

# Lecture 5: Macromolecules, polymers and DNA

## Introduction

In this lecture, we focus on a subfield of soft matter: macromolecules and more particularly on polymers. As for the previous chapter about surfactants and electro kinetics, we are interested in this chapter in molecular organization. On the one hand, this molecular organization has consequences for fluid mechanics at the milli and micro scale; on the other hand microfluidics has allowed the study of various such macromolecules from the biological field and life science. After a brief introduction of “soft matter”, basic concepts of polymer physics will be reviewed. Some applications in the field of flow mechanics at milli- and micro-meter scales will be presented at the end of this chapter.

## 1) Introduction to “soft matter”

### The field of Soft Matter

“Soft Matter” is a concept introduced by Pierre Gilles de Gennes (Nobel Prize 1991) and which is also referred to as “complex fluids” (American school). It can be seen as a subfield of condensed matter and comprises a variety of materials relevant for our lecture including liquids, colloids, polymers, foams, gels, granular media and most of the biological materials.

### Some characteristics:

#### Mesoscale

Typically from a few Å to 1000 Å → at this scale (meso-scale):

- continuous theory of matter,
- statistical physics ( $N \gg 1$ )

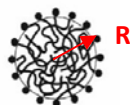
a polymer molecule:



$$N \sim 100 - 1000$$

$$R \sim N^{\nu} a \quad 100 - 500 \text{ \AA}$$

a micelle:



$$N \sim 100$$

$$R \sim 50 - 100 \text{ \AA}$$

## Weak interactions

Typical energy of interactions are weak in the order of magnitude of the energy of thermal agitation at room temperature ( $kT \sim 4 \cdot 10^{-21}$  J)

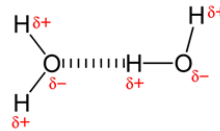
- Due to the weak interactions, these objects are fragile → break and re-build → biology (life)
- Due to the weak interactions: show important deformations (answers) under small forces/stimuli (sol-gel transitions, non Newtonian rheological behavior)

Interactions at play comprise:

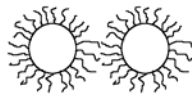
- Van der Waals attraction:  
Typically 1 to 10kJ/mole  
(0,4kT to 4kT at 25°C)



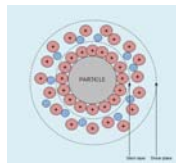
- Hydrogen bonds: with electronegative atoms (N, O, F)  
Typically 5 to 20kJ/mole (2kT to 8kT at 25°C)



- Steric interactions:  
Typically 1 to 10kJ/mole  
(0,4kT to 4kT at 25°C)



- Electrostatic interactions:  
Typically 10kJ/mole (4kT at 25°C)



## Examples

liquids, colloids (suspended particles in liquids), emulsions (suspended droplets in liquids), polymers (dilute, semi dilute, melt), foams, gels (polymers or colloids), granular materials, and a number of biological materials (proteins, vesicles, DNA,...)

## Applications

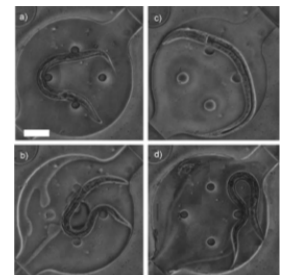
### the art of formulation or the science of mixtures of finalized properties

Painting: pigment + latex particles → “wet” stability, rheology and “dry” → coalescence: film formation

Tooth paste: charged silica beads + salt → gel (flocculation)

Gel in a microfluidic chip to culture, trap and immobilize *C. Elegans* (worm)

Very important for cosmetics and pharmaceuticals!



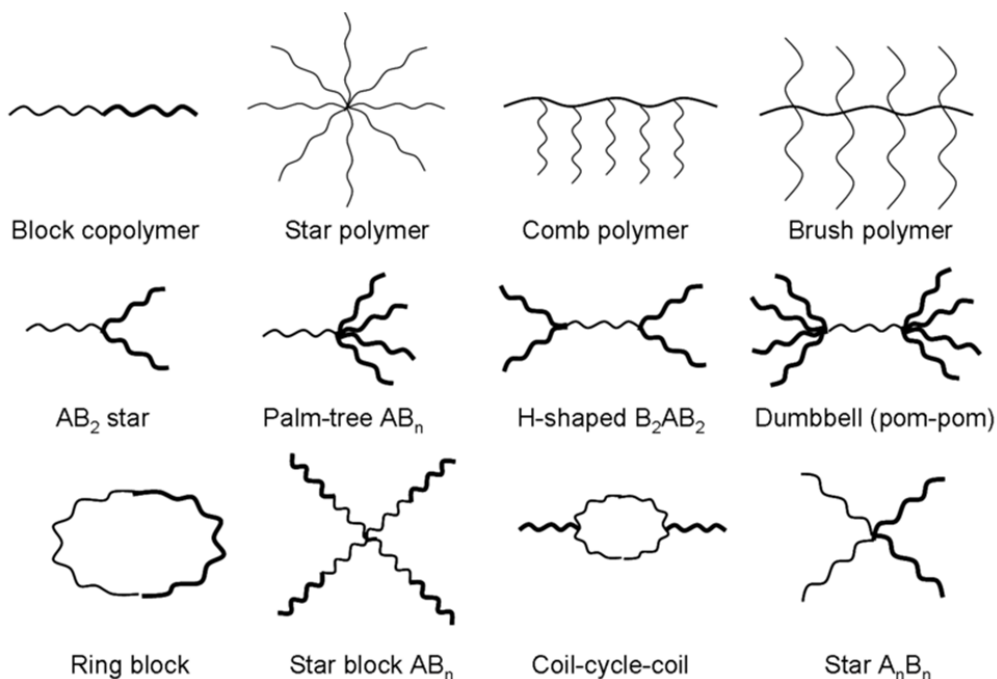
Sol-gel-sol transitions (+/-2°C)  
to immobilize *C. Elegans*,  
Krajniak and Lu 2010

## 2) Introduction to polymer physics

### 2)1) Generalities

**Definition of polymer:** is a large molecule, or macromolecule, composed of many repeated subunits, known as monomers (Staudinger 1926).

They can be linear or show different shapes such as branches and stars. They can be made of a single kind of monomer or present two or more blocks made by the repetition of a respective monomer. In this case, they are called block copolymer. Such molecules can have hydrophilic and hydrophobic (or lipophilic) blocks leading to the formation of microphases similar to what was introduced with surfactants → polymer engineering with many applications for daily life.



Source, Wikipedia

### 2)2) Properties of isolated polymer molecules

**The ideal chain:**

Kuhn (1940);  $\vec{R}$  is the end to end vector of the polymer molecule.

- Size R

Random walk  $\langle \vec{R} \rangle = 0$  but  $\langle \vec{R}^2 \rangle = Na^2$  with  $a$  the length of subunit (monomer) and  $N$  the number of monomers in the chain. The size of a polymer molecule is defined as  $R = \sqrt{\langle \vec{R}^2 \rangle} = \sqrt{Na}$

Typically  $R$  is measured with dynamic light scattering.

- Distribution of sizes

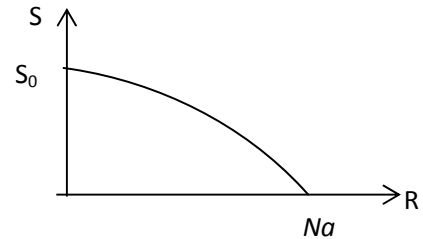
Probability to have an end-to-end vector  $\mathbf{R}(X,Y,Z)$  is  $P(\vec{R}) = Ce^{-3/2 R^2/Na^2}$

→ Gaussian distribution centered in zero

- Entropy

$$S = k \ln(\Gamma_N(\vec{R})) = S_0 - \frac{3}{2} k \frac{R^2}{R_0^2}$$

$\Gamma_N(\vec{R})$  is the number of paths of N units going from 0 to R



- Free energy

F=H-TS; without interactions (enthalpy H is zero if solvent=monomers):  $F = F_0 + \frac{3}{2} kT \frac{R^2}{R_0^2}$

→ minimum for  $\vec{R} = \vec{0}$ , quadratic with  $\vec{R}$

Important result: polymers are referred to as entropic spring with a constant  $k_H = 3 \frac{kT}{Na^2}$

- Stretching of a chain - constant force f



→ Minimization of  $G = F - \vec{f} \cdot \vec{R} = cste + \frac{3}{2} kT \frac{R^2}{R_0^2} - \vec{f} \cdot \vec{R}$

→  $\vec{R} = \frac{R_0^2}{3kT} \vec{f}$  → again entropic spring

**Deviations from the ideal chain**

**i) Short range interactions**

For the ideal chain:  $\vec{R} = \vec{a}_1 + \vec{a}_2 + \dots + \vec{a}_N$  and  $\langle \vec{R} \cdot \vec{R} \rangle = \sum \langle \vec{a}_i \cdot \vec{a}_j \rangle = Na^2$  since  $\langle \vec{a}_i \cdot \vec{a}_j \rangle = 0$  if  $i \neq j$

But practically, it is not the case; for example valence angle for a  $(-CH_2-)_N \rightarrow$  introduction of the coherence or persistence length noted  $l_p$  and defined as  $\sum_{i=1}^{\infty} \langle \vec{a}_1 \cdot \vec{a}_i \rangle = l_p a$

$$\rightarrow R^2 = N(2l_p a - a^2)$$

We find 2 extreme cases: (i)  $l_p = a$ ,  $R^2 = Na^2$  and (ii)  $l_p \gg a$ ,  $R^2 \sim 2Nl_p a = Nb^2$  with b the Kuhn segment

Order of magnitude: DNA 500 Å, Kevlar 1000 Å, PE 3 Å, actin 7µm.

**ii) Long range interactions (strong fundamental impact)**

Self Avoiding Walk (SAW) – notion of excluded volume v

Introduced by Flory (1949): since the chain cannot be several times at the same place, it gets swollen in a good solvent (good solvent = monomer → no contribution of enthalpy due to the mixture but only entropy) and the exponent 1/2 has to be replaced by another one.

Indeed, for a given solvent if the temperature T is high enough it is observed that  $\nu > 0$ : the molecule is swollen; if T is too low: segregation occurs (collapse of the macromolecule) and  $\nu < 0$ . From these observations, one can conclude that the term of excluded volume is function of the temperature (or of the solvent) and for a given solvent there exist a temperature ( $\theta$ ) for which the excluded volume contribution changes of sign.

Flory's approach consists in calculating the free energy of the chain taking into consideration 2 contributions: the **enthalpic term related to the excluded volume** and the **entropic term (ideal chain)** for a good solvent (can be generalized to a classical solvent → theory of Flory Huggins)



Within the polymer coil, the averaged monomer concentration is given by  $c = N/R^3$

$$\frac{F_{ev}}{kT} \sim \frac{1}{2} \nu c N$$

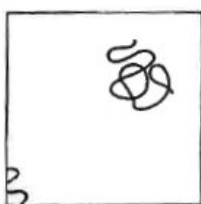
The entropic term remains:  $\frac{F_{ent}}{kT} \sim \frac{R^2}{R_0^2}$

Total free energy for the chain is:  $\frac{F_{tot}}{kT} = \frac{1}{2} \nu \frac{N^2}{R^3} + \frac{3}{2} \frac{R^2}{R_0^2}$

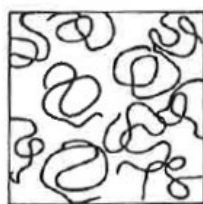
$F_{tot}$  is minimum for the so-called Flory radius:  $R_F \sim N^{3/5} a$

*Remark: both terms are false separately but the sum is correct, errors compensate themselves. Many attempts have been done to modify Flory without success so far.*

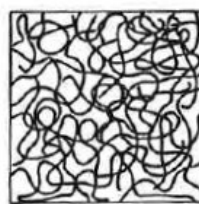
### 2)3) Concentrated solutions and melts



(a)  $c < c^*$



(b)  $c \approx c^*$



(c)  $c > c^*$

Doi, Introduction to polymer physics

$C^*$  is the number of segment per unit of volume when coils start to touch each other:

$C^* = N / R$  with  $R = N^{1/2} a$  for solvent theta (ideal chain) and;

$C^* = N / R$  with  $R = N^{3/5} a$  for good solvent (Flory)

### 3) Dynamic of polymers - Isolated chains and dilute solutions

Dynamic of isolated chain is governed by the chain mobility  $s_{chain}$  which is defined as the ratio between the force applied to the chain and the velocity of the chain.

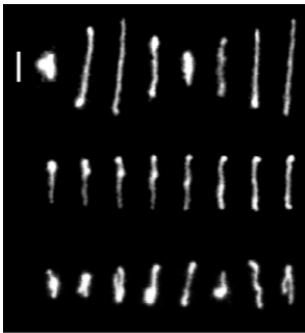
- if the solvent is immobile (Rouse model)  $F_{chain} = N F_{mono}$  and  $F_{mono} = 6 \pi \eta a V$  thus  $s_{chain} = N s_{mono}$

Diffusion coefficient (Einstein equation)  $D_{\text{rouse}} = kT / N s_{\text{mono}}$ . This prediction is not in agreement with experiment (except for melt)

- indeed, the solvent moves with the chain (Zimm theory)  $F_{\text{chain}} = \sum_n f_n \rightarrow$  concept of hydrodynamic radius  $R_{\text{hydro}}$ . It has been shown that  $D_{\text{hydro}} = kT / \eta_s R_{\text{hydro}}$  and  $R_{\text{hydro}} \sim N^\nu$  with  $\eta_s$  the solvent viscosity.

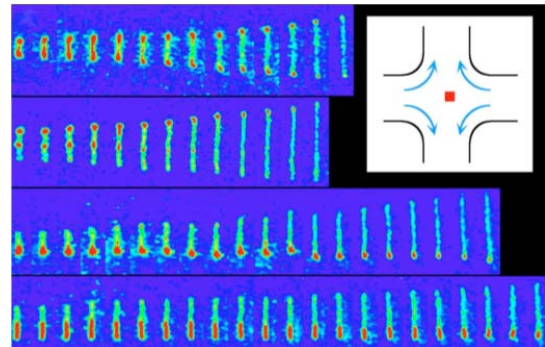
## Polymers and milli- micro-meter fluid mechanics – Examples (not exhaustive)

### 4)1) Microfluidic single-polymer studies

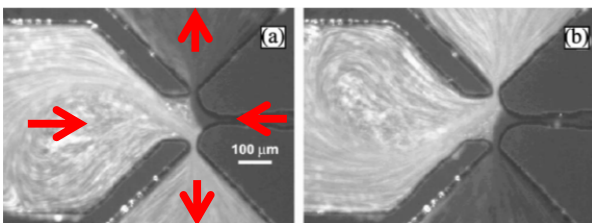


Stretched fluorescent DNA molecule, 3 (top to bottom) sequences (left to right) are shown. From Single Polymer Dynamics in steady shear flows, Smith et al, Science (1999)

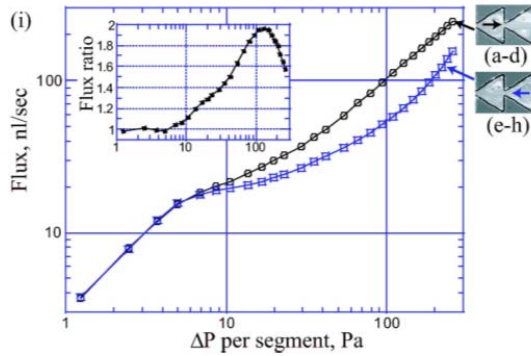
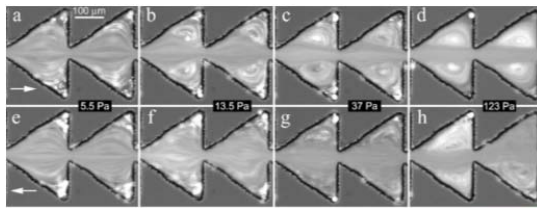
Stretched fluorescent DNA molecule, 4 (top to bottom) sequences (left to right) are shown. From Single Polymer Dynamics in an elongational flow, Perkins et al, Science (1997)



### 4)2) Elastic instabilities



Viscoelastic flip-flop memory device. Junction with two polymers solutions entering from opposite sides. Each solution exit in one output in contrary to Newtonian fluid which split. From Groisman et al, science 2003.



Viscoelastic dilute polymer solutions.

(a-d): flows in forward direction  
 (e-h): flows in the reverse direction

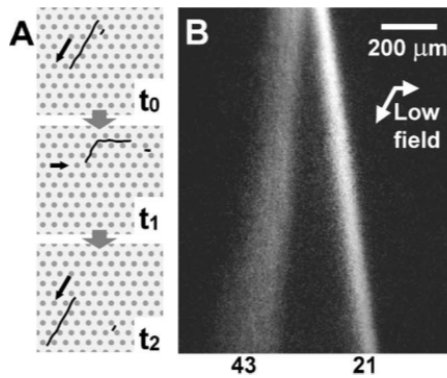
In contrast to Newtonian fluid, not reversible for small Re.

From Groisman and Quake (2004).

### 4)3) Controlled polymer deformation for separations

Ultrafiltration (see exercise)

Pulsed field electrophoresis



DNA molecules of different length can be separated – device shown in (A) with:  
 $t_0$ : electric field is applied to stretch the molecules along its direction.  
 $t_1$ : transverse (pulsed) electric field is applied

Result: smaller molecules encounter fewer obstacles than larger ones and progresses more in the transverse direction leading to their separation (B)

From Tegenfeldt et al (2002)