

# Material Chemistry KJM 3100/4100

## Lecture 1.

### Soft Materials:

- **Synthetic Polymers** (e.g., Polystyrene, Poly(vinyl chloride), Poly(ethylene oxide))
- **Biopolymers** (e.g., Cellulose derivatives, Polysaccharides, Proteins)
- **Liquid Crystals** (can behave like either a liquid or solid depending on the direction that is chosen within the material)
- **Polymeric Gels**
- **Polymeric Nanoparticles** (Core-shell particles)
- **Foams**

**Polymer Material**: A polymer material can also behave like either a liquid or a solid, depending on the time-scale of the measurement.

**Soft materials** exhibit physical properties that can be very different from conventional materials, giving rise to intriguing features.

**Polymers are used as materials in many different applications in pharmacy and medicine:**

- a) Implants**
- b) Oral drug delivery systems**
- c) Photochemical controlled drug delivery systems**
- d) Ocular and nasal administration**
- e) Vaginal administration**

**Hydrogels are often used in drug delivery. A hydrogel consists of an elastic three-dimensional polymer network that is swollen by water.**

**By changing structure of the polymer matrix, a controlled drug release can be established.**

**This unusual behavior can be attributed to several common features that these materials possess:**

**1. i) Usually weak bonding between the molecules (e.g., van der Waals forces, hydrogen bonds, and hydrophobic interactions).**

**ii) Large alterations of the materials can be accomplished by modest changes in the environmental conditions, such as concentration, temperature, and pH.**

**iii) The weak bonding promotes the molecules to self-assemble in response to intermolecular interactions to form unique and useful structures over large length scales.**

**2. The structure of soft materials is usually complex and it depends on the assembling of units and on which length scale the structure is probed.**

**In addition, many soft materials are built up of different components, where the physical properties of the individual component play an important role for the overall features of the material.**

**3. The physical properties of polymeric soft materials usually vary over a large range of time scales.**

**Molecules and assemblies of molecules can move on widely differing time scales from picoseconds- characteristic of the motion of individual polymer segments- to what can be called macroscopic time scales (seconds, minutes, years) corresponding to the slow flow or creep of the materials.**

**We should also bear in mind that the behavior of most soft materials is further complicated because they are typically far from equilibrium, that is, kinetics playing a dominant role in determining their structure and dynamics.**

**The complex nature of soft materials and their broad range of physical properties and technological applications make it impossible in this short course to give an overall account of soft materials.**

**In this course most of our attention will be focused on polymers, and aspects on the following topics will be given: Polymer gels, Polymer Nanoparticles, and Polymer Association Complexes (Polymer/Surfactant and Polymer/Cyclodextrin Systems).**

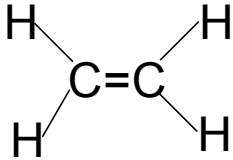
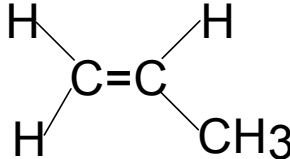
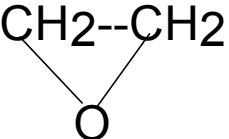
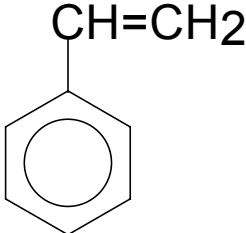


## Polymer- some basic concepts:

**What is a polymer?** A polymer consists of monomer units (repeating units) that are connected by covalent chemical bonds to form a chain.

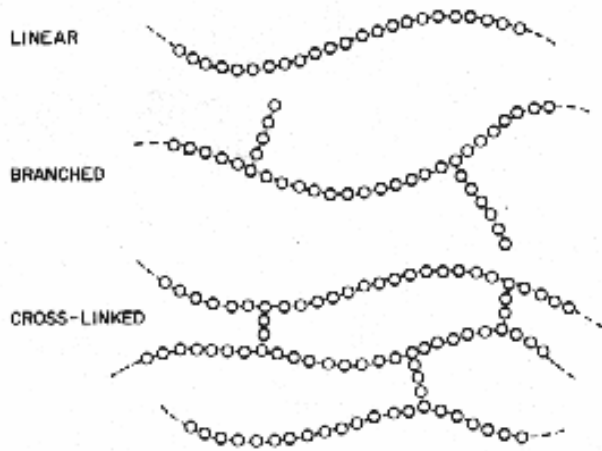
The connectivity is a central concept in the discussion of polymers, and it is important for the special properties of polymers.

The polymers discussed here are water-soluble and they are usually amphiphilic. Most of them are hydrophilic with a small amount of hydrophobic groups.

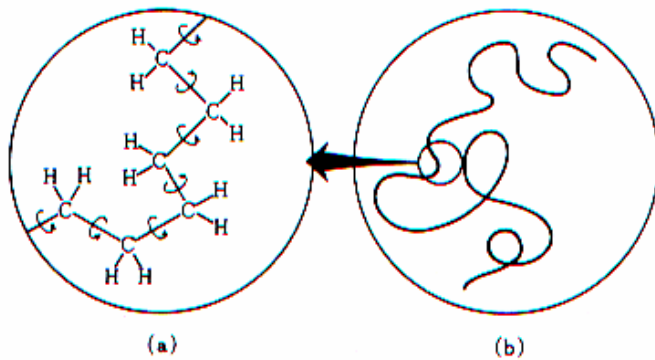
<u>Monomer</u>	<u>Structural unit</u>	<u>Name</u>
	$(-\text{CH}_2-\text{CH}_2-)_N$	Polyethylene
	$(-\text{CH}_2-\text{CH}(\text{CH}_3)-)_N$	Polypropylene
	$(-\text{O}-\text{CH}_2-\text{CH}_2-)_N$	Poly(ethylene oxide)
	$(-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-)_N$	Polystyrene
N=102-106	M = 104-108	

**Type of Polymers: Biopolymers (e.g., Proteins and Polysaccharides); Synthetic Polymers (e.g., Polystyrene and Poly(ethylene oxide))**

**Polymer Structures:**



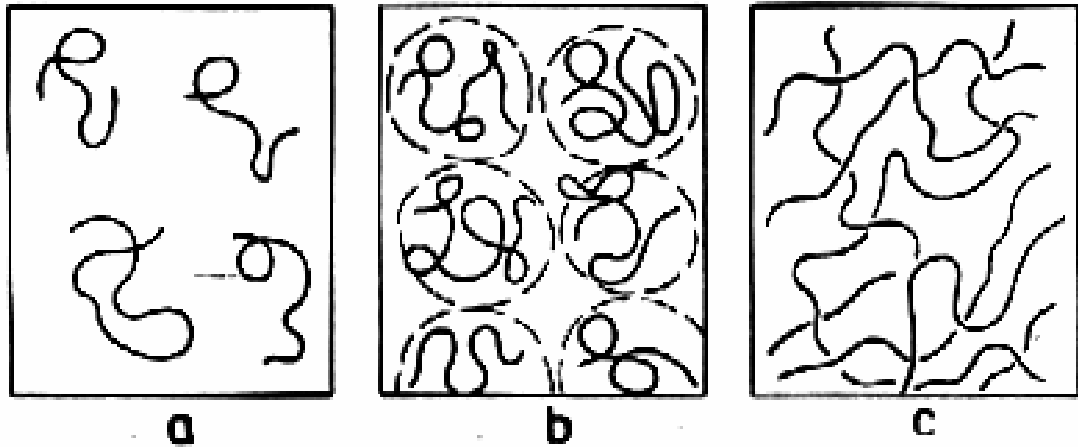
**Microscopic Structure versus Global Conformation:**



**(a) Microscopic Structure of Polyethylene**

**(b) Macroscopic conformation of Polyethylene**

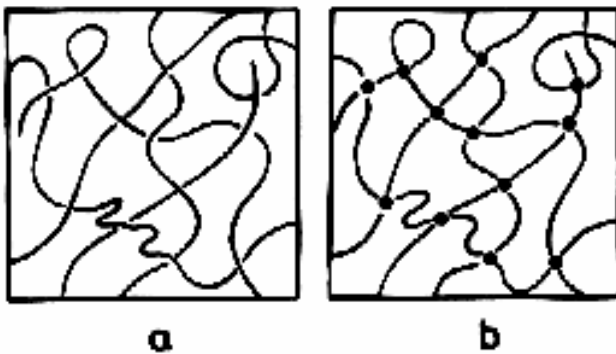
## Concentration Regimes:



- a) **Dilute regime**: In dilute polymer solutions, the molecules (coils) act as individual units without intermolecular interactions.
- b) **Intermediate regime** between a dilute and semidilute solution.
- c) **Semidilute regime**: In this regime, the polymer molecules overlap each other and form a transient network. *A semidilute solution is necessary for amacoscopic gel to evolve.*

**Different types of gel:** *Definition:* “A gel is a substantially diluted system which exhibits no steady state flow”. We will focus our attention on *hydrogels-gels that swell in aqueous solvents.*

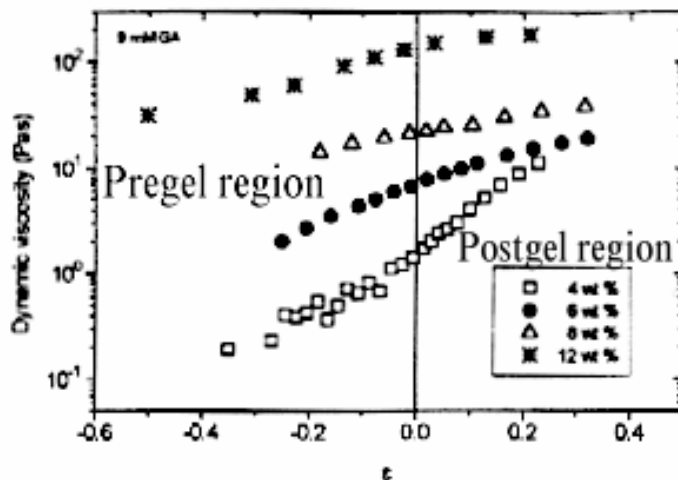
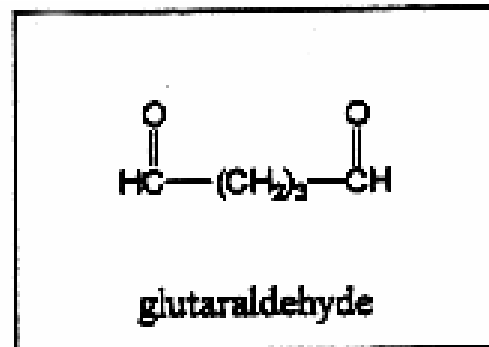
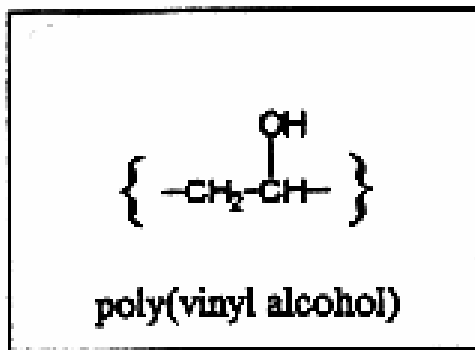
**Chemical gel:** The network is *covalently cross-linked* (a permanent network) with the aid of a *chemical cross-linking agent*. This is reminiscent of the *vulcanization process of rubber* with sulfur.



a) **Transient polymer network before cross-linking.**

b) **Gel-network as a result of *chemical cross-linking.***

**Example:** Cross-linking of semidilute aqueous solutions of *poly(vinyl alcohol)(PVA)* in the presence of the chemical agent *glutaraldehyde (GA)*.



We can see that the dynamic viscosity increases as the gelling reaction proceeds. Where  $\varepsilon \equiv (t-t_g)/t_g$  ( $t$  is time and  $t_g$  is the gelation time) is the distance to the gel point.

When GA is added to the semidilute PVA solution, cross-links will gradually start to form, and if enough cross-linker agent is present, the system becomes a gel after a certain time  $t_g$ .

The rheological methods used to determine the gel point of a gelling polymer system will be discussed later.

*Physical gel*(“*temporary*” *gel*): This type of gels (thermoreversible gels; responsive gels) is formed by *physical junctions* (e.g., ionic interactions, hydrophobic interactions, and hydrogen bonding) and they are usually weak as compared with chemical gels.

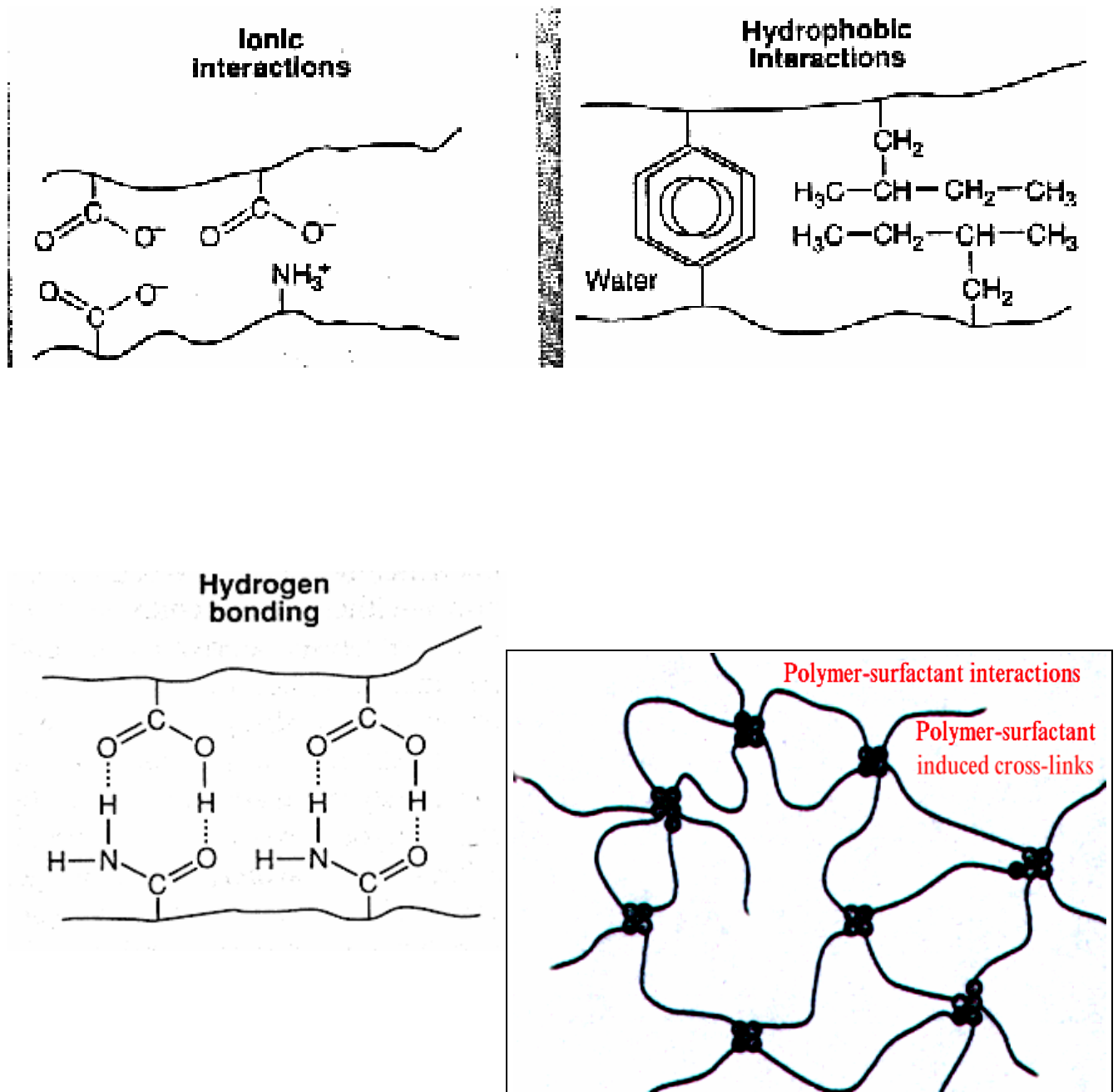
This type of gel may respond to *changes in temperature, pH or concentration of cosolute* (salt and surfactant).

For some semidilute aqueous solutions, a gel may be formed by *heating the solution*, while for other systems *gelation occurs upon cooling the solution*.



# Fundamental forces that control behavior of most

## responsive gels:



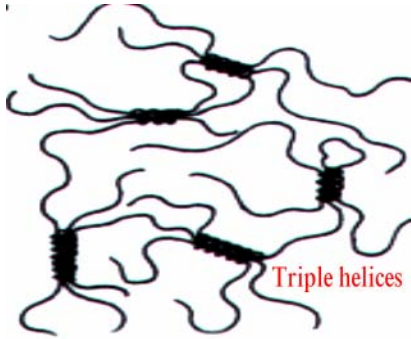
Some examples of gelation processes taking place upon cooling the solutions:

Gelatin/water: Gelatin is the name currently given to “*denatured*” collagen (*protein; polyamino-acids*).

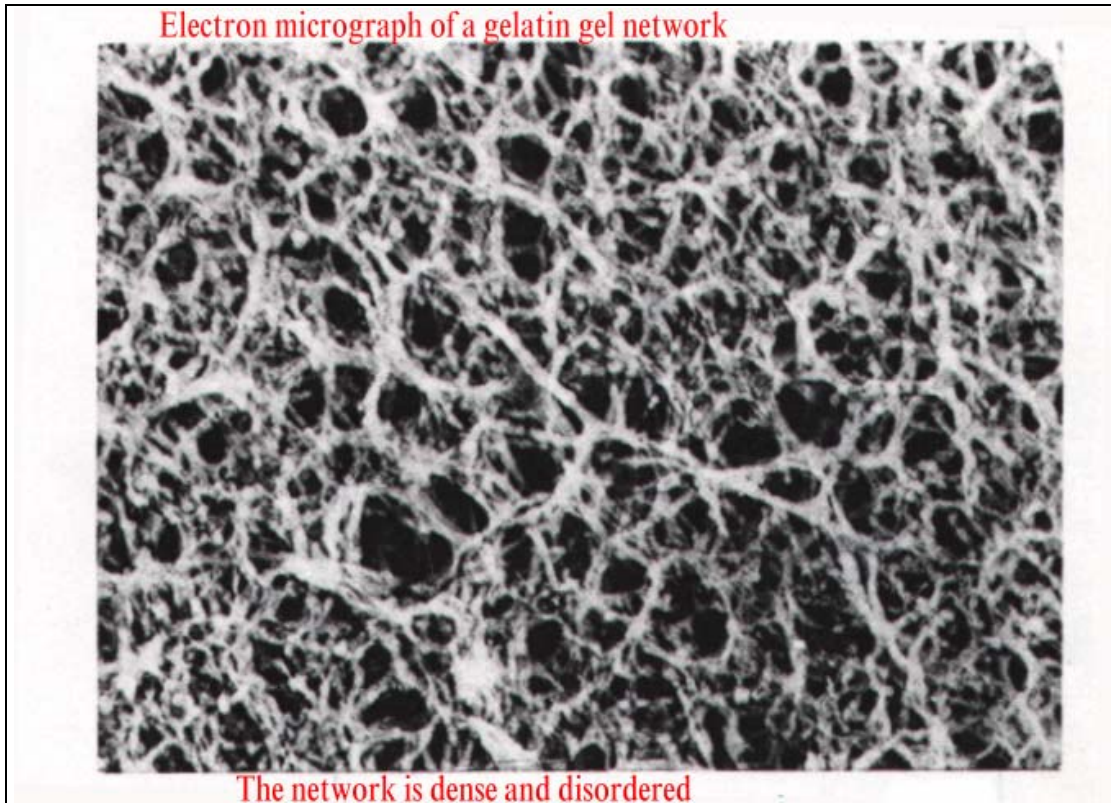
In this gelation process *junction zones of triple helices* are formed which act as physical cross-links upon cooling the solution. At higher temperatures (**above ca. 40 °C**) we have a solution and at lower temperatures a gel evolves.

--(Gly-X-Hypro)<sub>N</sub>-- (X is any amino-acid, Gly is glycine and Hypro is hydroxyproline)

## Schematic illustration of the gelatin gel structure

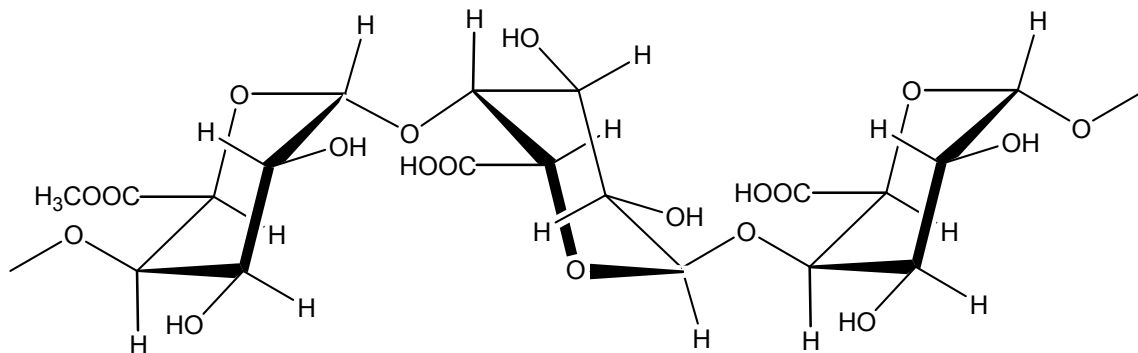


Electron micrograph of a gelatin gel network



The **polysaccharide pectin** is another water-soluble polymer that may through **hydrogen-bonded interactions** form a thermoreversible gel upon cooling.

### Pectin:



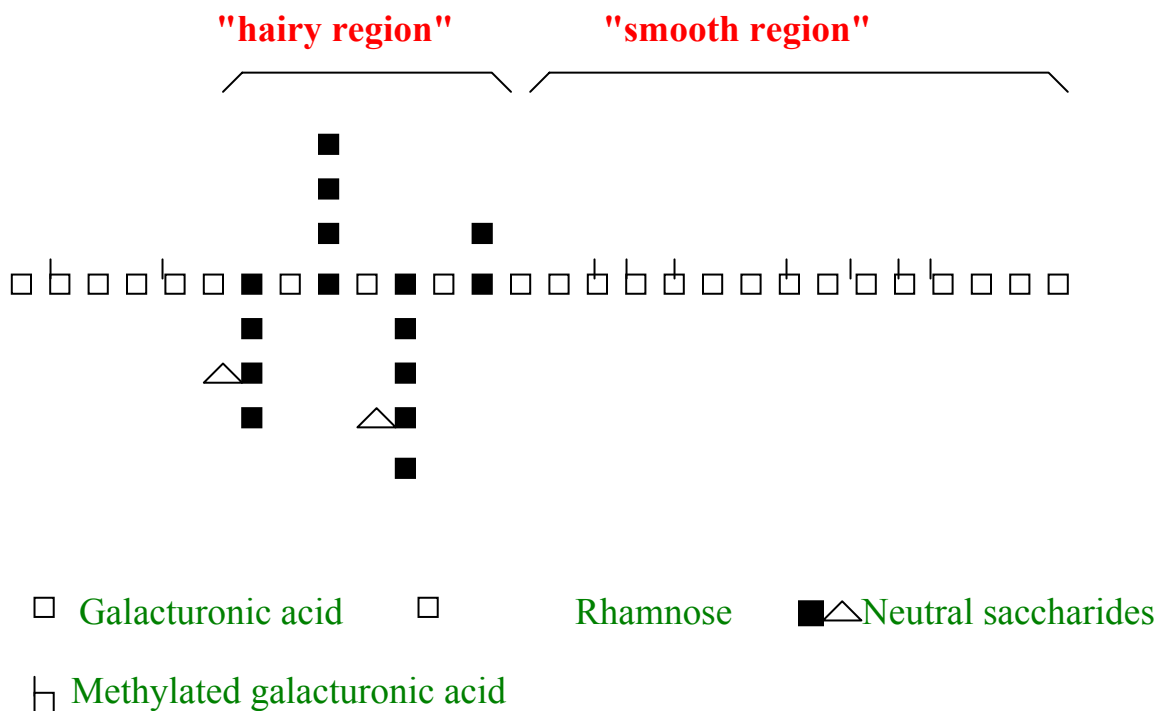
Molecular weight: ca. 40 000

Degree of methoxylation: 35 %

Galacturonic acid content: 88 %

**Gelation**: In the semidilute concentration regime, intermolecular hydrogen bonds between pectin chains (low methylated) may, upon cooling, generate a connected network which spans the whole sample volume (physical gel).

**Schematic drawing of pectin:**

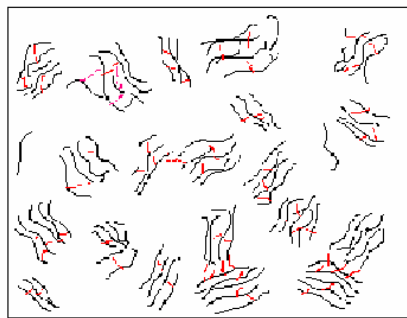


The **homogalacturonan parts** of the polymer are referred to as **"smooth"** regions while the **rhamnose-rich zones** are called **"hairy"** regions as the **rhamnopyranosyl residues** carry **oligosaccharide side-chains**. In native pectins about **70%** of the **galacturonan carboxyl groups** are **methylated**.

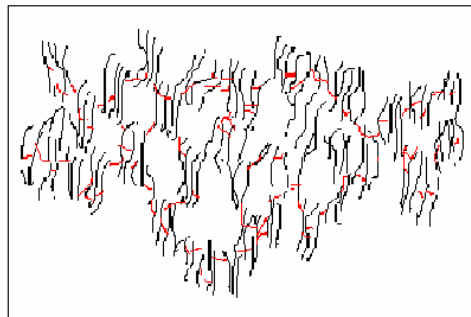
A **semidilute solution** of this pectin sample forms a **physical gel upon cooling** the **solution-intermolecular bonds** are established between the **chains**.

**For this sample a gel may also be induced if the sample is exposed to oscillation, shear or shaking.**

A simple schematic illustration of shear induced gelation in pectin solutions



Solution in the quiescent state



Shear induced gelation

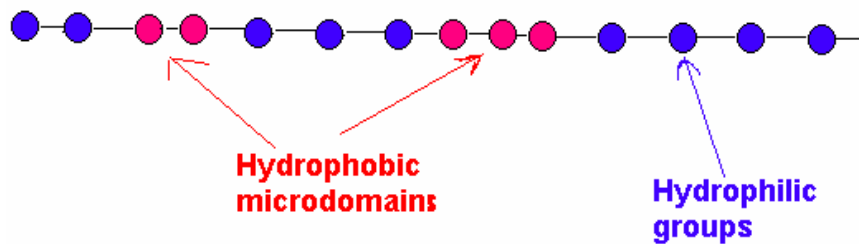
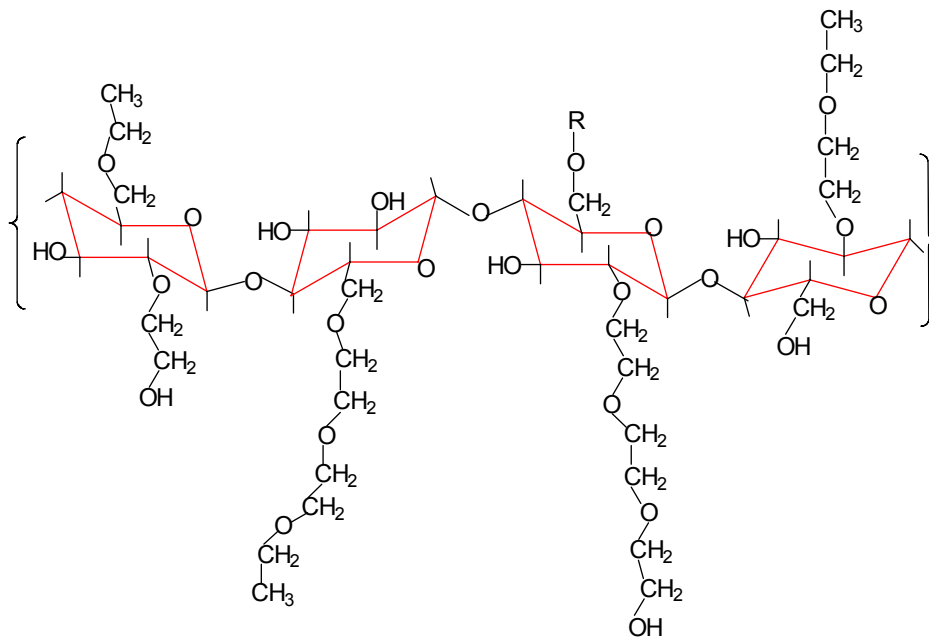
**The shear-induced stretching and alignment of polymer chains promote the formation of more sites becoming accessible for intermolecular hydrogen bonding and hydrophobic associations.**

## An example of a gelation process taking place

upon heating the solution:

System: Ethyl(hydroxyethyl)cellulose(EHEC)/ionic  
surfactant/water

### EHEC

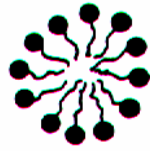




EHEC ( $M \approx 200\ 000$ ) is a **nonionic water-soluble cellulose ether**. This amphiphilic polymer consists of *hydrophobic* (ethyl) *hydrophilic* (2-hydroxyethyl) groups.

Surfactants: Molecules (reduce the surface tension) that are characterized by having two distinct regions in their structure, namely *hydrophilic* (“water-liking”; head) and *hydrophobic* (“water-hating”; tail) regions. At a certain concentration c.m.c. (critical micelle concentration) these amphiphilic molecules associate to form *micelles*.

Formation of micelle



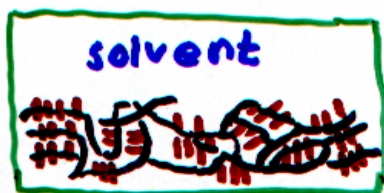
Semidilute solutions of EHEC in the presence of an ionic surfactant (moderate conc.) (SDS, CTAB) form thermoreversible gels at elevated temperature.

What happens when heating an EHEC-water solution *without an ionic surfactant*?

Semidilute EHEC solution in absence of surfactant:

Elevated temperature

CP  $\cong$  34 °C



macroscopic phase separation

In this case *large macroscopic aggregates* are formed and we observe a *phase separation* (polymer + solvent).

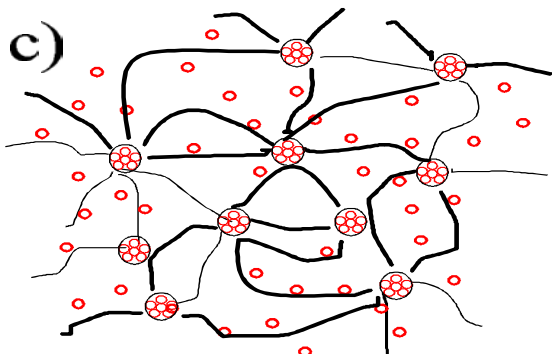
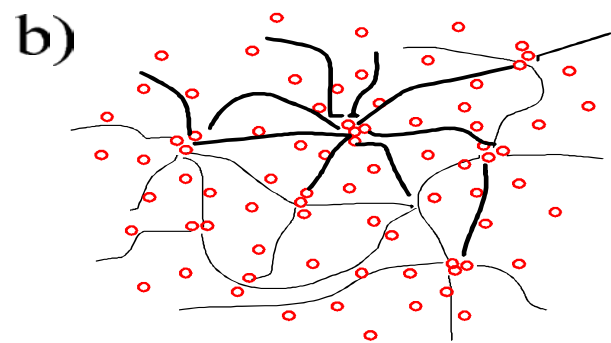
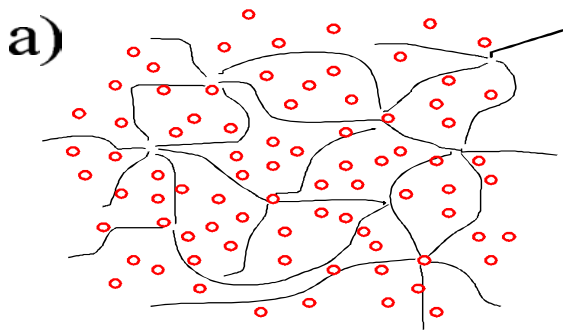
In the presence of *an ionic surfactant*, the phase behavior of the polymer is modified, because the surfactant causes *fragmentation of large domains* of the polymer-rich phase into *microscopic “lumps”* (microscopic phase separation).

The basic idea behind *gel formation* is that the gel has *connectivity* (hydrophobic associations or “lumps”) and *swelling properties* (caused by the ionic surfactant).


Thermoreversible gelation: A temperature increase promote the formation of “*lumps*” (connectivity) and these are kept apart through the *repulsive interactions* (swelling of the gel-network) generated by the ionic surfactant.

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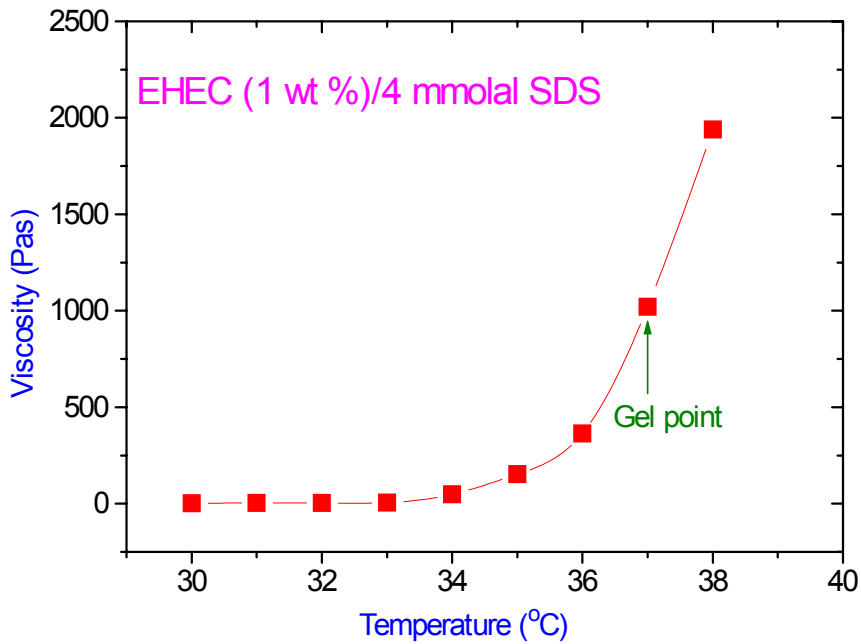
Thermoreversible gelation of aqueous EHEC solution in the presence of an ionic surfactant



Temp.increases a) → b) → c)

A rigid network (gel), where  act as cross-linking zones.

The change of the viscosity as the thermoreversible EHEC-surfactant gel evolves.



As the temperature increases a strong viscosity enhancement is observed and a gel is formed at 37 °C.