Hyperbranched Molecules: Surfaces and Self-assembly

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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...
- ... strung together into huge chains...
- ... which mostly ignore $h$...

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

- ... 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

\[ f = \text{fraction of A on molecule, controls symmetry:} \]

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

Schematic, G3 "core-shell" copolymer
Outline

- Introduction
  - Polymers, block copolymers, architectures
- Dendrimer brush
- Dendrimer copolymers
- Conclusions
Lots of polymers jammed together

\[ F = \text{conformation} + \text{insertion} \]

- **Stretching** (conformation) energy depends on just the red chain
- **Insertion** energy depends on what the neighboring chains are doing
- **Insertion** energy must be found consistent with what all the other chains are doing
- Self-consistent polymer brush
  - Anchored polymers

To insert red polymer:

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

Stretching Insertion

- Insertion, ok but why is stretching quadratic?
Stretching energy is quadratic

- Random walk, N steps covering an end-end distance L. How much energy?

- Apply a force F to each link.
  \[ \text{force} \propto L \quad \text{force} \propto \frac{1}{N} \]
  Double F, go twice as far \quad More steps, less force

- Work = force * distance: \( \left( \frac{L}{N} \right) L = \left( \frac{L}{N} \right)^2 N \)

- Generalization for non-uniform stretching
● Single-chain self-consistent field

- Lots of polymers jammed together

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

- **Stretching** is exact for the red test chain.

- **Insertion** energy averaged over conformations of all other chains

- **Insertion** energy must be found consistent with what all the other chains are doing
Classical mechanics

- Single-chain free energy
  \[ F[z(n)] = \frac{1}{2} \int_0^N \left( \left| \frac{dz}{dn} \right|^2 + P(z(n)) \right) dn \]

- Time, \( t \), is equivalent to "monomer number", \( n \)

- Minimize \( F \), extremize \( S \)

- Potential \( V(z) \) must have an "equal-time" property.

- If particle is released from rest, at a time \( T \) it will arrive at \( z=0 \), regardless of where it started.
• Only one “equal-time” potential will do

- Harmonic Oscillator

\[ z(t) = z_0 \cos \omega t \]

\[ z(n) = z_0 \cos \omega n \]

\[ V(z) = \frac{1}{2} \omega^2 z^2 \]

\[ P(z) = \text{const.} - \frac{1}{2} \omega^2 z^2 \]

- Strong constraint from self-consistency
What has to change for branched grafts?

- 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:

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

Generations

Number of equivalent branches

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

\[ G = 5 \]

\[ f = 16 \]

\[ f = 8 \]

\[ f = 4 \]

\[ f = 2 \]

\[ f = 1 \]
Lattice model

1. Start with empty lattice
2. Throw down copolymers at random
3. Calculate average monomer densities
4. Regrow the chains
5. Recalculate the monomer densities
6. Repeat

No “ground state” assumption!

What are potentials for G1-5?
Equal time potential is still harmonic
Trajectory depends on $G$

- Mass gets cut in half
- Momentum conserved
- Velocity doubles!
- Stretching doubles!
- Distribution of chain ends changes
Do the ends fold back into the brush?

- Filled core yes, backfolding no
Alexander de Gennes Model

Gross overestimation of stretching:

- Alexander, most branched part of chain is most stretched
- End-distributed, least branched part of chain is most stretched

End-confining radically alters brush layer.
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  - Dendrimer copolymers

Conclusions
- Flexible-dendrimer copolymers
  - 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
Agrees qualitatively with an Alexander model calculation:
Frischknecht and Fredrickson,
Macromolecules 1999 32 6831
Numerical lattice calculations

Ti foam photonic band gap forerunner

Conclusions

- Surfaces coated with dendrimers
  - Ends are buried, distributed
  - Don’t fold back, (poplars, not willows)
- Dendrimer copolymers
- Shift phase boundaries
- Photonics?
- Dendrimer-dendrimer block copolymers
  - Tip-tip
  - Trunk-trunk