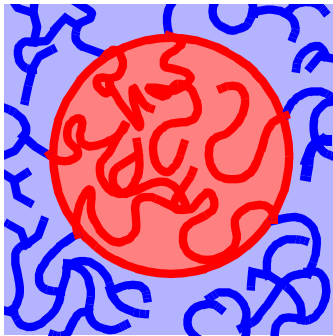


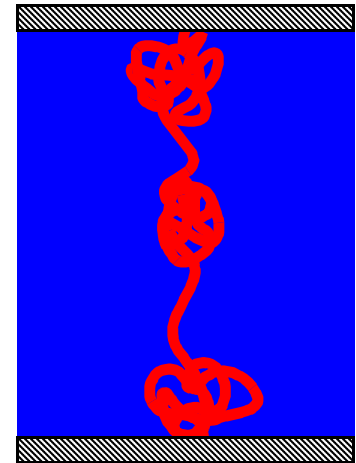
# Patterns in Polymers: Hyperbranching and Charged Blends



Galen T. Pickett

Department of Physics and Astronomy,

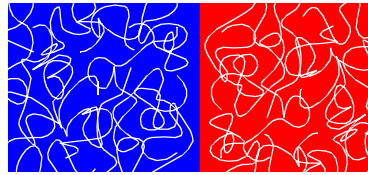
California State University Long Beach



● **Stuff we want to do:**

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□ **Strengthen mixtures of plastics**



- ☛ Incompatible plastics
- ☛ Combine properties (strength, flexibility)

□ **Lubricate/protect surfaces**

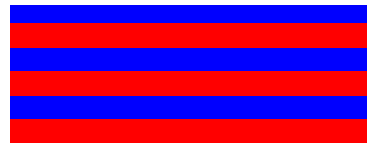
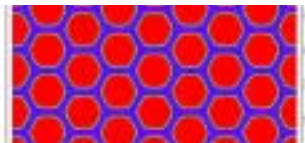


- ☛ Prevent contact
- ☛ Avoid damage

□ **Encapsulate drugs**



□ **Create patterns**

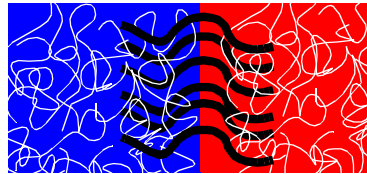


- ☛ Symmetry, scale

● **Stuff that can do it.**

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□ **Stitching polymers: reinforce mixtures**



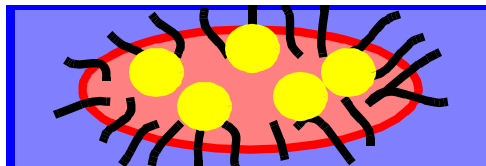
→ Half blue/half red reinforces interface.

□ **End-grafted polymers: lubrication**



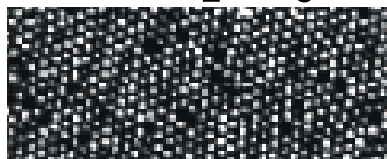
→ Trapped coating  
→ "Osmotic" barrier

□ **Amphiphilic polymers: housing for droplets**



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

□ **Block copolymers: templates for ordering**

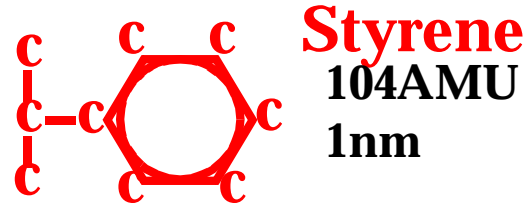


<http://www.princeton.edu/~polymer/>

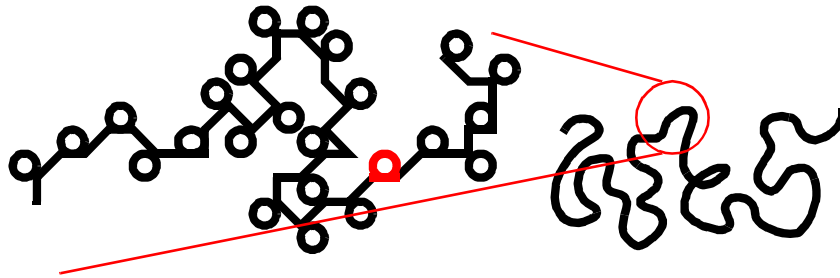
# ● Polymers

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- Are made of monomers...



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



## **Polystyrene**

1000 monomers: 104,000AMU  
1000nm = 1μm

- ... which mostly ignore  $h$ ...

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

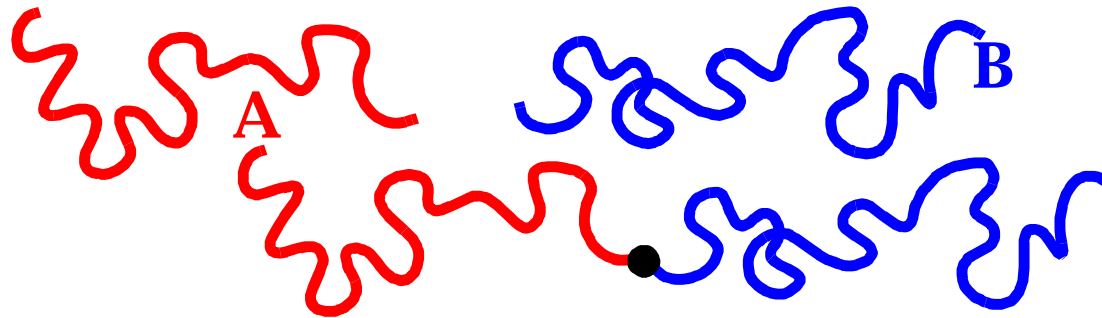
- ... and are all tangled up.



## ● Block copolymers

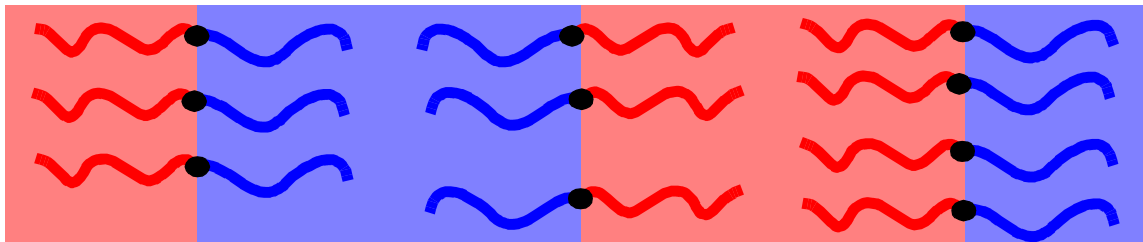
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- Two kinds of monomers strung together.



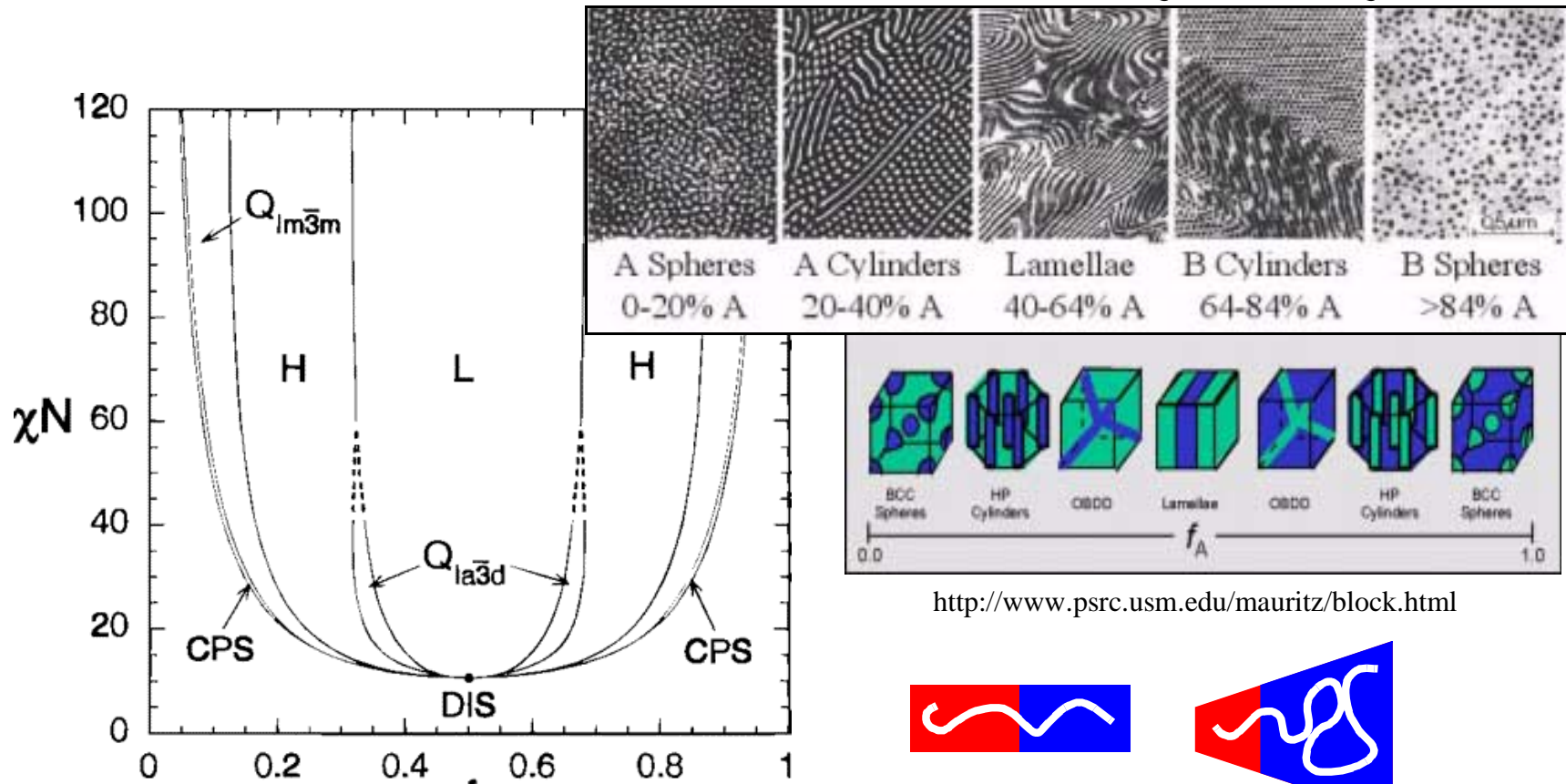
← A-block and B-block: “diblock”

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



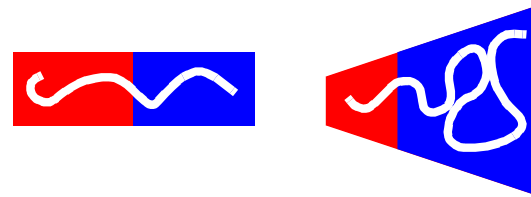
# ● Asymmetric diblocks

□  $f$  = fraction of A on molecule, controls symmetry:



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

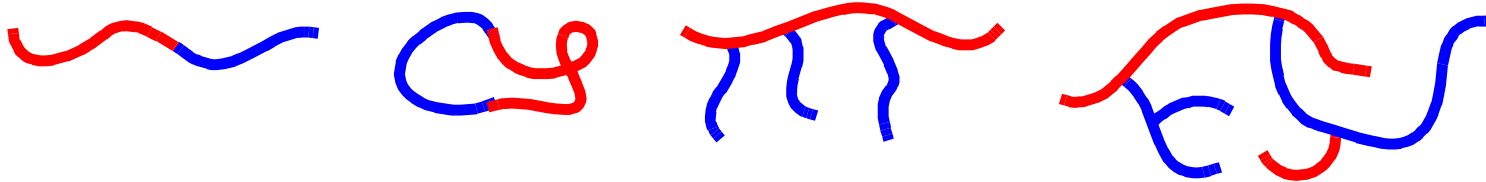
M. W. Matsen and F. S. Bates, *Macromolecules*; 1996; 29(4); 1091-1098.



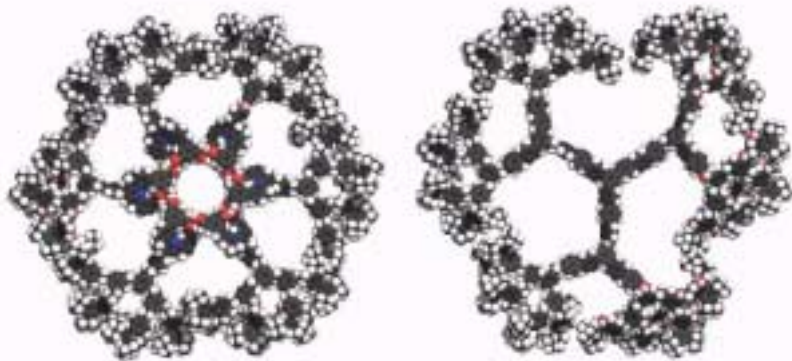
- **Architecture controls properties**

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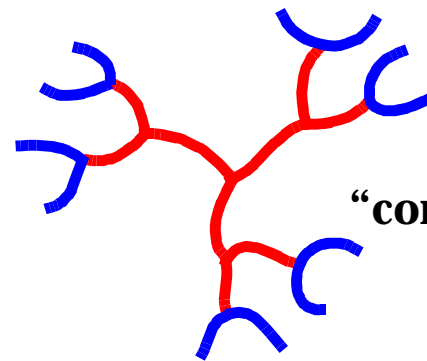
- **Diblocks, composition fraction is only control**
- **Chain topology is also something to consider:**



- **“Starburst” dendrimers**



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



Schematic, G3  
“core-shell” copolymer

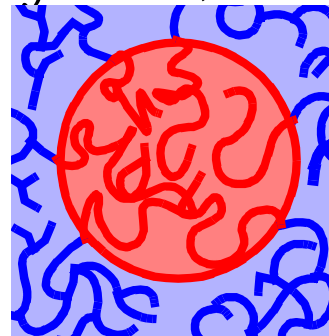
# ● Outline

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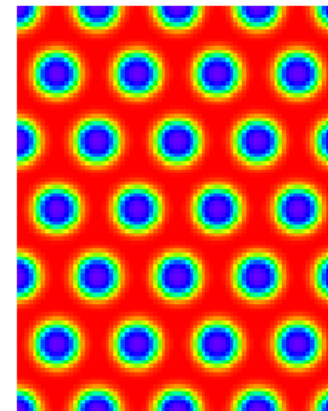
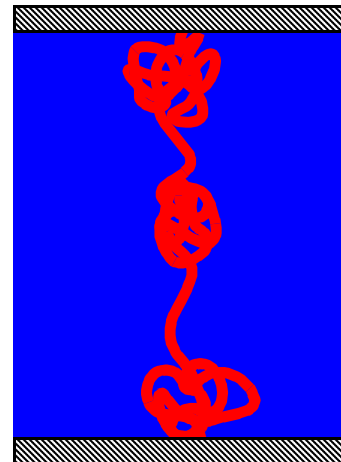
## □ Introduction

↳ Polymers, block copolymers, architectures

## □ Dendrimer copolymer



## □ Charged polymers



## □ Conclusions

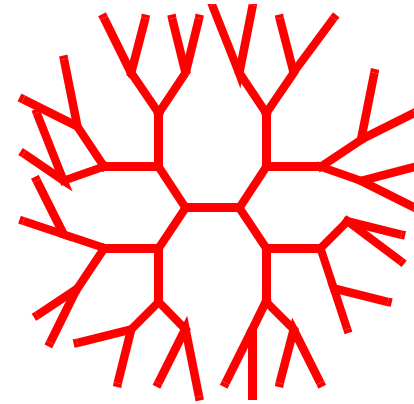


## ● **Single-dendrimer issues**

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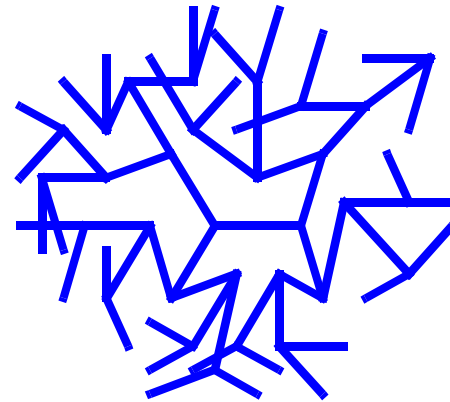
### □ **deGennes, single dendrimers**

- Hollow core
- Tips all exposed



### □ **Lescanec, single dendrimers**

- Core filled, backfolded
- Ends distributed



### □ **Where are the ends?**

### □ **Where are ends for a brush of dendrimer?**

- **Classical analog for dendrimer brush**

- **Single-chain free energy:**



**Generations**

$G_N$

$$F[z(n)] = \int_0^{G_N} f(n) \left[ \frac{1}{2} \left| \frac{dz}{dn} \right|^2 + P(z(n)) \right] dn$$

**Number of equivalent branches**

**G=5**

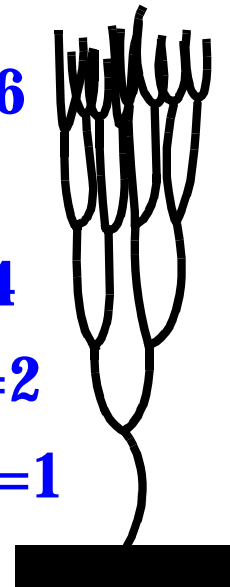
**f=16**

**f=8**

**f=4**

**f=2**

**f=1**

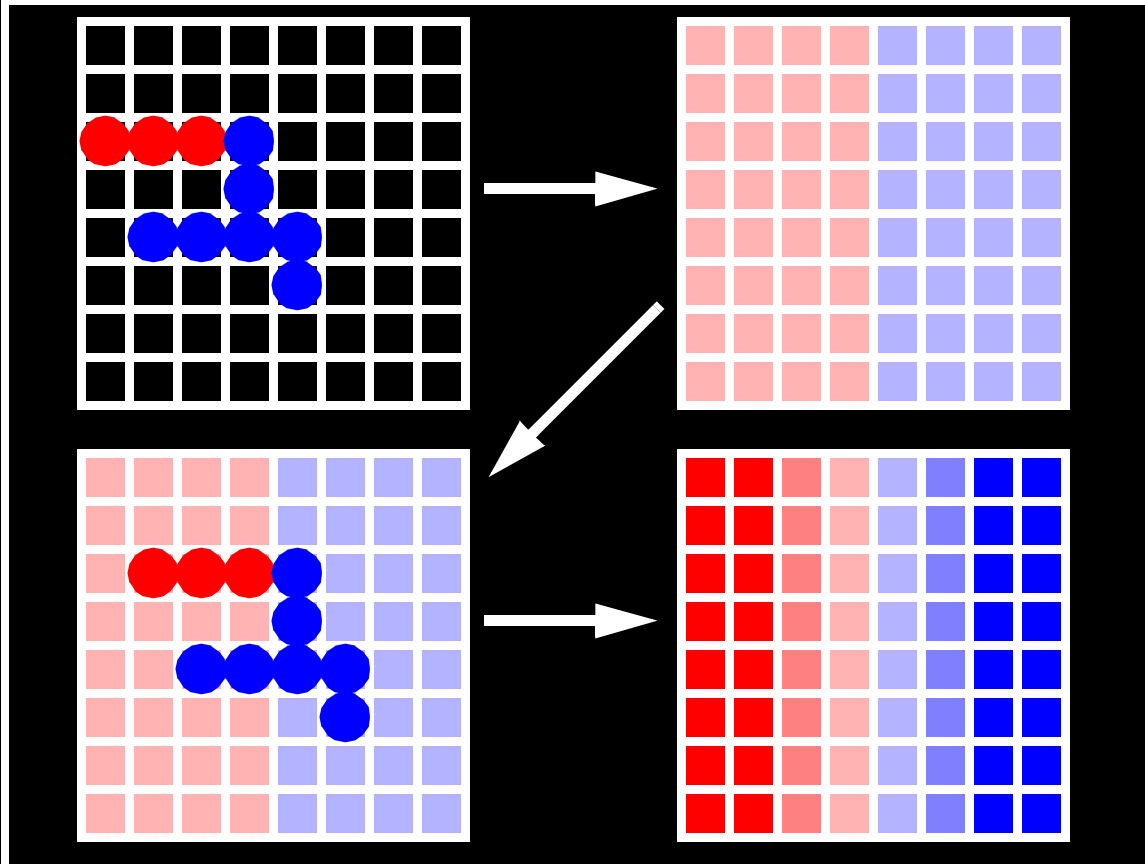


- **Time-dependent “mass”, in a time-dependent potential.**

## ● Clues from numerical work.

Fleer, Cohen, Scheutjens, Cosgrove, Vincent, *Polymers at Interfaces* Chapman and Hall, London 1993

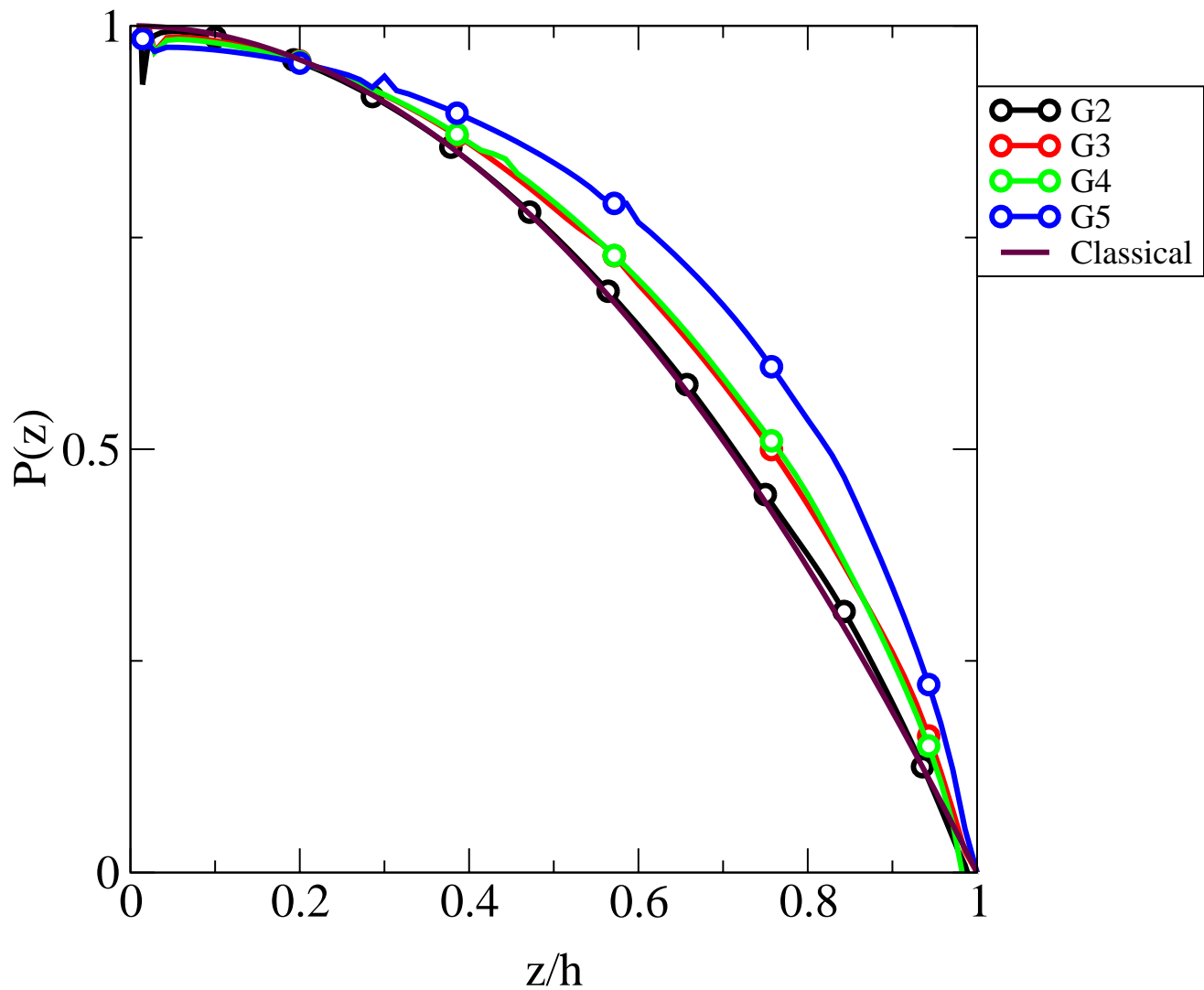
### □ Lattice model



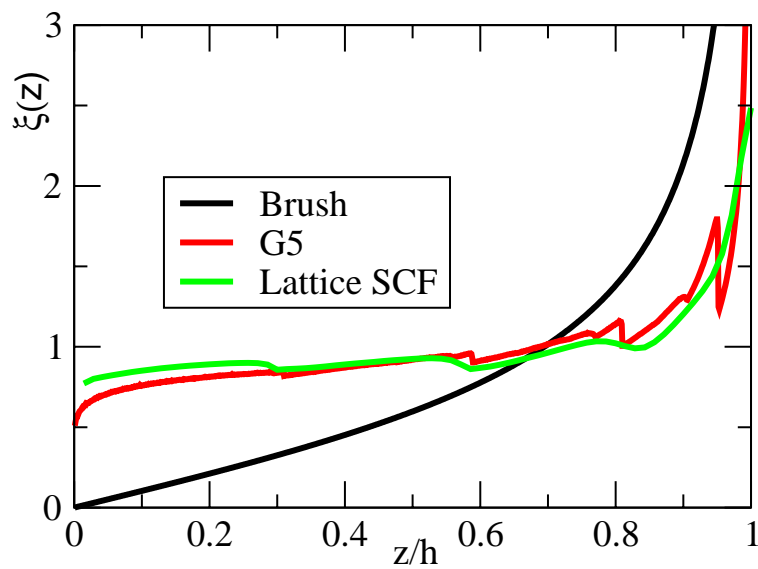
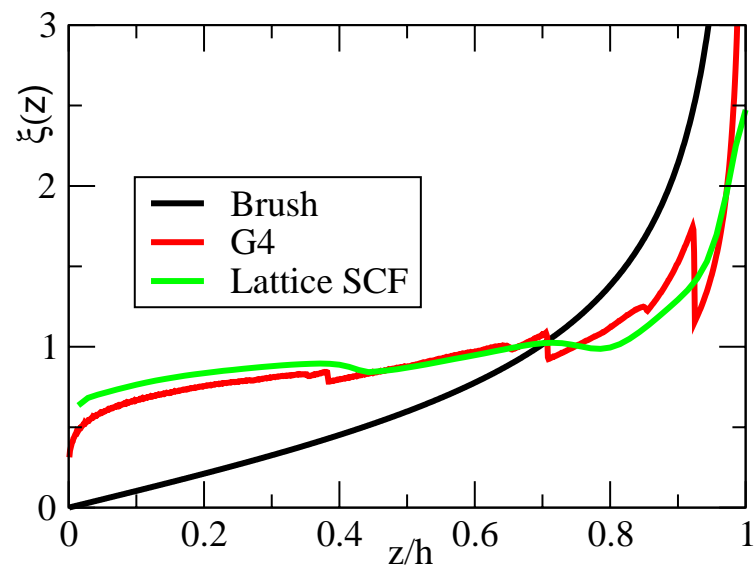
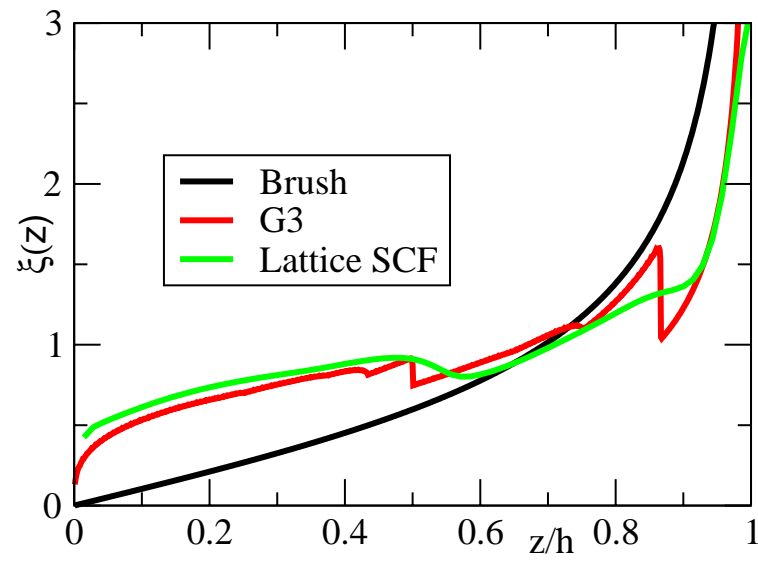
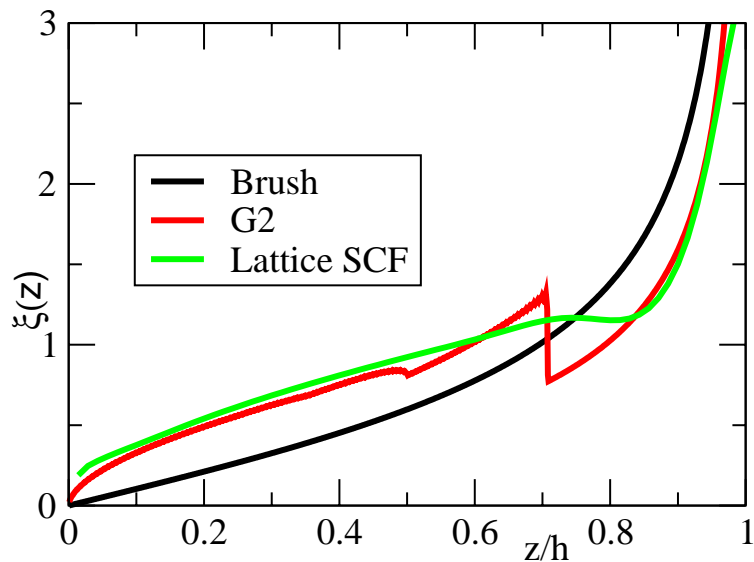
- Start with empty lattice
- Throw down copolymers at random
- Calculate average monomer densities
- Regrow the chains
- Recalculate the monomer densities
- Repeat

### □ What are potentials for G1-5?

● Equal time potential is harmonic (parabolic)

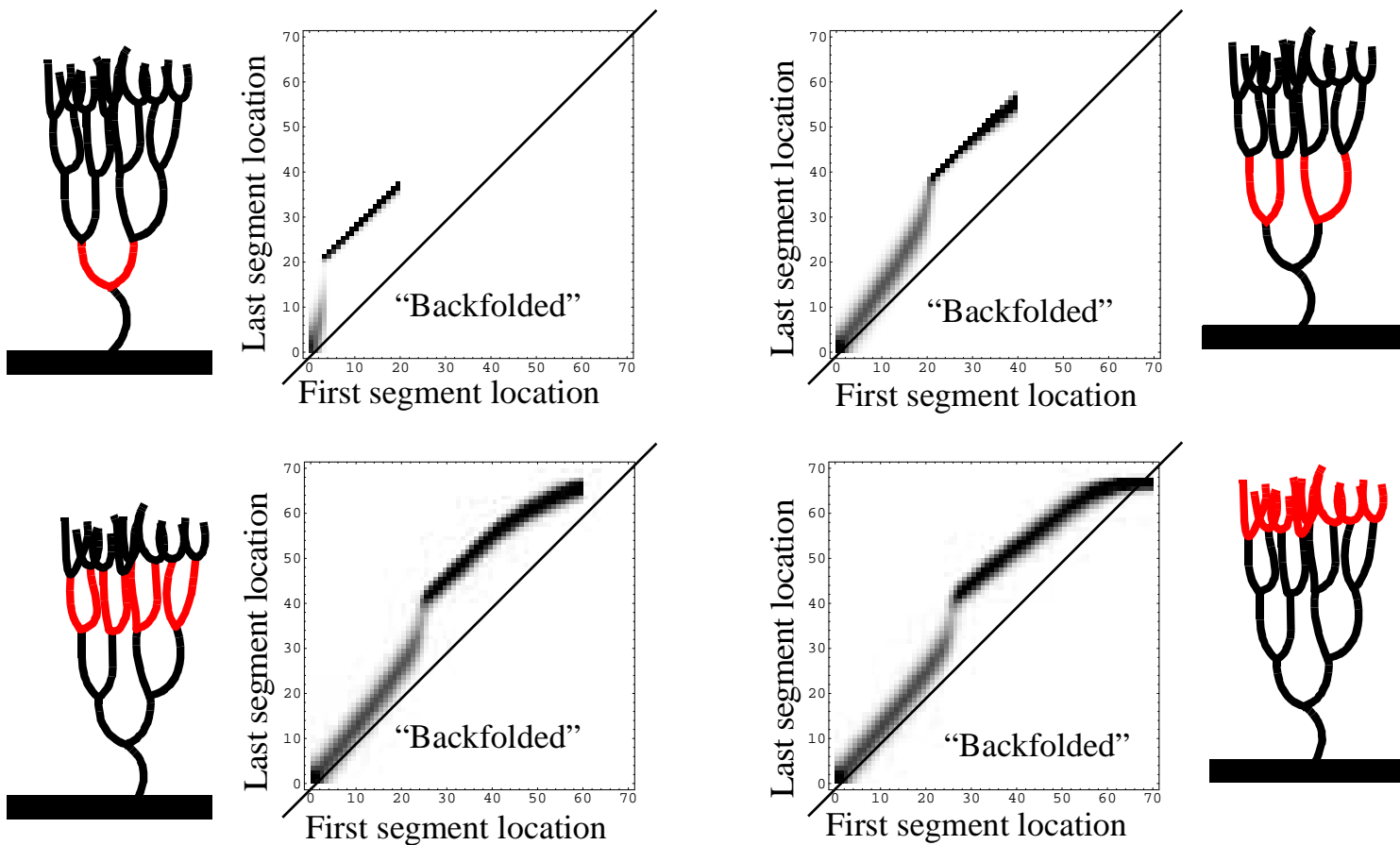


# ● Distribution of chain ends changes



● Do the ends fold back into the brush?

G5 dendrimer

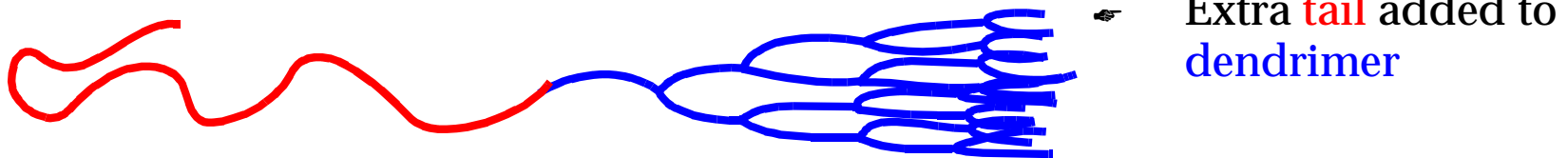


□ Filled core yes, backfolding no

## ● Flexible-dendrimer copolymers

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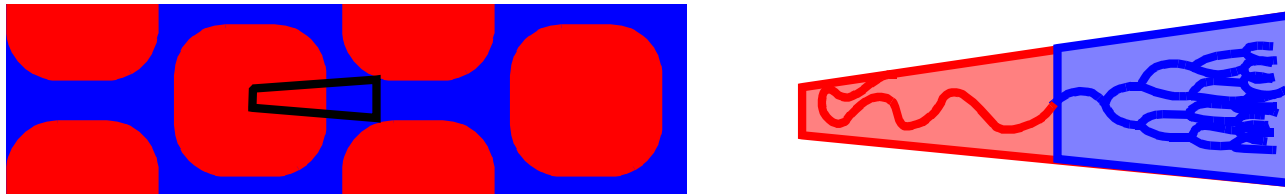
- Easy to synthesize



- Should bias phase diagrams

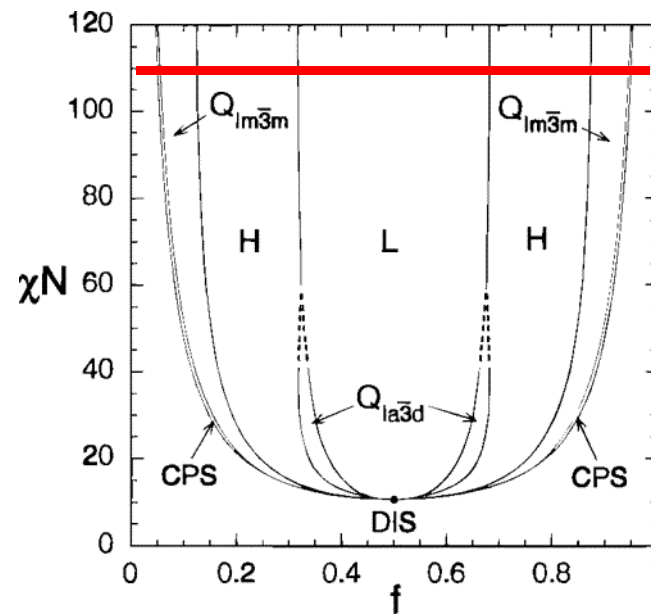
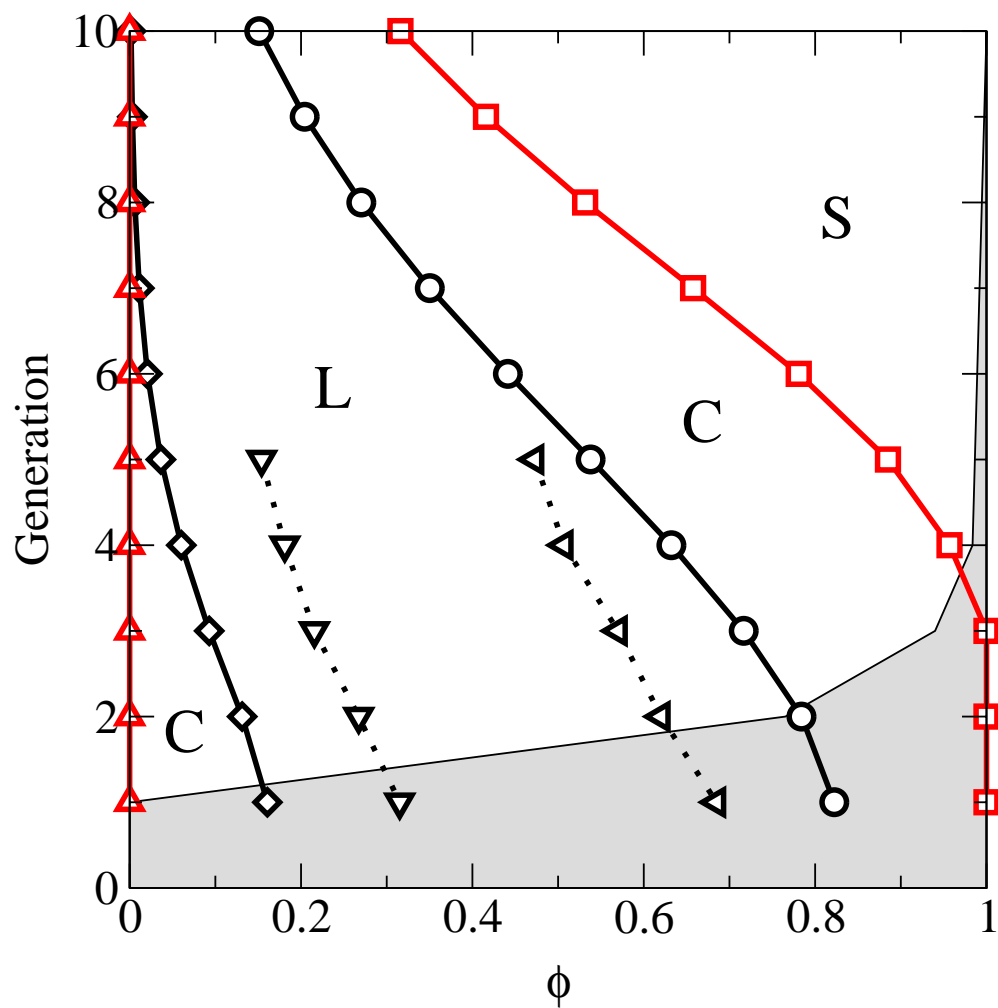
← Extra branchings splay outwards

- Micro segregated domains: 2 stacked brushes



- Branched block resides on convex side of domains

# ● Phase diagram

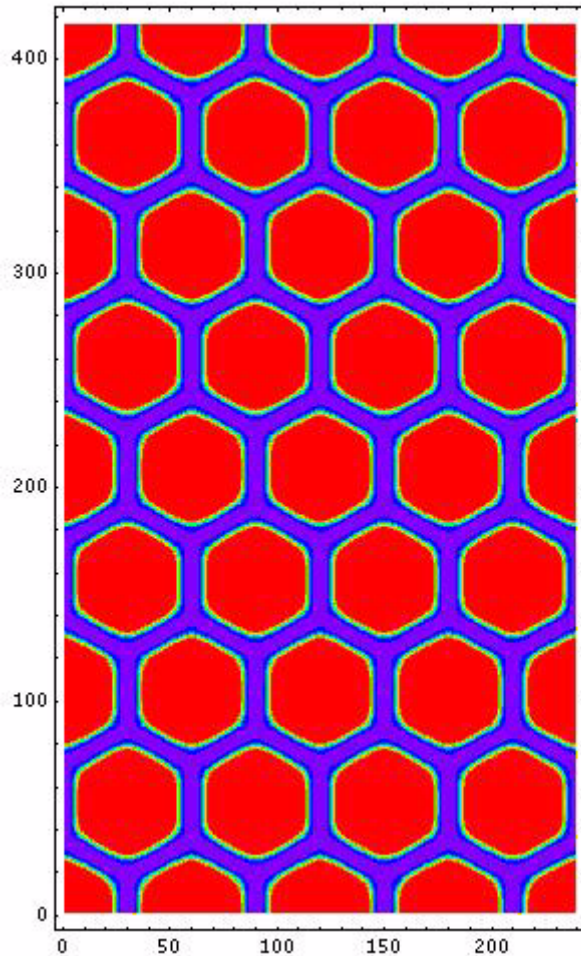


**Asymmetric diagram**

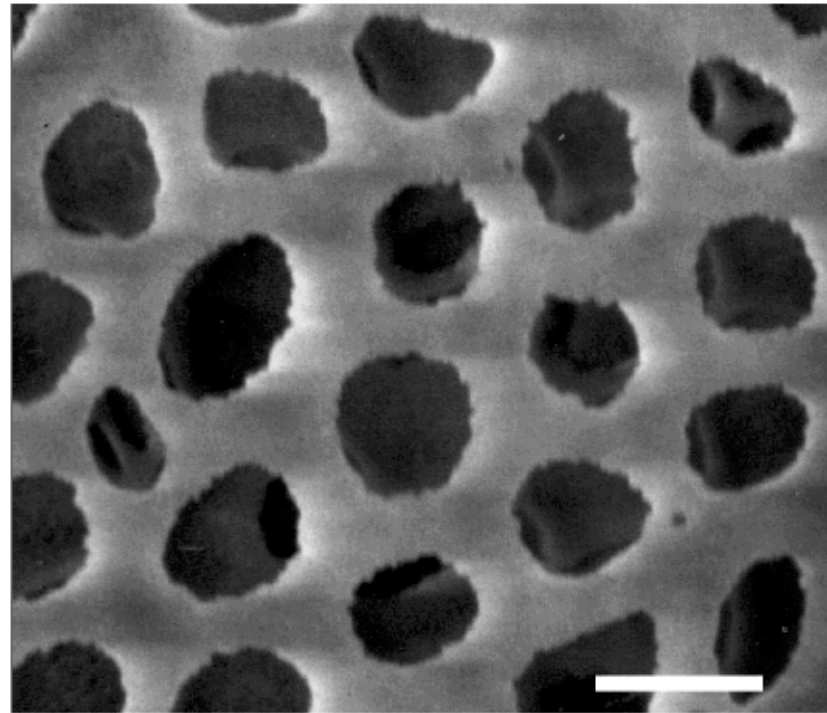


## ● Numerical lattice calculations

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**Dendrimer calculation**



**Ti foam photonic band gap forerunner**

Imhof and D.J. Pine, *Advanced Materials* 10, 697-700 (1998).

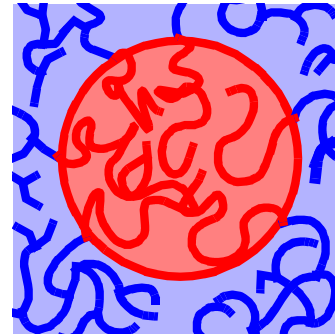
# ● Outline

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## □ Introduction

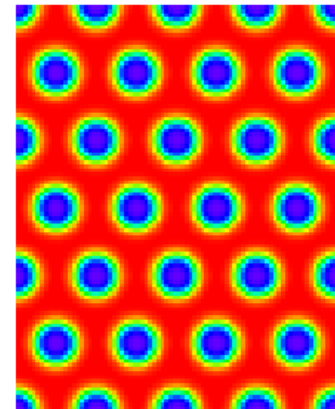
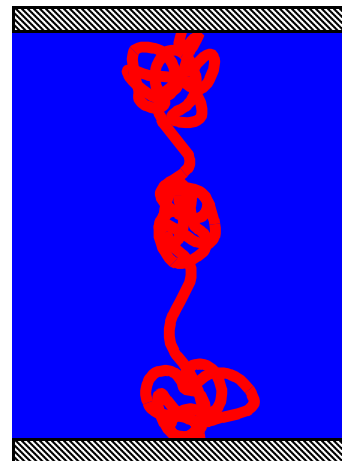
↳ Polymers, block copolymers, architectures

## □ Dendrimer copolymer



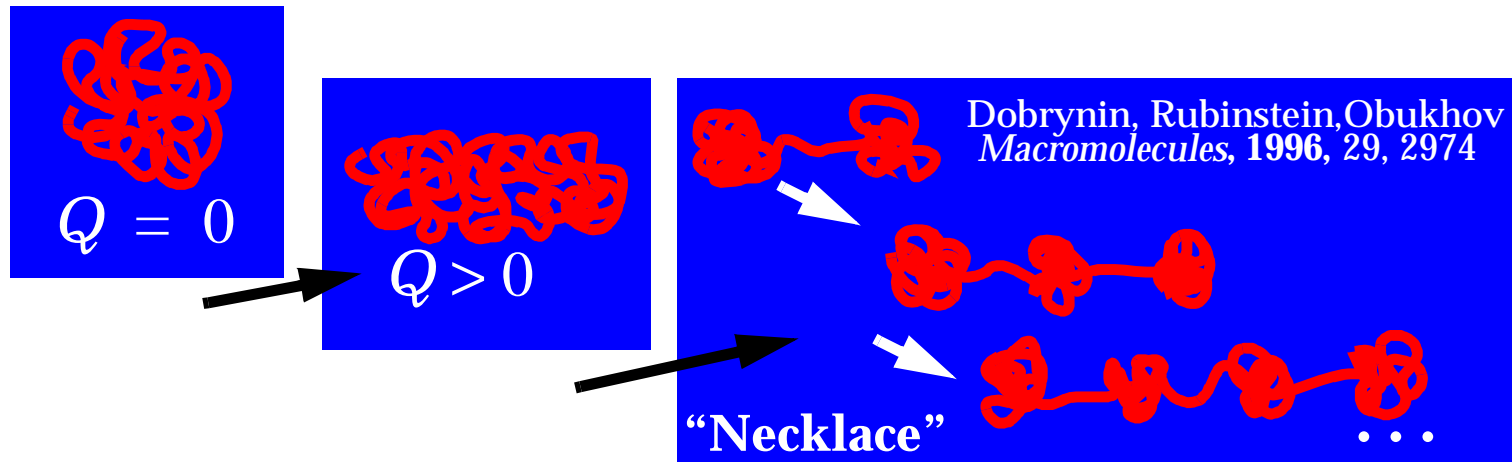
## □ Charged polymers

## □ Conclusions



## ● Polyelectrolyte, poor solvent

- Fixed charge  $Q = \alpha N$  on a flexible polymer,  $N$  monomers.
- Poor solvent:
  - ↳  $Q, N$  control conformation.

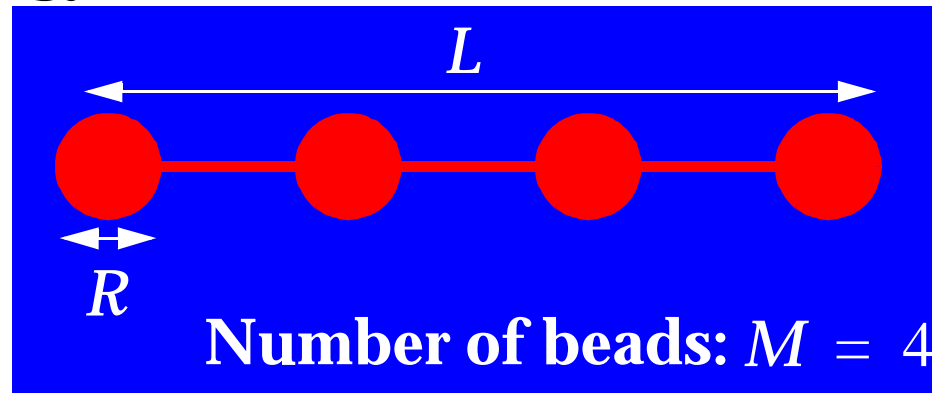


- Cascade of transitions.

- **Cartoon theory**

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- **Free energy of necklace conformation:**



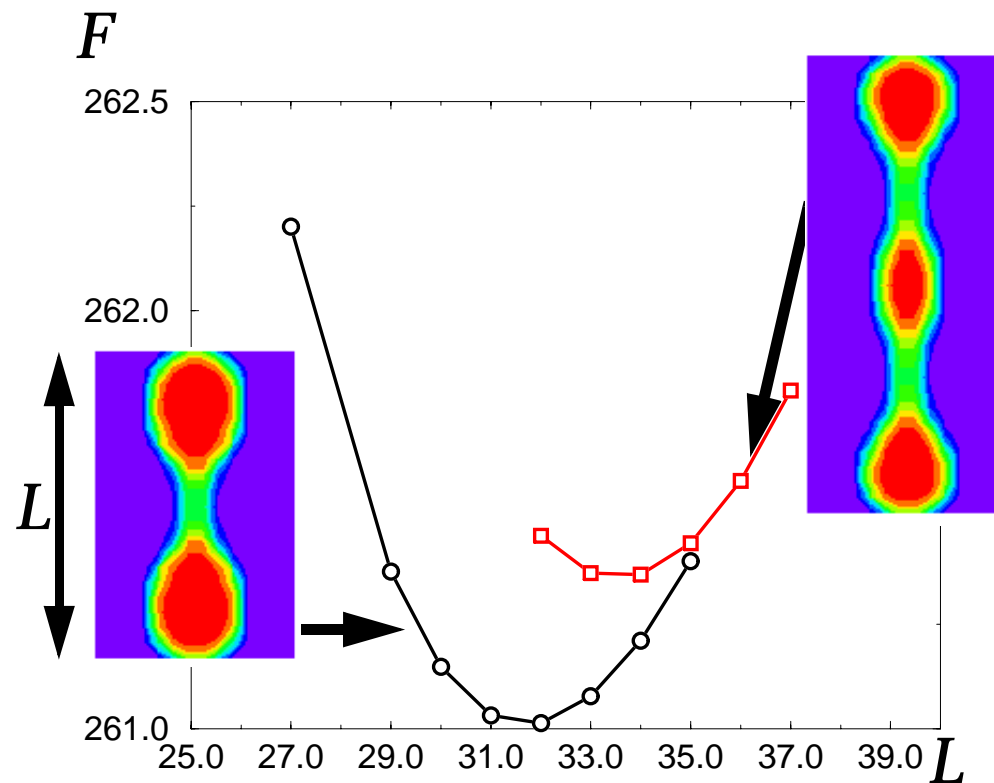
$$F = M \left( \gamma R^2 + \left( \frac{Q}{M} \right)^2 R^{-1} \right) +$$
$$L\gamma + \frac{Q^2}{L}$$

- **Predicts transitions from 1 to 2 to ...**

- **Compare structures:**

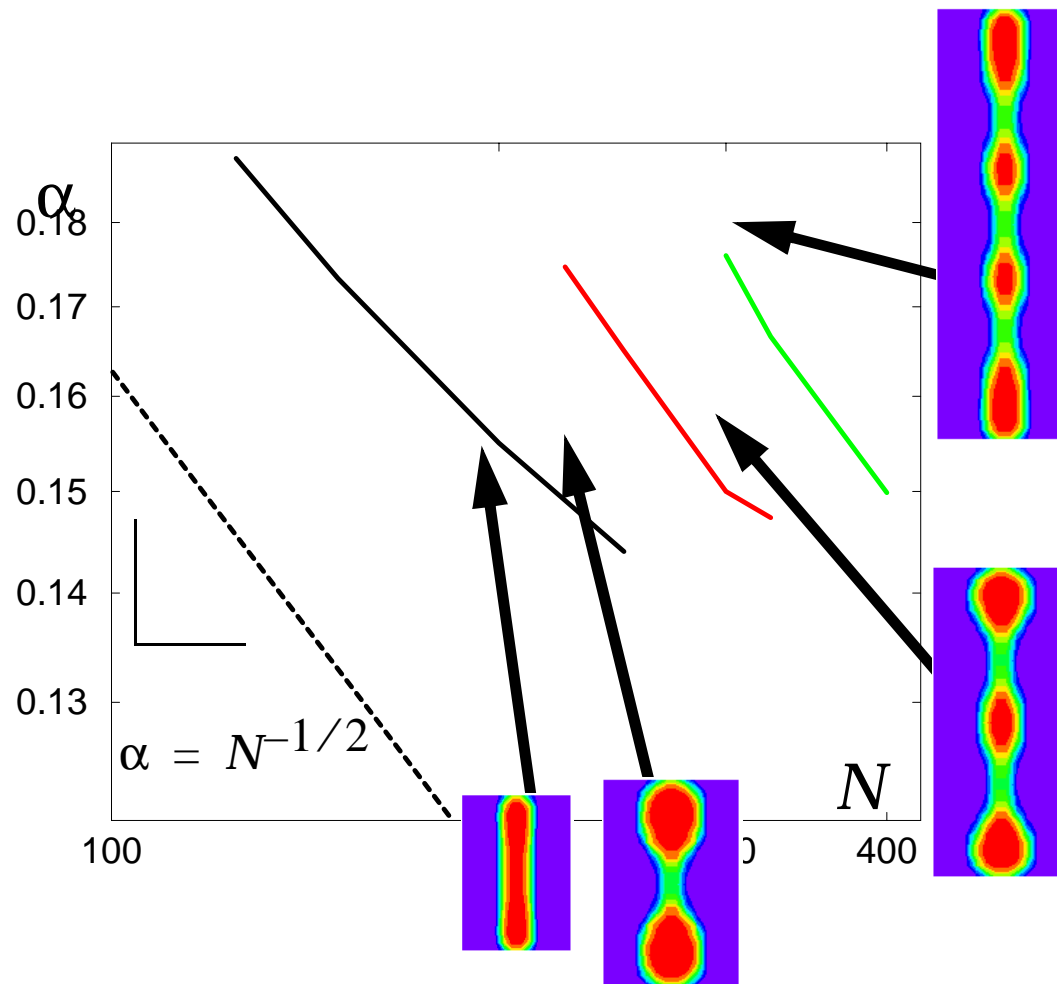
- **At fixed  $N$ ,  $\alpha$  vary  $L$  to find equilibrium structures.**

- ☛  $N = 250, \alpha = 0.16, \chi = 2.0:$



- ☛  $L_{eq}$  minimizes  $F$ . **Possible experiment.**

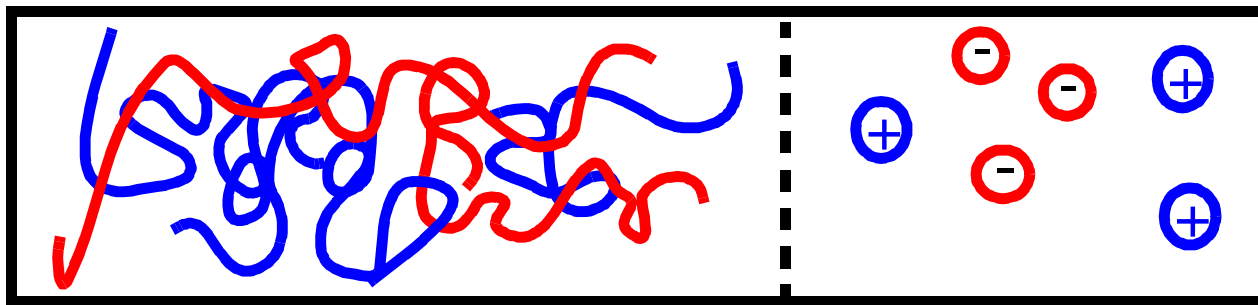
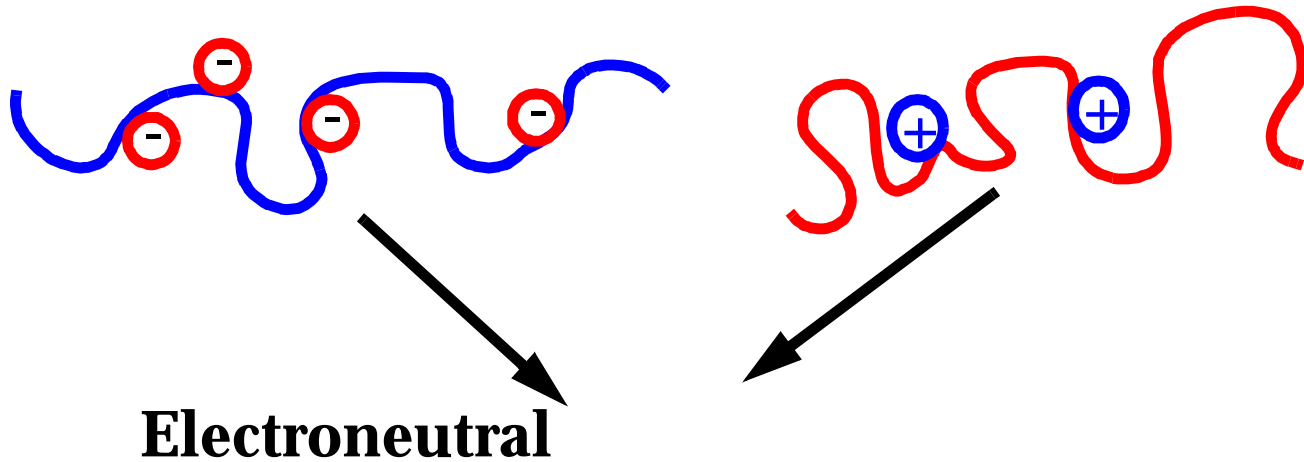
● **Diagram of states:**



□ **“Folded” conformations.**

- **Blend of polyelectrolytes:**

- **Polycation and polyanions mixed together:**



- **Poly-salt melt... what might it do. Phase separate?**

## ● **Blend to consider**

---

- **Let both chains have the same number of monomers (can be relaxed...)**
- **Let the CHARGE/monomer on the majority component be fixed.**
- **Electroneutrality then relates the CHARGE/monomer of minority component to composition:**

$$0 = \alpha_A f + \alpha_B (1 - f)$$

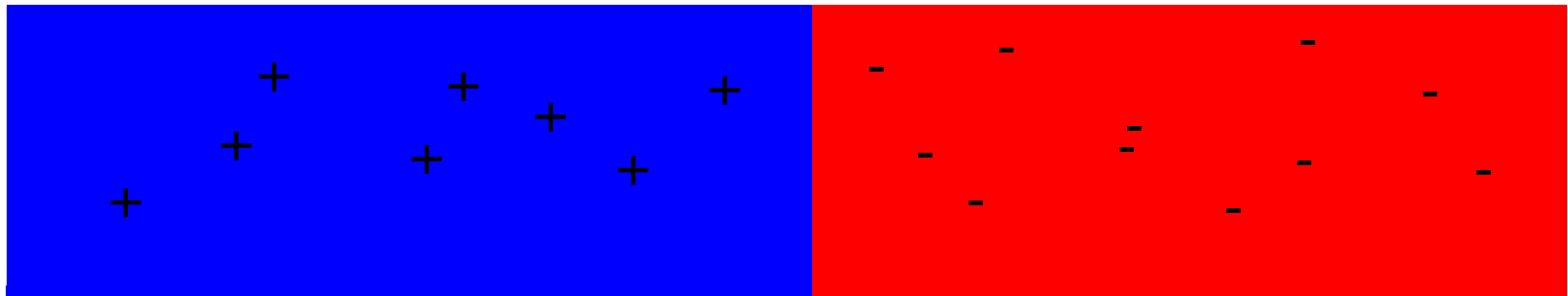
- **Minority chain is more strongly charged than majority chain ... synthetic chemistry.**



- **Can expect a mesophase.**

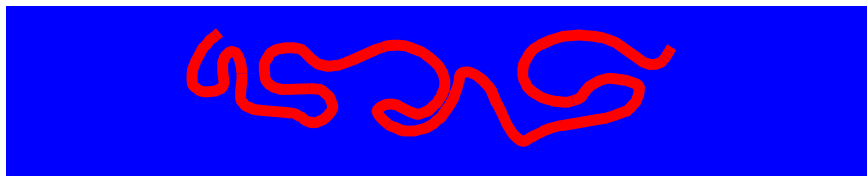
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- **Phase separation: huge electrostatic costs**



**“Collecting like charges”**

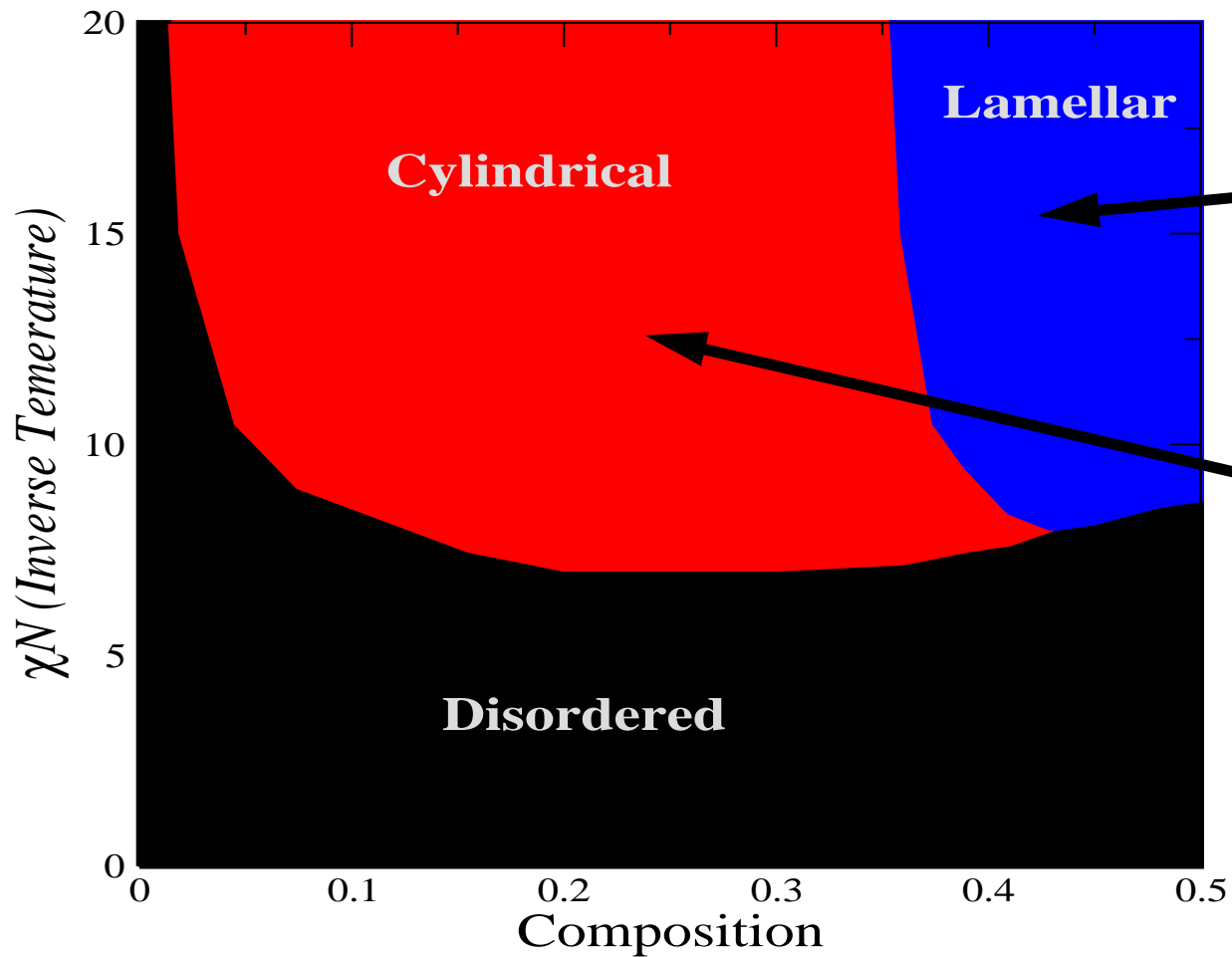
- **Single phase: huge specific interactions**



**N red monomers:  
total cost  $\chi N$**

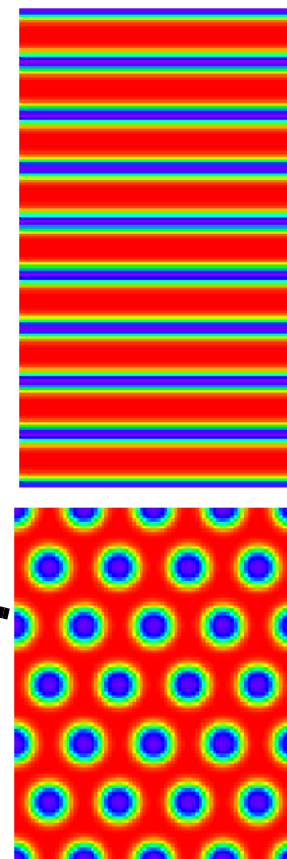
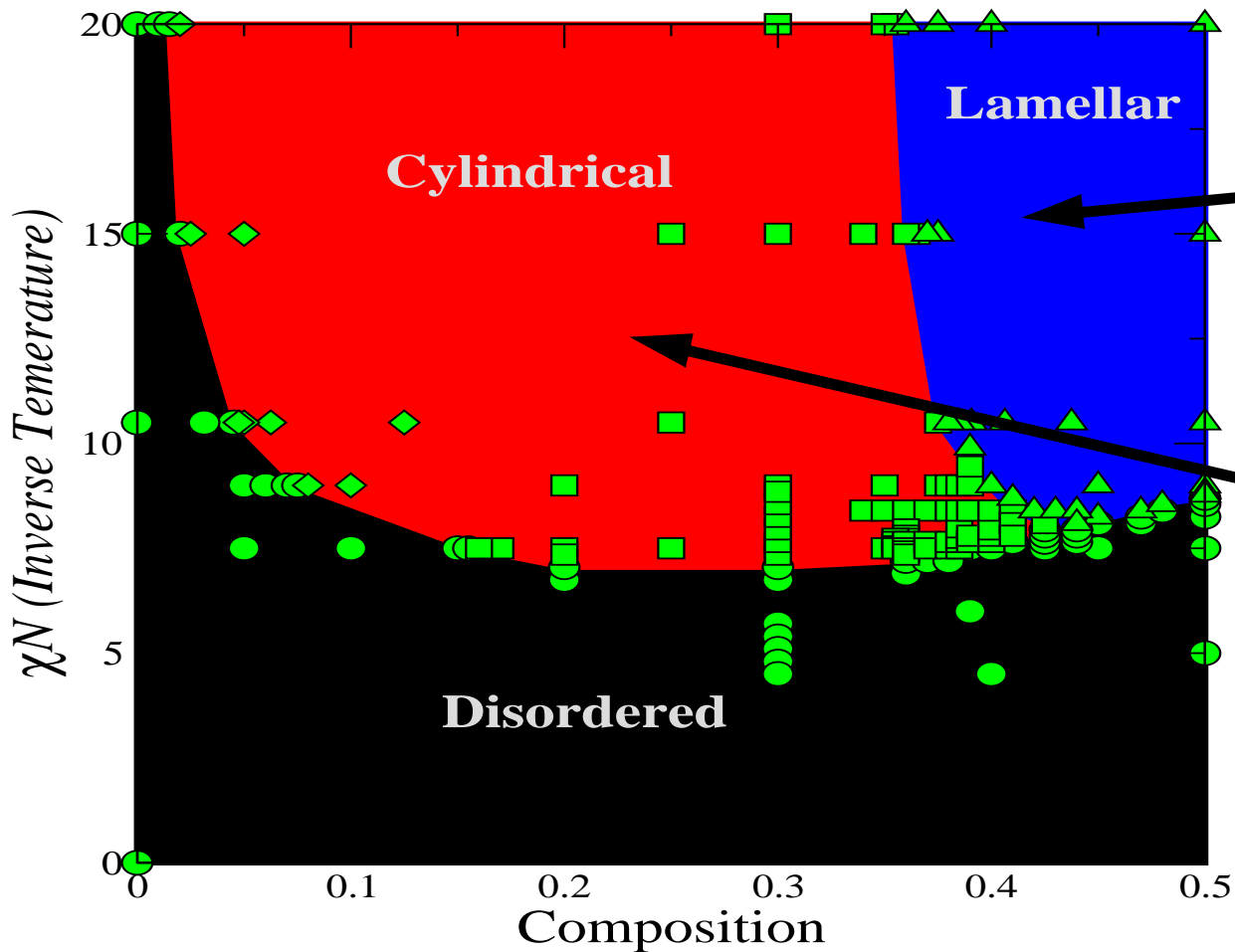
● **Microphases (just like block copolymers)**

Charge/monomer=0.01 N=150

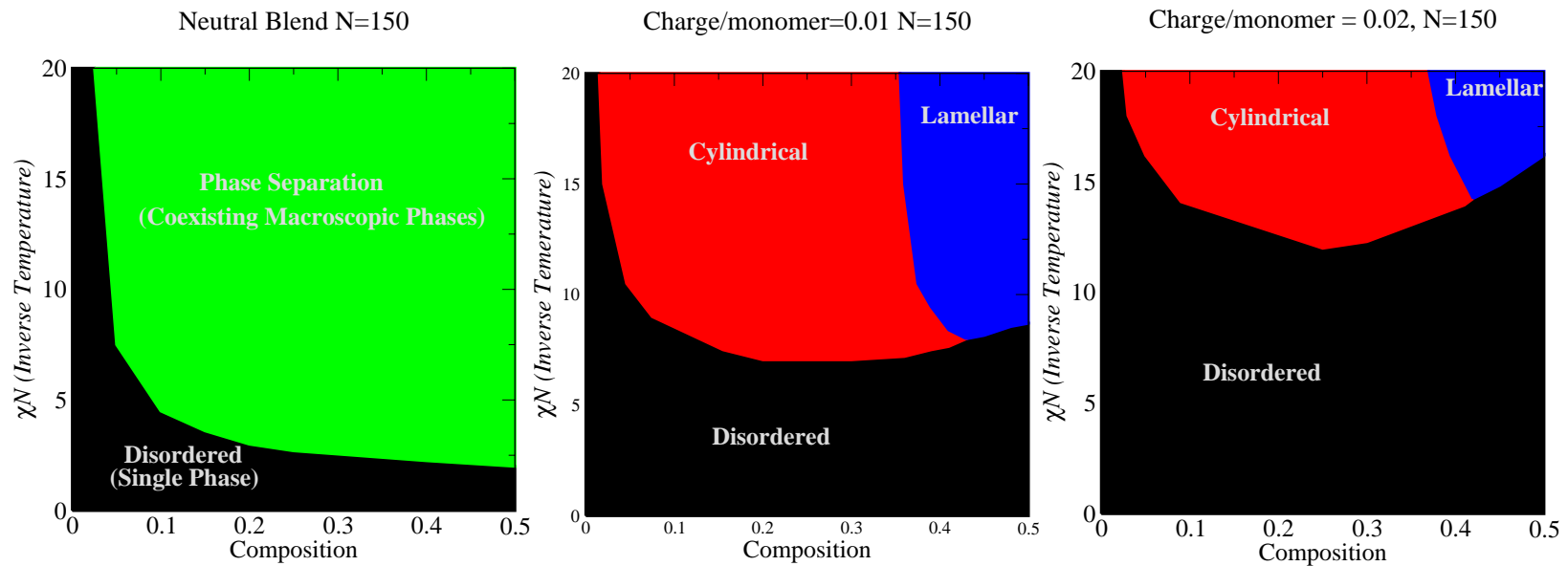


● **Microphases (just like block copolymers)**

Charge/monomer=0.01 N=150



## ● Charge compatibilizes the blend



Increasing charge  $\longrightarrow$

- Simple architectures (just homopolymers) but complex patterns.
- Long-range vs. short-range

## ● **Conclusions**

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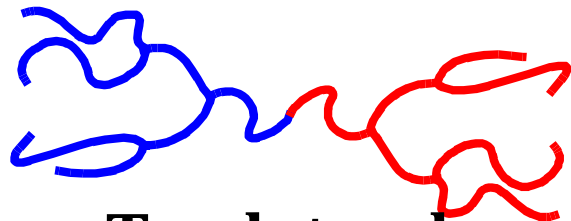
### □ **Dendrimer copolymers**

- ↳ Shift phase boundaries, ends get buried
- ↳ Photonics?

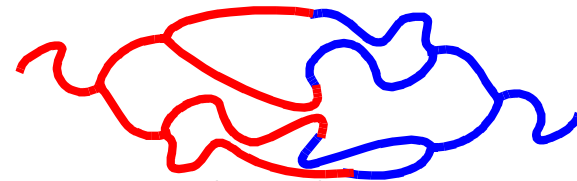
### □ **Charged Blends**

- ↳ Same kinds of patterns, big length scales.
- ↳ External fields for control of pattern.

### □ **Other dendrimer-dendrimer block copolymers**



**Trunk-trunk**



**Tip-tip**