Surface, Optical and Thermal Characterization of Nanoparticle Systems

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- Introduction, aim
- Wettability
- Optical properties
- Thermal properties
- Practical Example, current research

Materials Characterization:

✓Test of the synthezided nanocrystal
✓Well defined properties capture the useful characteristics of materials

✓The caracterization constitue an essential background for....
•Processing
•Designing the structure to achieve specific properties of materials
•Control of the performance

Polymers

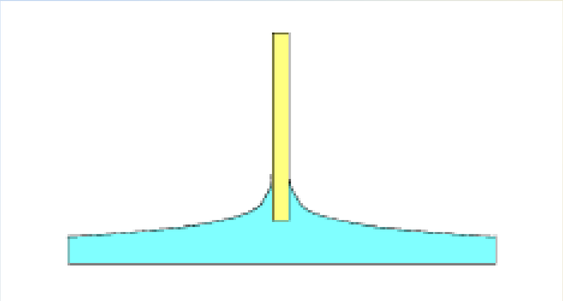
- Polymers are attractive because they are usually lightweight and inexpensive to make, and usually very easy to process, either in molds, as sheets, or as coatings.
- Most are very resistant to the environment.
- They are poor conductors of heat and electricity, and tend to be easy to bend, which makes them very useful as insulation for electrical wires.
- Polymers offer often a suitable matrix to insert nanoparticles

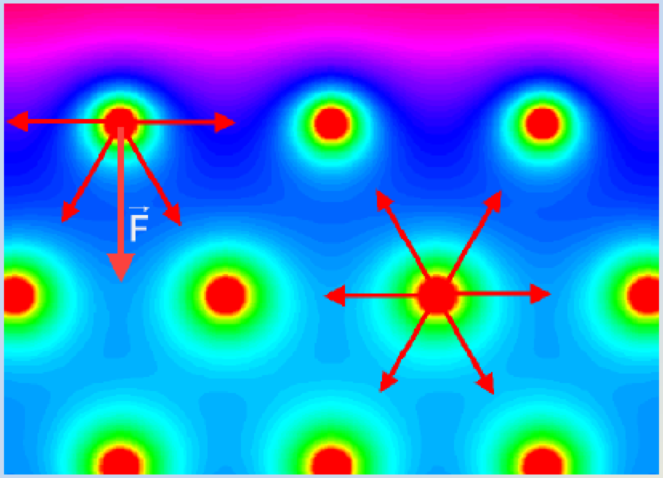
Nanoparticle Systems

- Doping polymers by nanoparticles in order to modify, enhance properties of materials.

Wetting and Adhesion Properties of materials

Surface tension (or surface energy) is the ammount of work necessary to form a new part of surface.

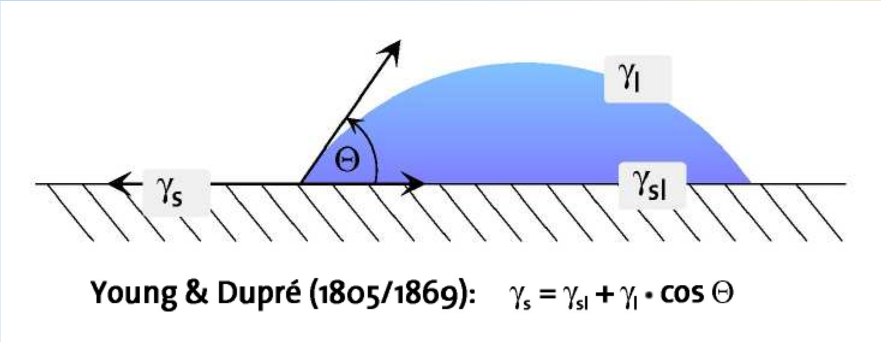




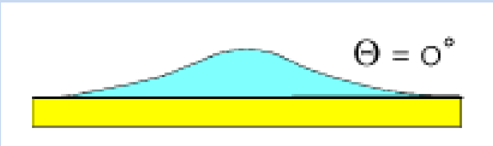
The surface tension is due to the different integrated molecular or atomic forces in the material interior and on the surface.

The surface of a material has a free energy larger then in the bulk material: the area of the material is therefore minimized.

The surface tension of solids (γ_s) is related to their wettability and is an usefull parameter for the study of the interactions between the solid surface and the biological surround.

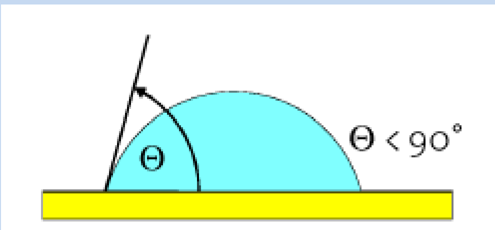


Wetting is the phenomenon of the adherent contact of liquids to the surface of solids (or other liquids). This can be evaluated by the measure of the contact-angle between a drop of liquid and a solid surface (Θ).
This is the **static contact-angle**, in this case the liquid should give rise to a symmetric drop on the solid surface.



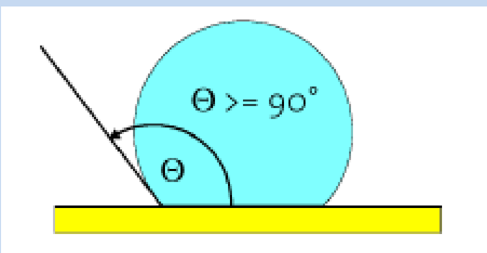
$\theta = 0°$ totally wetting

Hexane on polyethylene
Water on gold



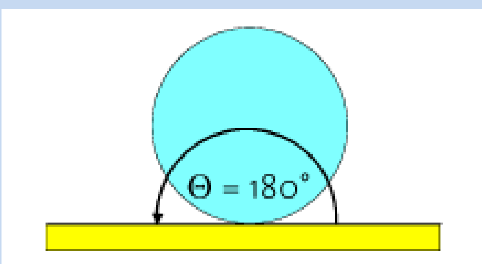
$\theta < 90°$ partially wetting

Water on glass (10° to 15°)
Water on PMMA (74°)



$\theta \geq 90°$ non wetting

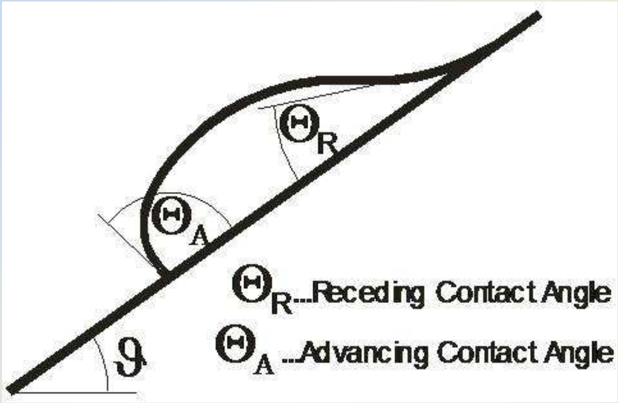
Water on teflon
Water on polypropilene



$\theta = 180°$ totally non wetting

180° not possible with gravity
Solid surfaces with contact angle above 150° are considered as super hydrophobic.

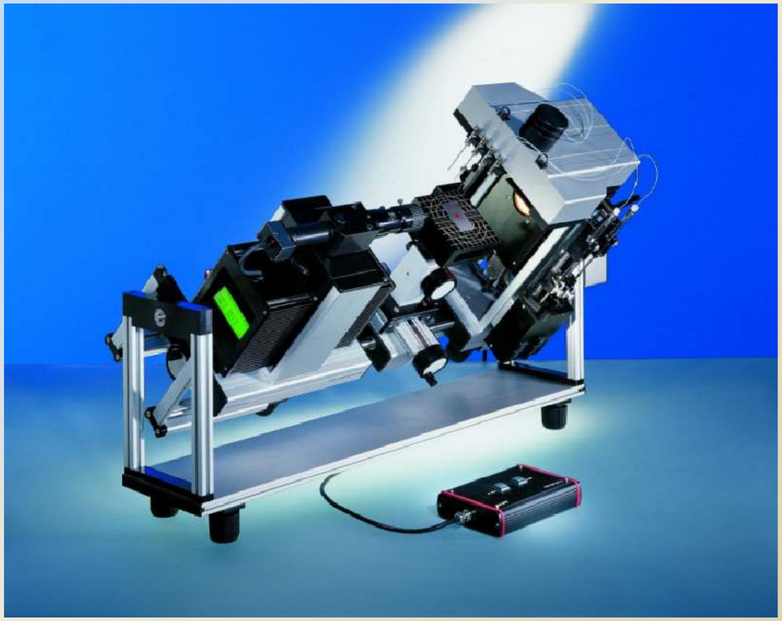
We refer to a dynamic **contact-angle** in case of a liquid drop mouving on a solid surface. In particular we can define an advancing contact angle (Θ_A) and a receding contact angle (Θ_R).
The difference between these two angles (Θ_A- Θ_R) is called **hysteresis** of the contact-angle and determines the pinning force of the drop on the surface.



The measure of the hysteresis of the contact-angle is a measure of the morphological properties of the surface.

Drop Shape Analysis Method

- Takes images of the droplet at hight magnification
- Analyse the immage to determine the droplet profile
- Fits the experimental profile with the theoretical profile
- Determines the surface tension γ and the contact angle Θ as fitting parameters



Printing:

the ink must not spread out → Large contact-angle
the ink has to be absorbed → time dependence of the contact-angle

Coating and varnishes:

coating/varnish should be continous → small contact angle

Contact adhesives:

the knoledge of the surface tension of both adhering components and their polarities is important for a correct choice of the adhesive

Biocompatibility:

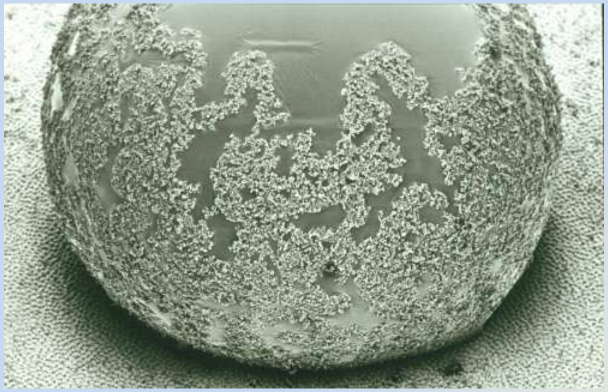
hydrofillicity of a surface is an important characteristic of biocompatibles materials

Self-cleaning surfaces,
What we can learn from Nature

Chemical modification of smooth solid surfaces can tipically lead to water contact angle up to 120° by using fluore polymeric or silane layes, but not more.

How to produce a super-hydrophobic surface (θ >150°)?

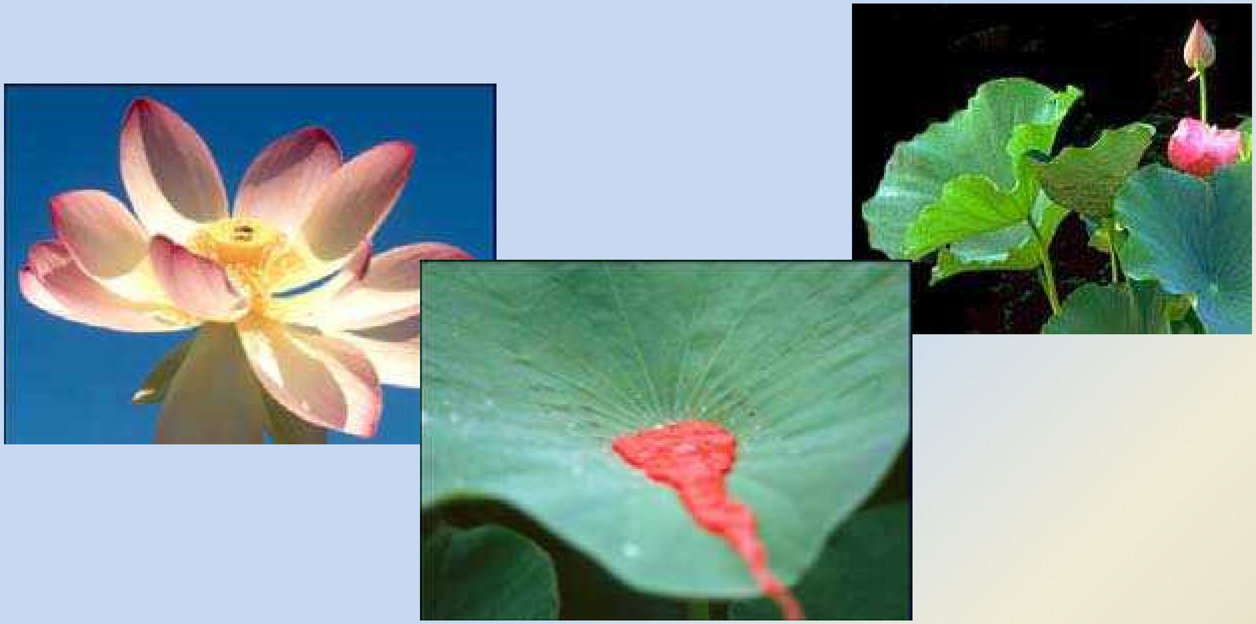
The equilibrium shape of the drops on solid surface is only half of the story - to clean the surface the material (dirt) has to be transported along the surface and best off it.



Lotus self-cleaning effect

Water drops rolling down the lotus leaf surface pick up the dirt particles and effectively clean the leaf surface.

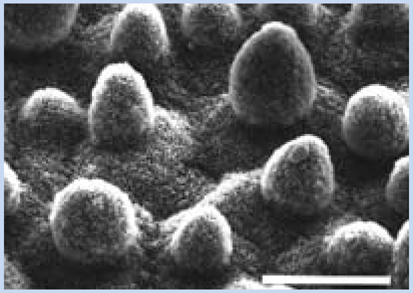
Lotus plant-Nelumbo Nucifera



Some plant leafs have contact angles approaching 180° (Lotus effect)

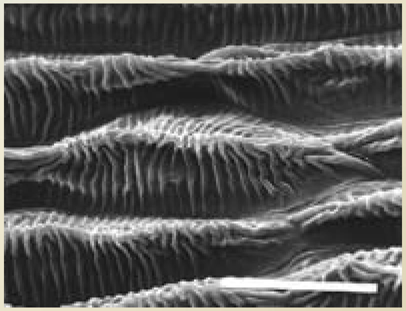
To reach the extreme values of the contact angle near 180° the surface must be not only hydrophobic but also must have a special structure

Super hydrophobic surfaces, such as lotus leaves, with micro/nano combined structures found in nature have attracted many researchers' interest because of their importance in fundamental research and practical applications such as self cleaning, anti-fogging/snowing, drag reduction effect etc. In this regard, diverse methods have been proposed to produce such surfaces.



Nelumbo Nucifera
the rough surface is characterized by papillose epidermal cells and aditional layer of epicuticular waxes

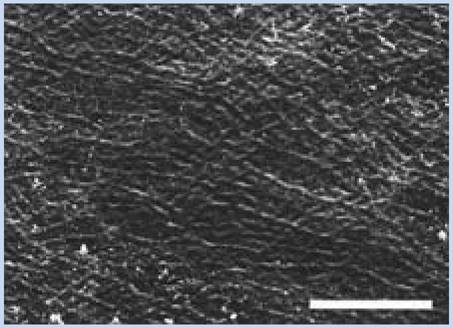
Mutisia Decurrens
the petal surface is characterized by cuticular folds



For low- energy surface roughness promotes drying:
It becomes energetically 'expensive' for the liquid to follow the surface corrugations. For hydrophobic materials surface nanostructuring enhance hydrophobicity.

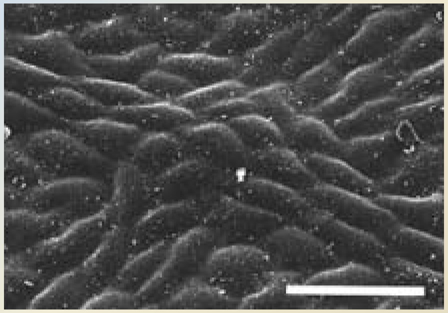
Hydrophilic surfaces

If the surface has a high interfacial free energy, roughness promotes wetting and liquid will accumulate within the corrugation.



Gnetum Gnemon
the smooth leaves are almost lacking microstructures

Magnolia Denudata
the leaves are characterized by sunken and raised nervatures



Summarizing: wettability is improved by roughness for hydrophilic surfaces ($\theta^* < \theta$ for $\theta < 90°$) but gets worse for hydrophobic surfaces ($\theta^* > \theta$ for $\theta > 90°$).

Optical Properties of materials

Refractive index

- Refractive index (*n*) measures how fast light propagates through a medium. This describe how different particles affect light propagation, measured with respect to air.
- The refractive index *n* of a dielectric medium is:

$$n = \frac{c}{v}$$

where c is the speed of light in vacuum, and v is the speed in the medium.

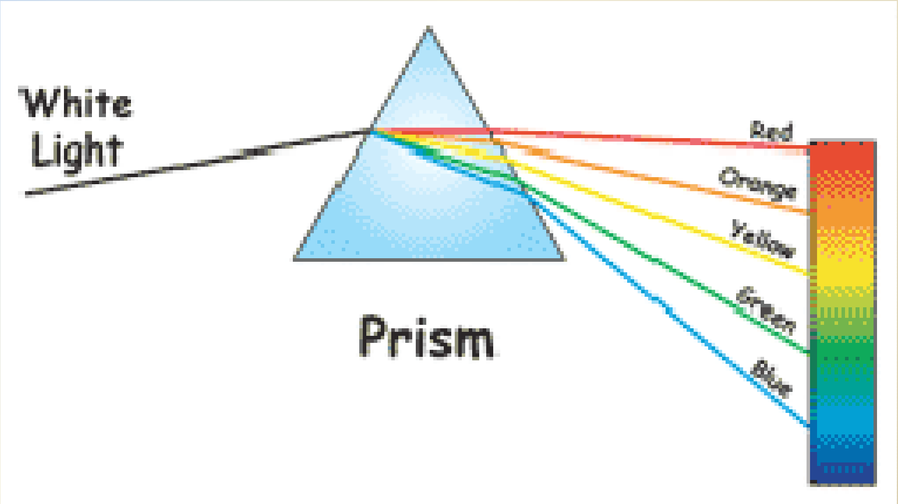
•Due to dielectric loss in real material the refractive index can be complex, with a real and imaginary part.

$\tilde{n}(\lambda) = n(\lambda) + ik(\lambda)$

Value of the imaginary part is a measure of the absorption strength.

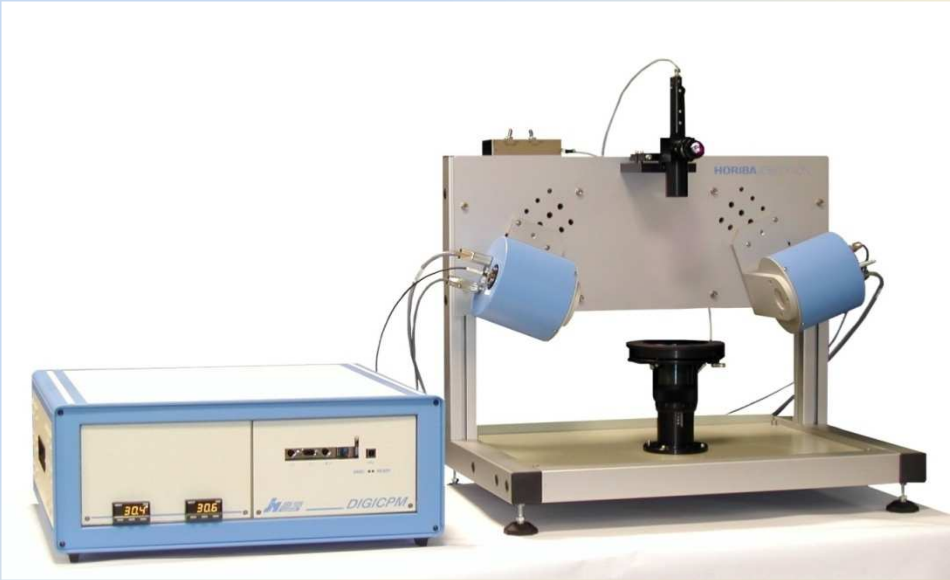
•For most media, refractive index varies with wavelength.

This gives the familiar rainbow spectrum with white light in glass or water.



Ellipsometry Overview

- Technique that determines the change in polarization state of light reflected from a sample.
- Typically used for characterizing thin films.
- Used in a wide range of applications.
- Non contact, non destructive method.



CAPABILITIES
Characterization of thin films, surface and interface

- **Thickness**

- Accurate thin film measurement from a few angstroms to several microns

- Characterization of single layer and complex multilayer stacks

- Characterization of surface and interface

- **Optical properties**

- Refractive index (n) and extinction coefficient (k) from the far-UV to near-IR for complex materials, graded and anisotropic layers

- **Material properties**

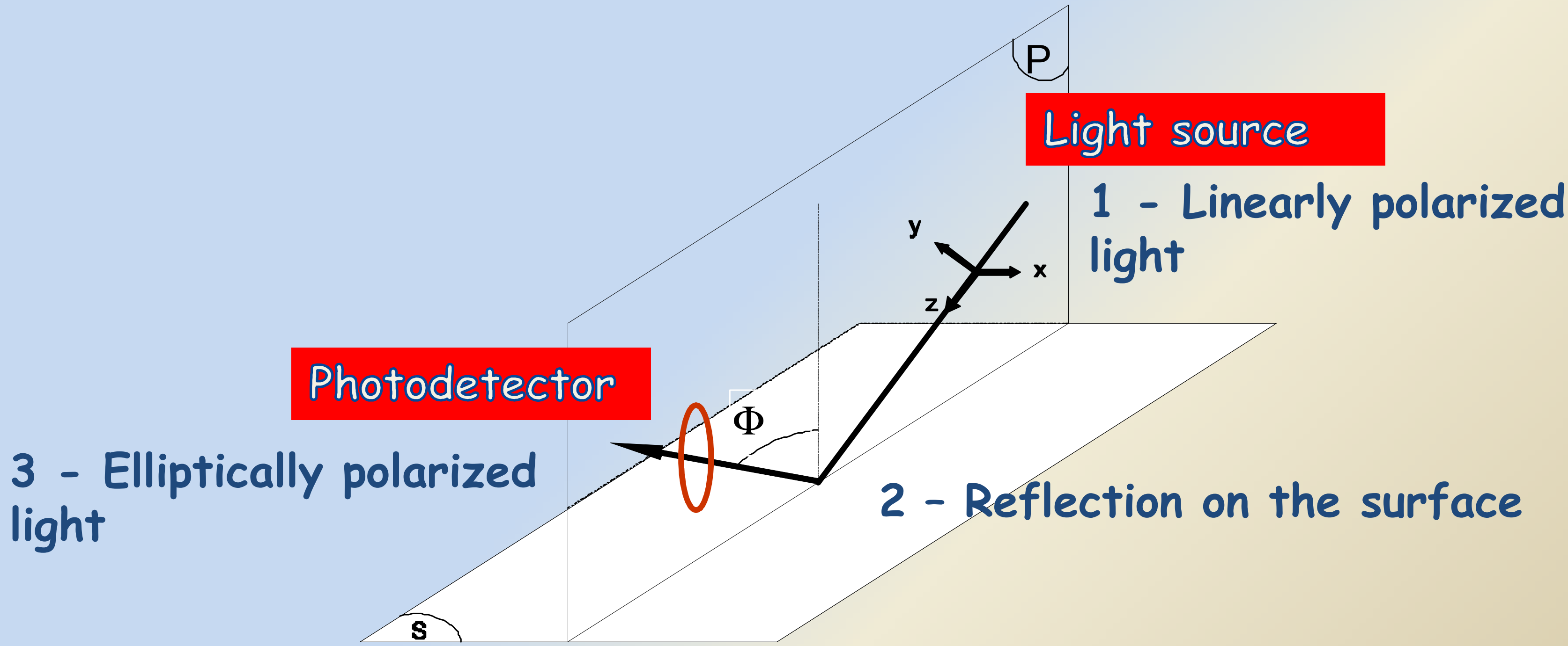
- Composition / crystallinity

- Microstructure

- Film uniformity by area and depth

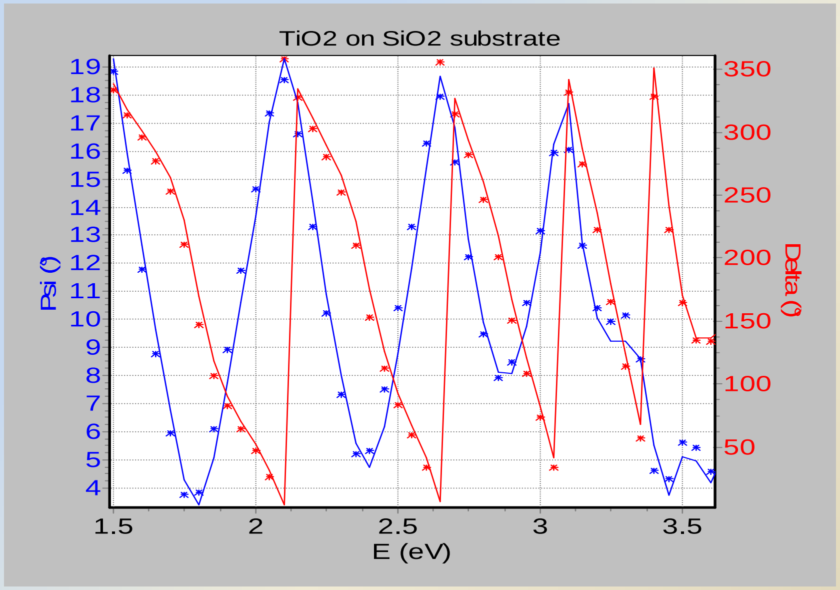
Technique

Measurement of the polarization change of light reflected from a sample in terms of two parameters Δ and Ψ.



ANALYSIS OF DATA

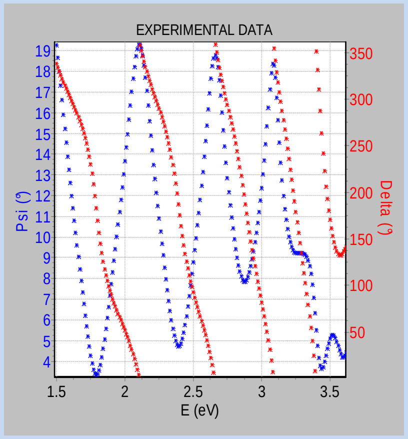
- Ellipsometry does not measure film thicknesses or optical constants, it measures Ψ and Δ



- To extract these informations from a sample, it is necessary to perform a **model dependant analysis** of the ellipsometric angles In this step, the number of layers is fixed, and the basic structure concerning the contents of each layer is set.

SE DATA ANALYSIS FLOWCHART

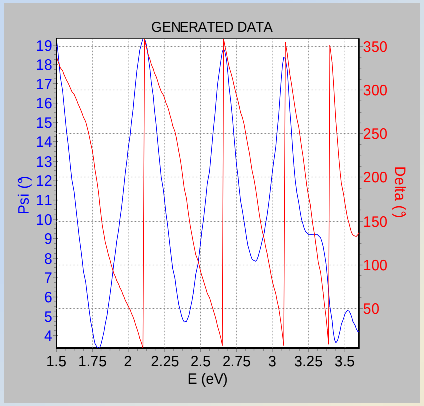
1 Measurement → **2 Model** → **3 Fit** → **4 Results**

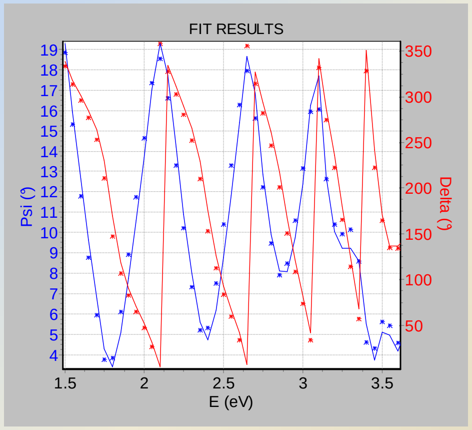


roughness

TiO_2

SiO_2 substrate

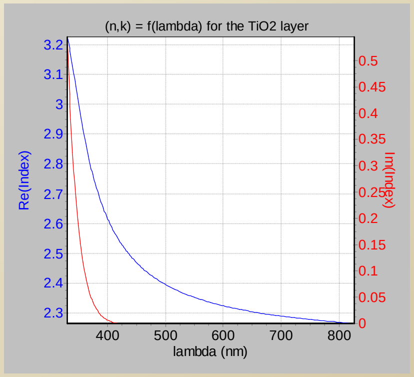




$\chi^2 = 1.6$

$d_{TiO2} = 4200$ Å

$d_{rough} = 20$ Å



Thermal Properties of materials

Well defined properties/characteristics which allow us to answer questions like

•How does an engineering component change size when heated?

•How well does it transmit heat?

•How will its temperature change when heated?

•At what temperatures can I use it?

Thermal Analysis

- Differential Scanning Calorimetry (DSC)
  - Measure difference of heat absorbed or liberated during heating or cooling in respect to a reference

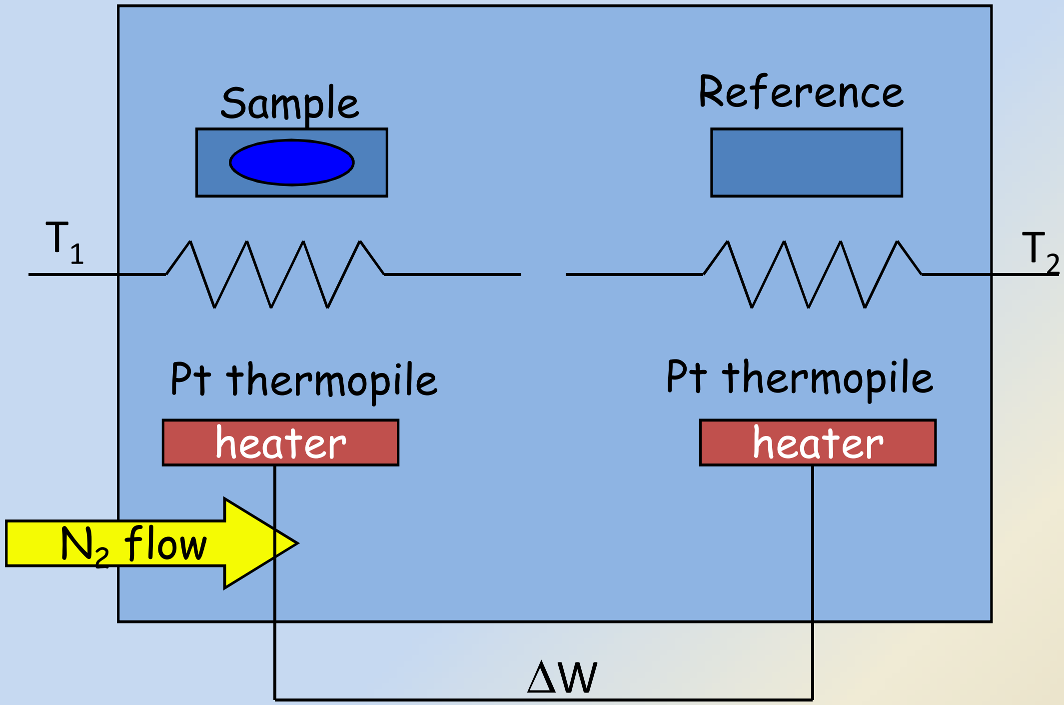
What Can You Measure with DSC?

- Qualitative analysis
  - Fingerprinting of minerals, clays, polymers
- Sample purity
  - Melting points
- Heat capacity, c_p
- Glass transition temperature, T_g
- Crystallization temperature, T_c
- Phase diagrams

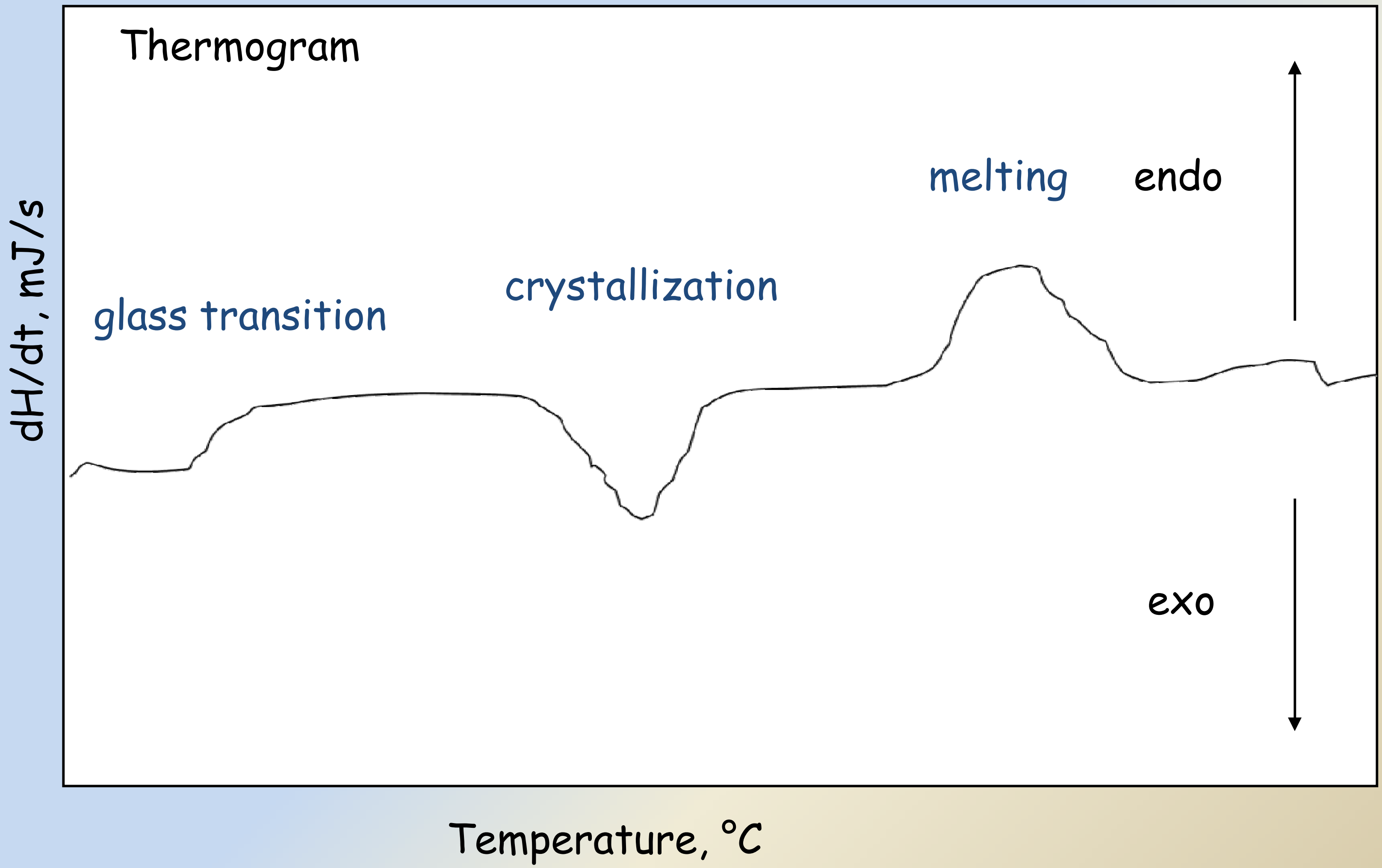
Where Used?

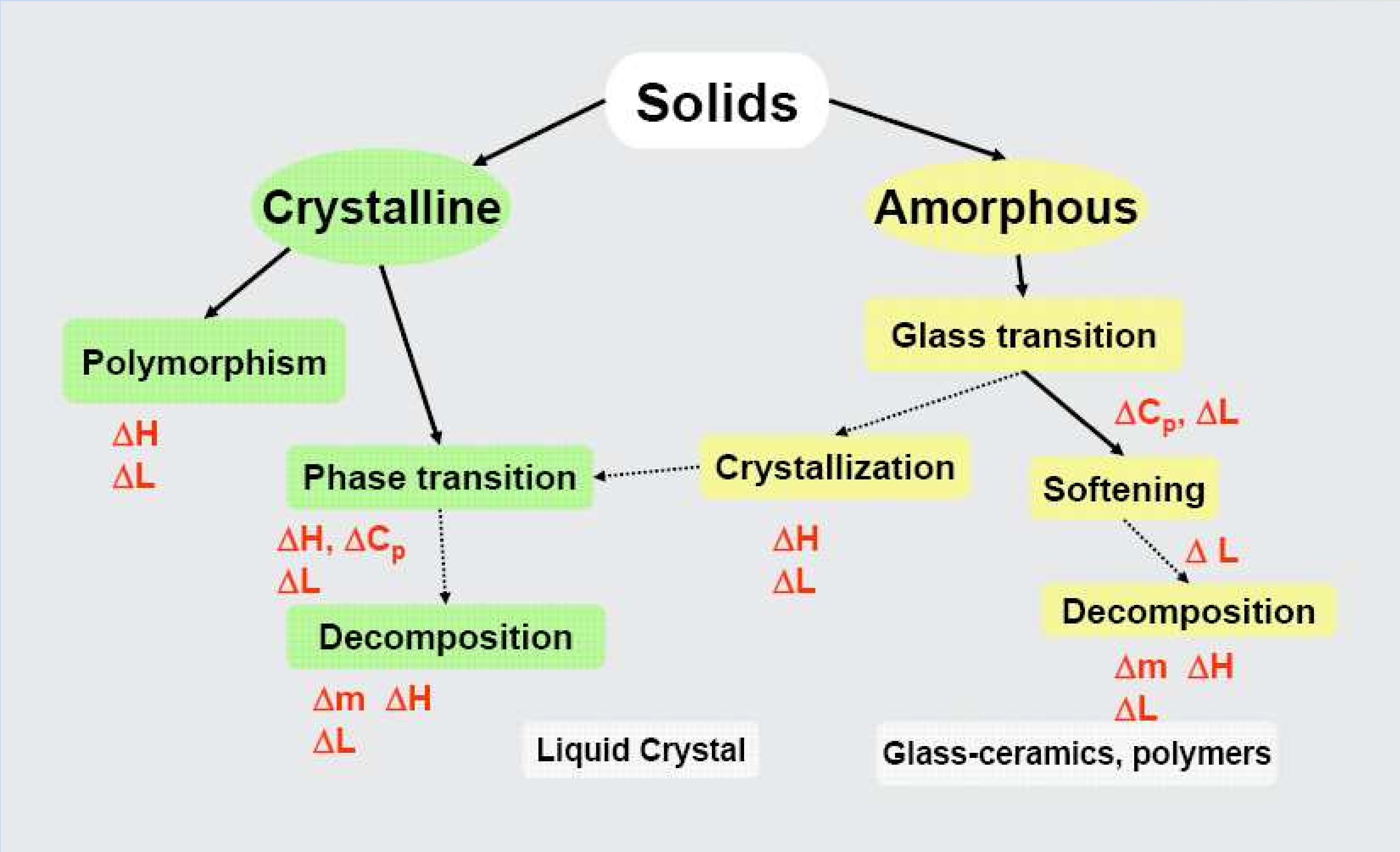
- Pharmaceutical industry
  - Purity
- Food industry
  - Characterization of fats and oils
- Polymer industry
  - Synthetic blends

Schematic of DSC Instrument



Output of DSC





Solids
Crystalline
Amorphous
Polymorphism
ΔH
ΔL
Phase transition
ΔH, ΔCp
ΔL
Decomposition
Δm ΔH
ΔL
Glass transition
ΔCp, ΔL
Crystallization
ΔH
ΔL
Softening
Δ L
Decomposition
Δm ΔH
ΔL
Liquid Crystal
Glass-ceramics, polymers

Phase Diagrams

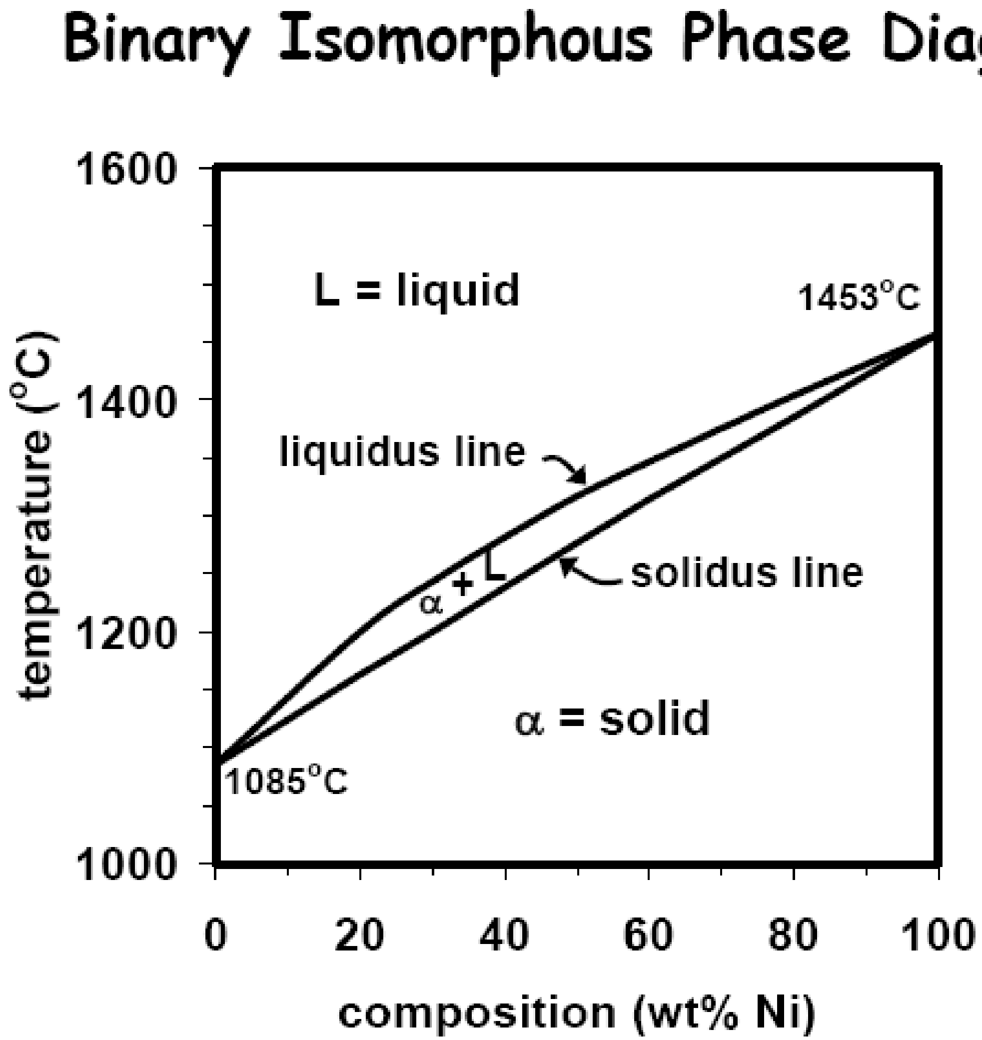
• Graphical representation of relationship between phase composition and a state variable (often temperature).

• The phase diagram allows to determine phase compositions and phase amounts at any point on a binary diagram.

• Phase a homogeneous, physically distinct, region of matter (solid, liquid).

Completelly soluble mixture,

same shape so can substitute each other



2 phases:
L, α

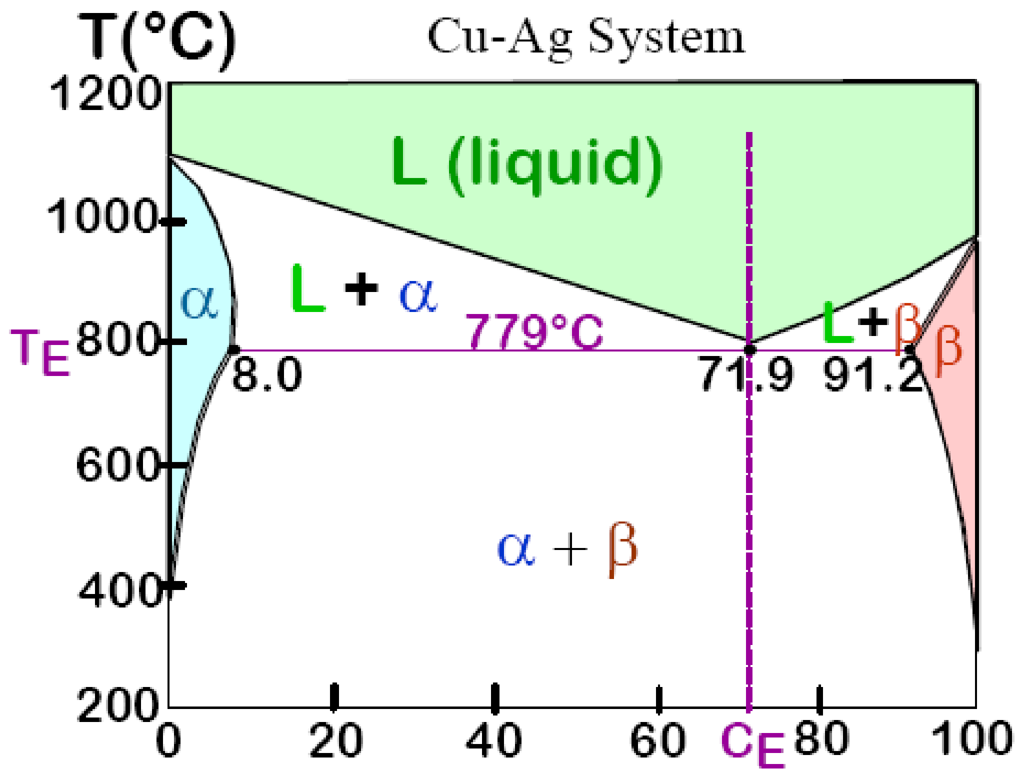
3 phase fields:
L, α + L, α

Binary Eutectic Phase Diagrams

- for 2 components with limited solubility in each other
- can form two different solid phases (eutectic)

α: Cu containing fraction of Ag

β: Ag containing fraction of Cu



Callister 2003

The example:
PEMMA+SP

The idea

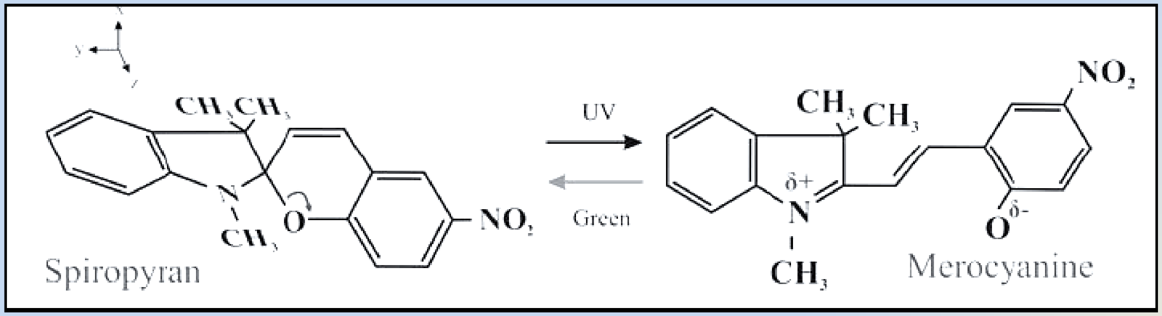
enhance the properties of the copolymer (PEMMA) by mixing it with photocromic molecule (SP).

Poly(ethyl methacrylate)co-poly(methyl acrylate), shortly called here PEMMA

+

1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole, shortly called here SP

The propertes of the resulting material can be furtherly enhanced by surface nanostructuring.



The embedded non-polar spiropyran molecules can be converted to their polar merocyanine, upon UV laser irradiation; the process can also be reversed upon green laser irradiation.

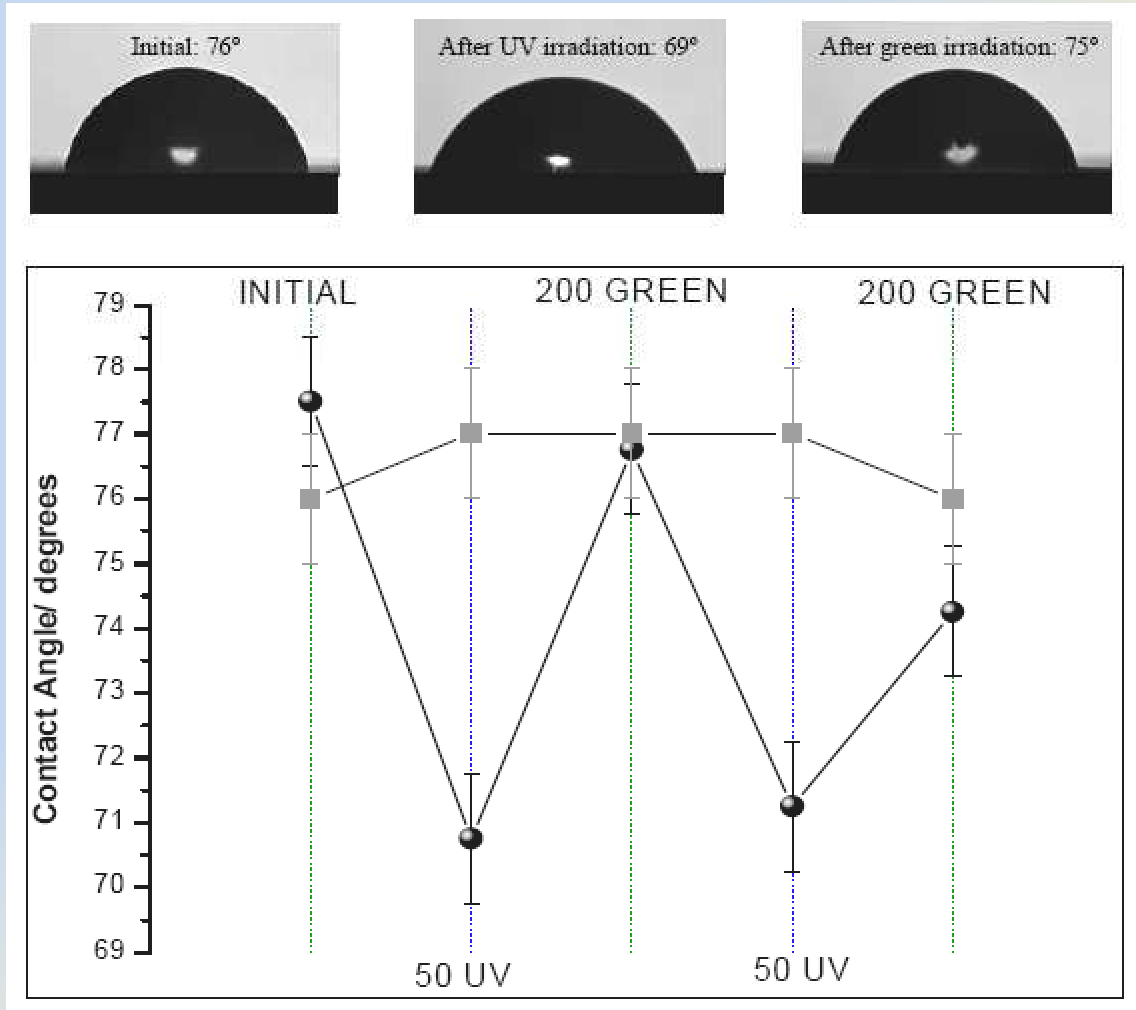
Insering the photocromic molecules in a polymeric matrix and eventually nanostructuring the surface of the film can allow for

⇒ Enhancing the different properties of the sample.

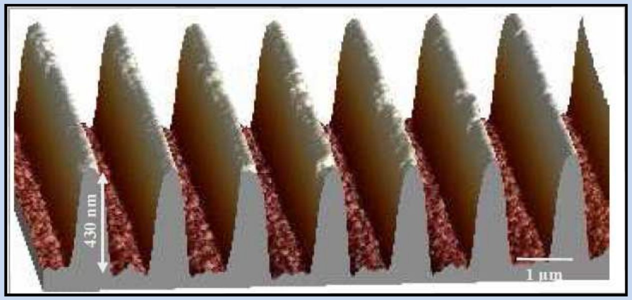
⇒ Optical control of the properties.

Photocontrolled variations in the wetting capability of photocromic polymer

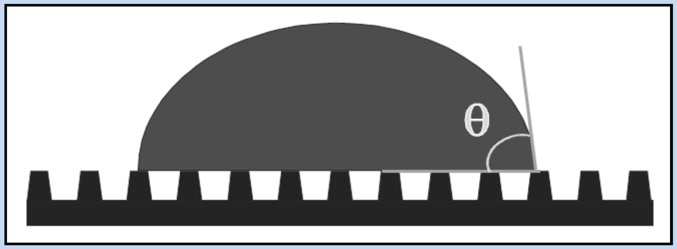
PEMMA + 5% SP
Due to the dipolar moment of the MC isomers the surface of the sample becomes more hydrophillic



Enhancement by surface nanostructuring

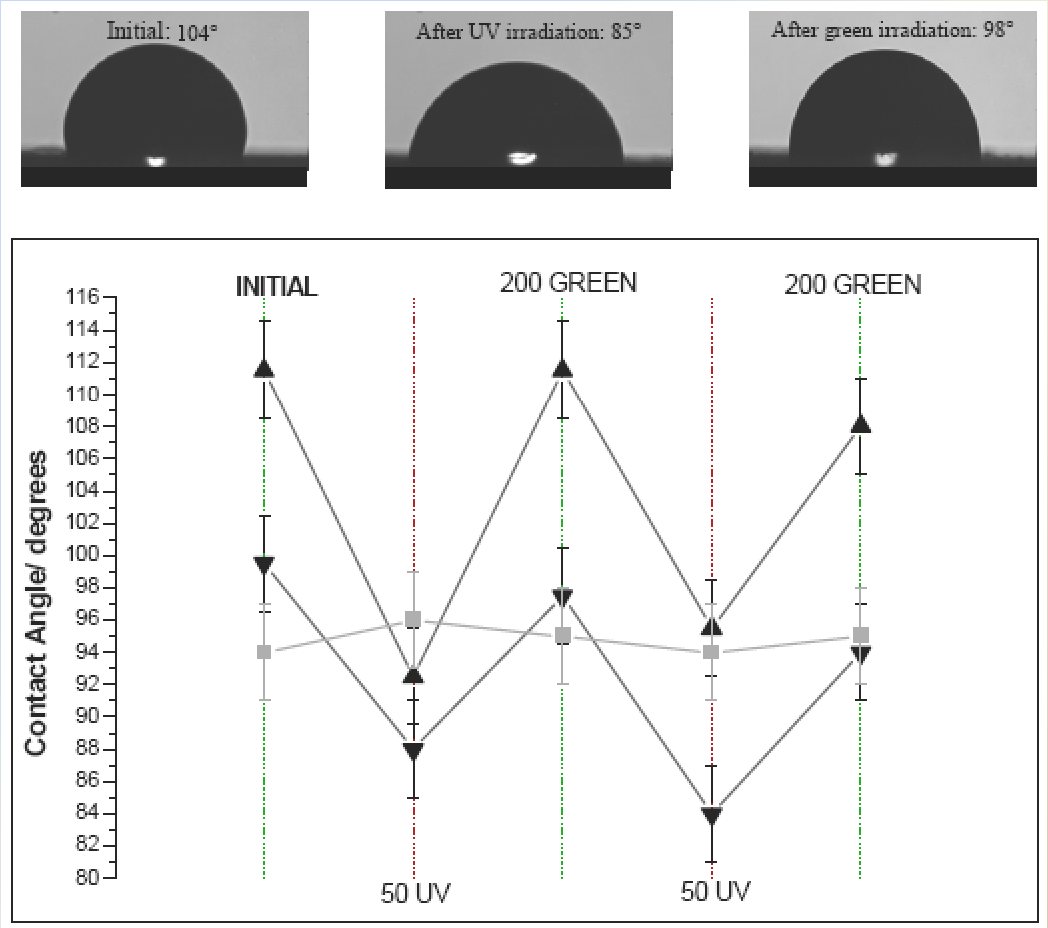


Nanoimprinted grating



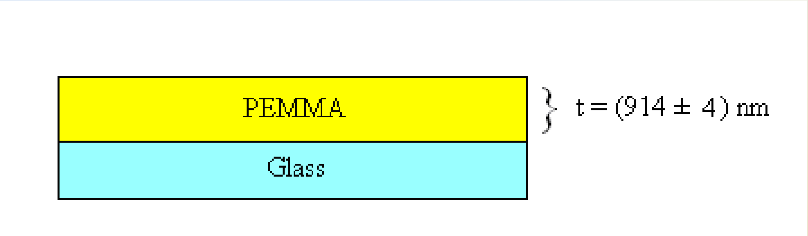
Cassie-Baxter model

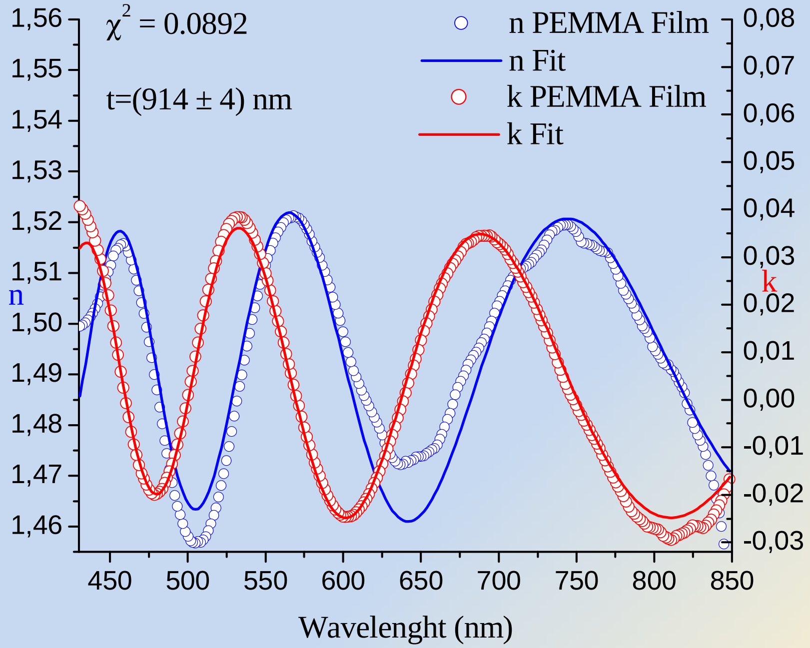
The surface roughness give rise to enhanced contact angle photo-induced differences.

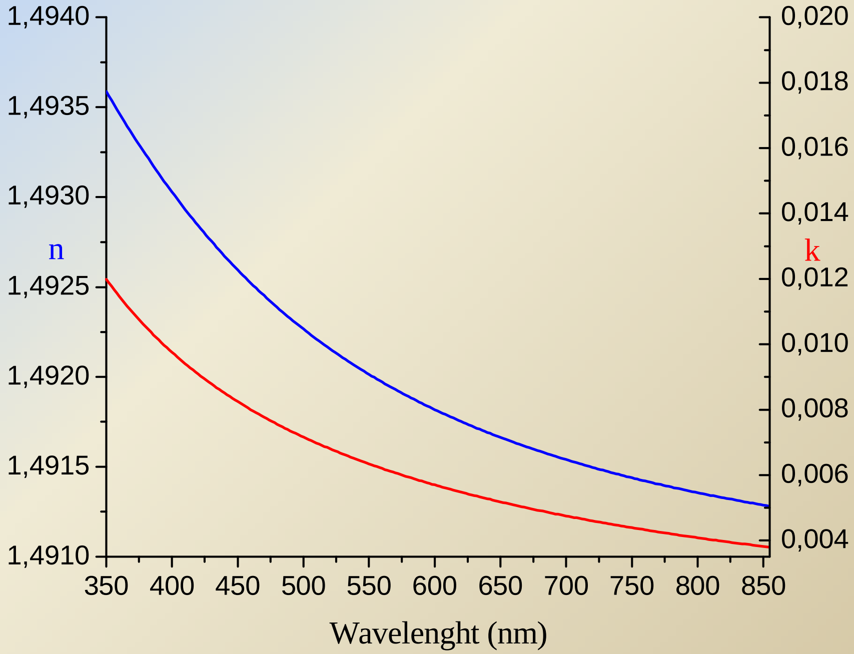


Photocontrolled changes in the optical properties of the photocromic polymer

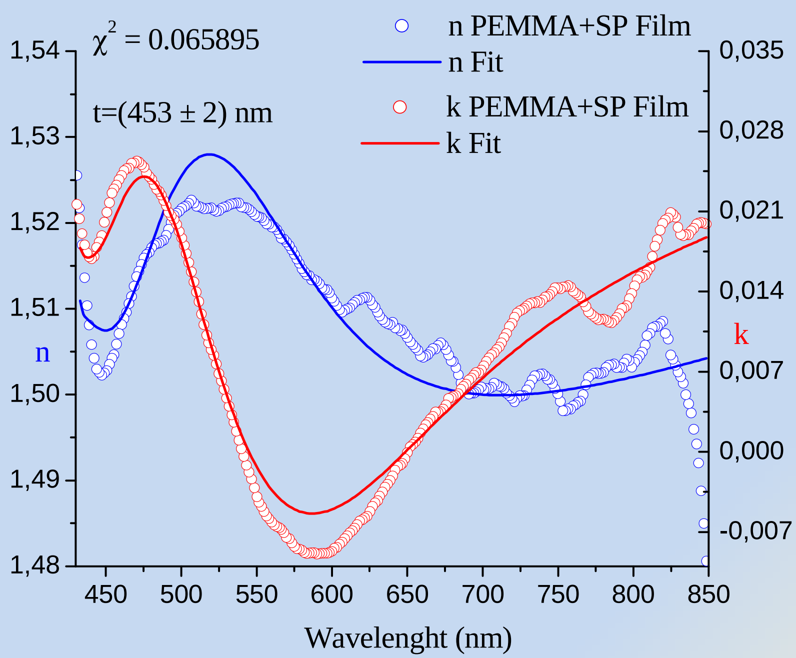
Polyethylmethacrylate-*co*-methylacrylate (PEMMA)

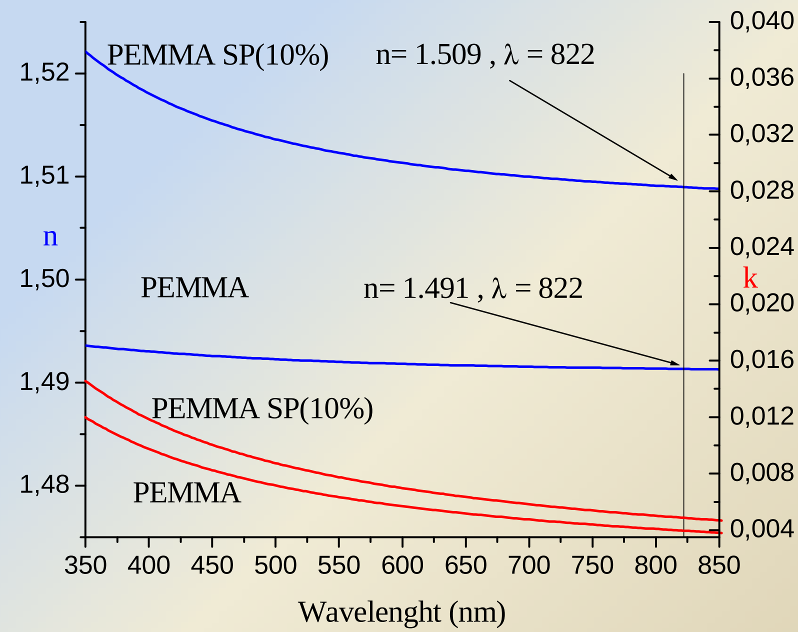






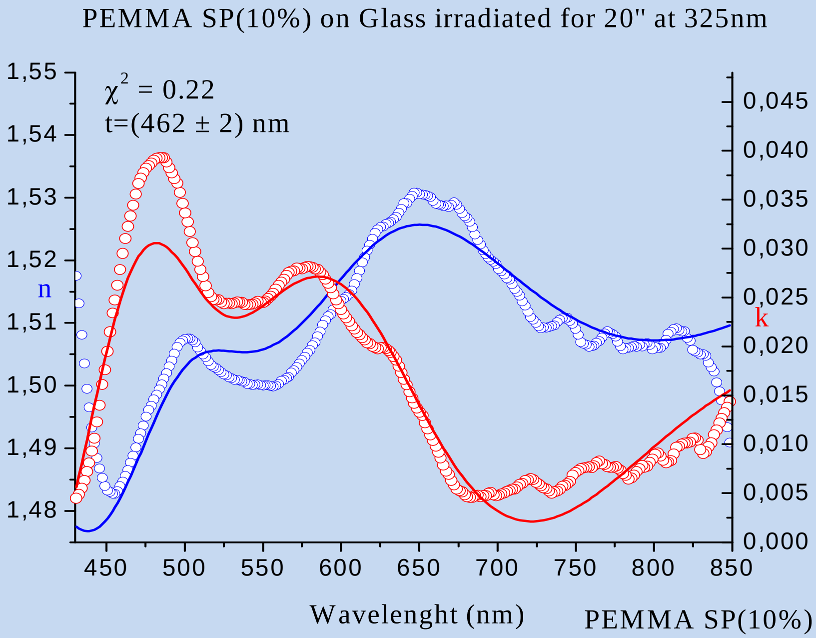
PEMMA + photochromic Spiropyran (10%)

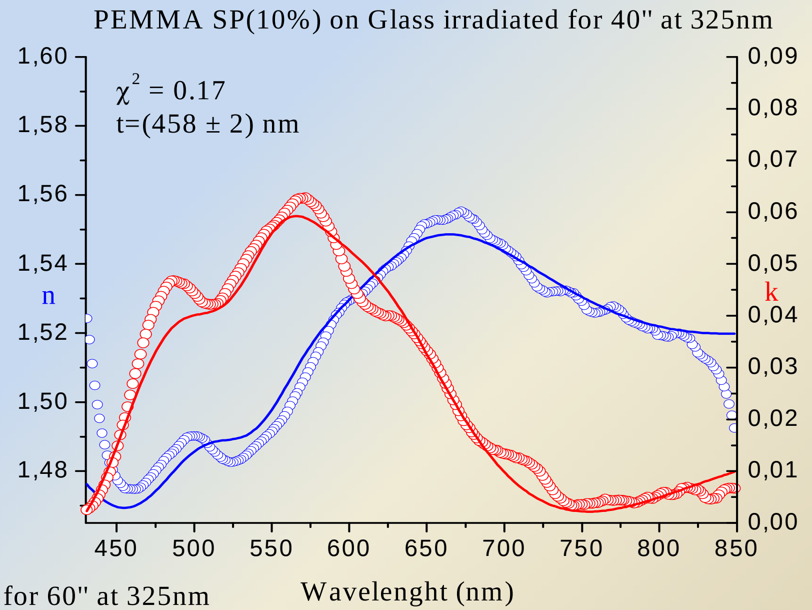


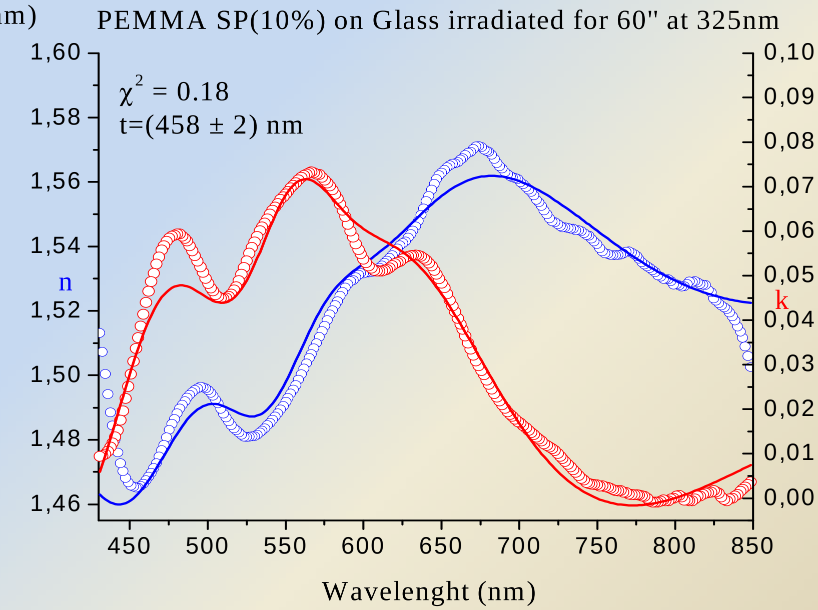


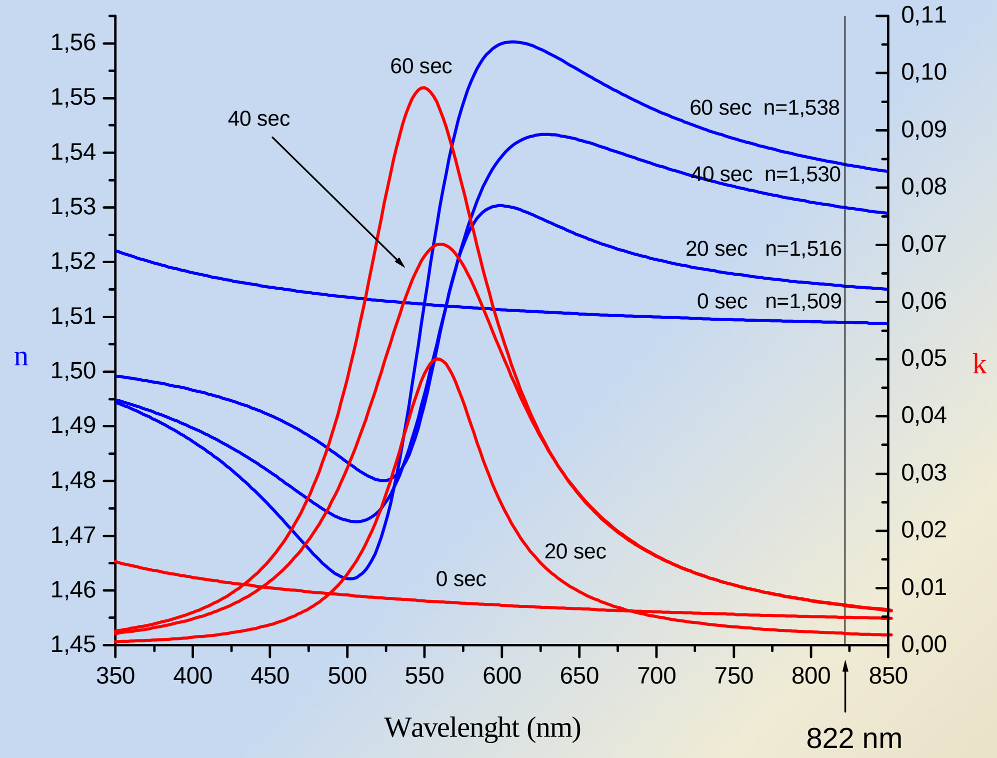
Doping the polymer the refractive index is slightly increased.

After cw He-Cd laser irradiation (325nm) the film shows an absorption peak around 550nm.



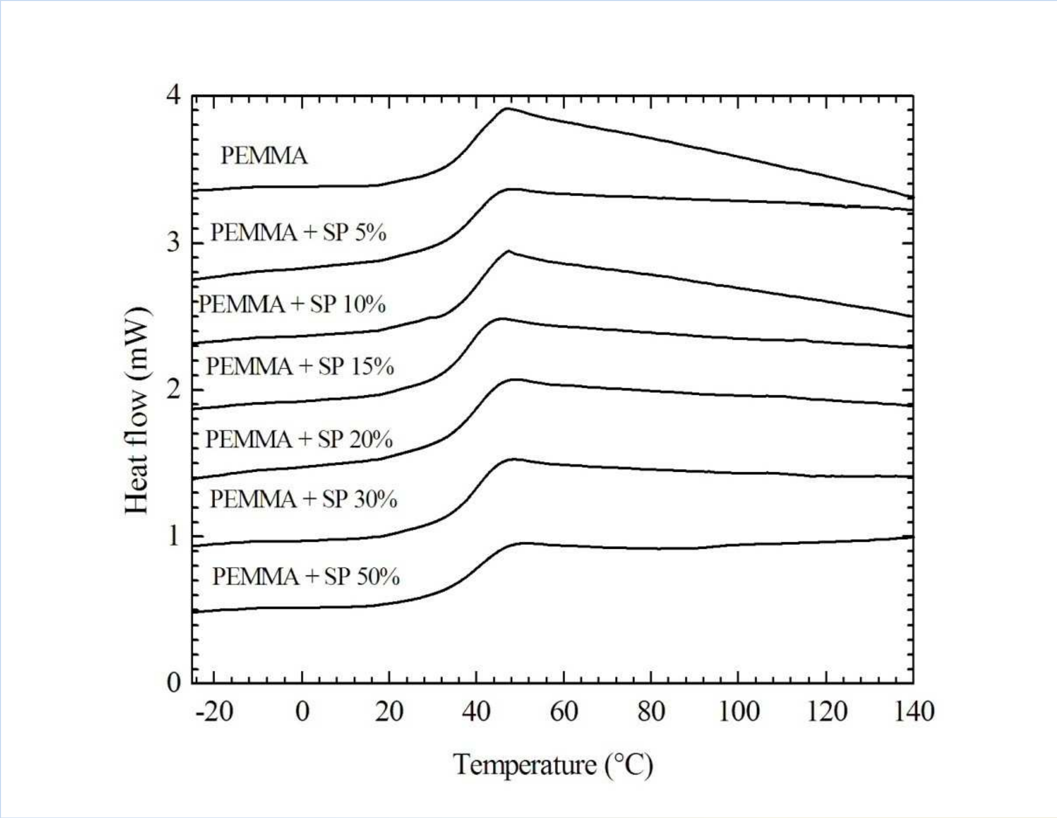






Increasing of the index of refraction and is absorption coefficient in function of the laser exposure time of the film. After 60 sec it reaches the saturation value. The sample change from transparent to red coloured.

Thermal characterization



Addition of small amount of SP in the polymeric matrix (5%, 10%, 15% and 20%) does not affect the T_g of the sample (39°C) while at higher concentrations the increase of the SP concentration causes the decrease of the T_g (for 30% T_g =38°C and 37°C for 50%)

Possible Applications?

- Microfluidic devices

The polymetric matrix doped with photocromic SP molecules can alter its macroscopic volume reversibily upon UV irradiation and green laser.

- Controlable drug delivery

Controllable surface absorption can allow for controllable release of drug.

- Self cleaning surfaces

Control droplet positioning and motion on a prepatterned substrate.

- Optical switch

The photocromic transformation between the SP and MC ,olecules can alter the macroscopic volume of their host polymer matrices.