripped down as a synthesis tool.
  - Controlled chains, exotic architectures.
  - Topological control (almost).
  - Speculation: Drug Delivery

