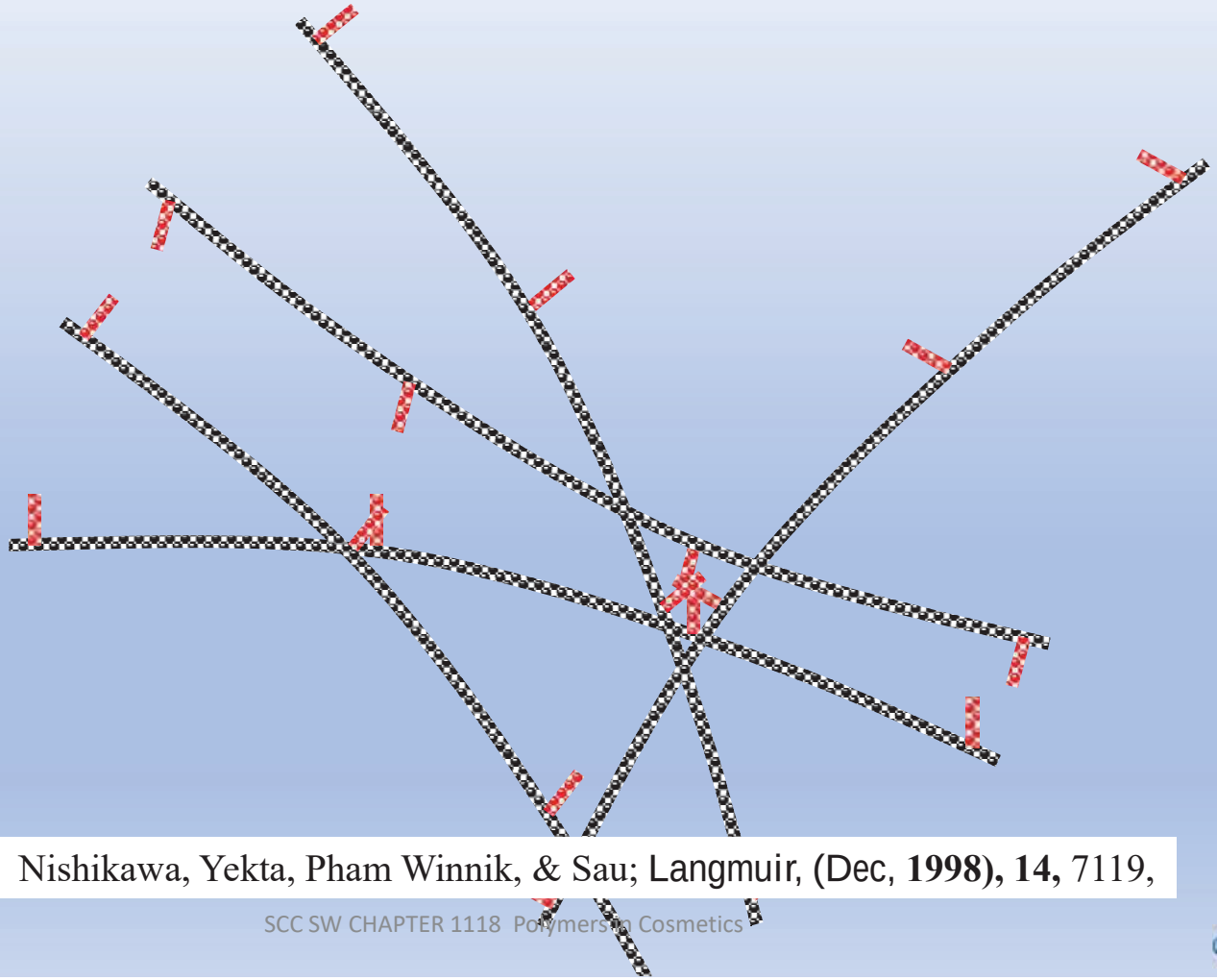
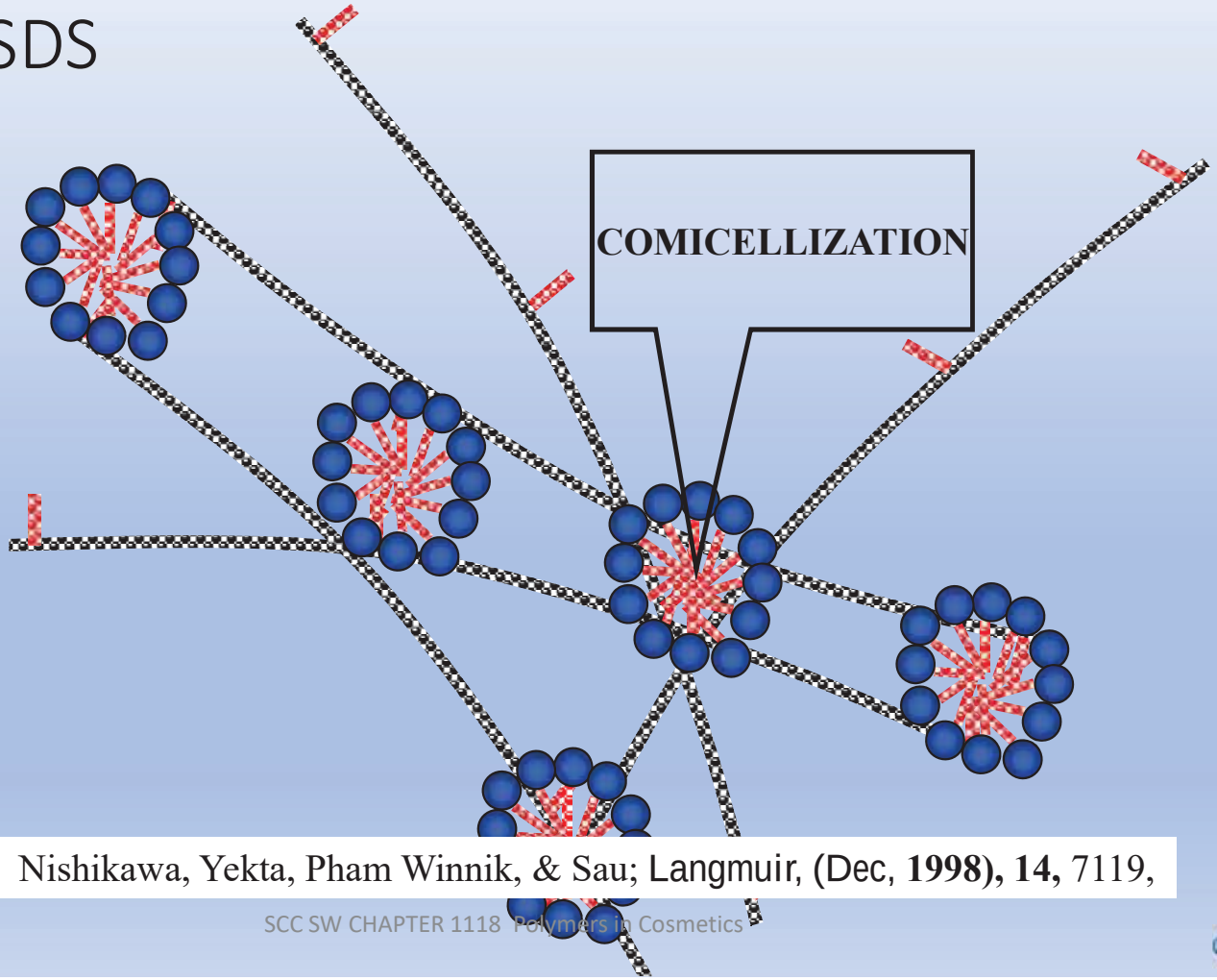
HYDROPHOBICALLY MODIFIED HYDROXYETHYL CELLULOSE



Nishikawa, Yekta, Pham Winnik, & Sau; Langmuir, (Dec, **1998), 14,** 7119,

HMHEC
EFFECT OF SDS



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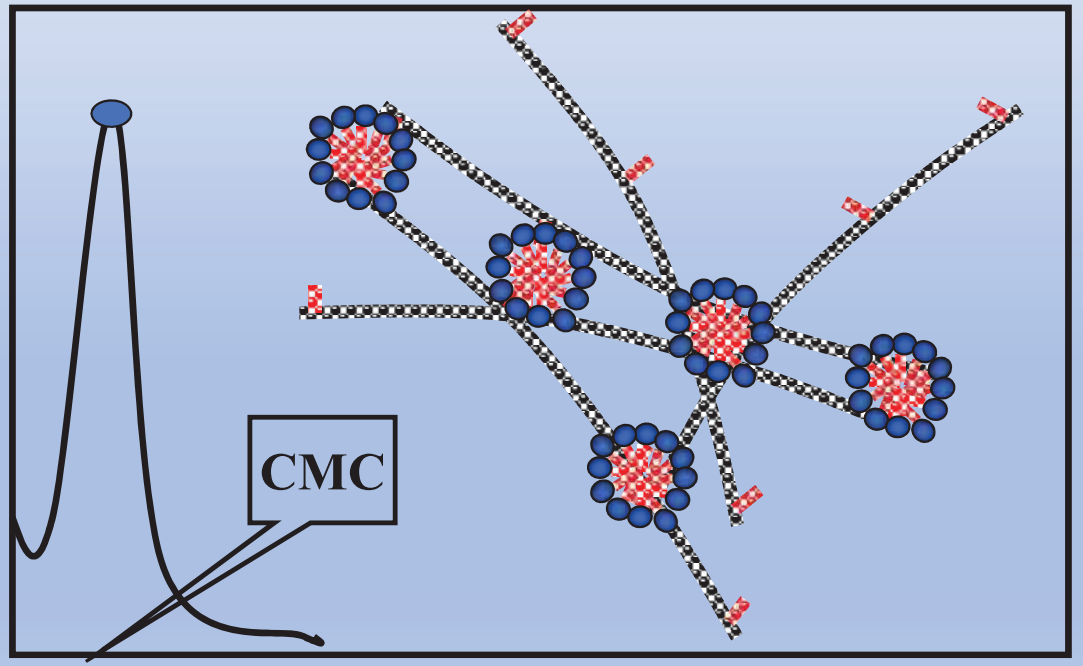

Landoll & Sau; ACS Adv. Chem Ser, 213; (1986) 343

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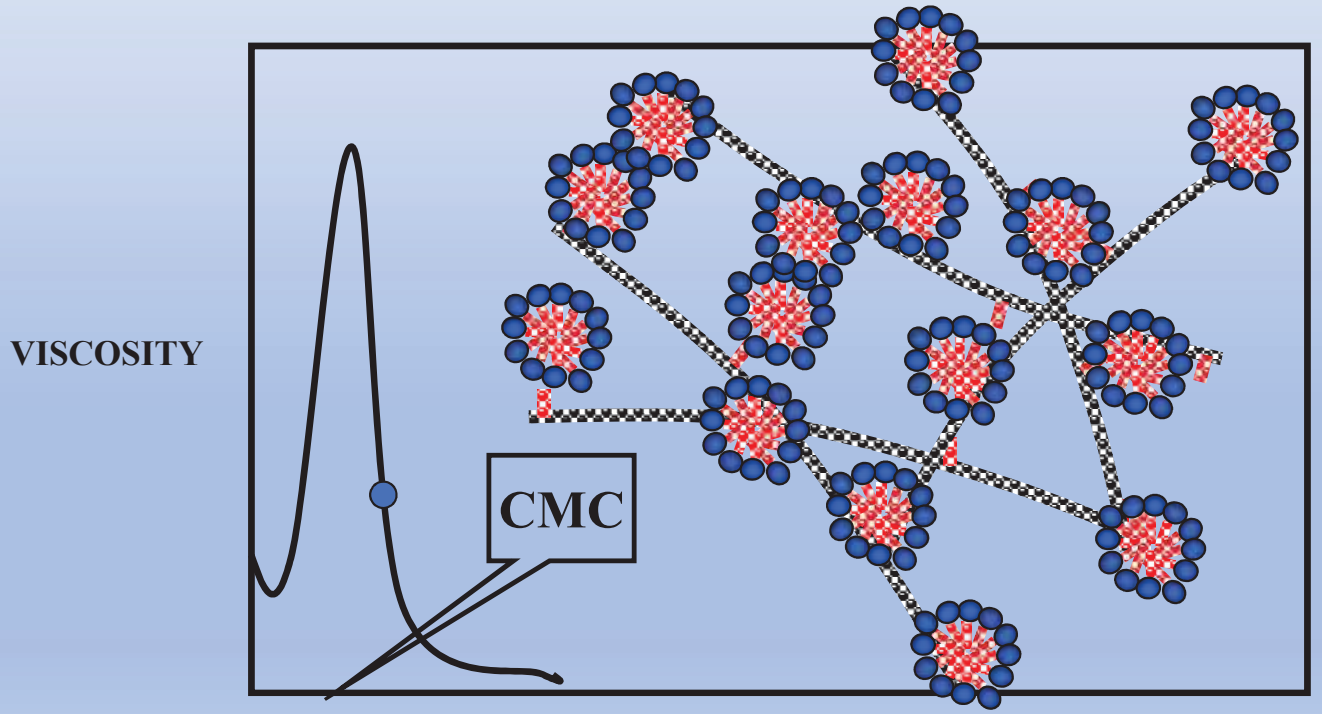

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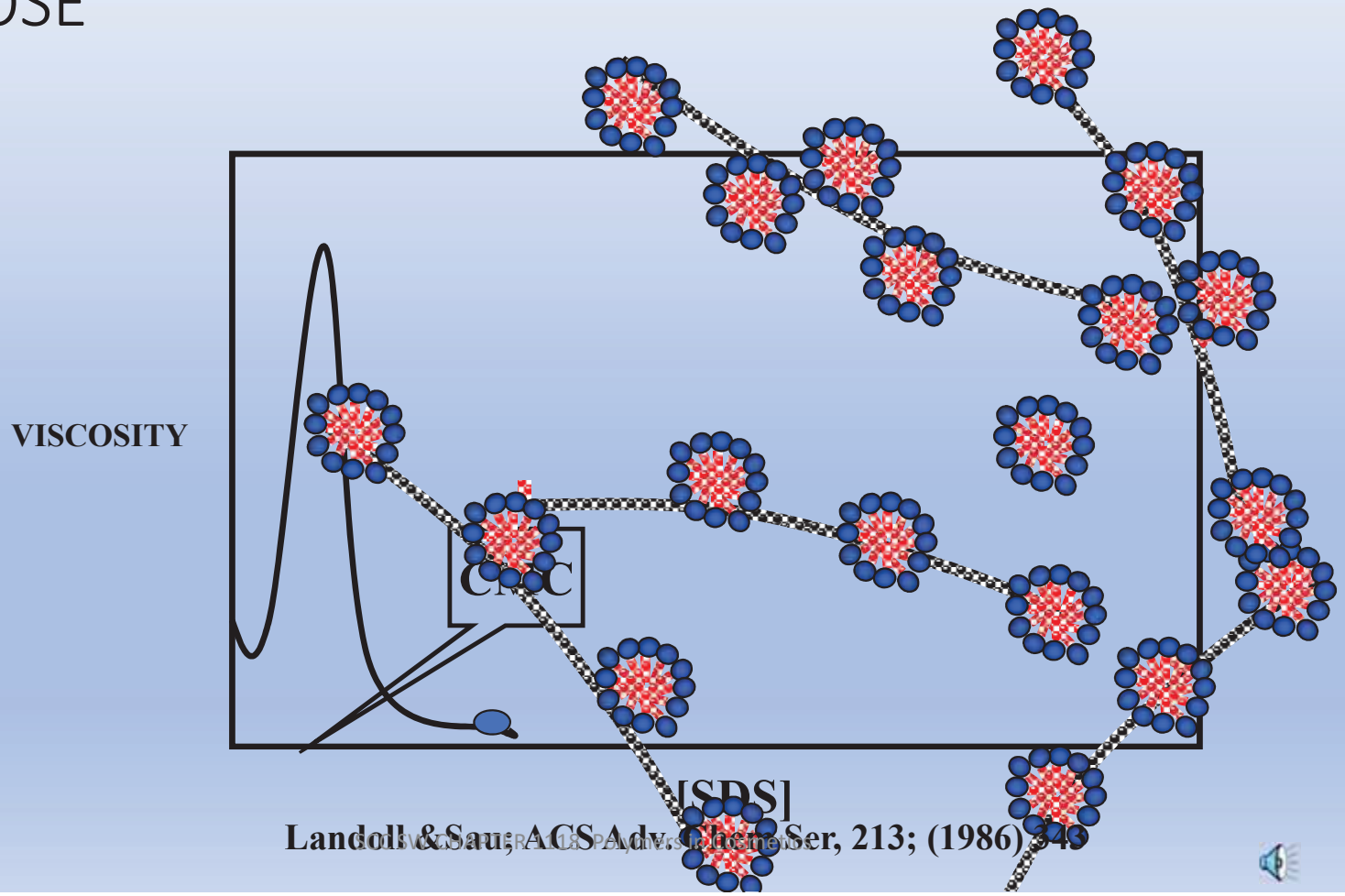

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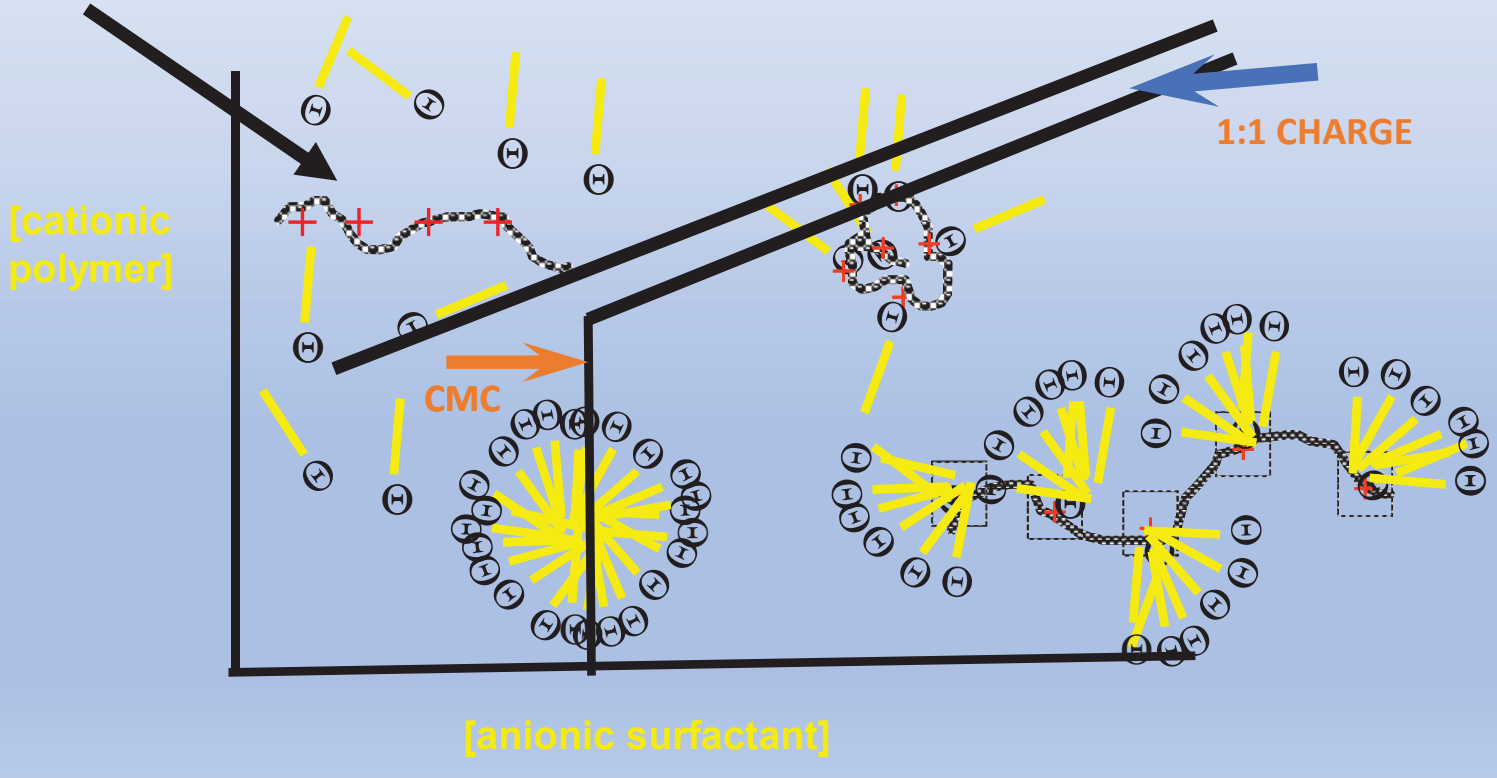
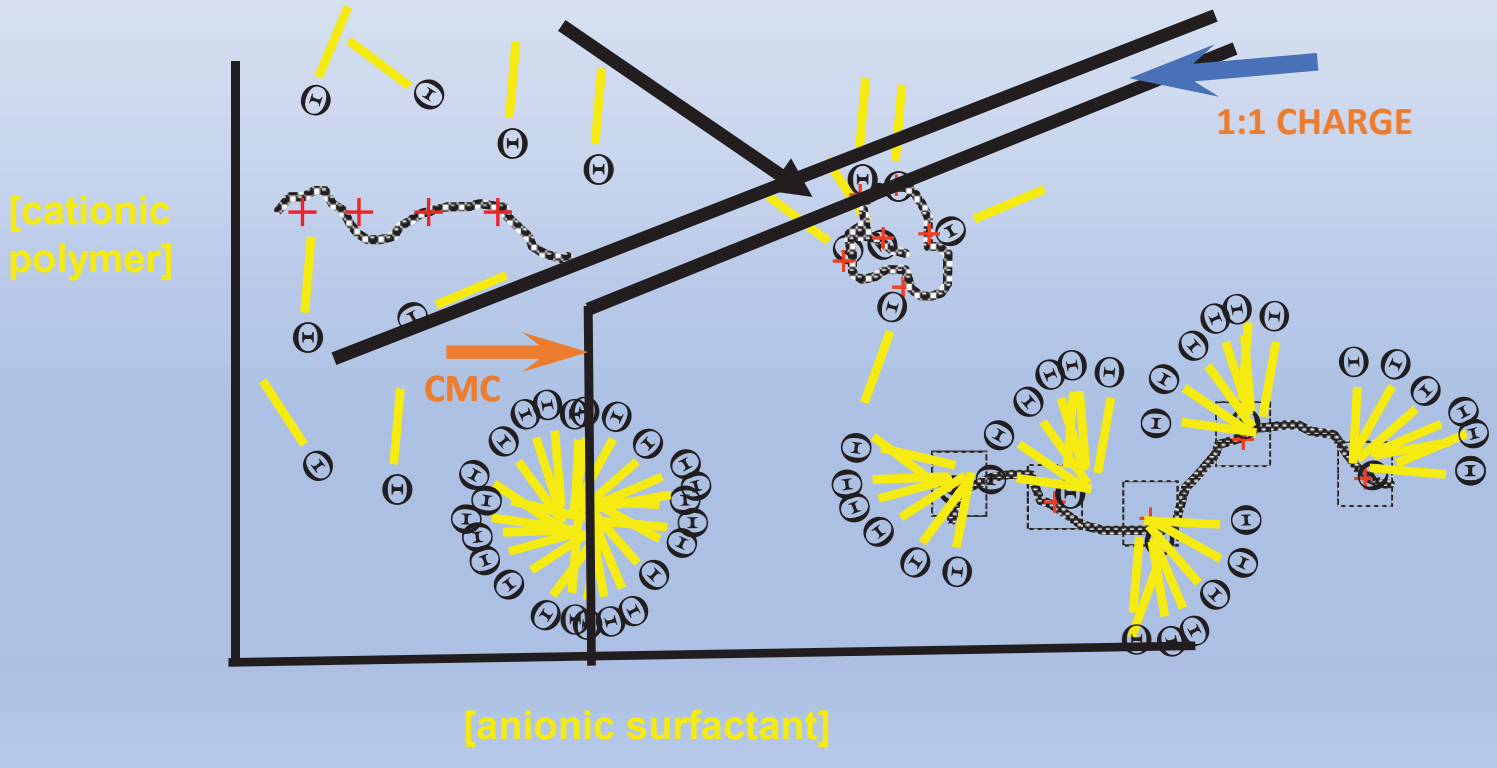
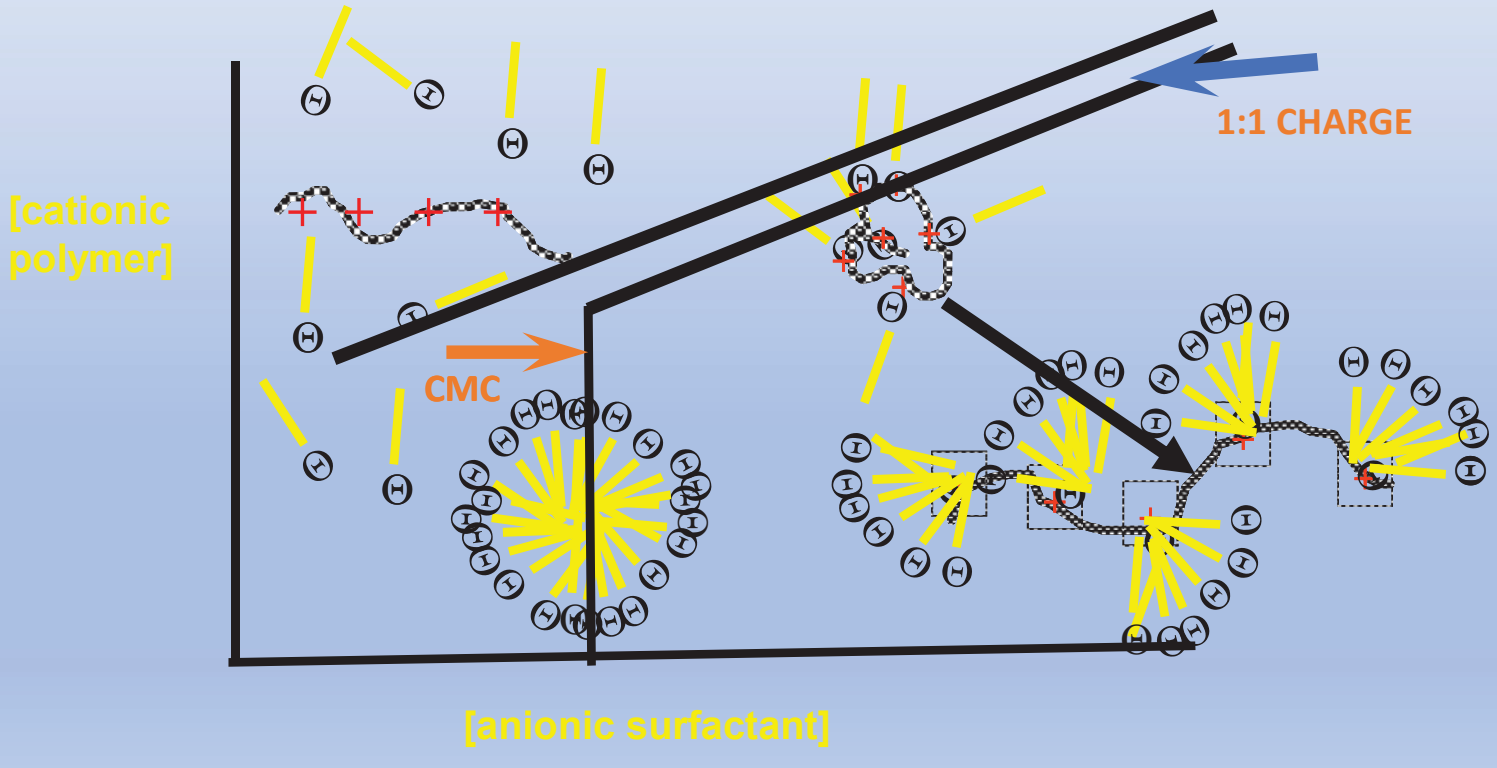
Polymer-Surfactant Interaction



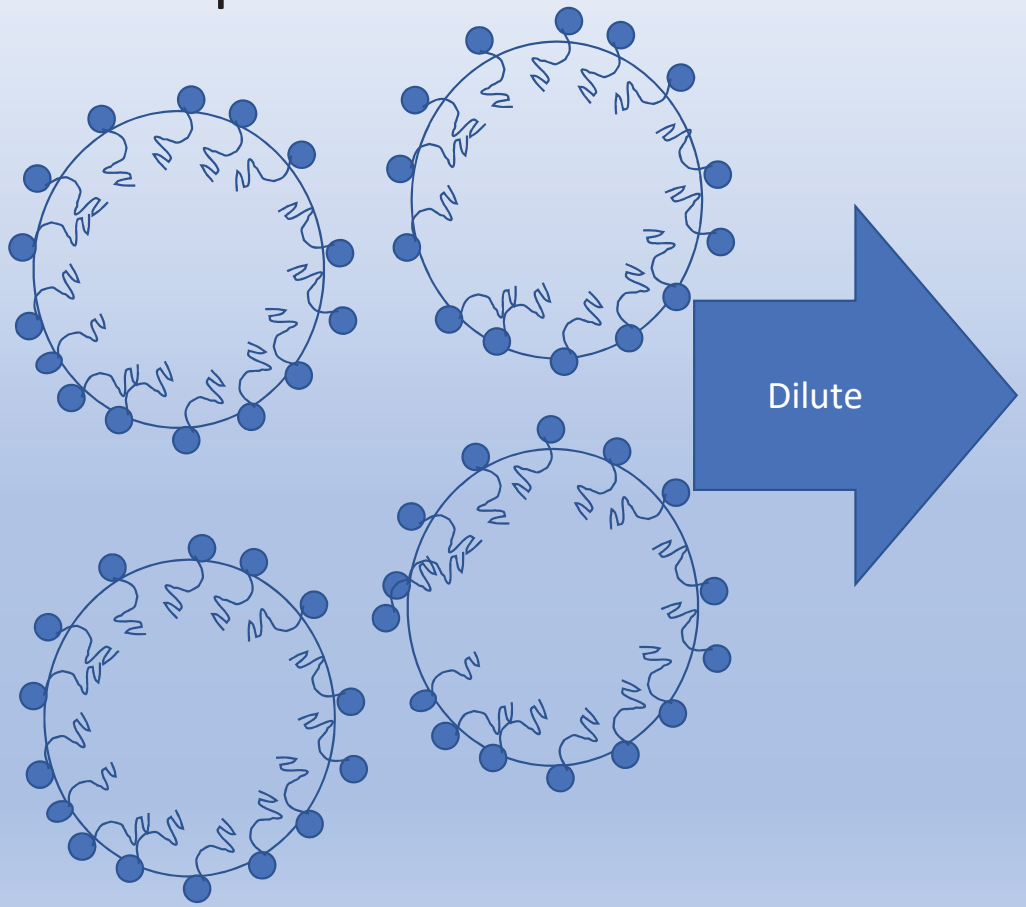
Polymer-Surfactant Interaction



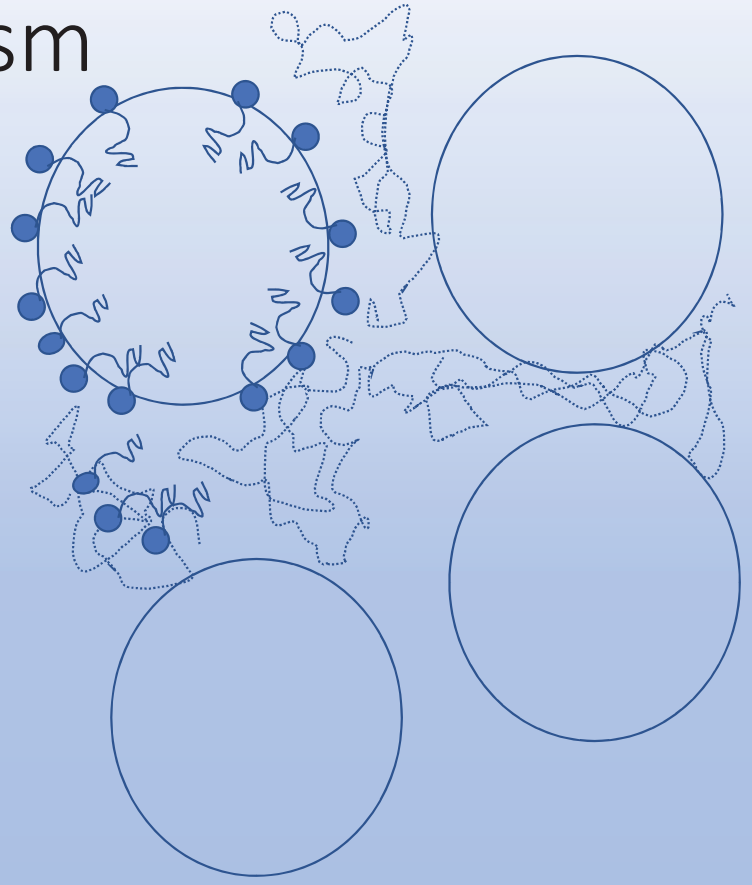
Polymer-Surfactant Interaction



Proposed Mechanism



Proposed Mechanism



Coacervate Forms
Surfactant desorbed from foam interface

Fixatives and Films

Cosmetic Polymers

Desired Attributes of Hair Fixatives

- Hairstyle hold improvement
- Ease of application on wet hair
- Easy combing
- No sticky feel
- Quick drying
- Not powdery when groomed
- Ensures hair body and bounce
- Increased hair volume
- Hairs do not clump
- Non-hygroscopic film
- Better hair gloss
- No excessive stiffness

C. Zviak, ‘ The Science of Hair Care’

The Challenges

- Hairstyle hold improvement
  - This must be achieved with a minimal amount of fixative resin conveniently applied
    - Aerosol spray
    - Pump spray
    - Gel
    - Mousse

The Challenges

- Ease of application on wet hair
  - The solvent medium must be compatible with water
  - Also it must be generally recognized as safe
    - Ocular
    - Inhalation

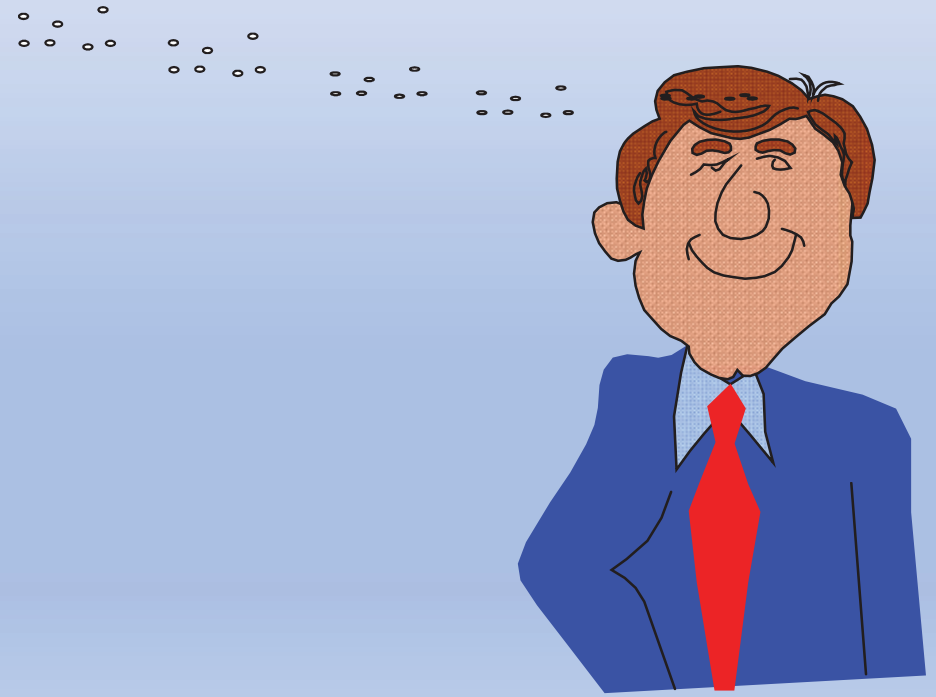
The Challenges

- Easy combing
  - The cohesive strength of the polymer film must be less than the tensile strength and shear strength of the hair
  - The adhesive bond of the film to the hair must be weaker than the shear strength of the hair

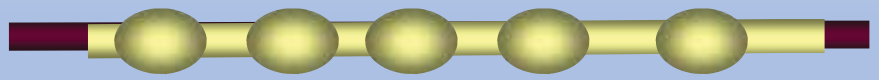
Hairspray Components

- Fixative Polymer
- Solvent
- Propellants
- Adjuvants
- Valve System

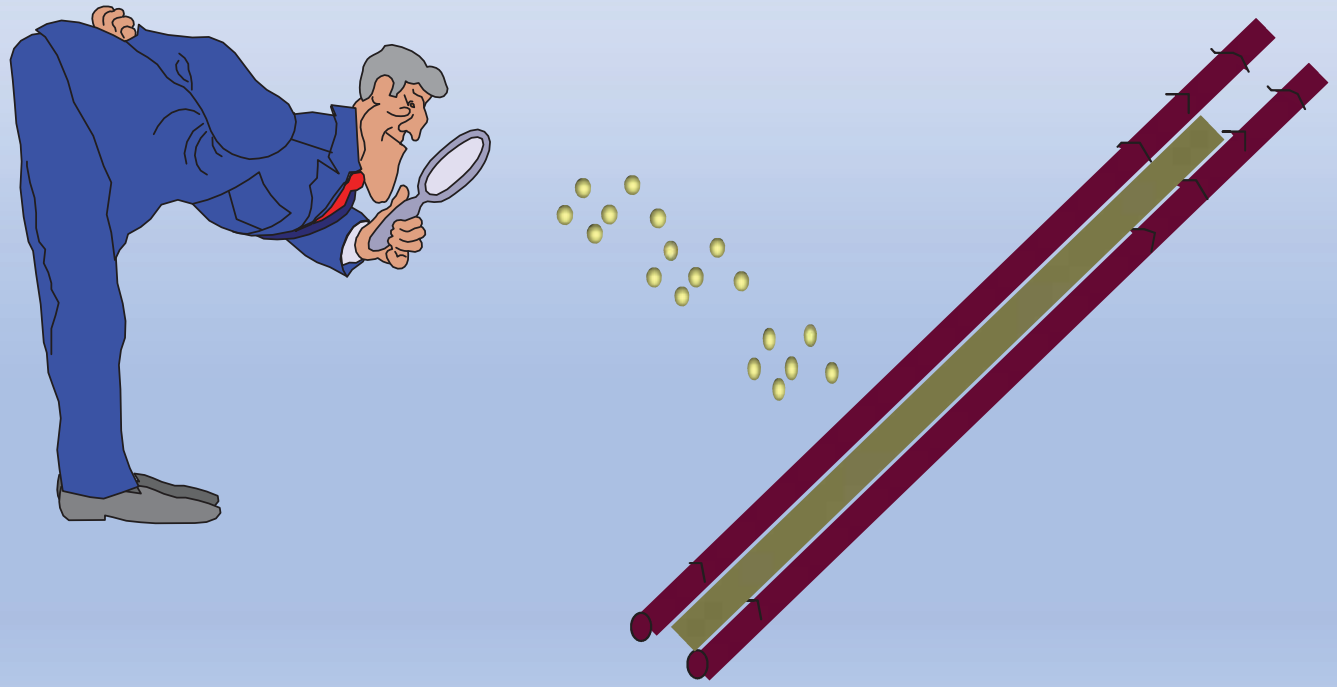
Hairspray Mechanism



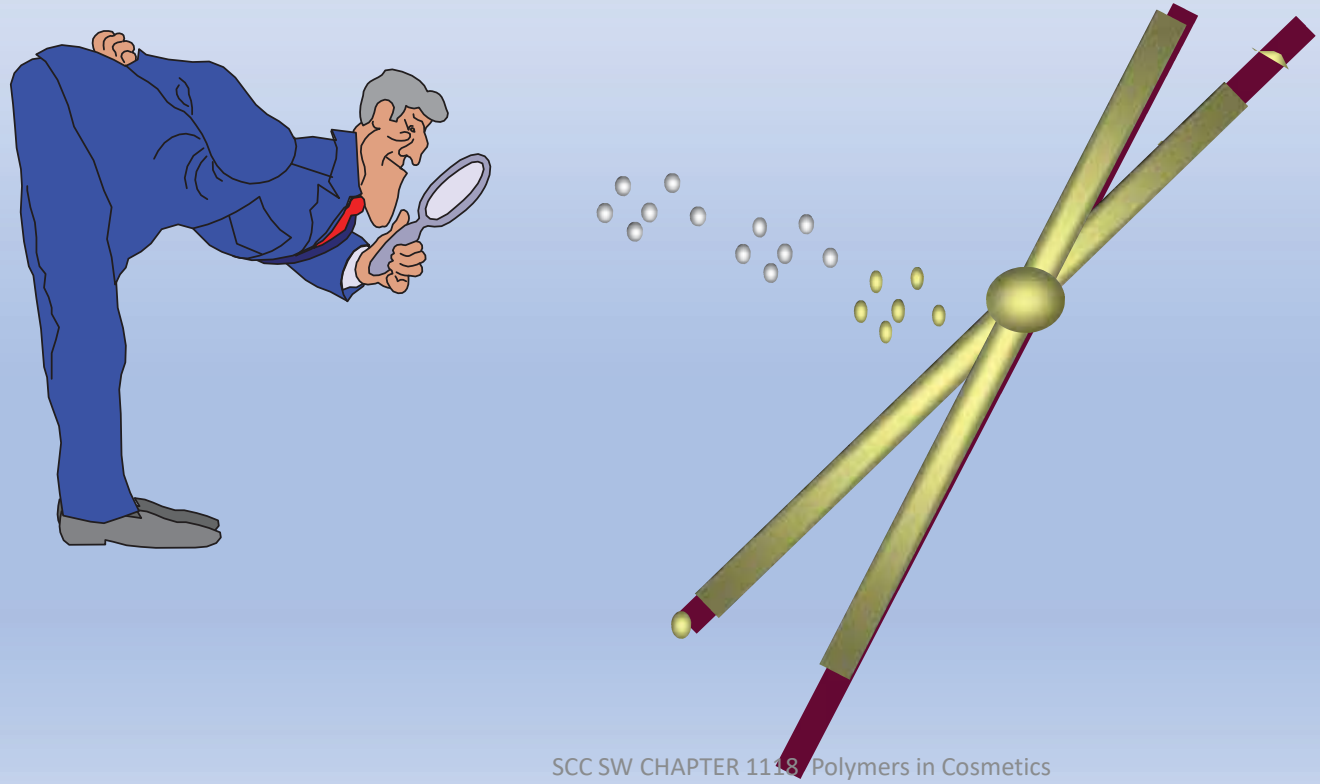
Rayleigh Instability



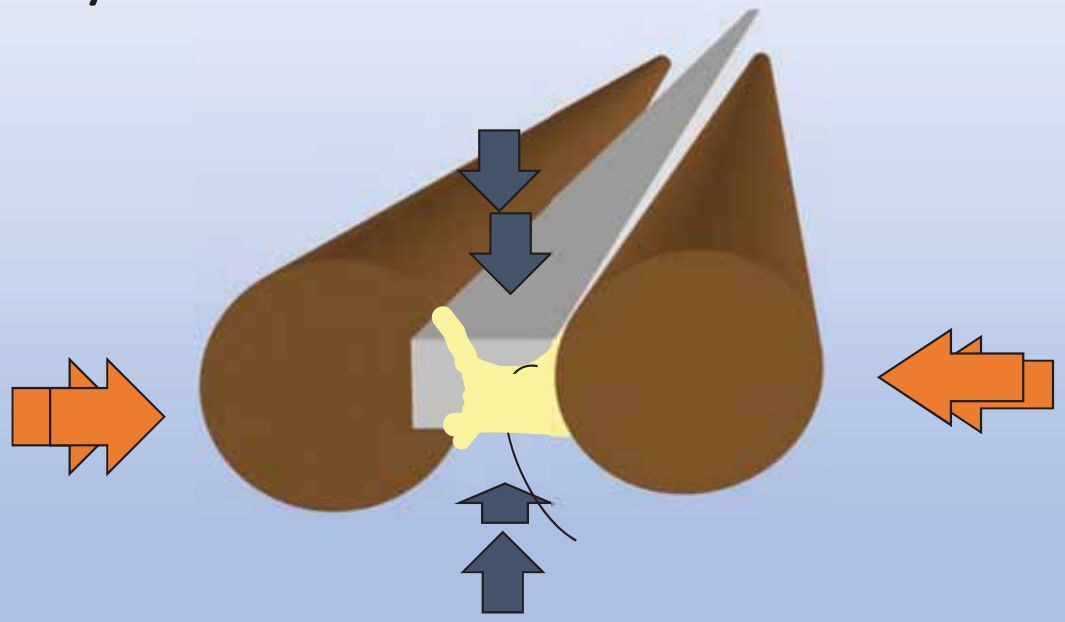
Hairspray Mechanism



Hairspray Mechanism



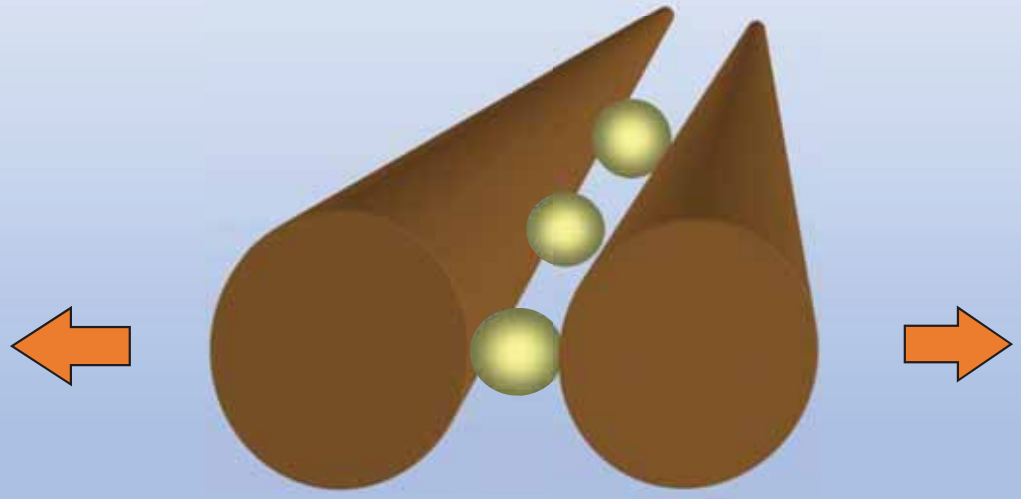
Hairspray Mechanism



Laplace Pressure

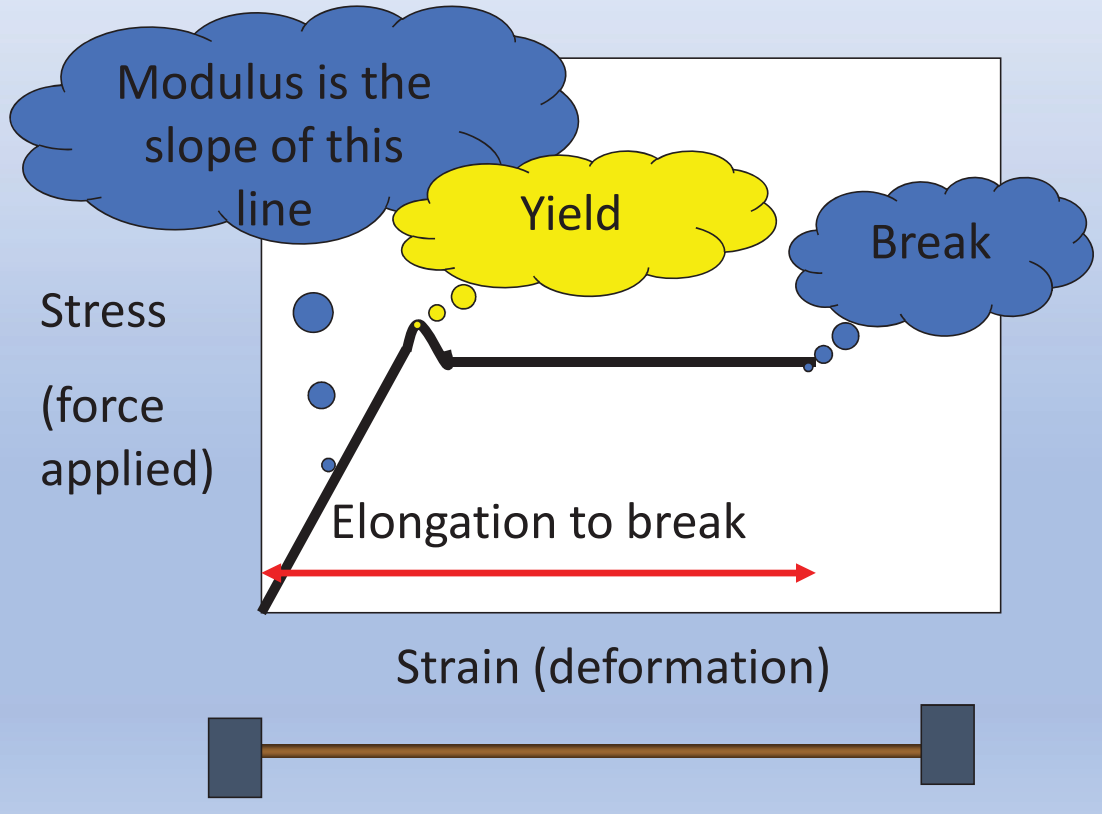
Causes Hair to be driven together

Hairspray Mechanism



Contact Angle > 90^{o} causes the fibers to be pushed apart

Strength and Toughness



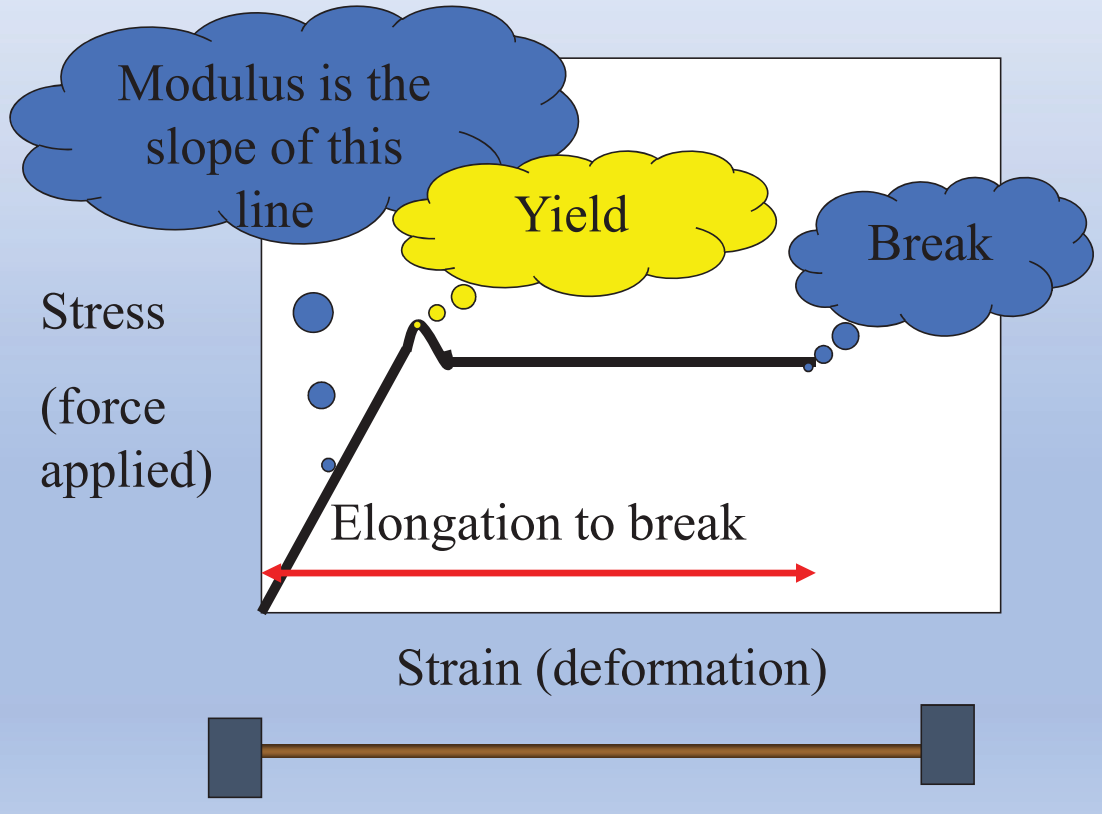
Reptation

- Above the chain entanglement threshold
  - The polymer molecules wriggle past each other
  - Like a snake moving along a tube made up of snakes
- Viscosity = $(\text{concn})^{2.2 - 3.4}$

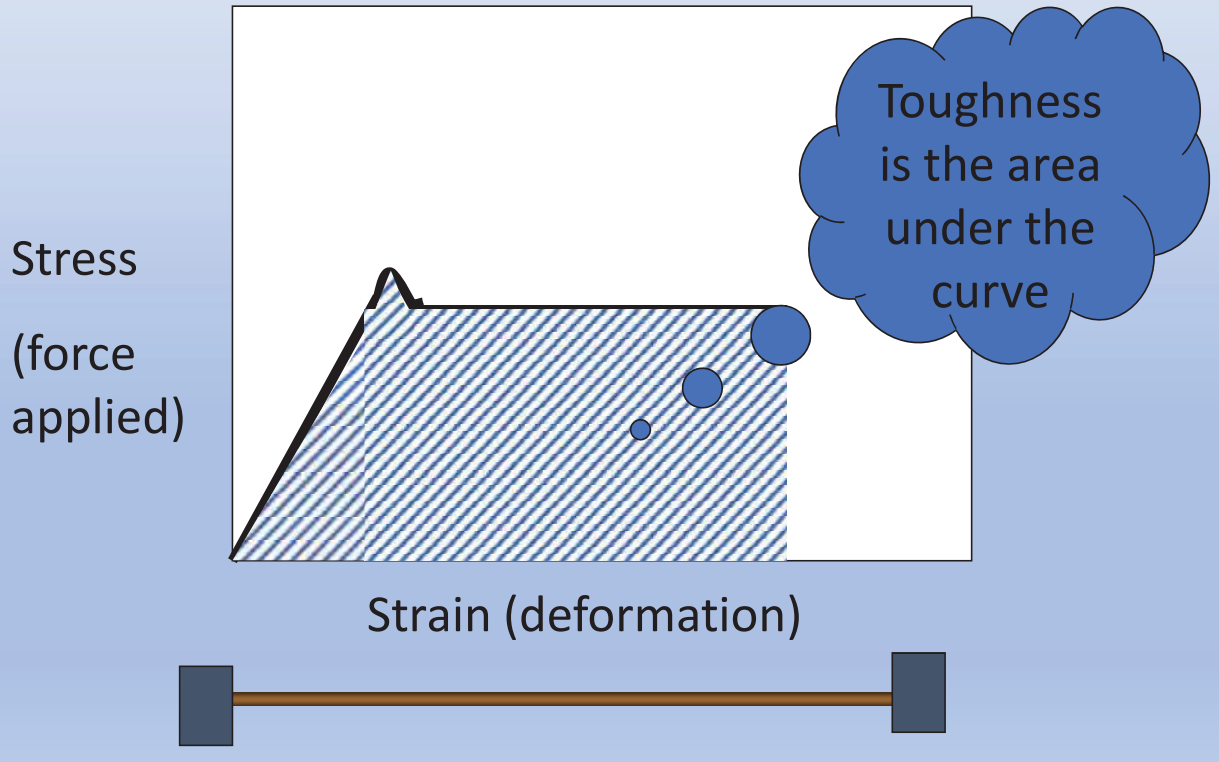
Plasticization

- Small molecules interspersed between the polymer molecules can assist repatation
  - This is plasticization
- There is a time element
  - If the applied force must last long enough for the polymers to move
  - If the force is of short duration, elastic deformation and recovery will occur
    - Debra Number

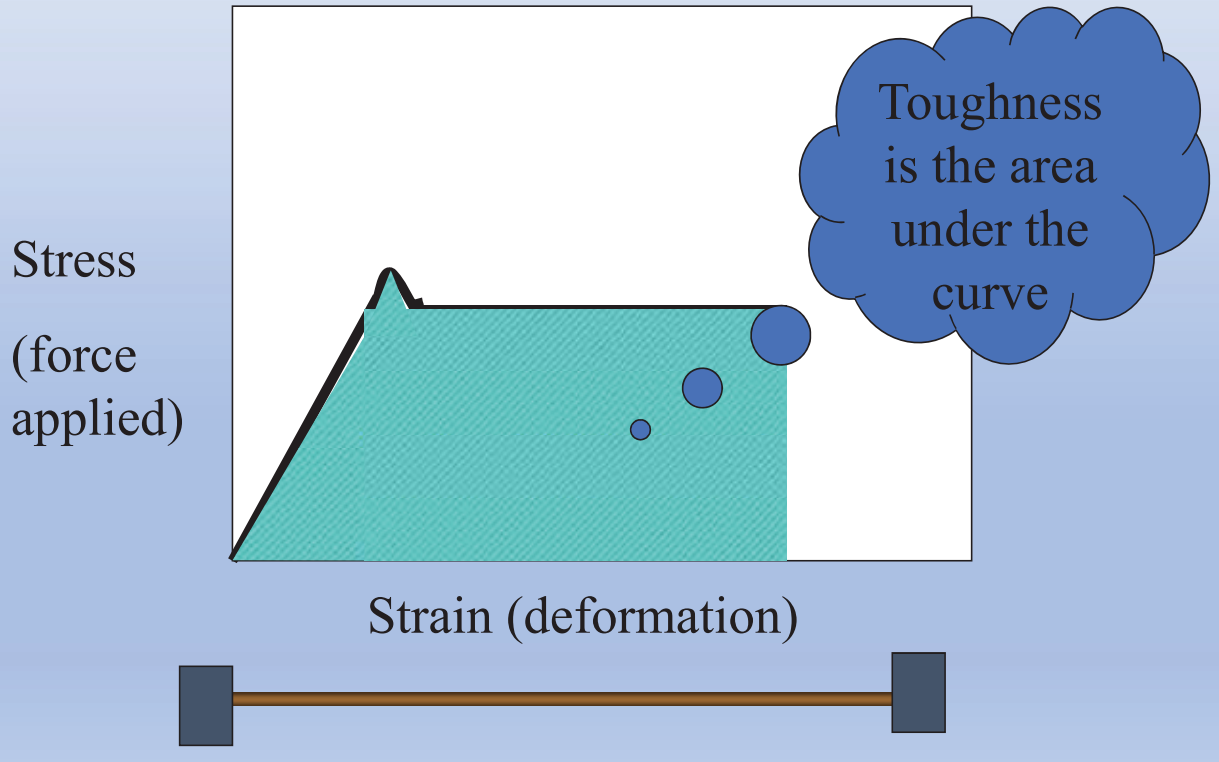
Strength and Toughness



Strength and Toughness



Strength and Toughness



No Sticky Feel

- The polymer in the dried film should be immobile during the time of ‘touch’ and should have insufficient time to interact with the stratum corneum of the fingertips
- Quick Drying
  - volatile solvent and propellant
  - gellant

Mechanical Property Aesthetics

- Ensures hair body and bounce
- Increased hair volume
- Hairs do not clump
- No excessive stiffness

- The polymer film must ‘crosslink’ the hair matrix in place, rather than coat the hair

Non-hygroscopic Film

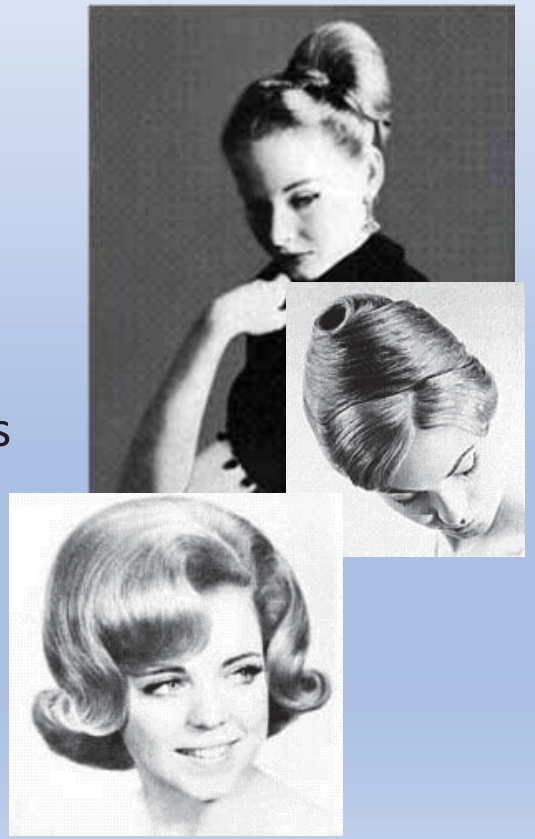
- The reason for this is to avoid plasticization of the film by absorbed water vapor.
- This begs the question " what is plasticization?"
  - It merely means that small molecules within the polymer matrix make it easier for the polymer chains to wriggle past each other
  - This lowers Tg and makes the polymer 'softer'

Desired Properties of a Hairspray

- Better hair gloss
  - This means that the polymer system must show no phase separation during the process of film formation.

Poly(vinylpyrrolidone) [PVP]

- 1950's -Hairstyles ascend
- Hairspray becomes necessary
- Shellac is used as the fixative polymer
  - but shellac is insoluble in water
  - cannot be removed by shampoos



Poly(vinylpyrrolidone) [PVP]

- PVP IS WATER SOLUBLE
- PVP IS SUBSTANTIVE TO KERATIN
- THEREFORE THE MODERN HAIRSPRAY WAS BORN
  - USING PVP AS FIXATIVE
- PVP WAS SAVED AS A COMMERCIAL MATERIAL

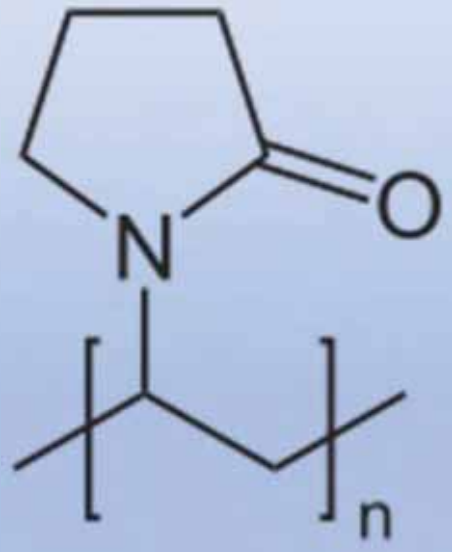
Poly(vinylpyrrolidone) [PVP]

- PVP is provided as K15, K30, K60, K90 etc.
- The Firkentscher ‘K’ value
  - An early measure of polymer molecular weight
  - $\eta_{sp}/c = [(75\ k^2)/(1+1.5kc)] + k$
    - Where K = 1000k

Poly(vinylpyrrolidone) [PVP]

- However, PVP was plasticized by atmospheric humidity
  - p.m. 'hairstyle droop' on humid days
- Copolymers were introduced to provide the desired properties.

Poly(N-2-vinylpyrrolidone)
PVP



Copolymers

- Random copolymers consist of two monomers randomly positioned along the chain.
  - True random copolymers display ‘weighted average’ properties
- The properties of interest for early hairsprays were:
  - Hardness or softness (translated as low Tg or high Tg)
  - Polar or Nonpolar (for control of sensitivity to humidity)

PVP/VA

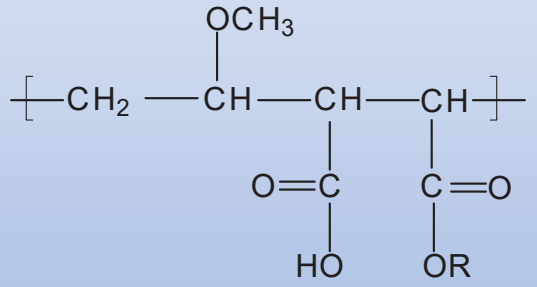
(*PVP/VA from ISP; Luviskol from BASF*)

- Polyvinylpyrrolidine/vinyl acetate copolymer
  - PVP is polar and ‘hard’ (Tg below room temperature)
  - VA is nonpolar and ‘soft’(Tg above room temperature)
- Introduced to overcome the extreme moisture sensitivity of PVP homopolymer.
- VA content of commercial resins varies from 30 to 70 percent
  - Hairsprays 70% VA
  - Hairgels 30% VA

PVP/VA

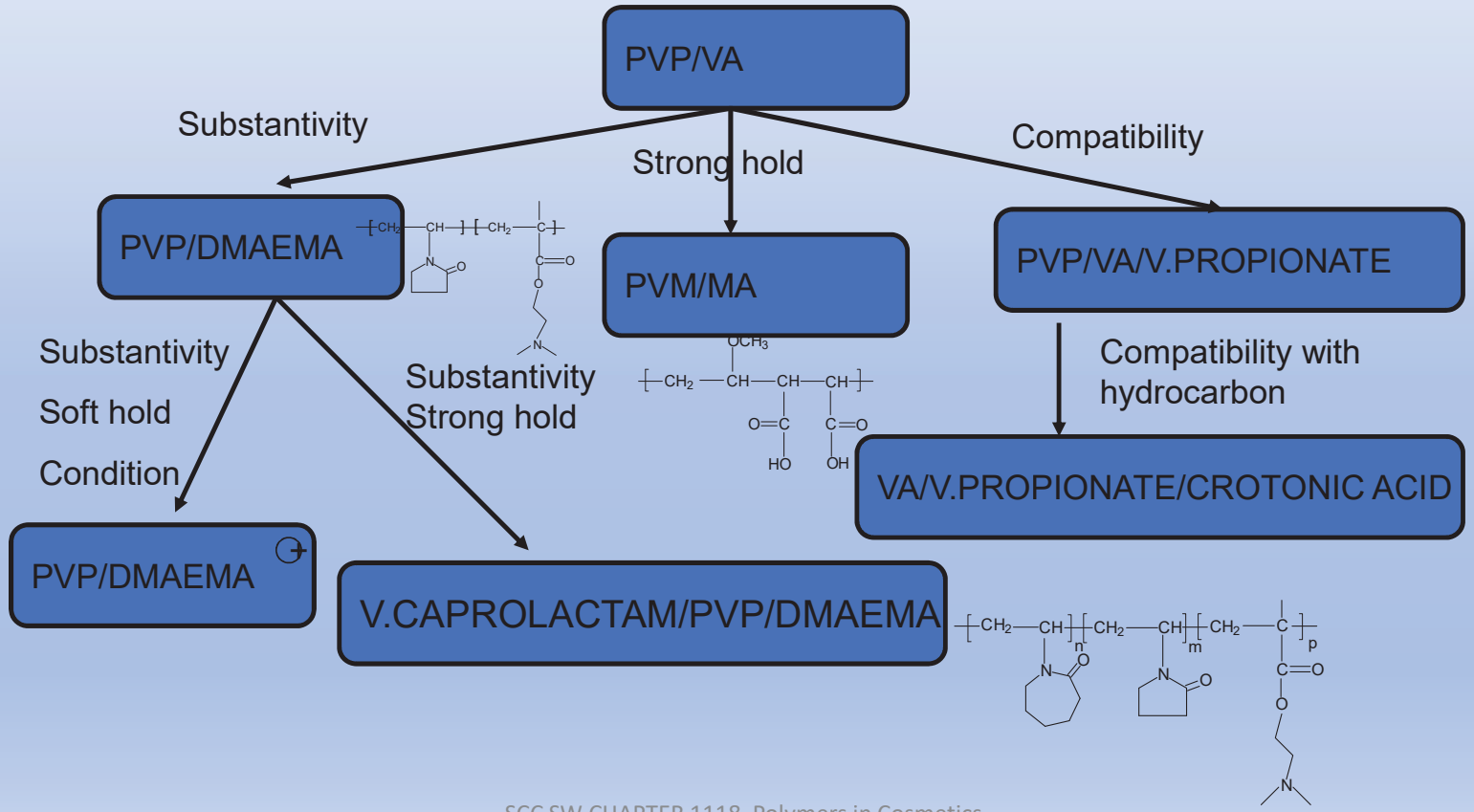
- Below pH 4.5, PVP forms and insoluble, hydrogen-bonded complex with poly(acrylic acid)
  - Carbomer Gels need special care
  - Clarity is best obtained at pH neutral

PVP/VA

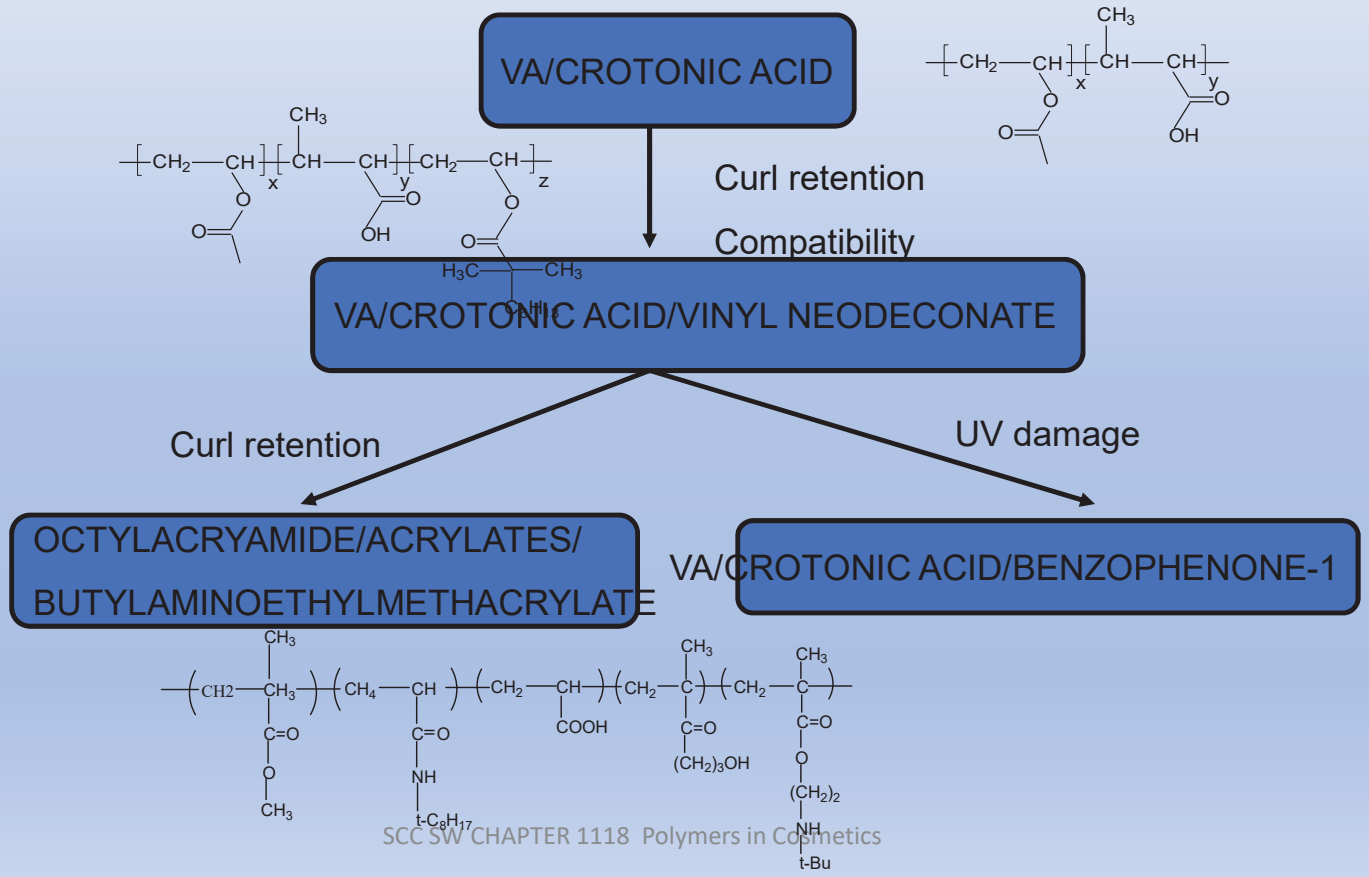


R=ethyl, isopropyl,butyl

Evolution of Hair Fixative Resins from PVP/VA

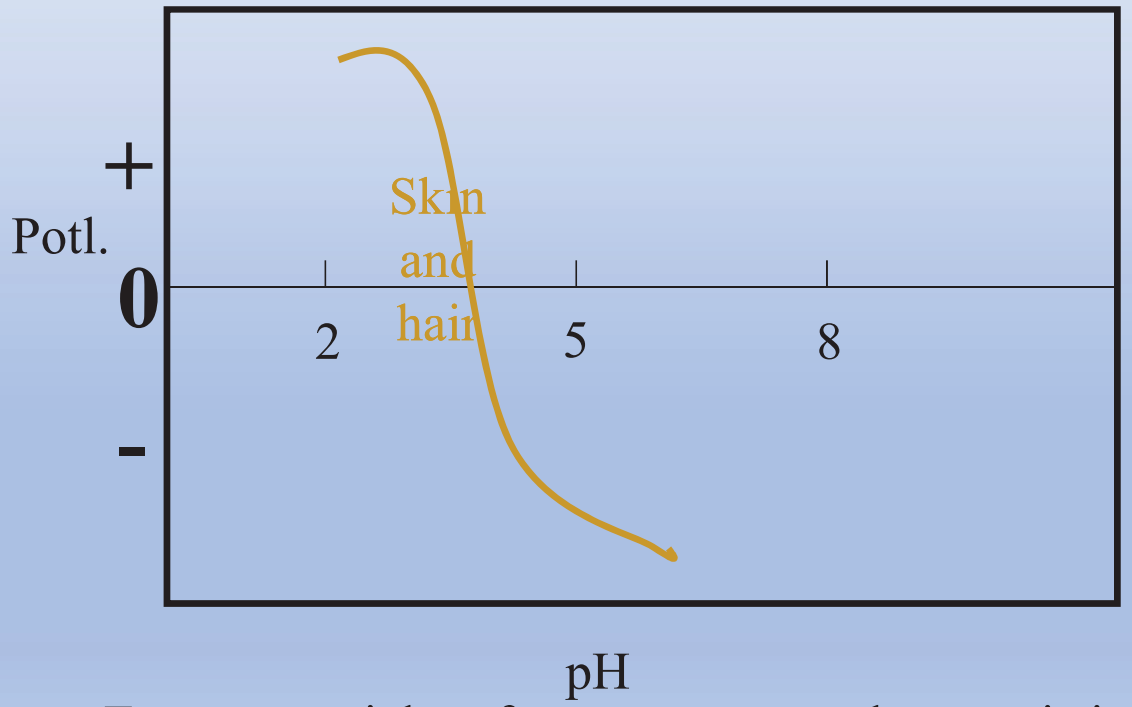


Evolution of Hair Fixative Resins from VA/Crotonic Acid



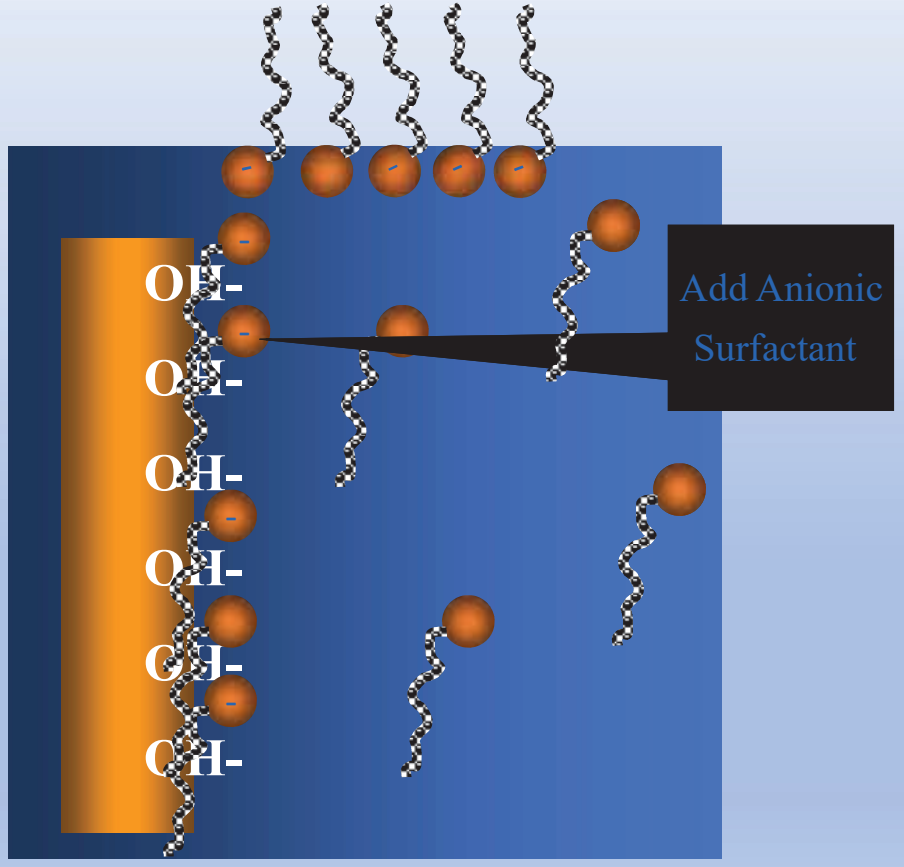
Conditioning Polymers

Electrical Charges Associated with Surfaces



Every material surface possesses a characteristic Point of Zero Charge

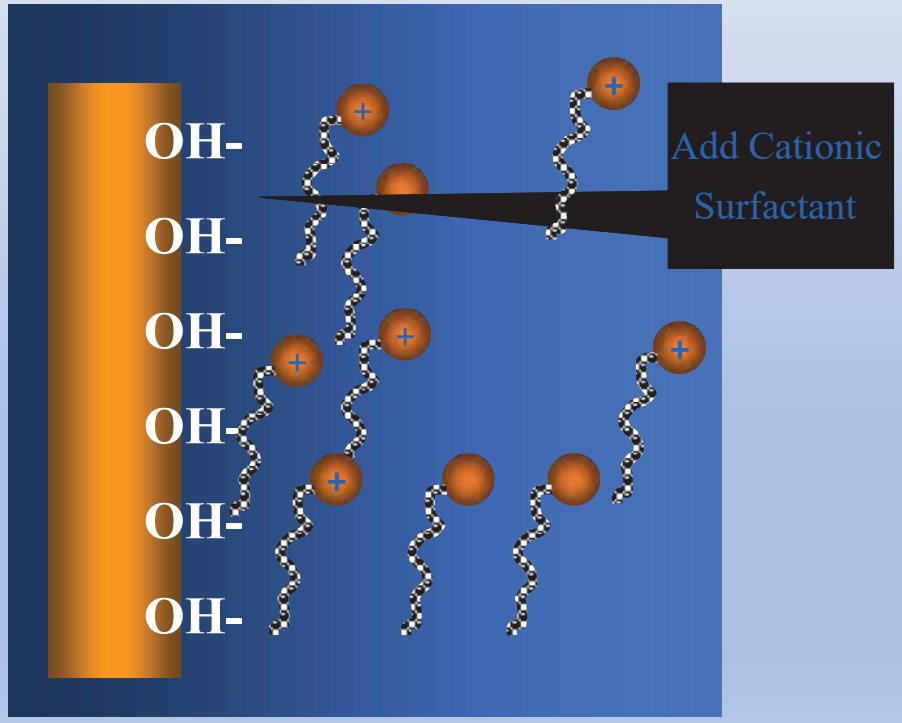
Surfactants and Conditioning



Adsorption at liquid/vapor interface reduces $\gamma_{s/l}$.

Adsorption on Hair enhances wetting

Surfactants and Dispersion



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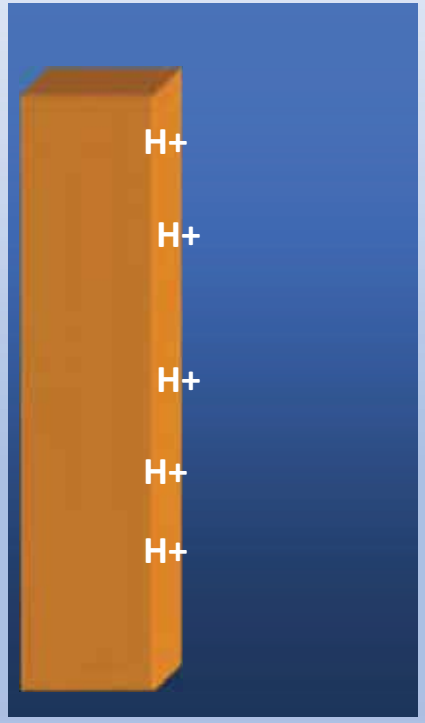
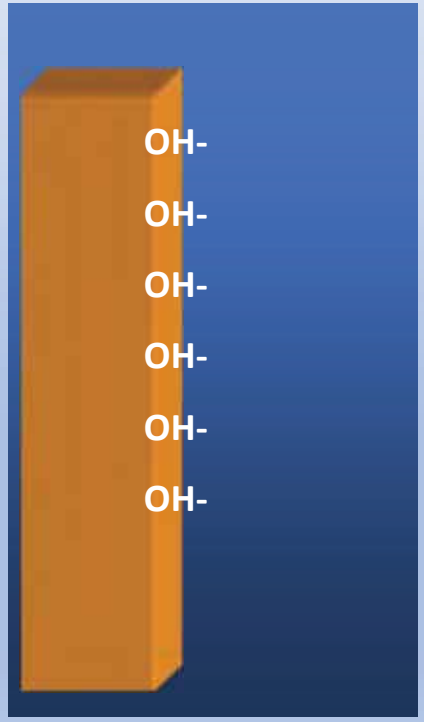
Electrical Charges Associated with Surfaces

- When immersed in aqueous solution, all surfaces interact with the hydrogen ions or hydroxyl ions of the water and also with other ions in solution.
- These ions can adsorb or desorb and an electrical potential is conferred on the surface.

Electrical Charges Associated with Surfaces

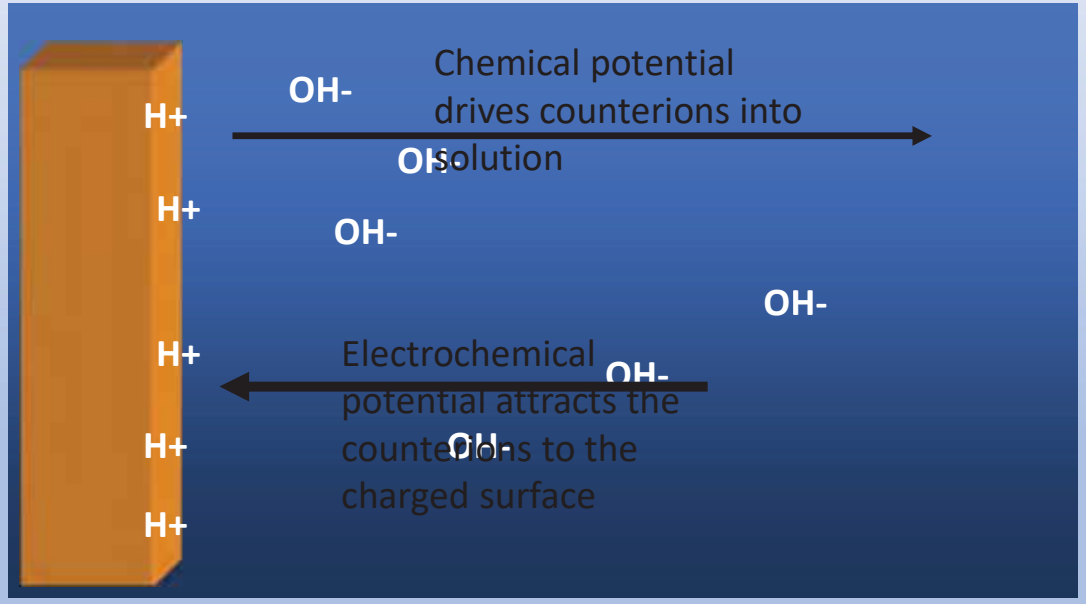


Adsorbed Cations confer positive surface potential



Adsorbed Anions confer negative surface potential

Electrical Charges Associated with Surfaces



Adsorbed Cations confer positive surface potential

and soluble counterions diffuse from the surface but are held in proximity by the need for electrical neutrality