SVILUPPO DI NUOVI MATERIALI PER OLOGRAFIA: DALLA MOLECOLA AL MATERIALE

Andrea Bianco
INAF – Osservatorio Astronomico di Brera, via Bianchi 46, 23807, Merate. Italy

Andrea.bianco@brera.inaf.it

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Merate (LC)

Milano

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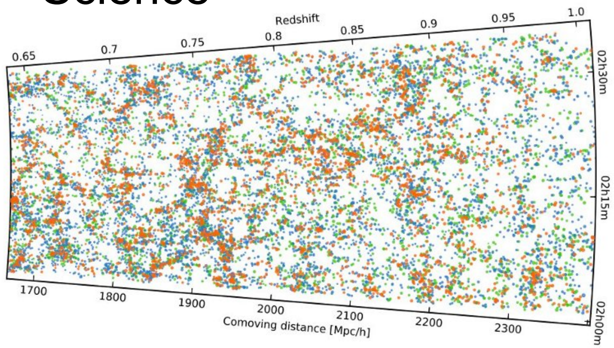
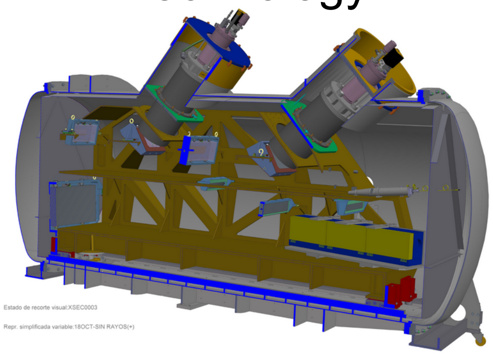
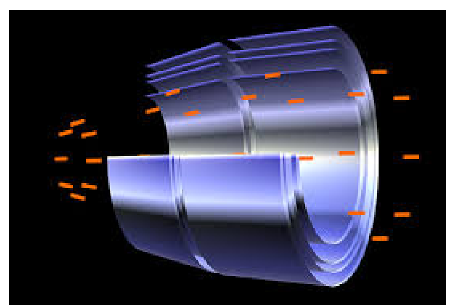
Science

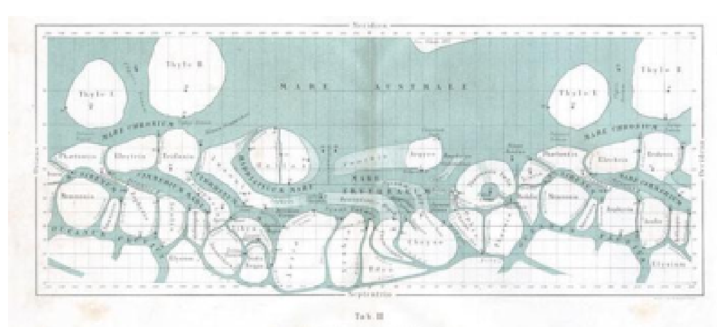


Technology





Museum, historical library



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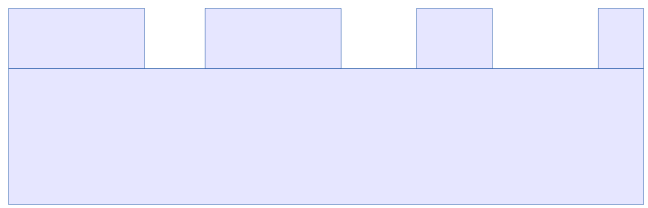
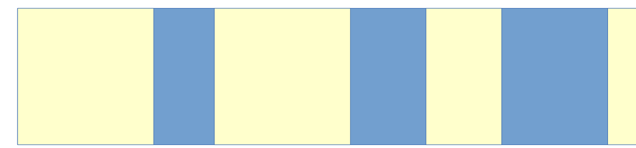
Hologram: families

An hologram is an optical element where it has been stored the light field of a scene.

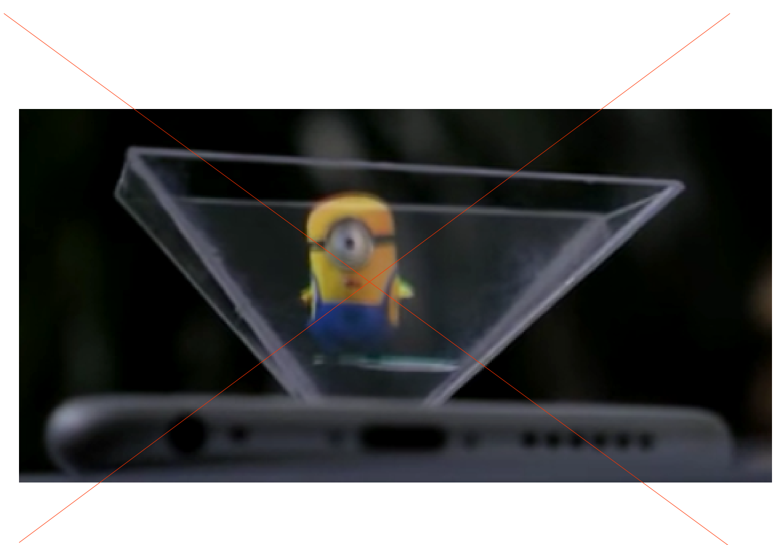




Amplitude Hologram
(opaque/transparent)

Surface Phase Hologram
(thickness modulation)

Volume Phase Hologram
(refr. index modulation)



Hologram: families

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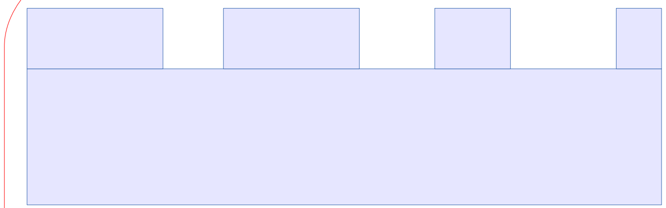

Surface Phase Hologram
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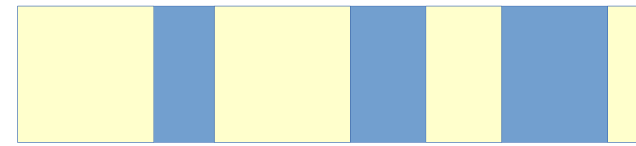

Volume Phase Hologram
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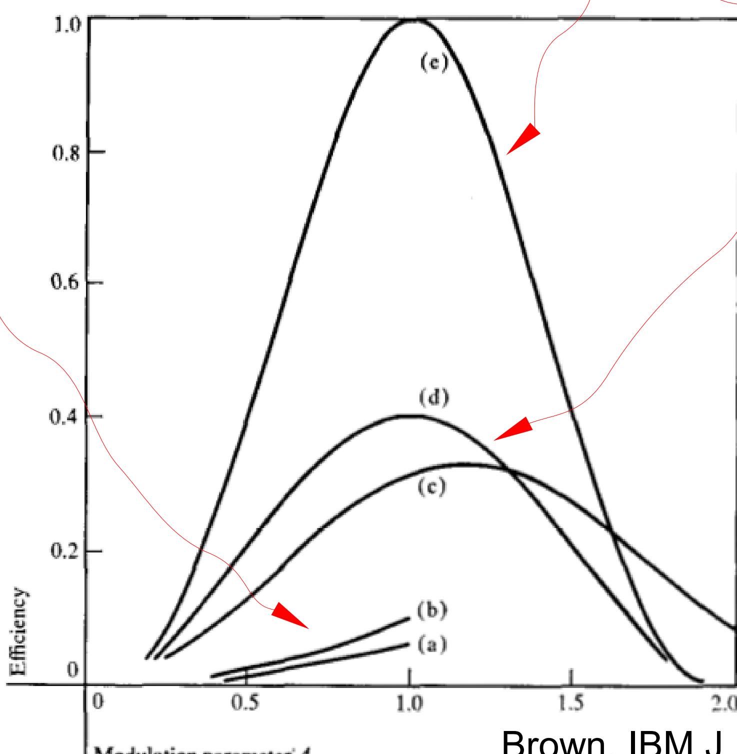
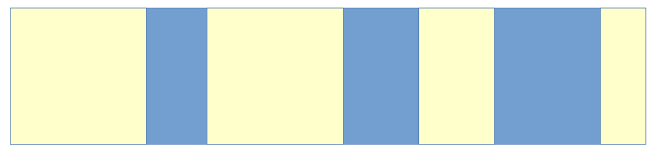


Brown, IBM J Res. Develop., 1969

The efficiency is really different between the holograms:
Amplitude holograms < 11%
Phase holograms up to 100%

Hologram:
Volume Phase



Volume Phase Hologram
(refr. index modulation)

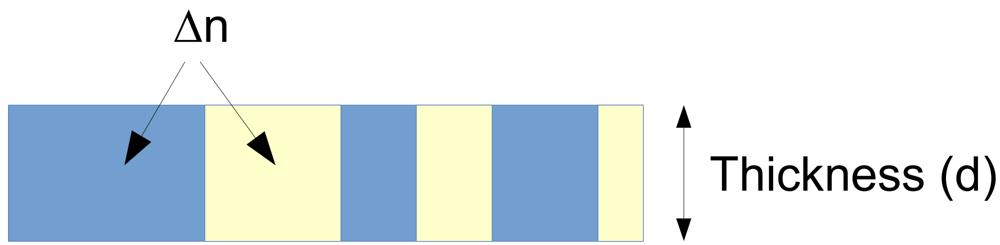
The holographic material must show:
- A modulation of the refractive index (large enough)
- Such modulation induced by light
- Fixation of the hologram (freeze the situation, no further reactions)

2.1. The ideal holographic recording material

There are several criteria, which an ideal material would satisfy:

1. The material must have a high resolution and a flat spatial frequency response. This will ensure that the desired interference pattern is completely stored, i.e. that no fine fringe detail is lost.
2. There must be a linear relationship between exposure and the amplitude of the reconstructed wave. This ensures the fidelity of the image at replay.
3. The material's dynamic range must be large enough for a sufficient modulation to be formed during recording, which will lead to a good signal to noise ratio.
4. The material should be of high optical quality and lossless. This will lead to high optical efficiencies (bright images).
5. Changes in environmental conditions should not affect the material and the recorded hologram should be stable for long periods of time.
6. The material should be sensitive enough to react to a low energy exposure.

What kind of hologram? Volume Phase



Volume Phase Hologram
(refr. index modulation)

Hologram efficiency: $d \times \Delta n \approx \frac{\lambda}{2}$

The holographic material must show:
- A modulation of the **refractive index** (large enough)
- Such modulation induced by light
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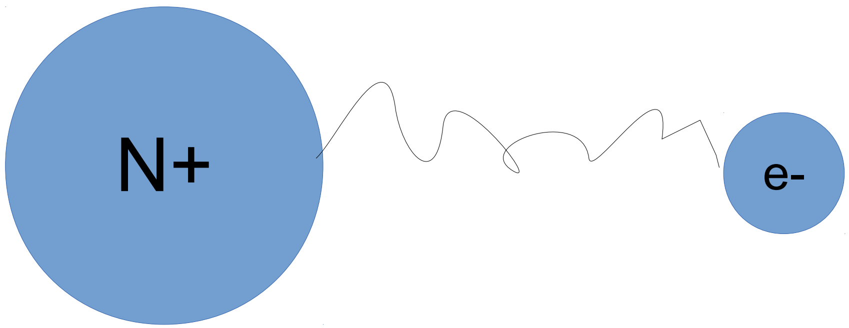
Refractive index in dielectrics

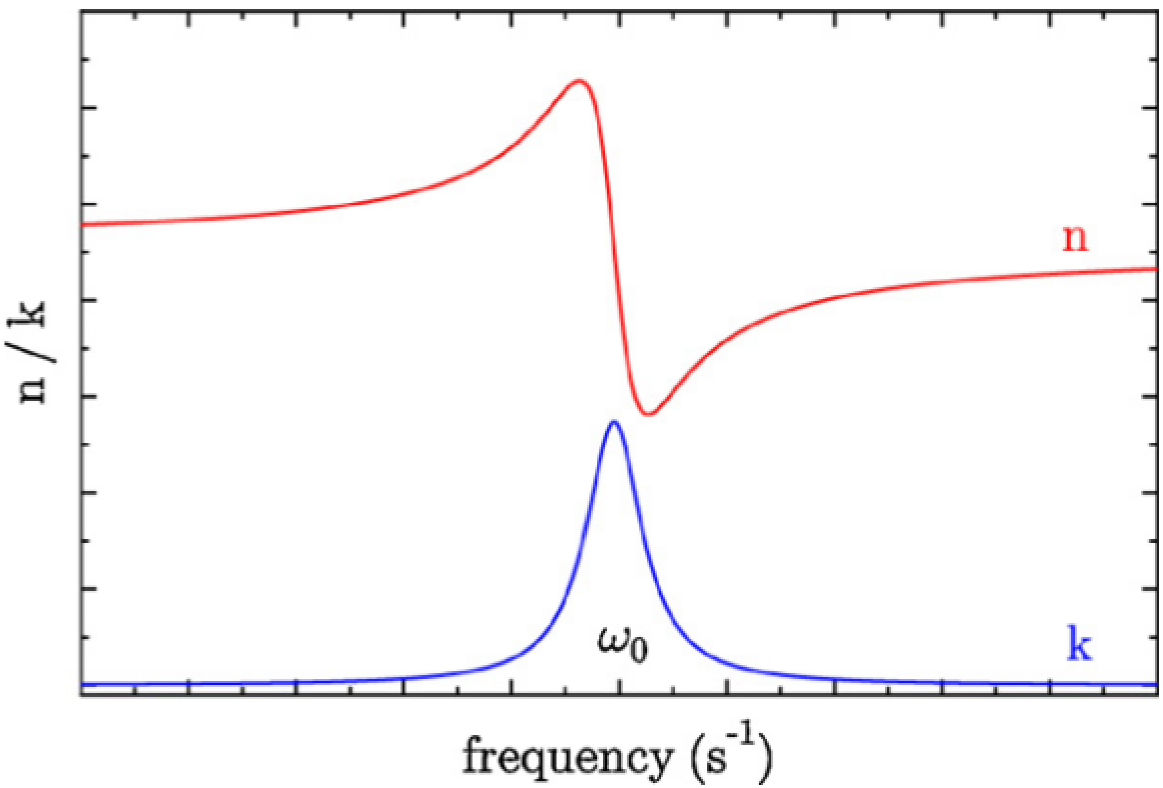
Lorentz model: the material is considered as a set of harmonic oscillators.



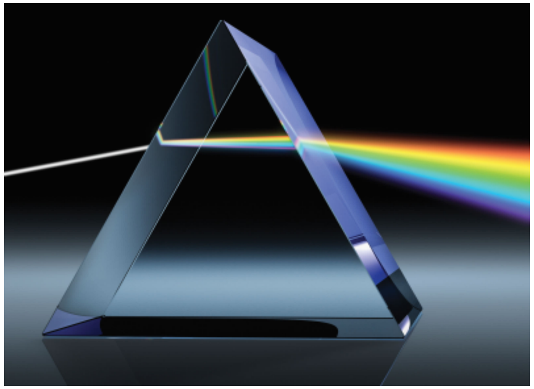
Complex refractive index

$$N = n + ik$$

Propagation — Absorption



The refractive index is a function of the light frequency/wavelength



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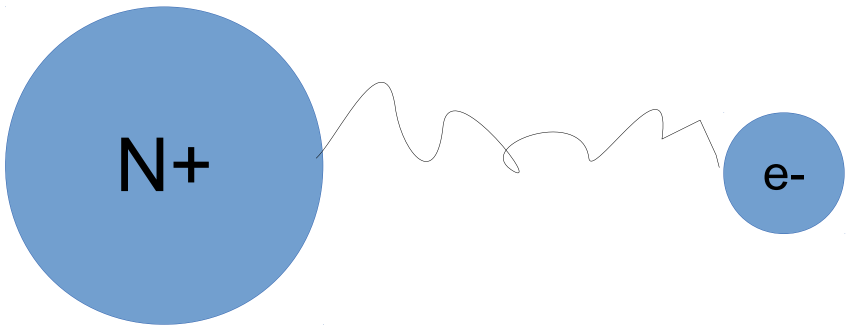

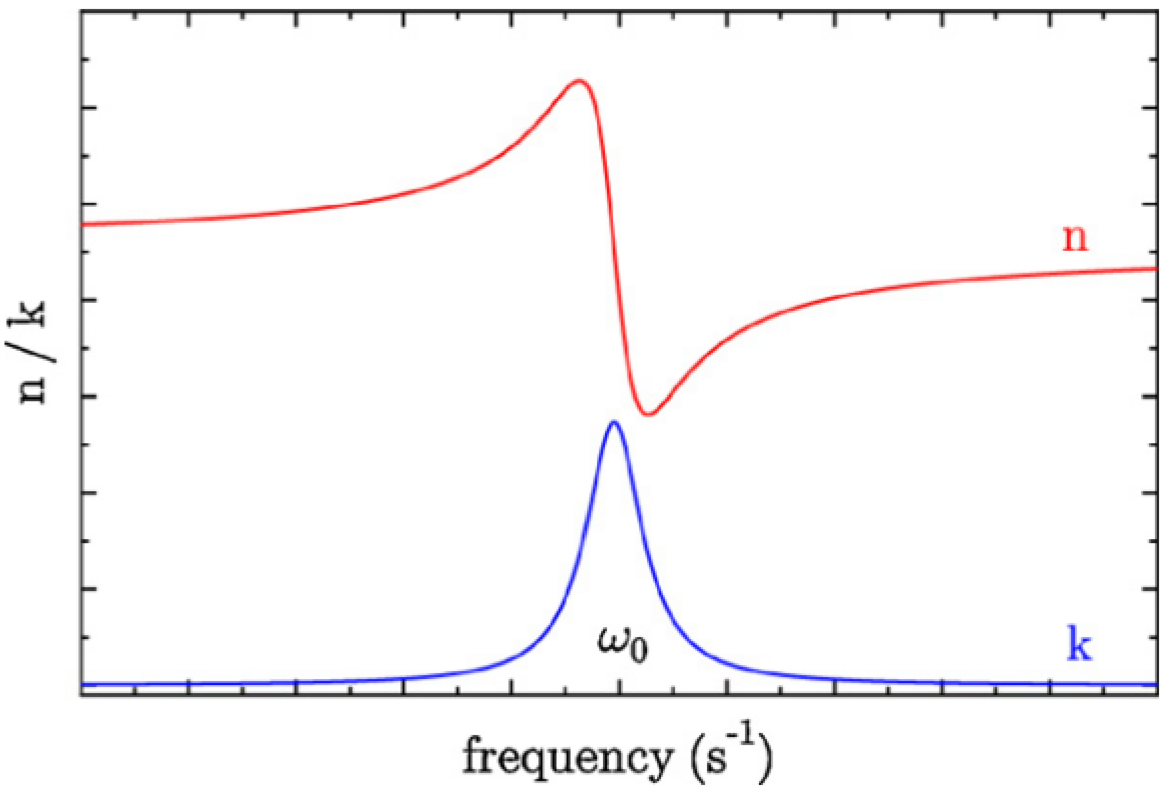

Complex refractive index

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Propagation — Absorption

What are the material properties that determine the refractive index?
We are interested in the real part!

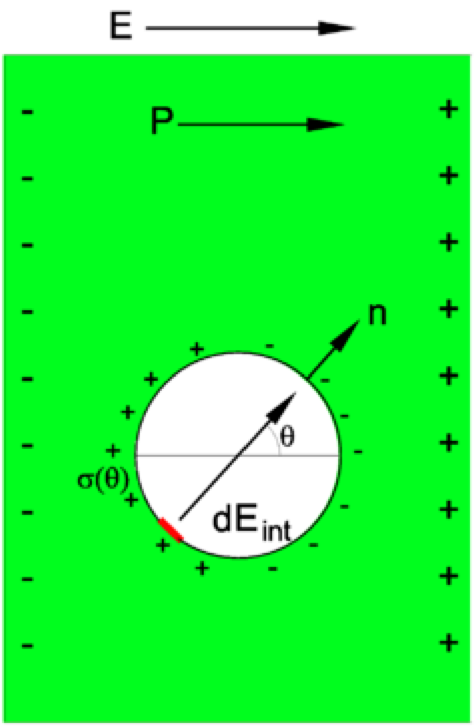
Refractive index in dielectrics

The local electric field is due to the external field + a field due to the surrounding material:

$$\underline{E}_{loc} = \underline{E}_{ex} + \underline{E}_{mat}$$

$$\mathbf{E}_{loc} = E_0 + \frac{P}{3e_o}$$

Lorentz internal field



Molecular Polarizability

$$\frac{n^2-1}{n^2+2} = \frac{1}{3\epsilon_0} N\alpha \qquad N = \frac{N_A \rho}{M}$$

Well-known Lorentz-Lorenz equation

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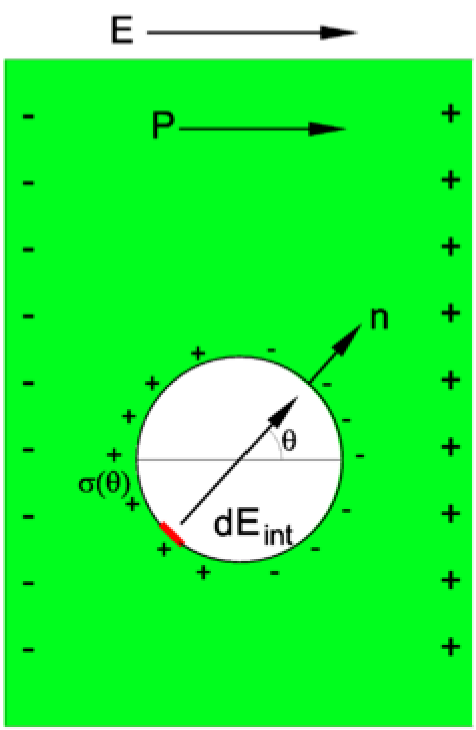


$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\epsilon_0} N\alpha$$

Well-known Lorentz-Lorenz equation

$$N = \frac{N_A \rho}{M}$$

Avogadro's Number

Material density

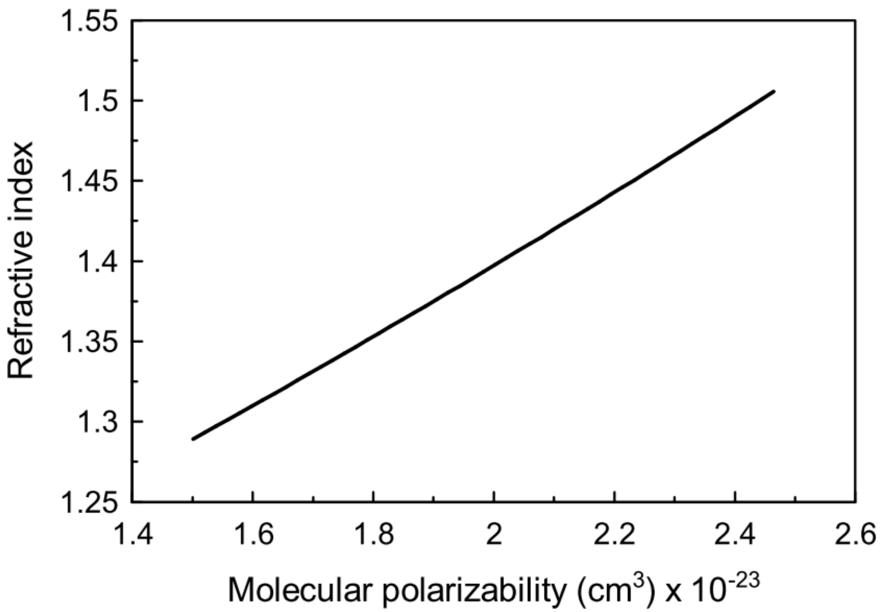
Molar mass

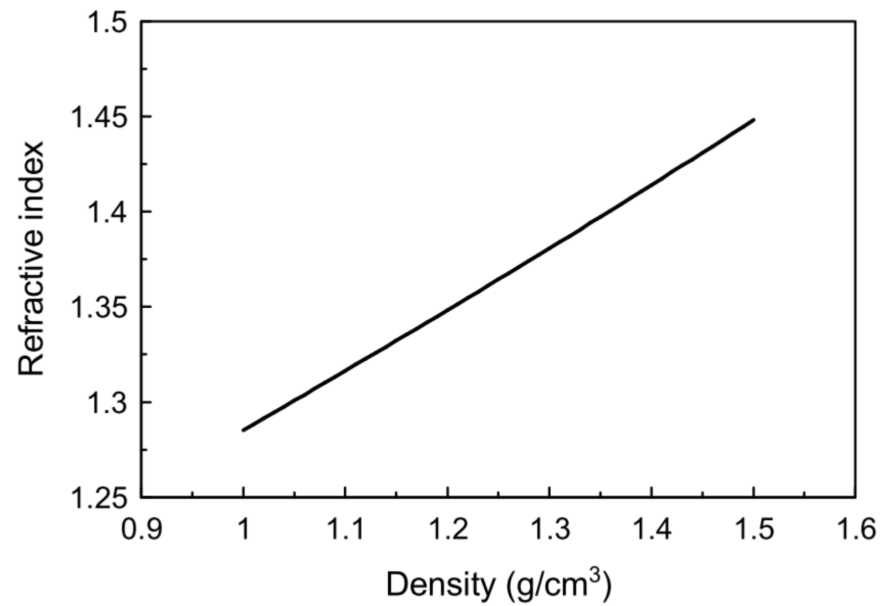
Refractive index in dielectrics

The refractive index then becomes:

$$n = \sqrt{\frac{3\epsilon_0 + 2N\alpha}{3\epsilon_0 - N\alpha}} \qquad N = \frac{N_A \rho}{M}$$

n depends on molecular polarizabilty (α) and material density (ρ)





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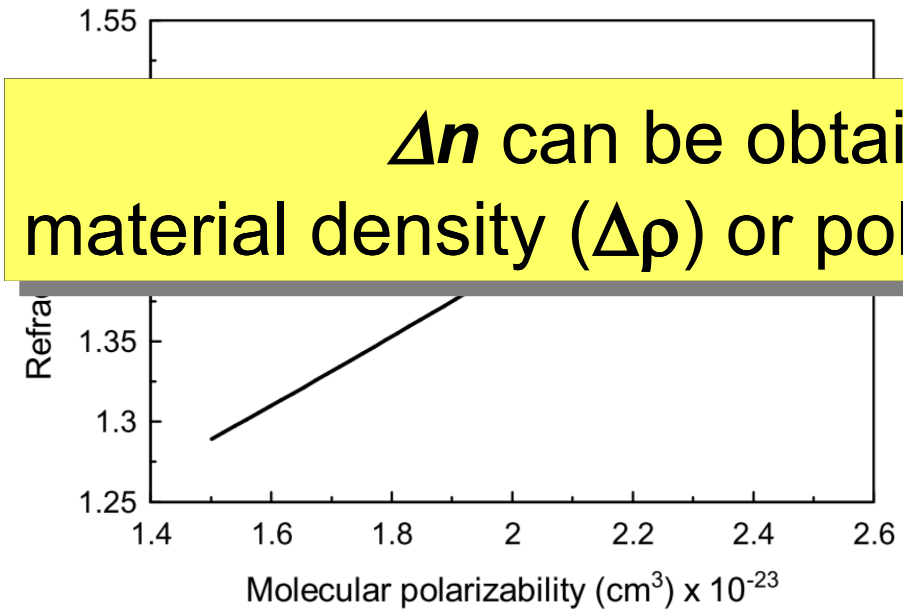
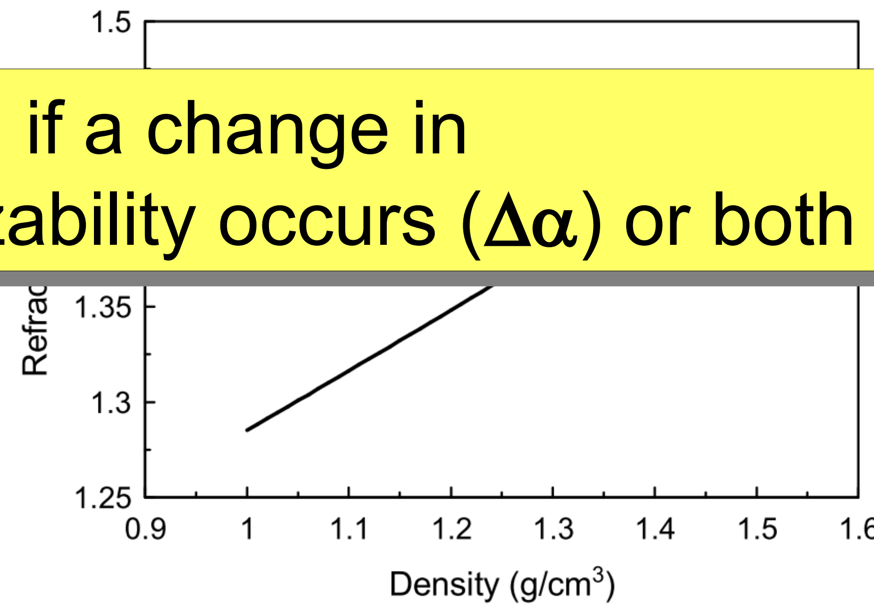
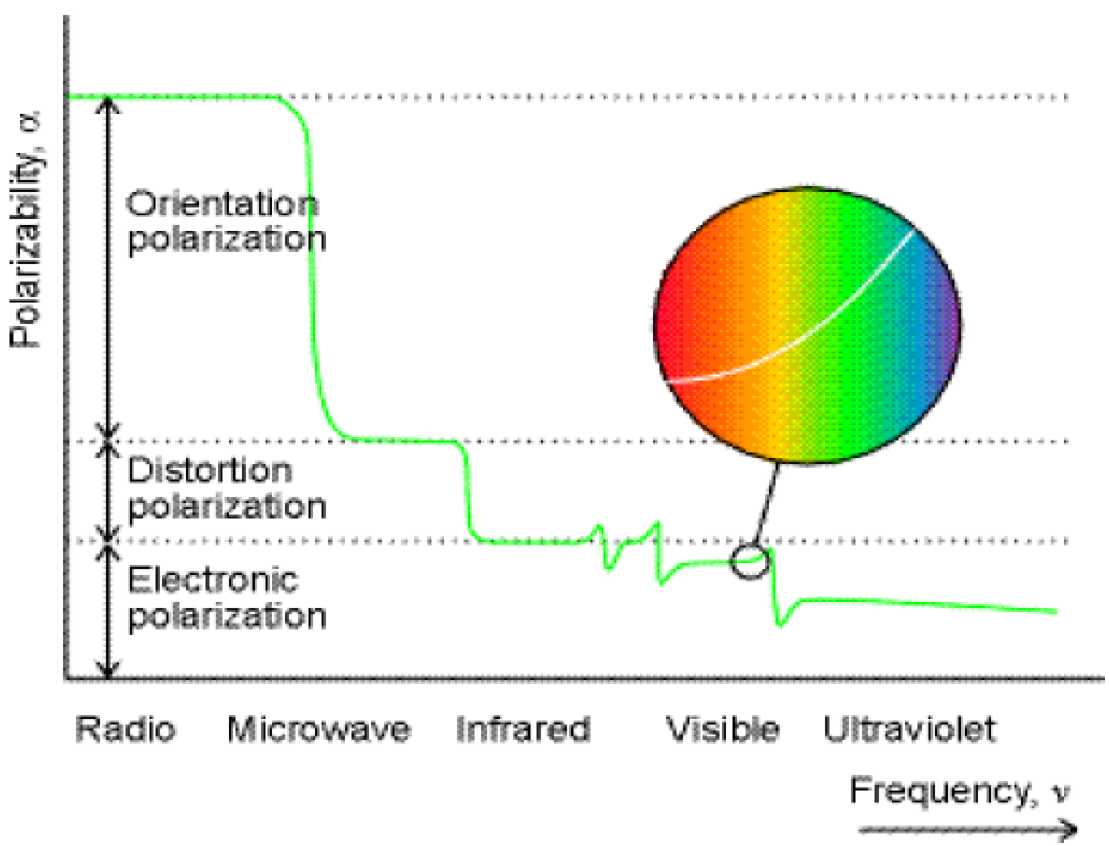


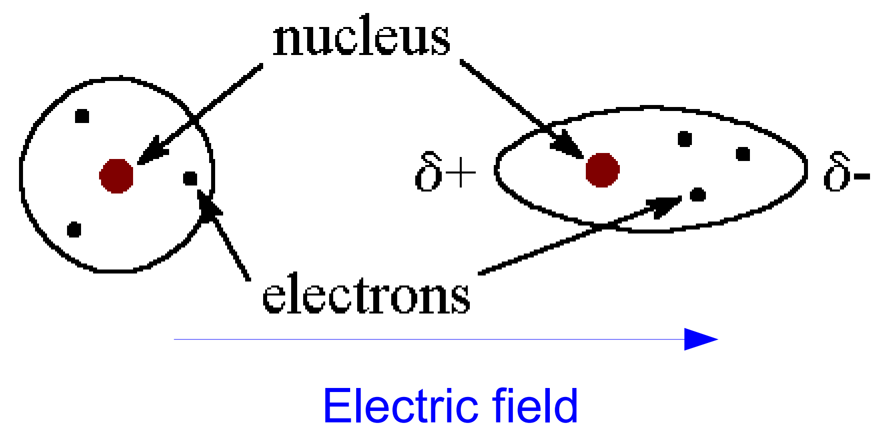


Δn can be obtained if a change in material density (Δρ) or polarizability occurs (Δα) or both

Molecular polarizability α

Molecular polarizability tells you how easy the electronic cloud can be perturbed by an external electric field.
It depends on the frequency of the electric field:





Since we work at optical frequencies, only the electronic contribution is active.

Molecular polarizability α

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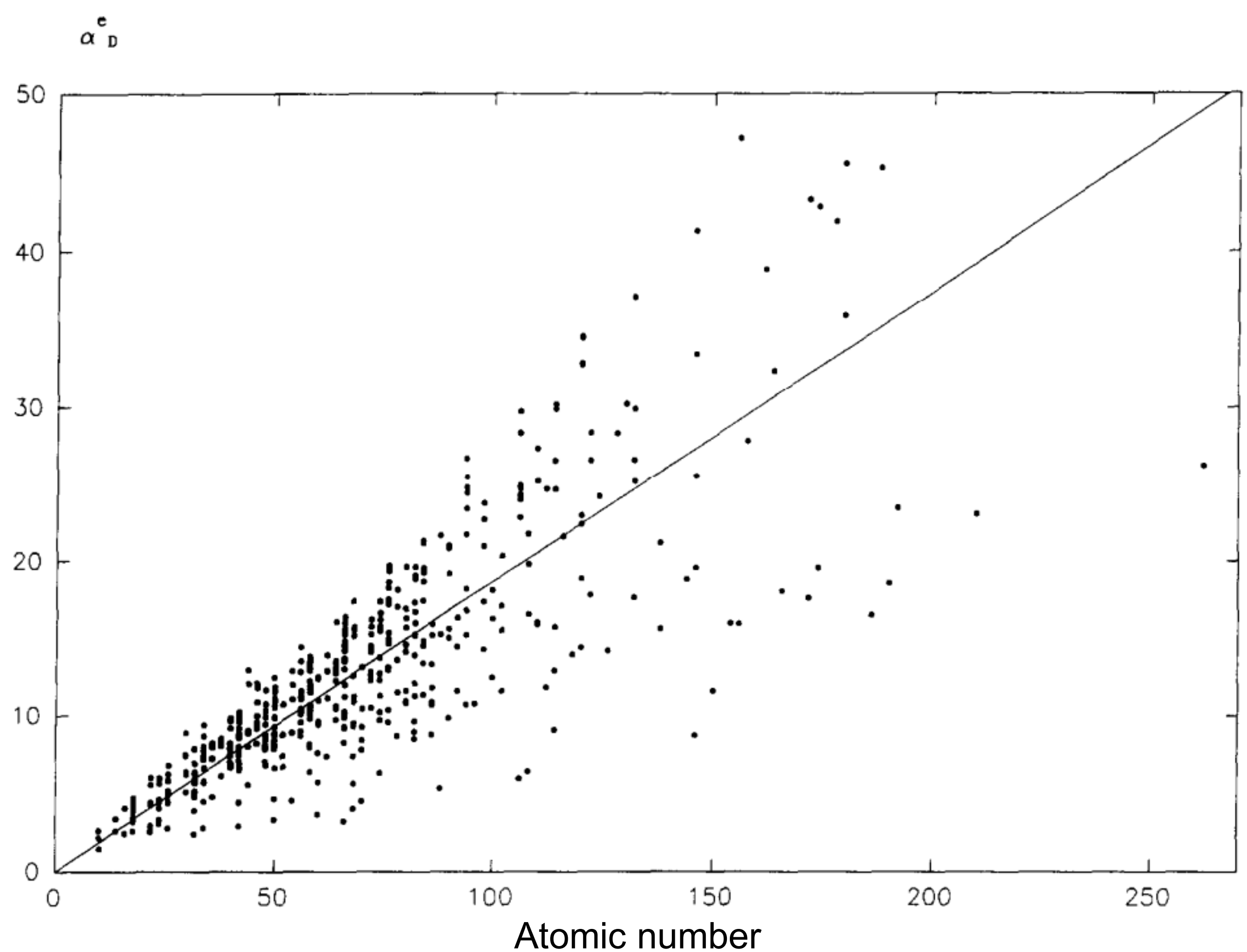
Have a look at the molecular polarizability for different systems:



Polarizability vs.
total atomic number (Z)

An Increase in Z turns into an increase of α almost linear.

An increase in Z means an increase in molecule size.

Molecular polarizability α

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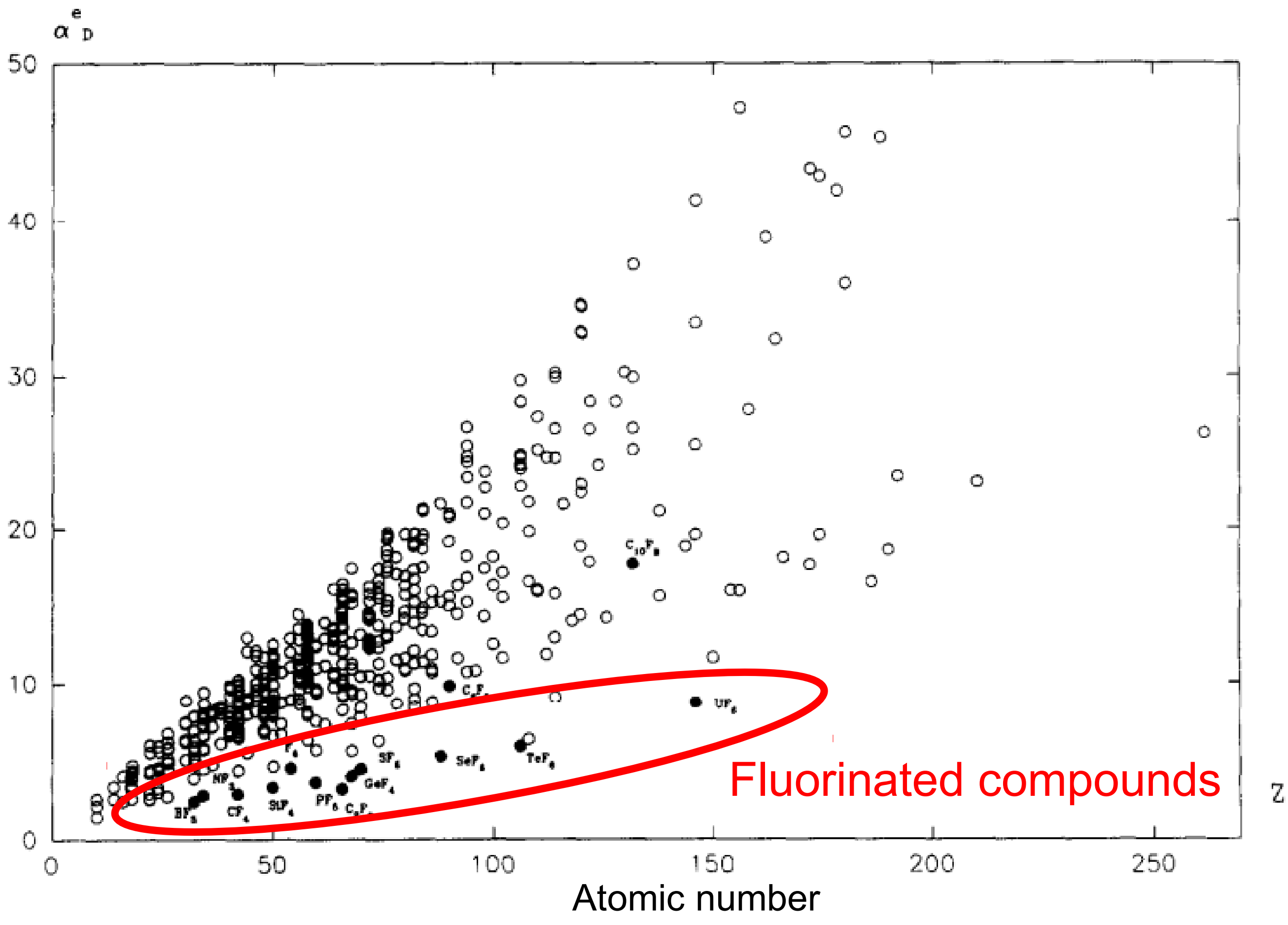

Polarizability vs.
total atomic number (Z)

Fluorinated molecules show low polarizability.
Tight bonded electrons.

Molecular polarizability α

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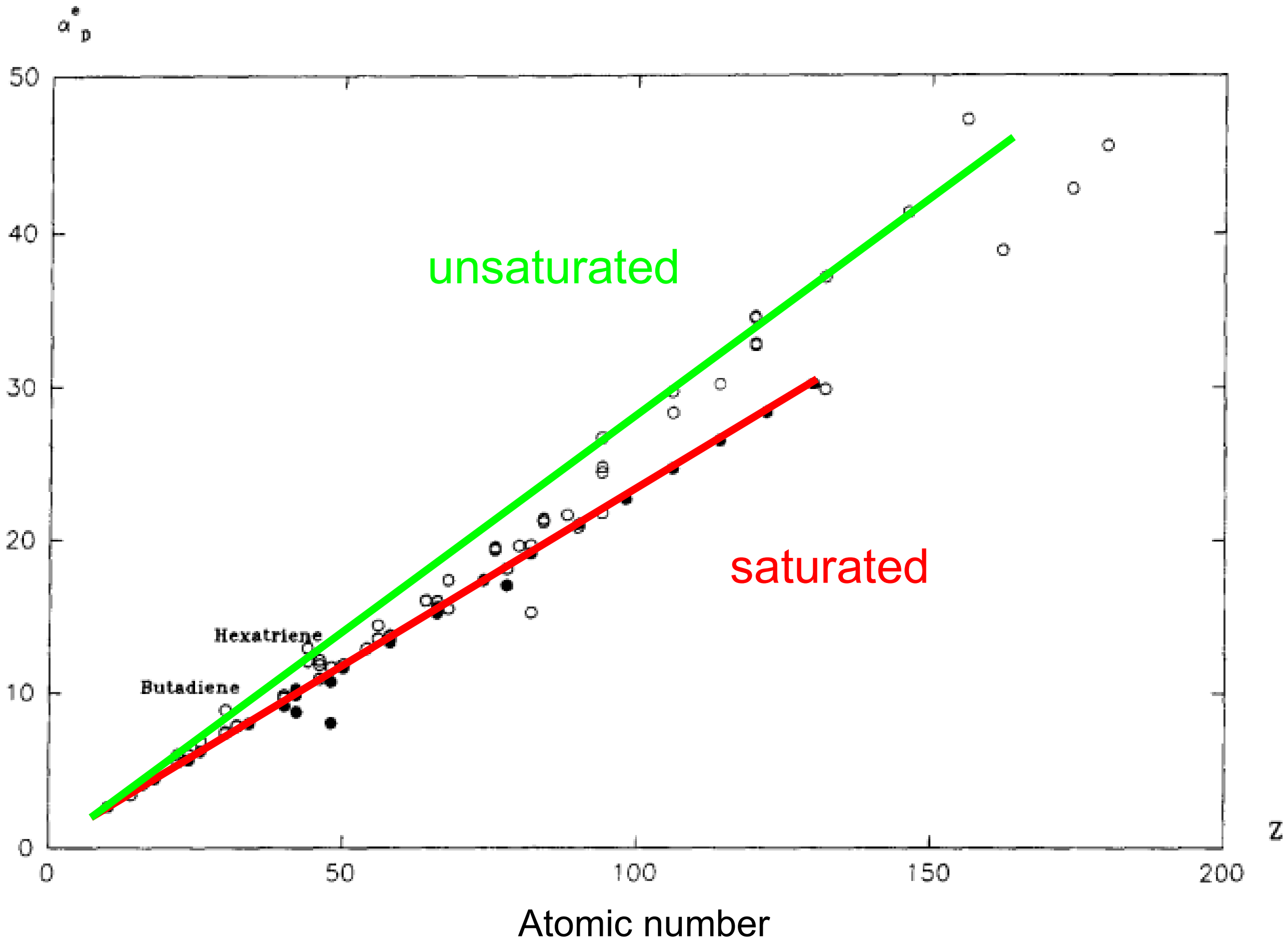
Have a look at the molecular polarizability for different systems:



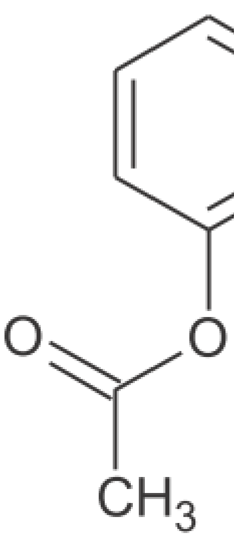
Polarizability of hydrocarbons vs. total atomic number (Z).

The presence of π electrons increases the polarizability at constant Z.

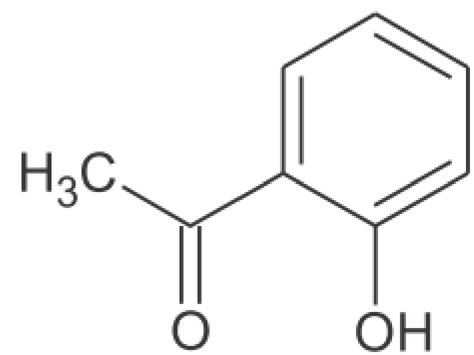
π electrons are more polarizable as expected.

Refractive index α/ρ

- A better benchmark is the polarizability weighted on the total number of electrons of the molecule;
- The polarizability is just one half of the problem, the density is important!
- We can have highly polarizable molecules, but a low density, at the end we will have a low refractive index.



Refractive index = 1.501
Density = 1.073 g/cm^3

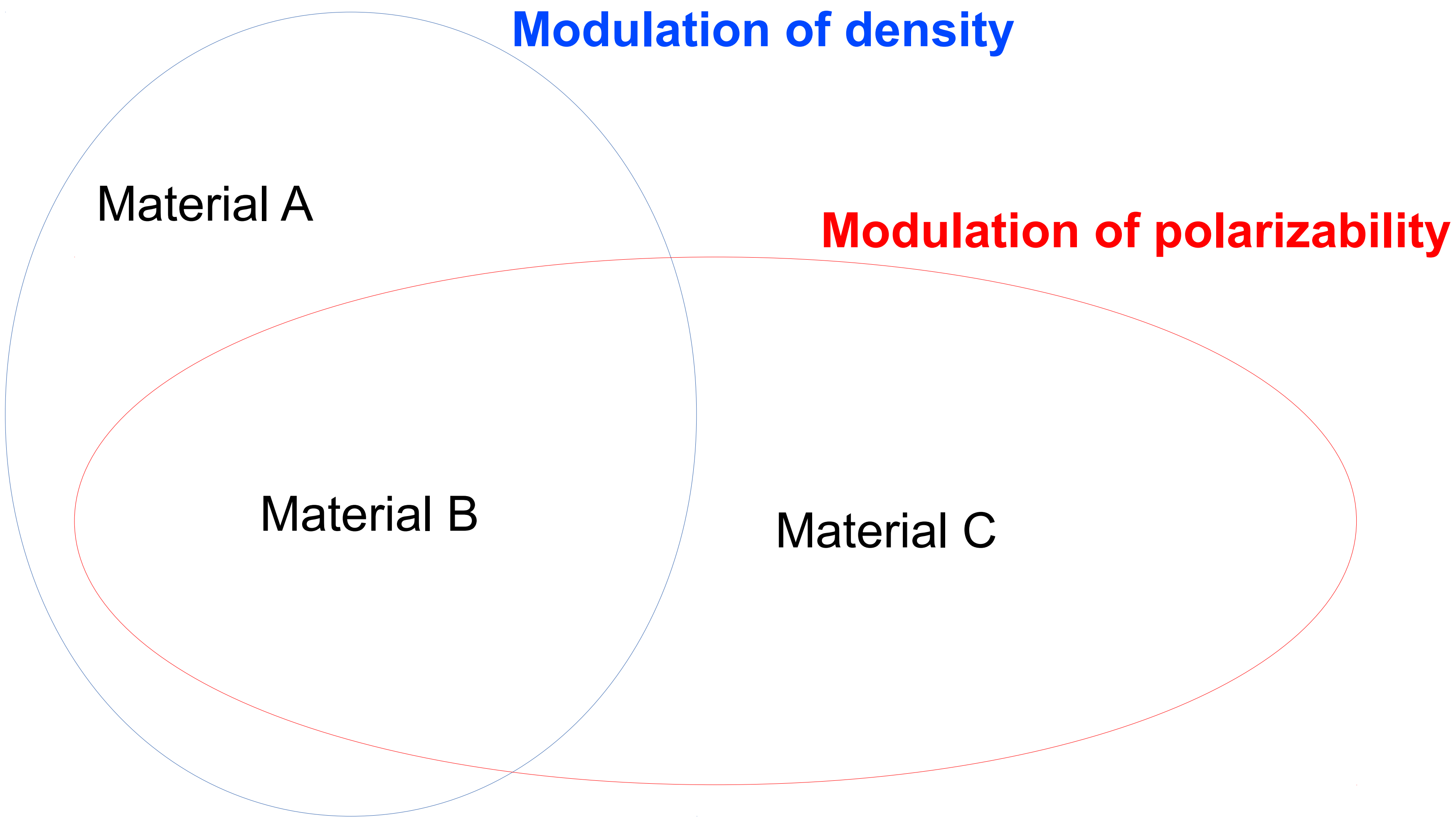


Refractive index = 1.558
Density = 1.1378 g/cm^3

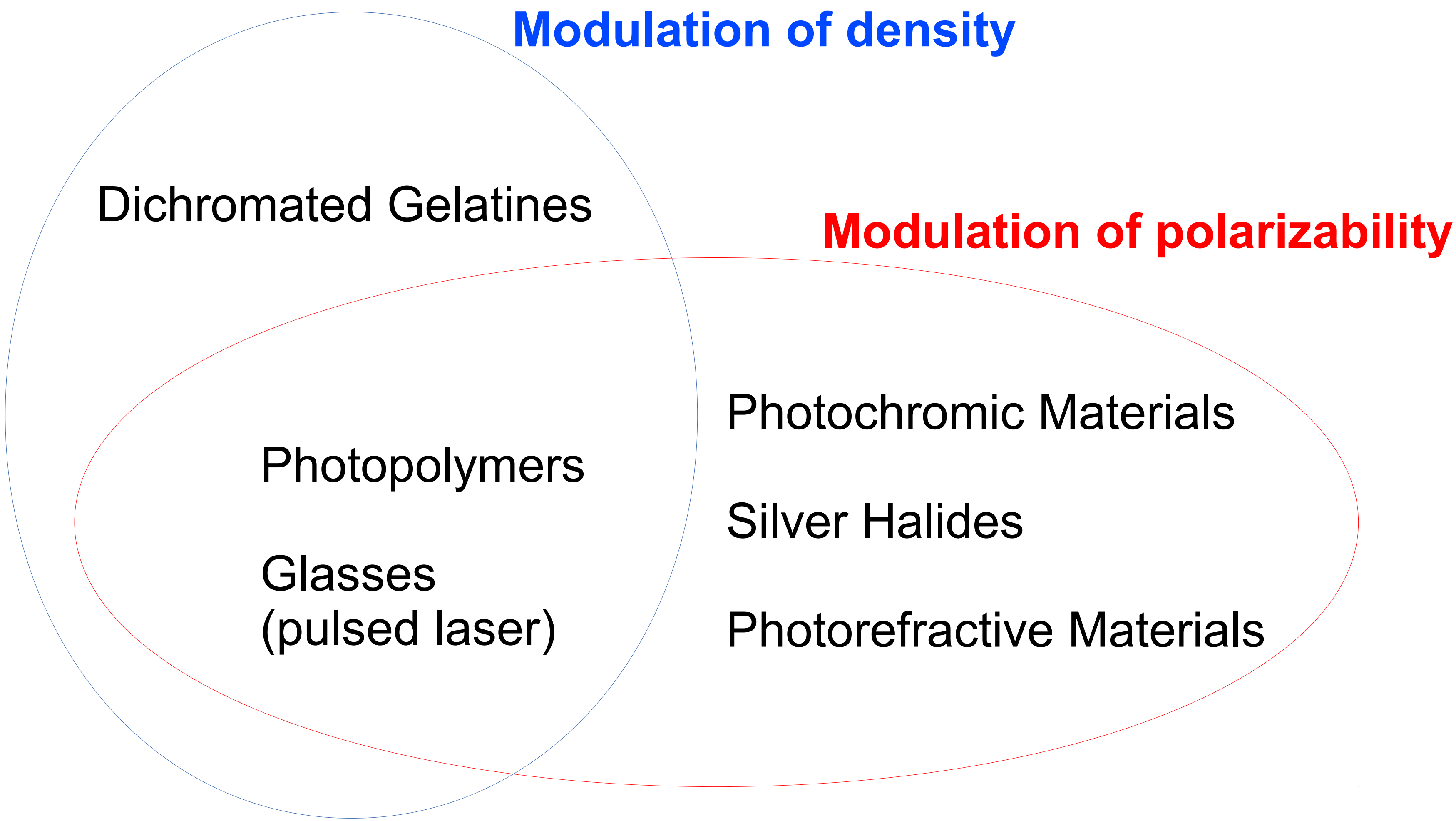
The two molecules (isomers) are two liquid with very similar structure, we do not expect a dramatic change in polarizability:

The refractive index difference is due to the different density.

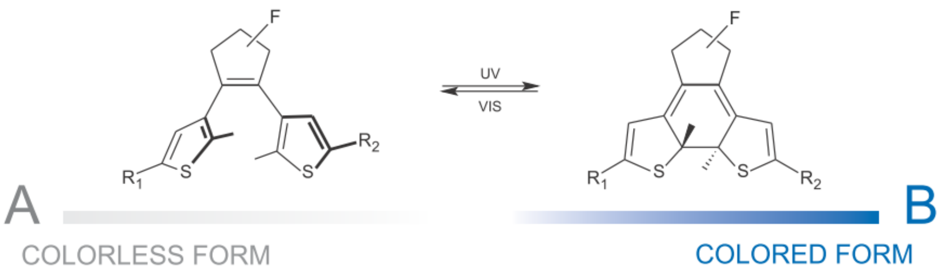
How to induce a Δn?



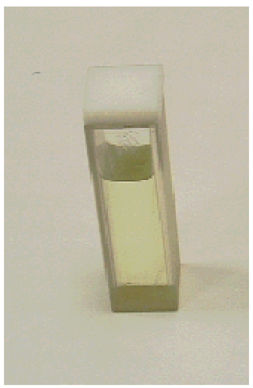
How to induce a Δn?

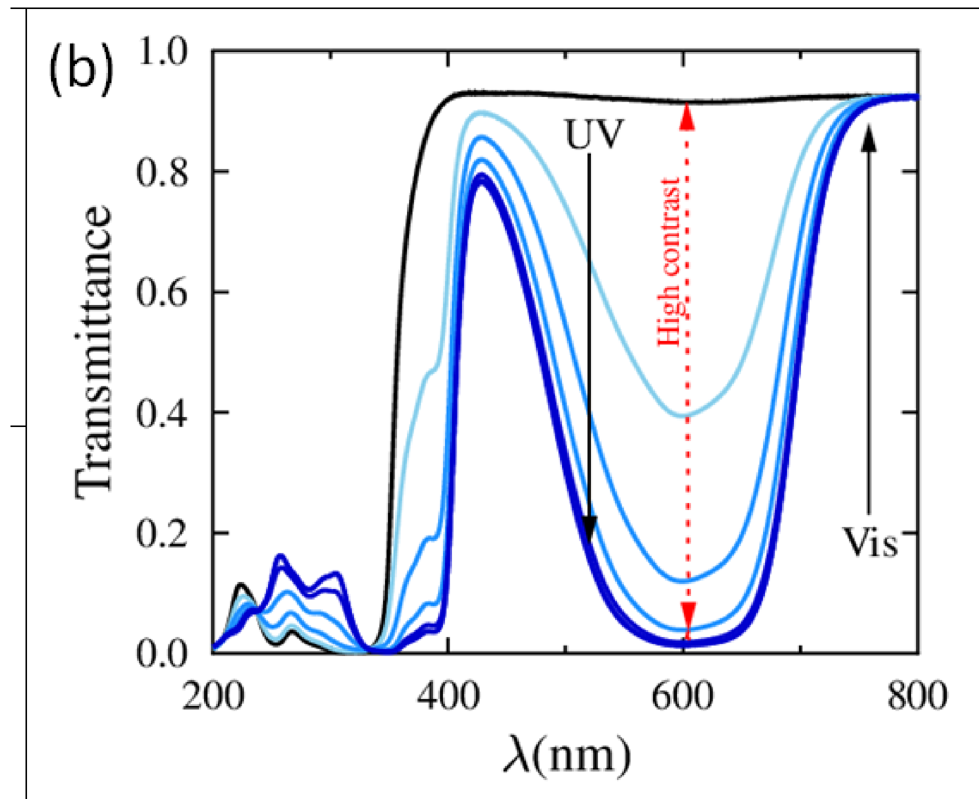


Photochromic Materials



Reversible chemical transformation between two stable forms induced (at least in one direction) by photons.





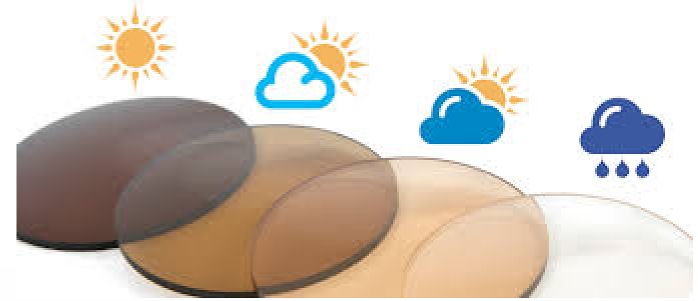
Many properties change…

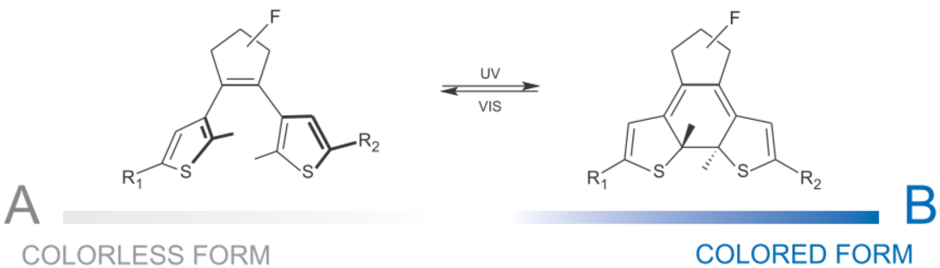
- Absorption UV-vis spectrum (color);
- Vibrational spectrum (IR and Raman);
- Luminescence;
- Dipole Moment;
- **Refractive index;**

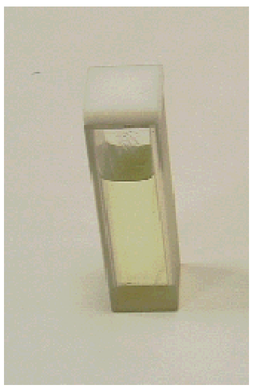
A. Bianco, et.al, *Laser and Photonics Reviews* 5(**6**), 711, 2011

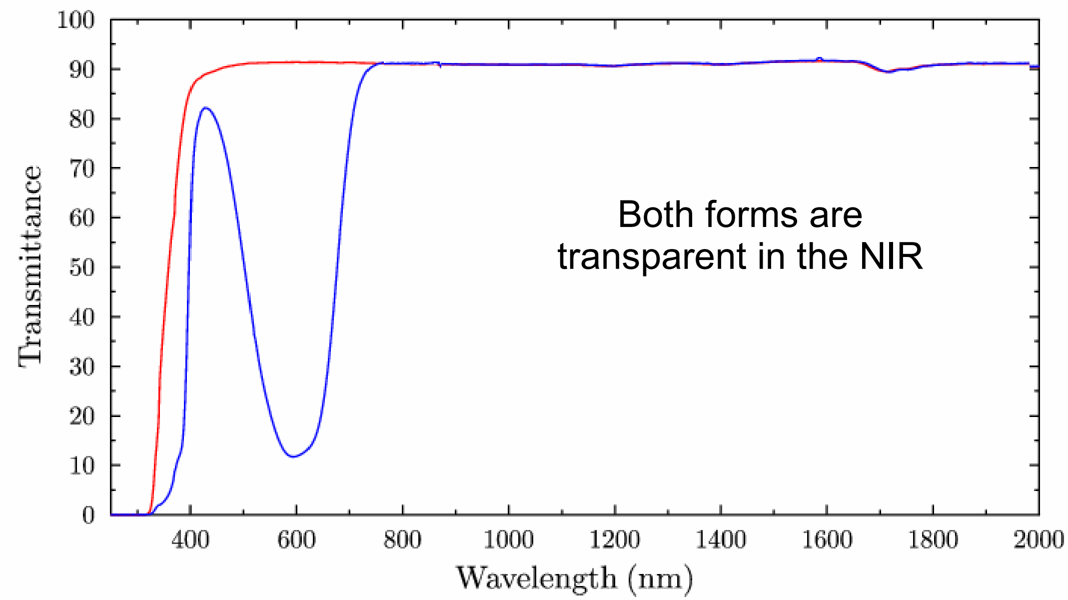
C. Bertarelli, et. al, *J. Photochem. Photobiol. C: Photochemistry Reviews* **12**, 2011

Photochromic Materials

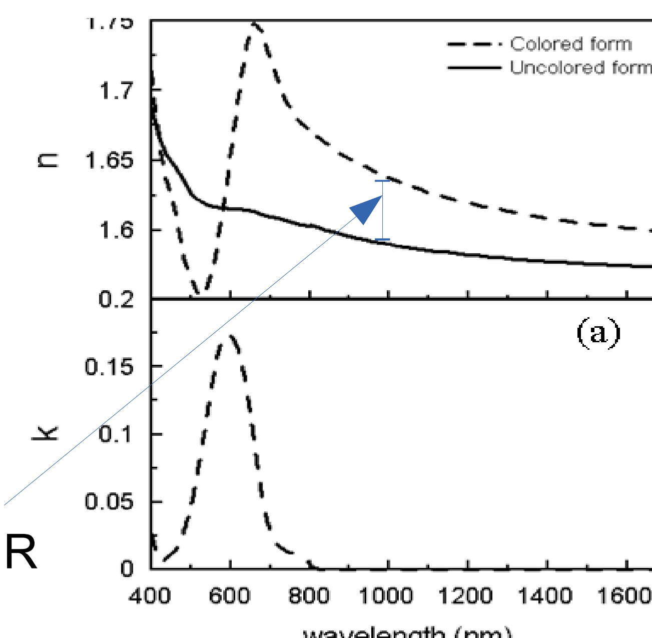






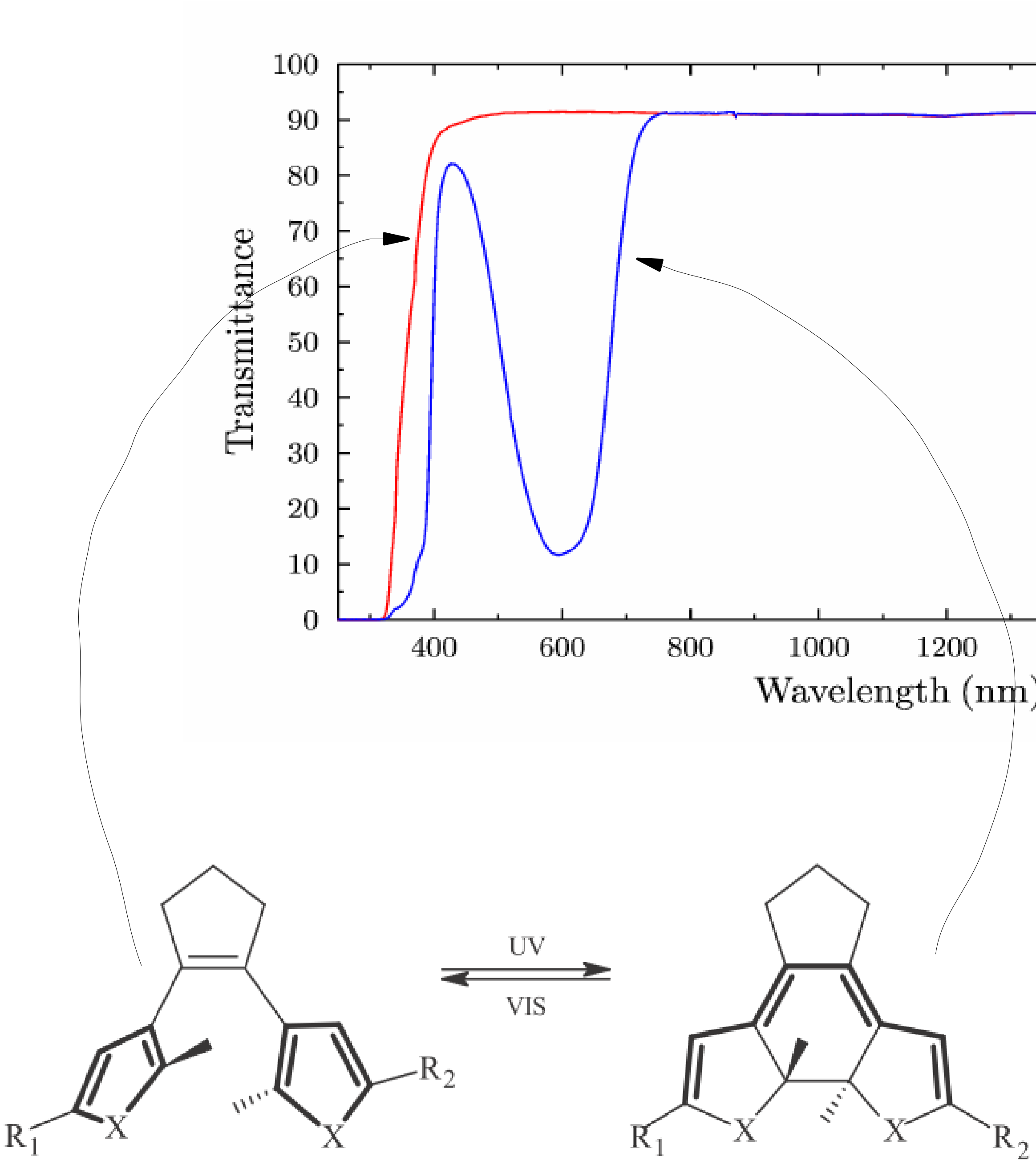


- They are reversible, so reconfigurable holography;
- Self-developing (no chemical developing);
- They can be used only in the transparent region (NIR);
- The material must be converted in the volume.



Δn up to 0.04 in the NIR

Photochromic Materials



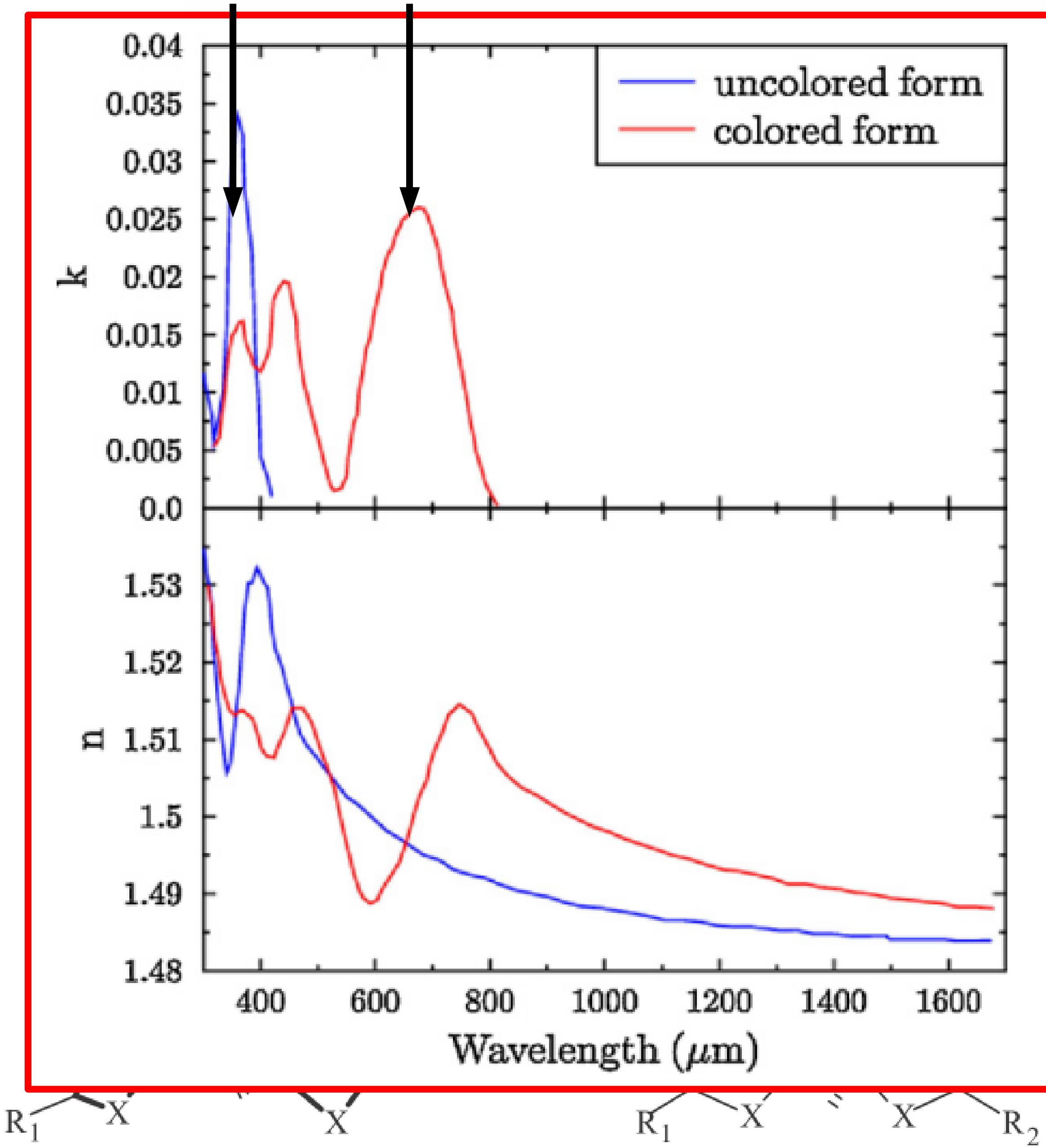
The conjugation of π electron strongly increase going from uncolored to colored form!

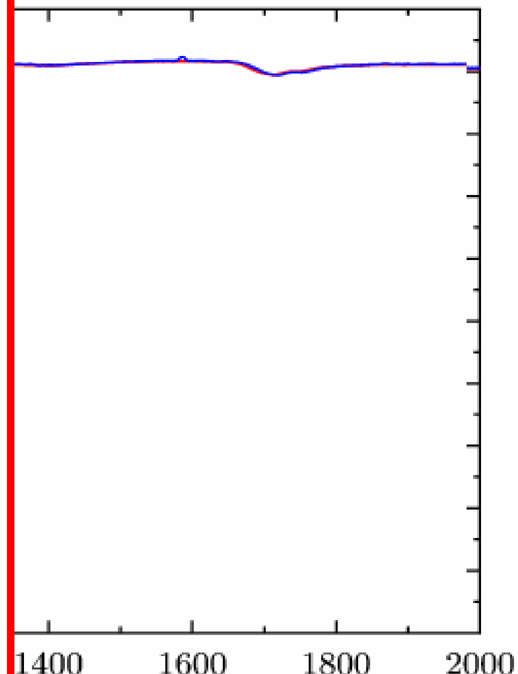
Indeed an absorption at low energy (in the visible) occurs.

The polarizability should increase too!

A resonance effect is also active

Photochromic Materials





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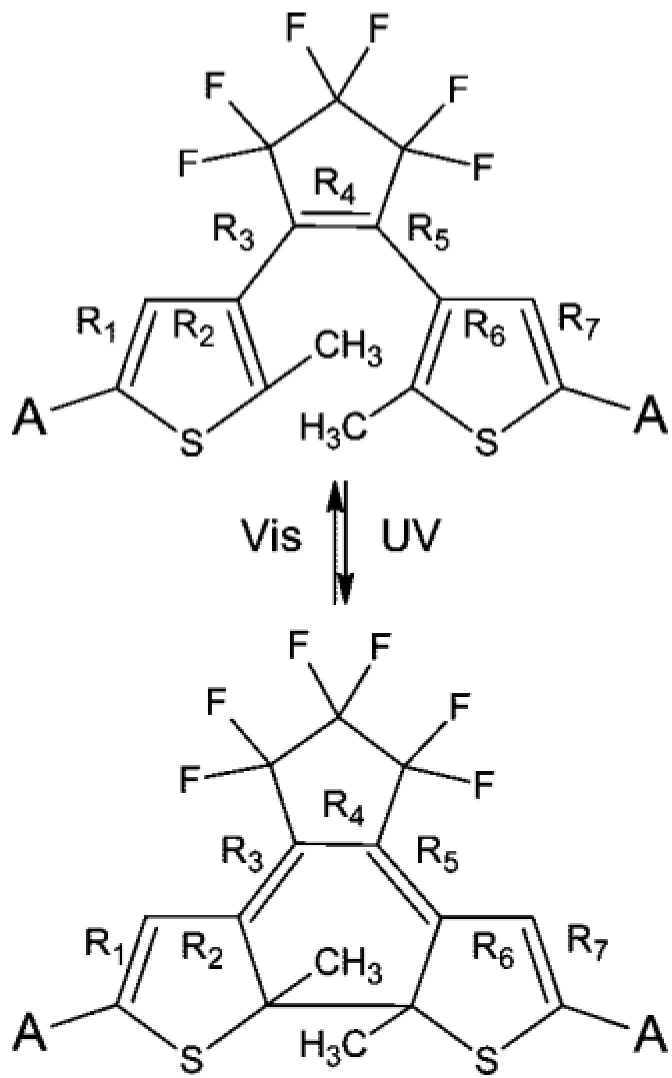
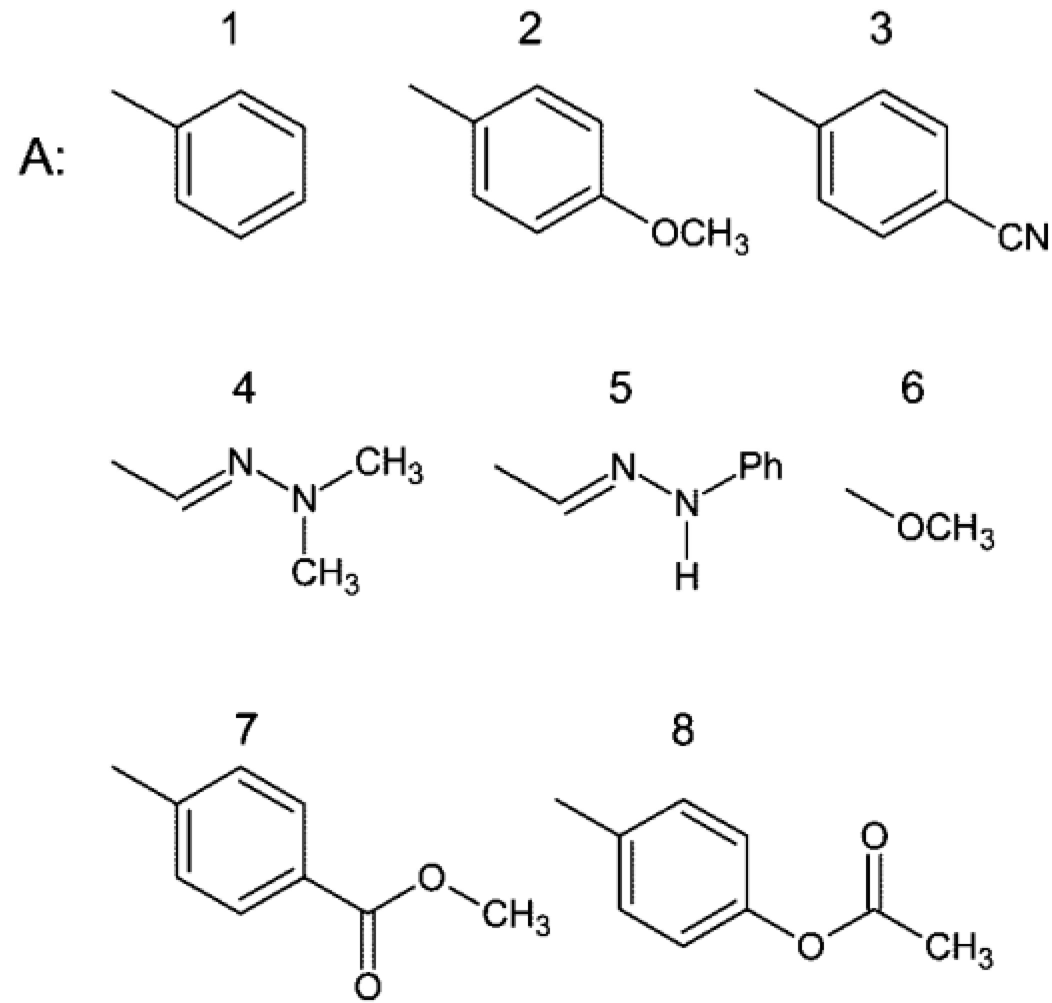
Photochromic Materials: Polarizability



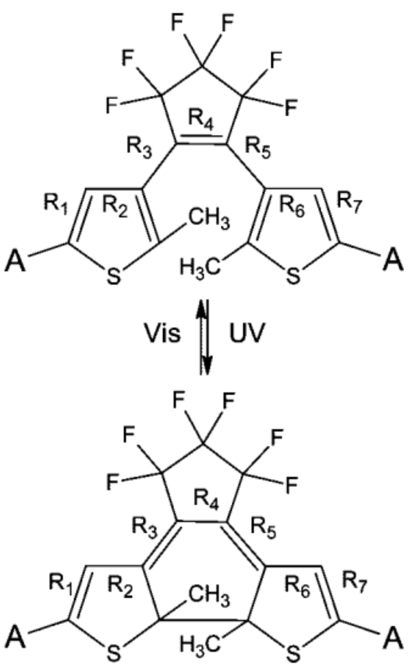


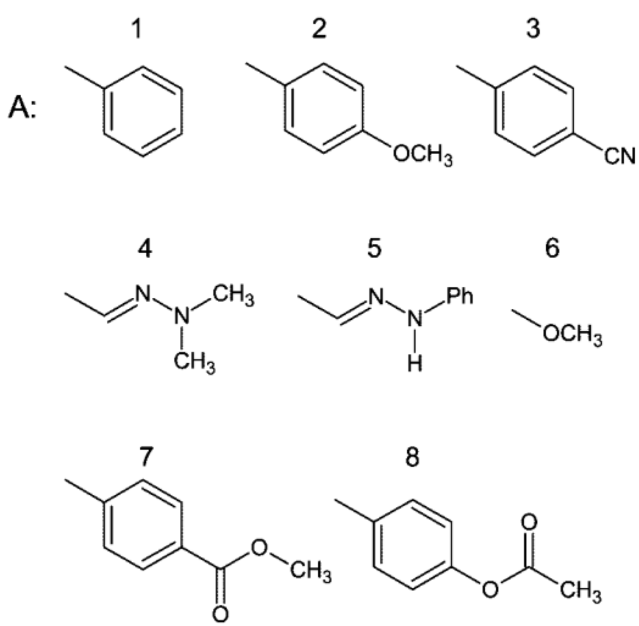
How does the polarizability change with the chemical structure?

Photochromic Materials: Polarizability

Molecule	Uncolored form		Colored Form		Δ polarizability	
	α (bohr³)	PPE(bohr³)	α (bohr³)	PPE(bohr³)	α (bohr³)	PPE(bohr³)
1	343	1.29	407	1.53	64	0.24
2	392	1.32	481	1.61	89	0.30
3	402	1.39	489	1.68	87	0.30
4	341	1.30	432	1.65	91	0.35
5	469	1.51	631	2.03	162	0.52
6	225	1.03	244	1.12	19	0.09
7	433	1.33	523	1.60	90	0.28
8	418	1.28	507	1.55	89	0.27

DFT calculations





- The polarizability of uncolored form smaller than the polarizability colored form;

Callierotti G., et al. J. Phys. Chem. A vol. 112, 2008

Photochromic Materials: Polarizability

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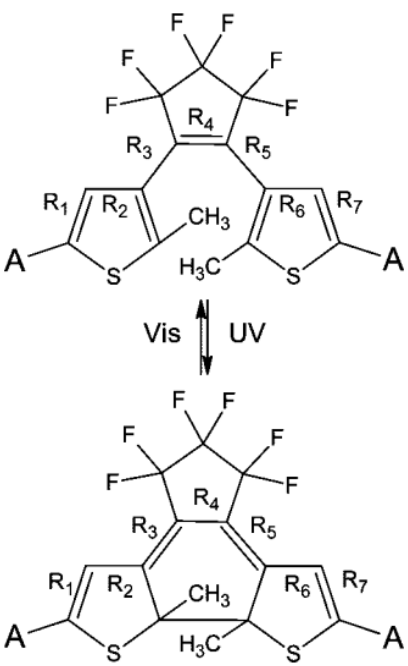

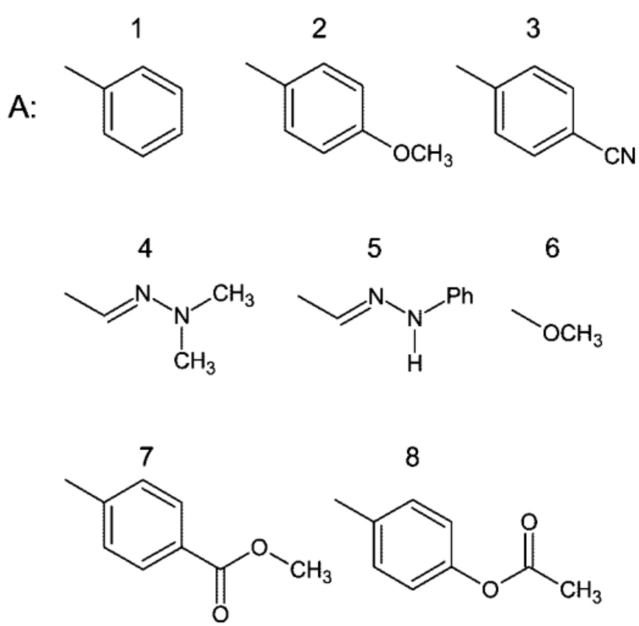

- The polarizability of uncolored form smaller than the polarizability colored form;

- Increase of contribution of single electron;

Callierotti G., et al. J. Phys. Chem. A vol. 112, 2008

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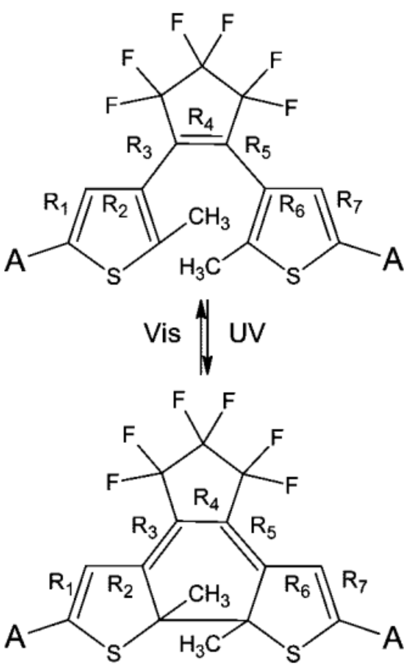
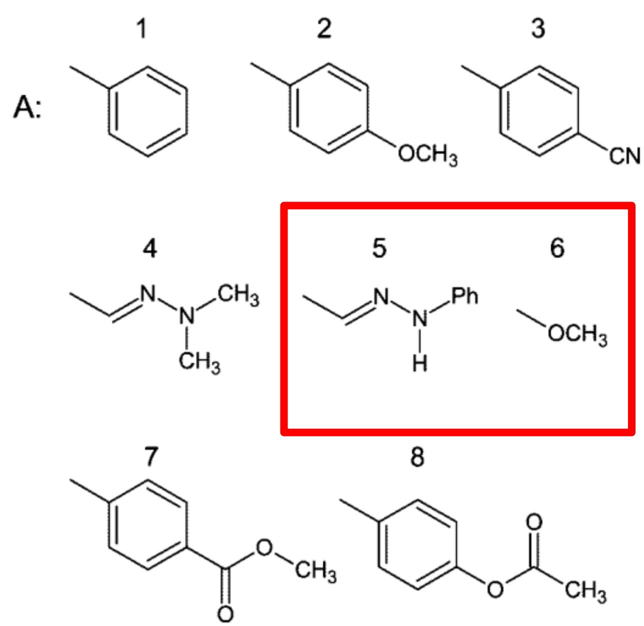
8	418	1.28	507	1.55	89	0.27

DFT calculations





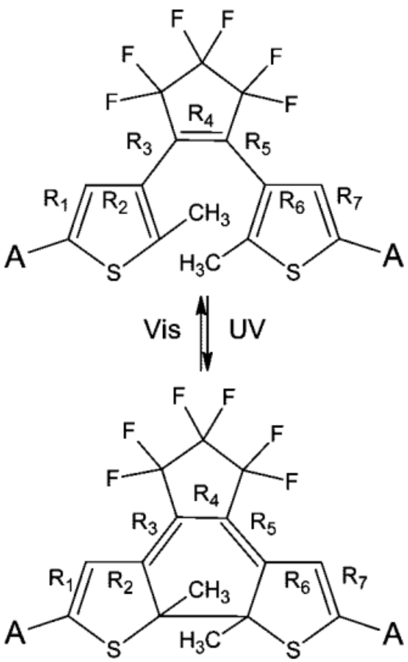
- The polarizability of uncolored form smaller than the polarizability colored form;

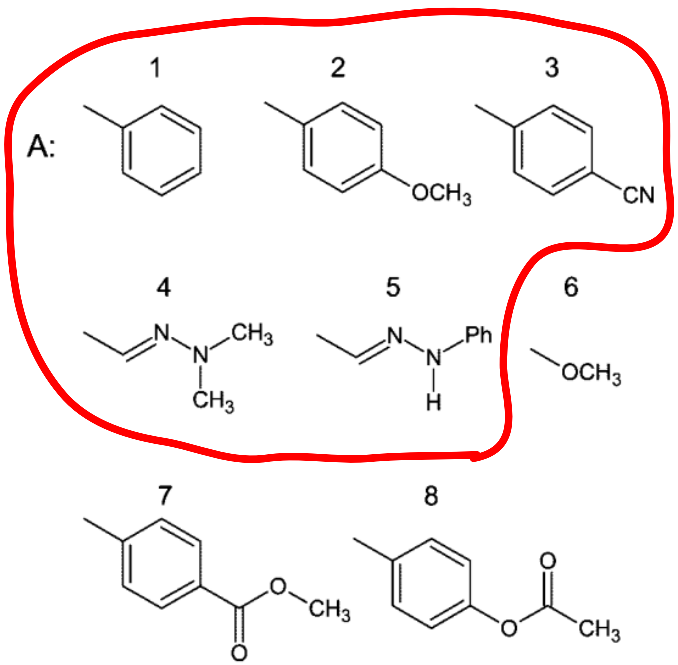
- Increase of contribution of single electron;

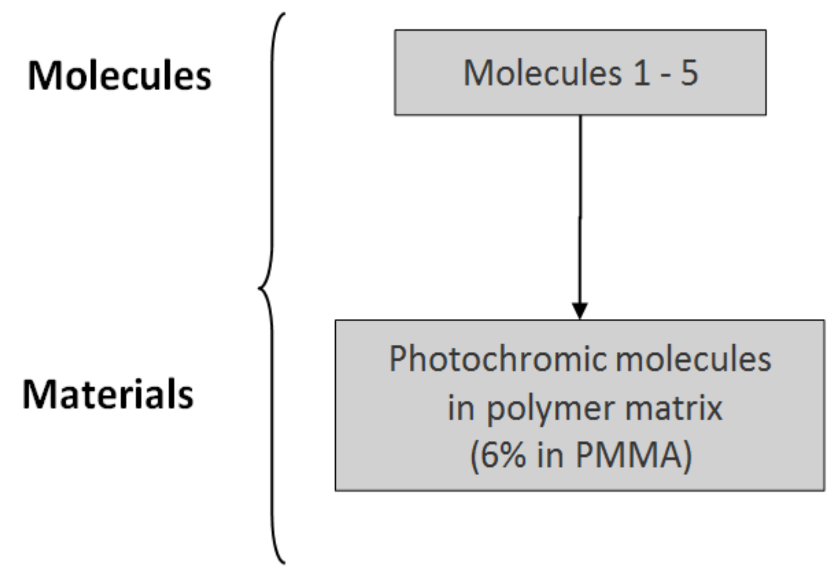
- Different chemical groups provide different modulations: molecular optimization.

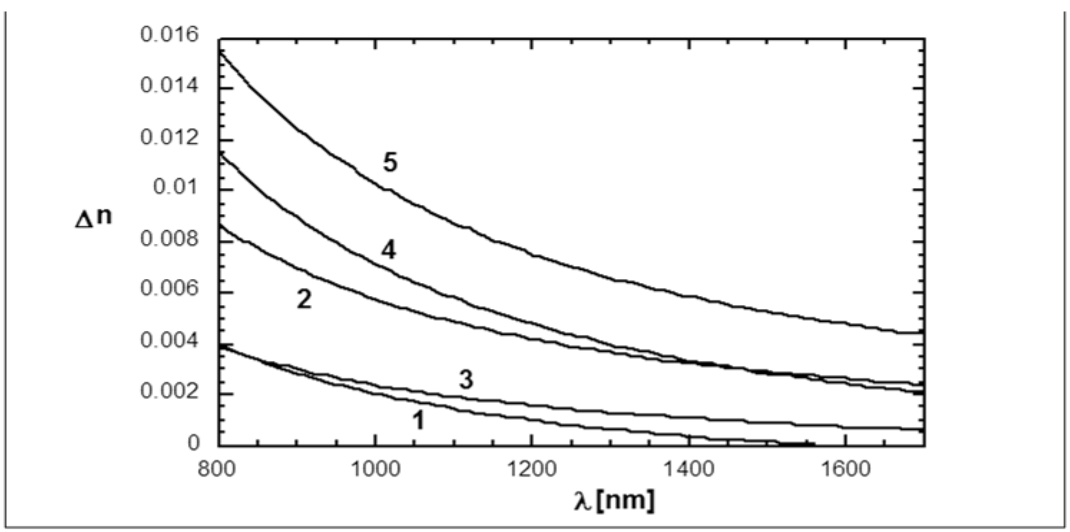
Callierotti G., et al. J. Phys. Chem. A vol. 112, 2008

Photochromic Materials: Δn, polymer matrix









C. Bertarelli et al. *Adv. Fuct. Mater.*, 2004

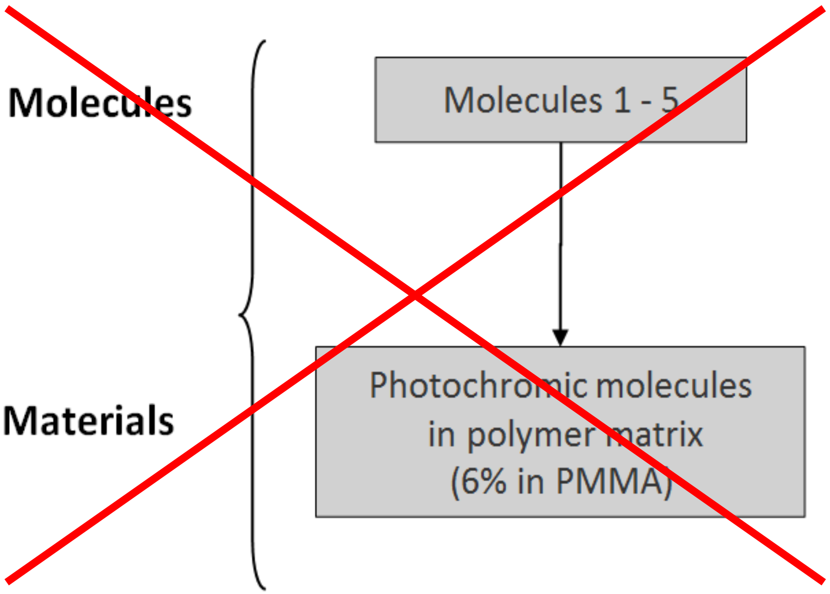
- A polymer matrix is required;

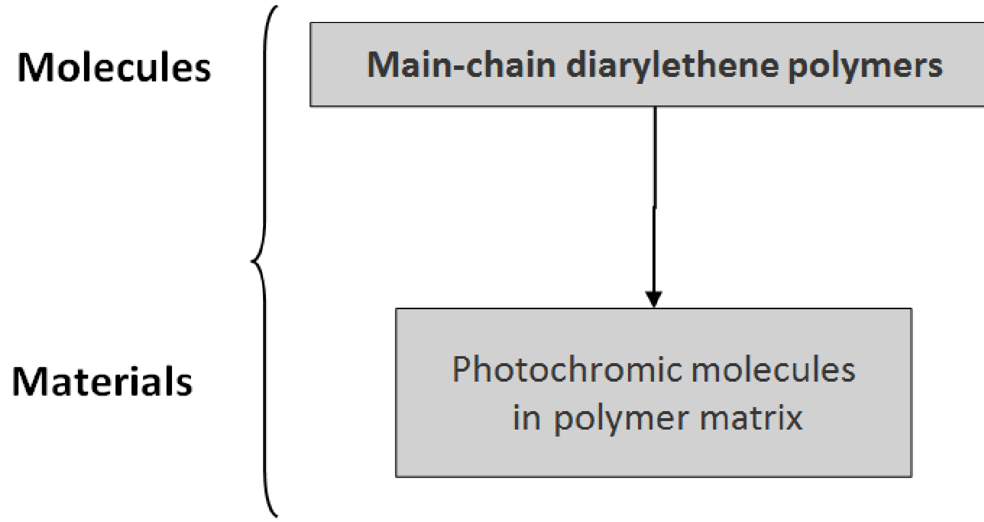
- Different Δn are obtained according to the chemical group resembling the polarizability trend;

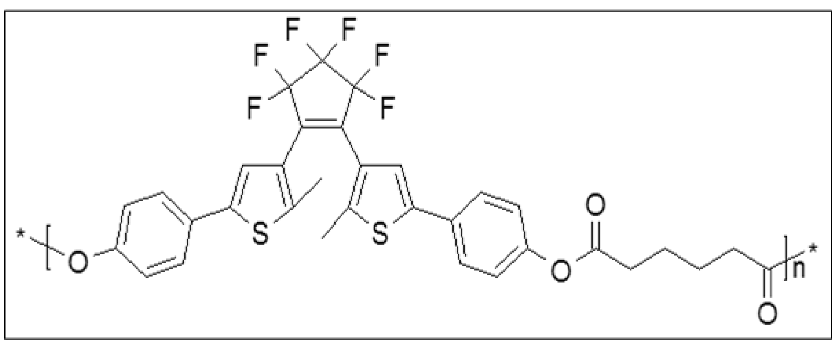
- Not so large Δn (< 0.01)!

- But 6% of active molecule in the polymer matrix (PMMA), not so much....

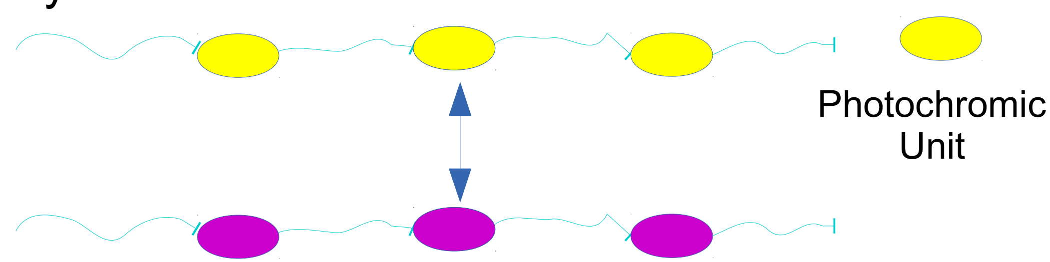
Photochromic Materials: Δn, backbone polymer





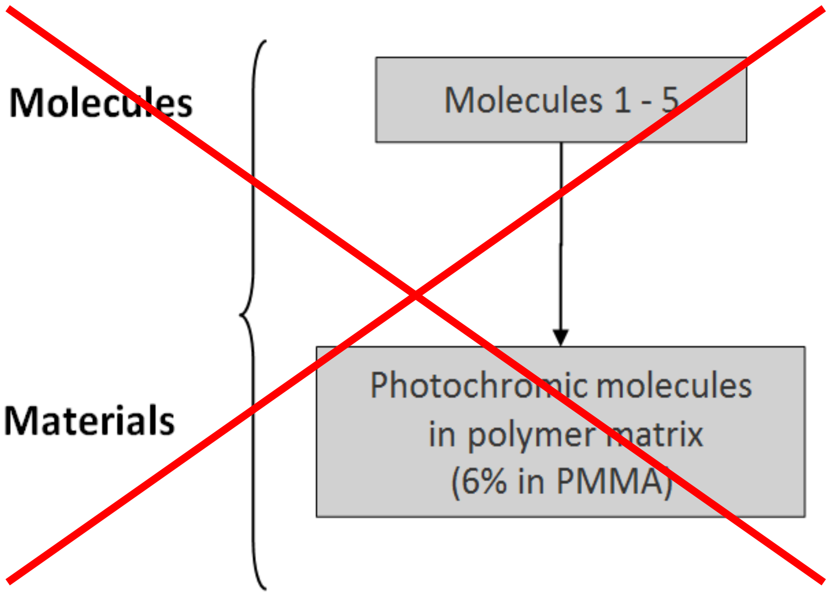


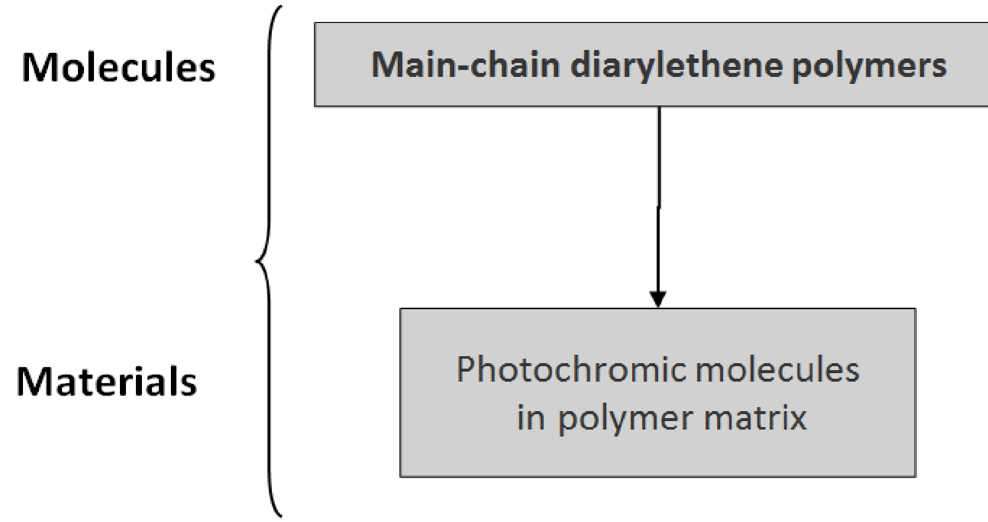
Polymer chain

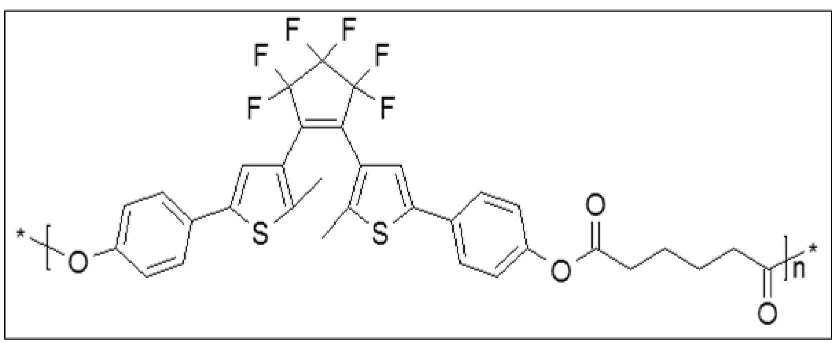


- The monomer is photochromic;
- The concentration of the photochromic unit strongly increases;
- More difficult to optimize the photochromic unit.

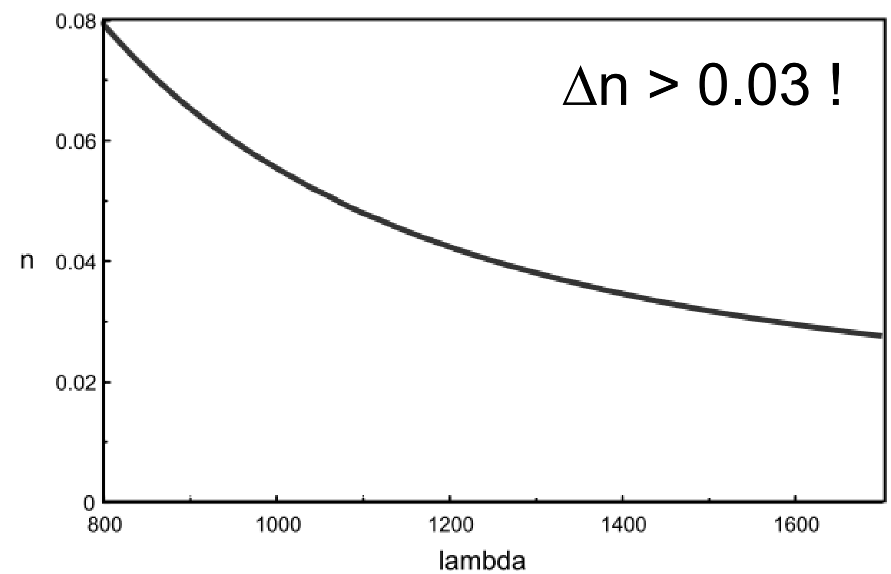
Photochromic Materials: Δn, backbone polymer







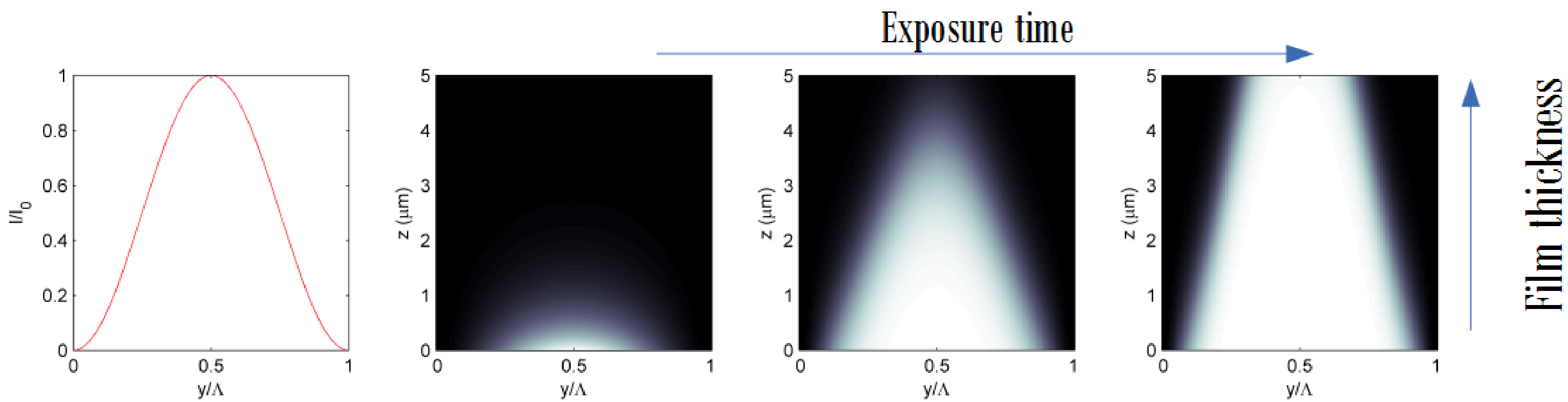
Δn (1.5 μm)=0.03



It is more important the concentration than the polarizability.

Photochromic Materials: write the hologram

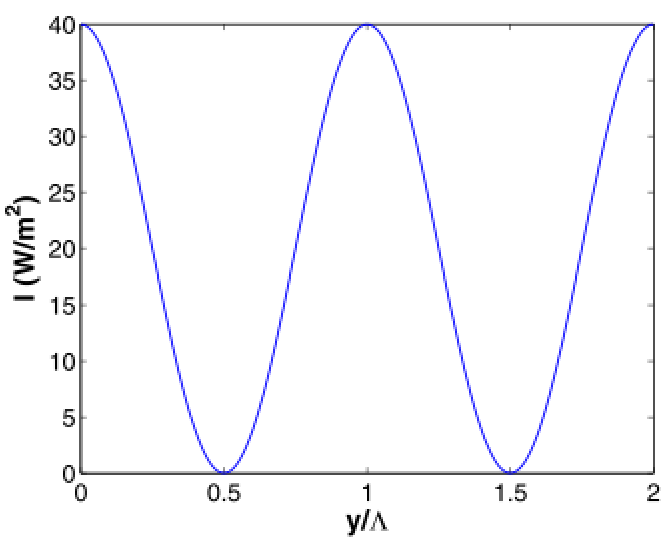
The optical writing of a photochromic material is highly non-linear. You have “to dig” optically the photochromic material through the film thickness

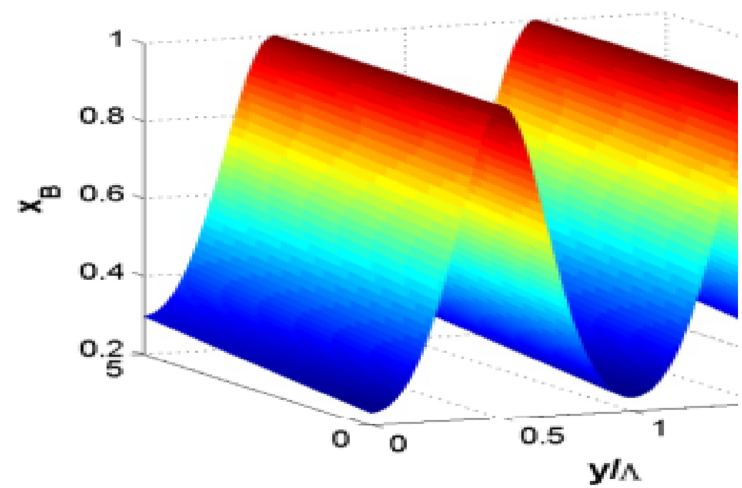


Pariani, G.; et. al *J. Phys. Chem. A, 115,* **2011**.
Bianco A., et al. Proc. of SPIE Vol. 8281, 828104 (2012)

Photochromic Materials: write the hologram

The optical writing of a photochromic material is highly non-linear. You have “to dig” optically the photochromic material through the film thickness



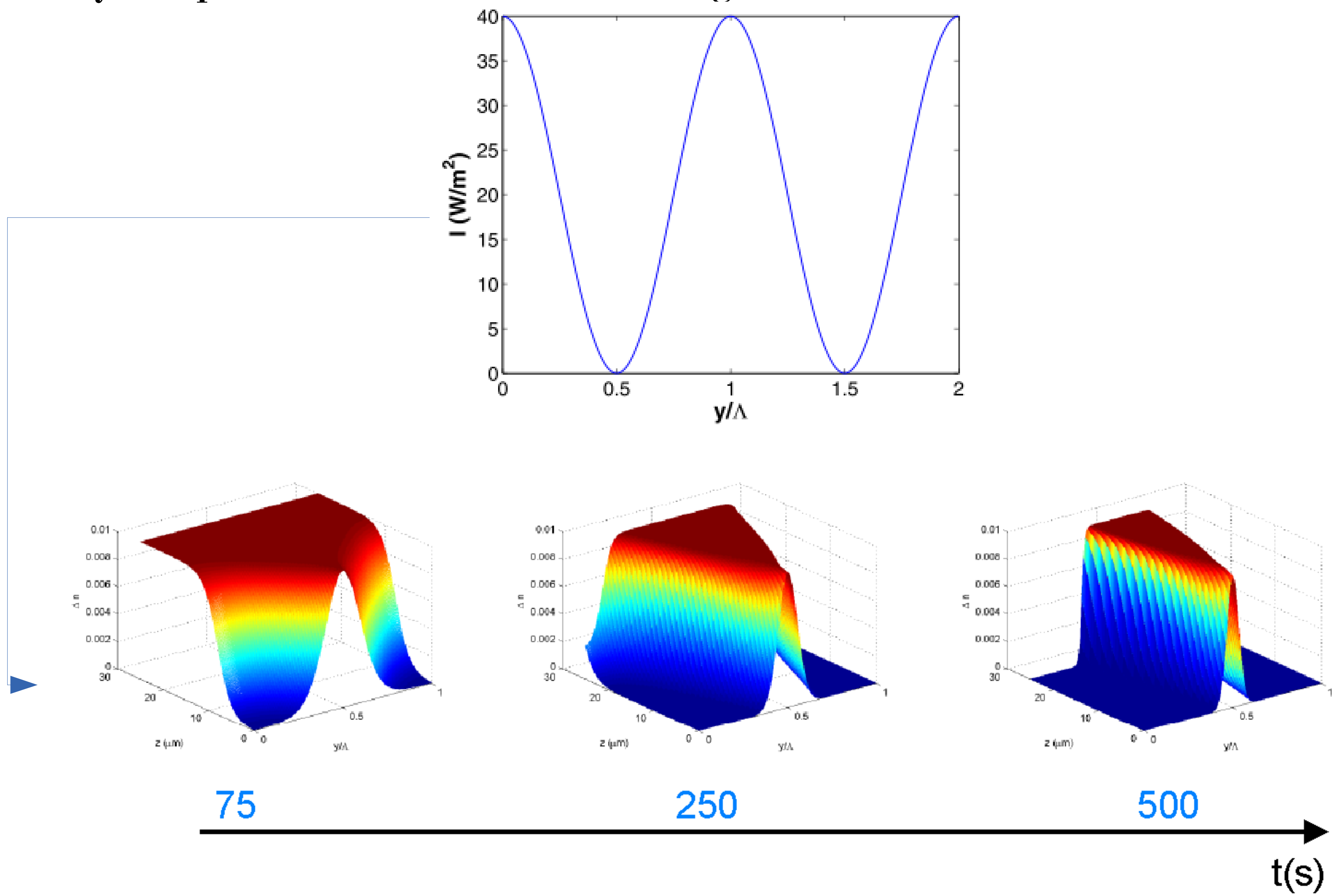


Illumination conditions:
Sinusoidal pattern coming from the two beams interference

We've learned that the pattern in the photochromic film is not sinusoidal

Photochromic Materials: write the hologram

The optical writing of a photochromic material is highly non-linear. You have "to dig" optically the photochromic material through the film thickness



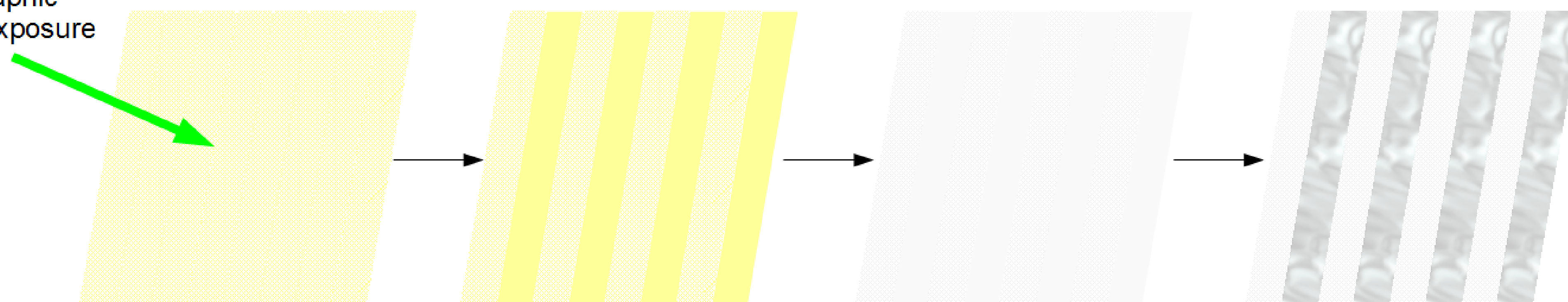
Photochromic Materials - summary

- The modulation of refractive index in photochromic materials in due to a modulation of polarizability;
- The chemical structure of the molecule can be optimized to enhance the change in polarizability;
- The main issue is the content of photochromic unit in the holographic material;
- It is better to play with the concentration than the polarizability, for example using photochromic polymers;
- The response to light exposure is highly non linear and all the material thickness must be written, so very low sensitivity and complex profiles.

Dichromated Gelatine (DCG)

Phillips, N. J., et al. Proc. SPIE Vol. 1914 (1993).
Xiong, L. et al. Applied Optics, 37(17), 3678-3684 (1998)
Chang, B. J., et al. Applied Optics, 18(14), 2407-17 (1979).

How does the DCG work?



- Simple gelatin layer added with dichromated (usually ammonium)
- After the exposure only a latent image has been impressed on the DCG (gelatin cross-linking)
- Development: different swelling with water for exposed and unexposed areas
- Development: drying with alcohol with formation of micro-voids => n decreases
- The amount of micro-voids = f(cross-linkage) => less/no microvoid in the exposed area
- Δn ✪ Δmicro-voids => easy to have large Δn since $n_{void} = 1$!

Dichromated Gelatine (DCG)

Phase Holograms in Dichromated Gelatin

T. A. Shankoff

October 1968 / Vol. 7, No. 10 / APPLIED OPTICS

The gelatin–dichromate photosensitive system has been shown to be very efficient as a recording medium for both two- and three-dimensional holographic gratings. Upon development, as much as 33% of incident reading light is diffracted into the first order for the unmodulated thin phase gratings and 95% for the thick holograms. The material can record a grating spacing at least as small as 2600 Å, and gives reconstructions comparable with those obtained in 649F film. The air–gelatin index differential of 0.54 is considered responsible for the high diffracted powers found. Exposures vary from 3 mJ to 150 mJ at 4880 Å. Certain films have speeds within two orders of magnitude of 649F holographic film.

- Dichromated gelatine (DCG) has been studied for making phase holograms for more than 40 years.
- It is surely **the best** material for holography and the benchmark.
- Modulation of the refractive index very large => Δn up to 0.15!
- Fine tuning of Δn
- Good transparency up to 2.8 μm
- Good homogeneity => very low scattering => high S/N
- Reference material for VPHG in astronomy

VPHG materials: Dichromated Gelatine (DCG)

- Dichromated gelatine (DCG) has been studied for making phase holograms for more than 40 years.
- It is surely **the best** material for holography and then the benchmark.
- Modulation of the refractive index very large => Δn up to 0.15!
- Fine tuning of Δn
- Good control of film thickness
- Transparent up to 2.5 μm
- Good homogeneity => very low scattering => high S/N
- Reference material for VPHG in astronomy

BUT…

- Low sensitivity
- Narrow spectral response
- Sensitive to moisture
- Complex chemical developing process

Photopolymers

Photopolymer Material for Holography

B. L. Booth

March 1975 / Vol. 14, No. 3 / APPLIED OPTICS

An experimental Du Pont holographic photopolymer material produces an index modulation in excess of 10^{-2} utilizing a diffusion mechanism. Optimum exposure in air is typically 30 mJ/cm^2, in nitrogen 3 mJ/cm^2. Composition, beam ratio, and exposure power all affect the index modulation. This, combined with thickness variations, permits diffraction efficiency to be preadjusted for a variety of desired angular responses and spatial frequencies. The material can be easily overmodulated according to Kogelnik's phase grating theory. No wet processing is required. After total polymerization, storage at 100°C, −60°C, and under water does not significantly affect the diffraction efficiency. Image-object superposition is exact for real-time holography. Excellent copies of silver halide holograms with four times the original efficiency have been made. Grating devices with tailored peak or flat wavelength response can be constructed.

Why interesting?

- High sensitivity;
- Large spectral response, by choosing the dye (488, 532, 633 nm);
- **Self-developing (no chemical post exposure process)**;
- Easy control of the film thickness (especially with liquid photopolymer)
- Flexible, self-standing films

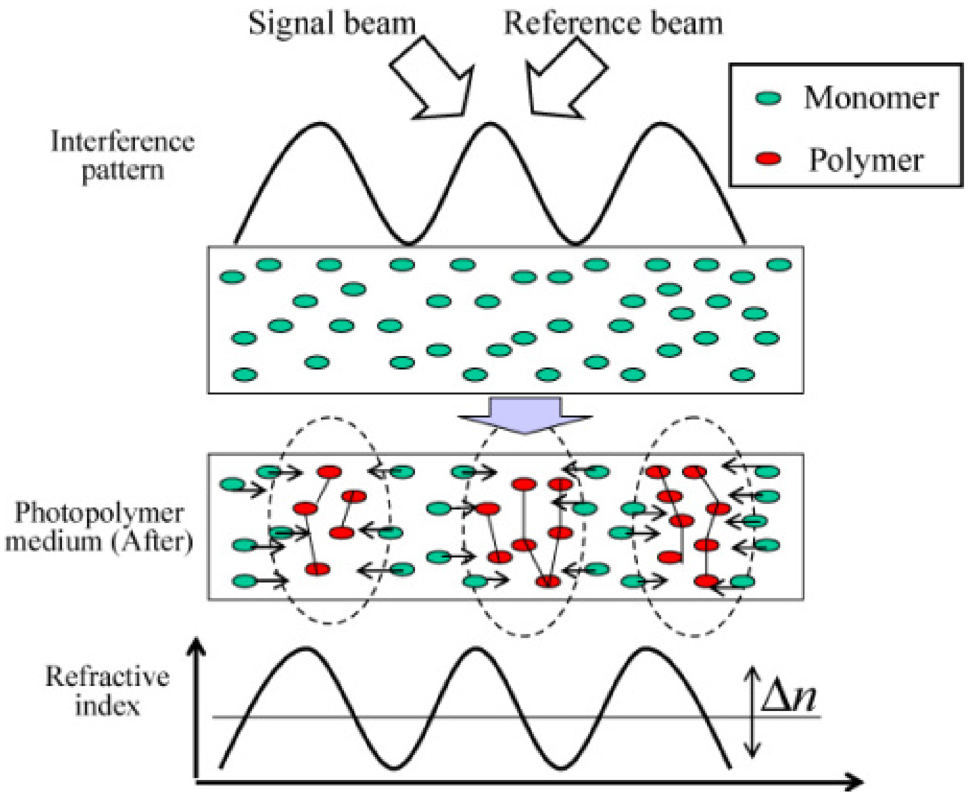
Photopolymers

What's inside a photopolymer?

- Active monomer/s;
- Photoinitiation system (dye + initiator);
- Binder (in solid photopolymer, usually PVA, CAB, PVAc,...);
- Other components (cross-linkable monomers, co-initiator,...)

Photopolymers: mechanism

- Uniform mixture
- Light exposure: monomers react in the bright areas
- Diffusion of the monomers from dark to bright areas => density change
- A modulation of the refractive index that resembles the illuminating conditions is obtained



The monomers are the refractive index carriers

Photopolymers: chemical amplification

A key problem with organic materials for holography is their general low sensitivity to light.
We have to find mechanisms that mimic to the reaction in silver halide.

Free radical polymerization

Photopolymers: chemical amplification

Starting System:

- Sensitizing Dye (D)
- Initiator Electron Donor (ED): triethanolamine
- Monomer (M): vinyl monomer (acrylamide)

The reaction has to start...we have to create radicals with light

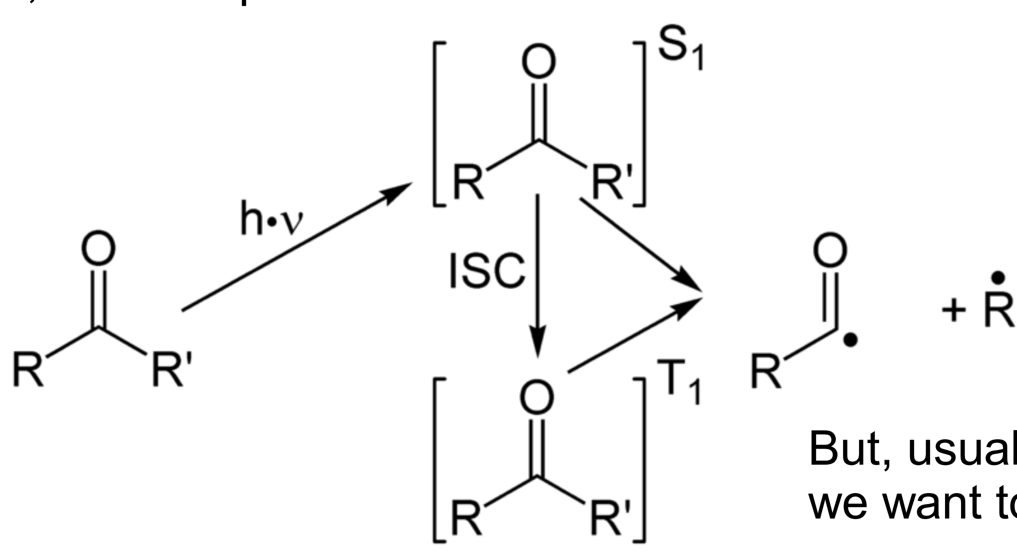
Photopolymers: chemical amplification

Starting System:

- Sensitizing Dye (D)
- Initiator Electron Donor (ED): triethanolamine
- Monomer (M): vinyl monomer (acrylamide)

The reaction has to start...we have to create radicals with light

No a big issue, for example the Norrish's reaction on ketons and aldehydes



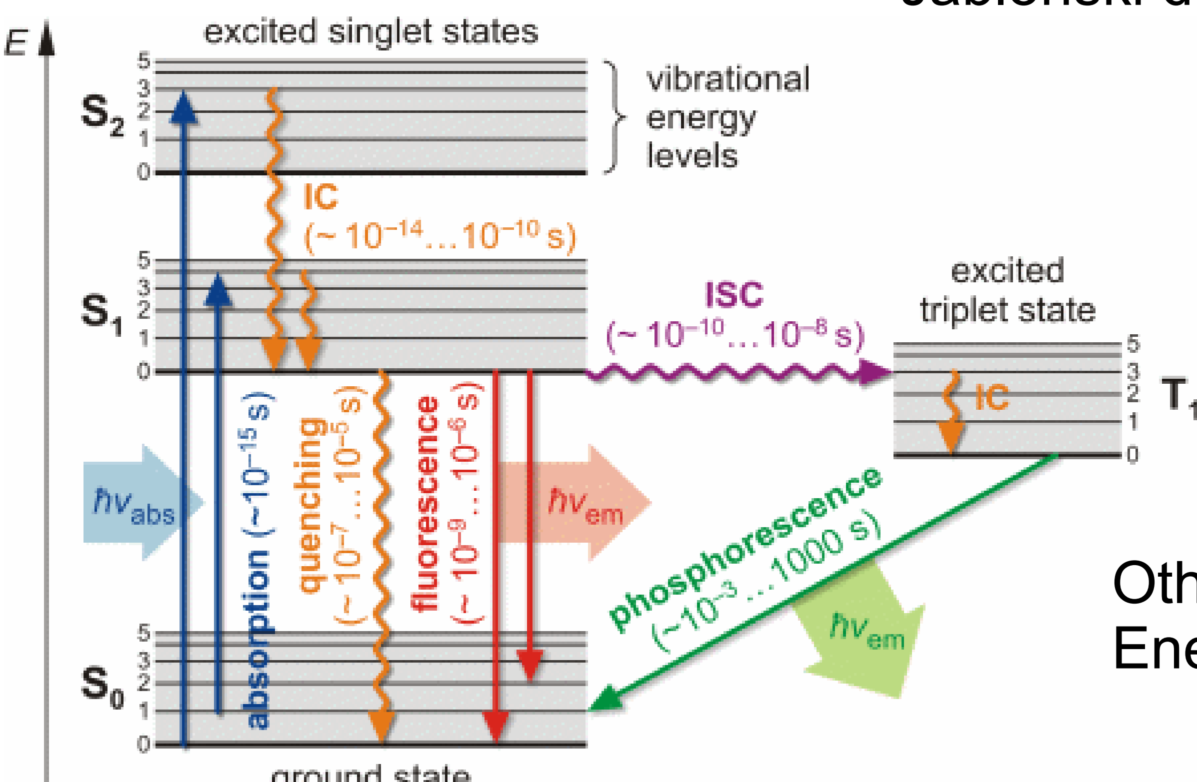
But, usually they work in the UV and we want to use laser in the visible....

Photopolymers: chemical amplification

We can use a Dye to make the system sensitive to visible light.
The Dye absorbs a photon in the visible:

$$D + hv \rightarrow {}^1D^*$$

Jablonski diagram tells us the possibilities



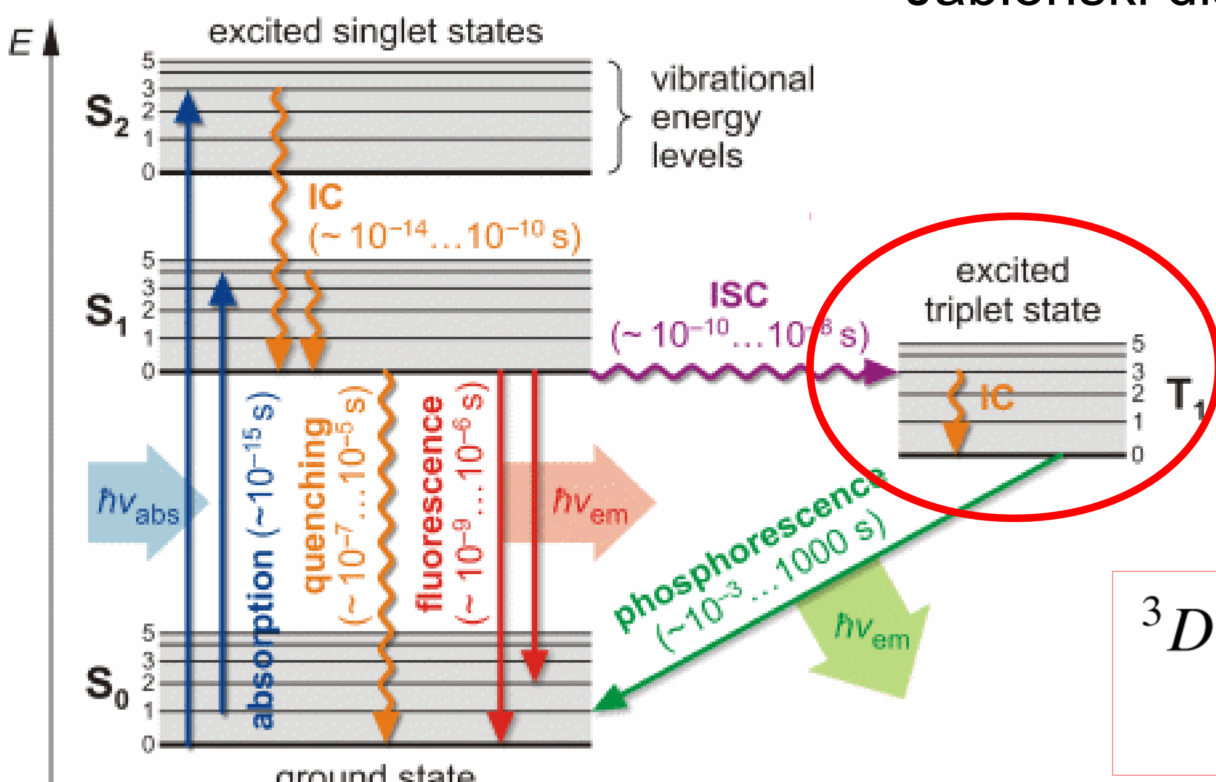
Other possibilities:
Energy transfer, electron transfer

Photopolymers: chemical amplification

We can use a Dye to make the system sensitive to visible light.
The Dye absorbs a photon in the visible:

$$D + h\nu \rightarrow {}^1D^*$$

Jablonski diagram tells us the possibilities



Common example:

Reaction with Electron Donor (TEA)

Electron transfer

$$ {}^3D^* + (\mathrm{HOCH_2CH_2})_3\mathrm{N}: \rightarrow D^{\cdot -} + (\mathrm{HOCH_2CH_2})_3\mathrm{N}^{\cdot +}\,. $$

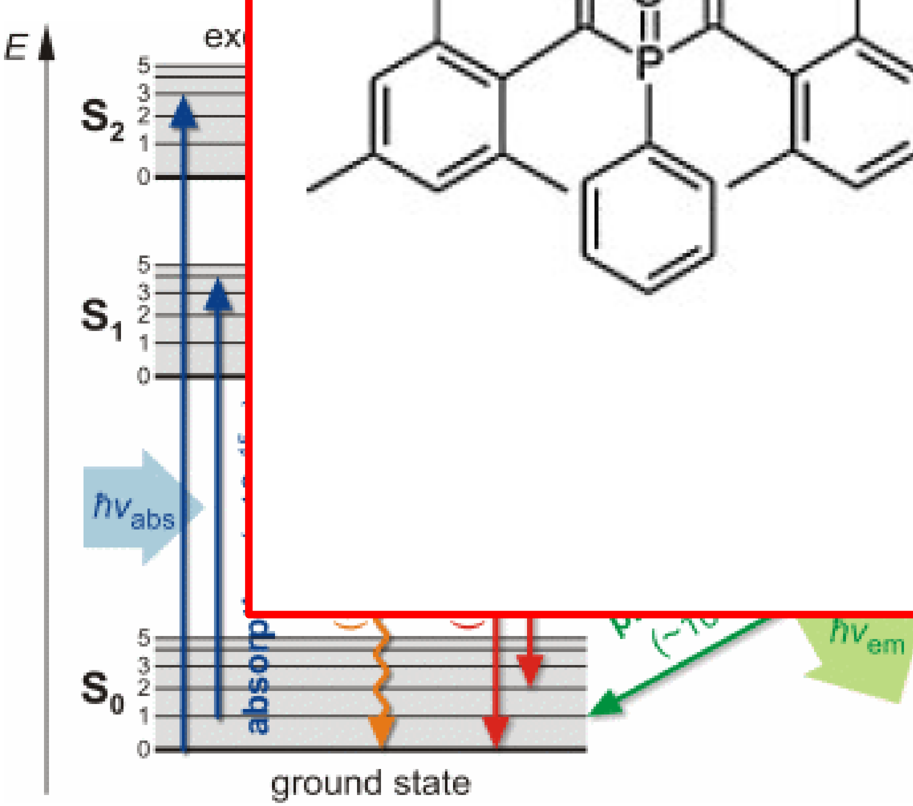
Photopolymers: chemical amplification

1^{st} step: t

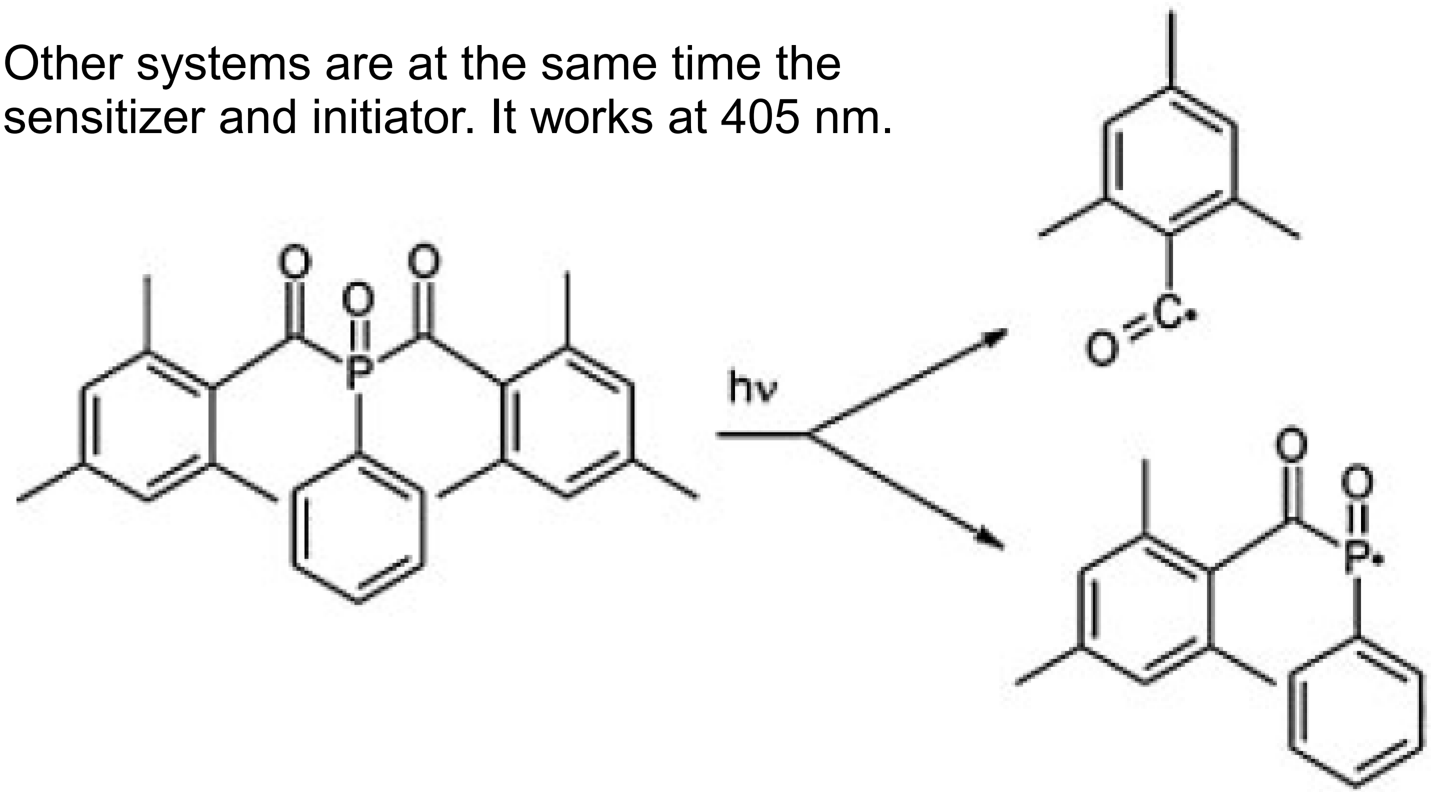
…ssibilities

…onor (TEA)

…n transfer



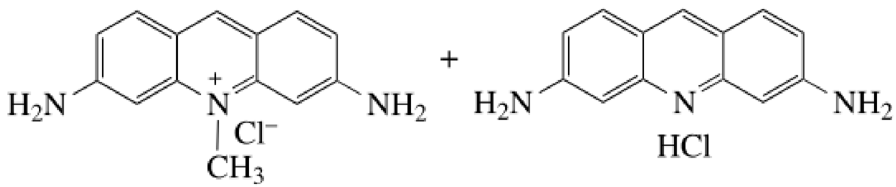
Other systems are at the same time the sensitizer and initiator. It works at 405 nm.



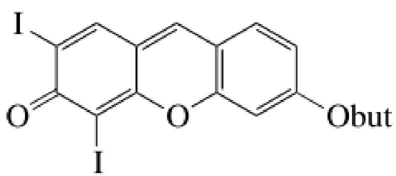
Irgacure 819

$$^3D^{*} + (\mathrm{HOCH_2CH_2})_3\mathrm{N}: \rightarrow D^{\cdot -} + (\mathrm{HOCH_2CH_2})_3\mathrm{N}^{\cdot +}.$$

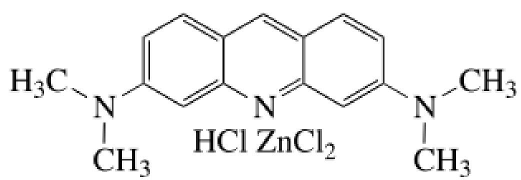
Photopolymers: Dyes



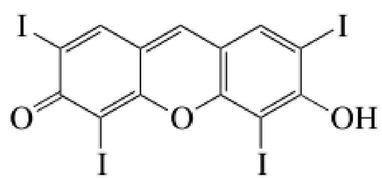
65% (1) 35%



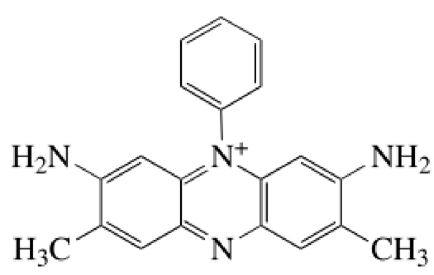
(2)



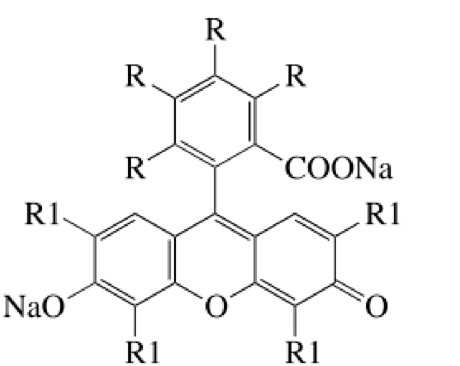
(3)



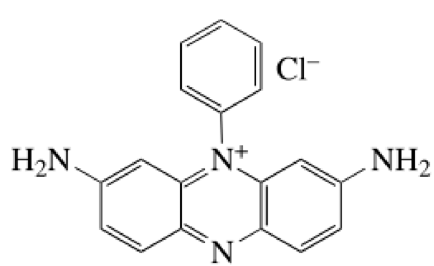
(4)



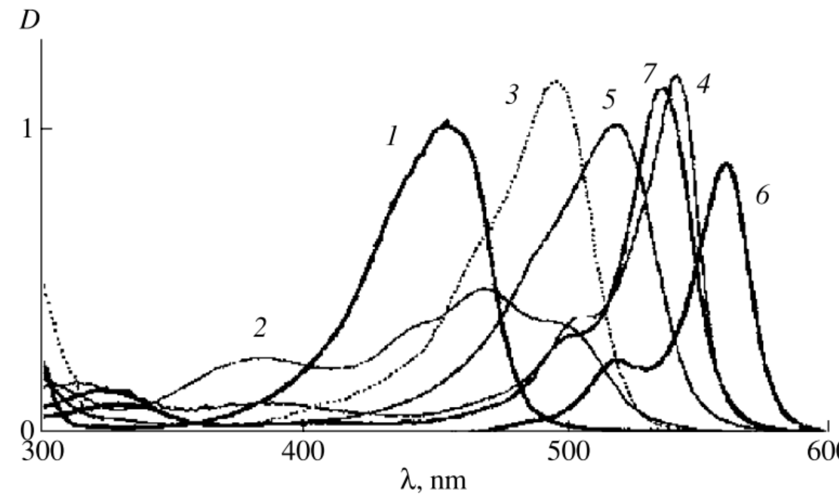
(5)



R = Cl; R1 = I (6) R = H; R1 = Br (7)
R = H; R1 = I (8)



(9)

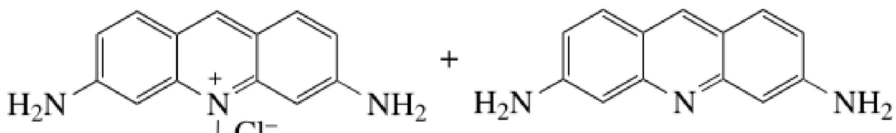


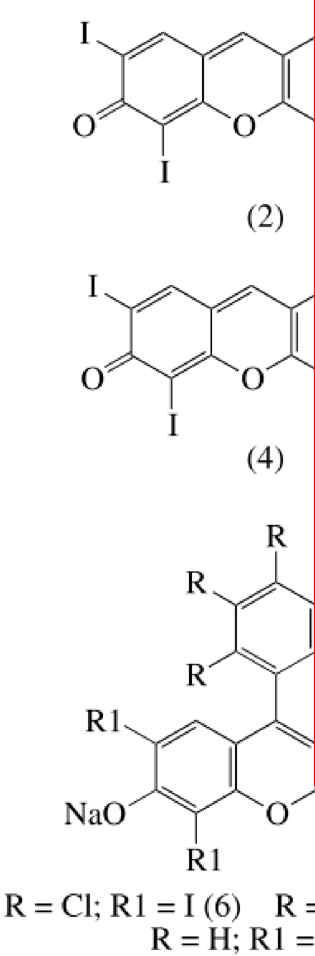
Dye must be choose according to:
- Wavelength sensitivity;
- Efficiency;
- Absorption coefficient.

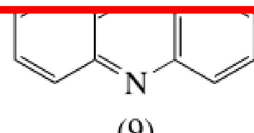
This in important especially for panchromatic materials.

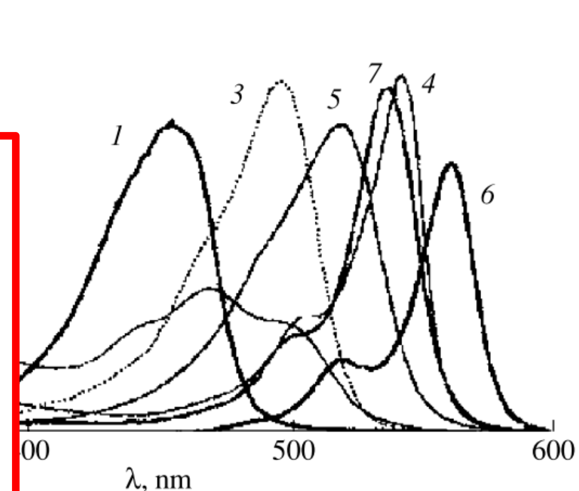
High Energy Chemistry, 2006, Vol. 40, No. 3, pp. 131–141

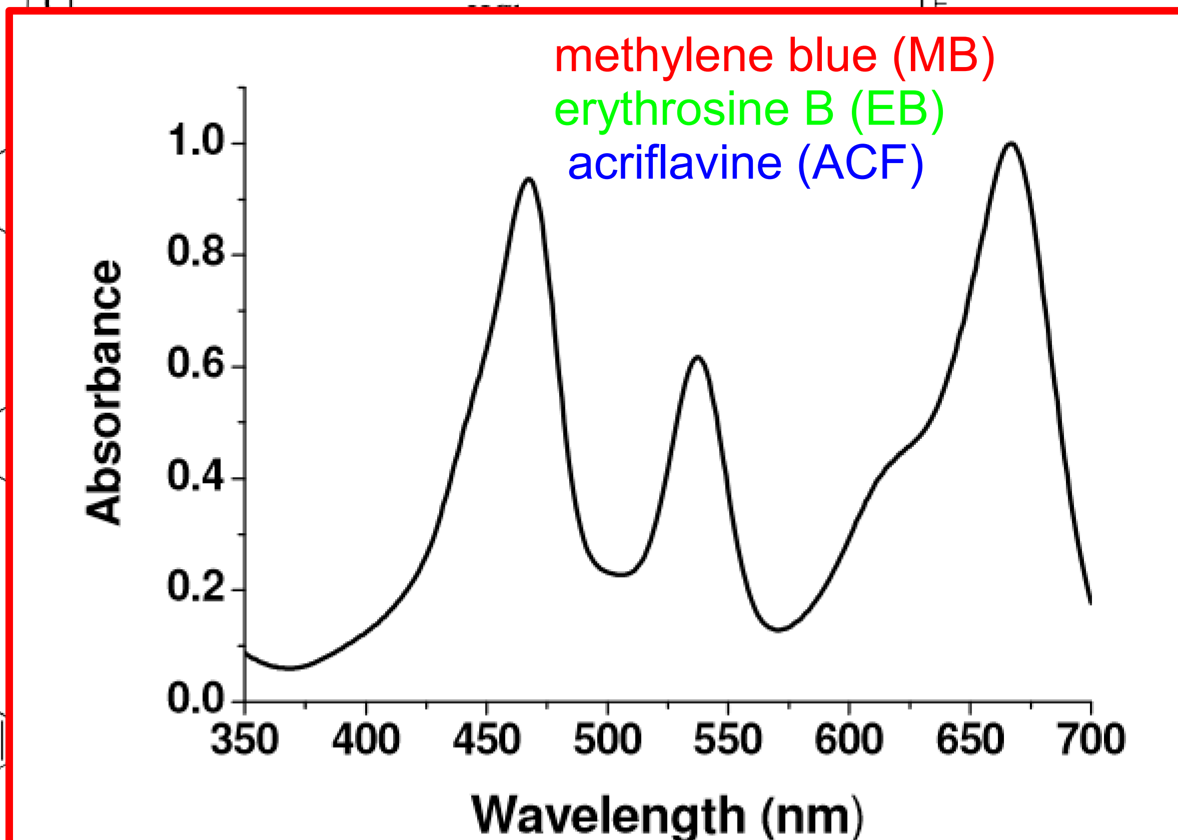
Photopolymers: Dyes











Meka et al. Appl Opt. 2010 10;49(8)

choose according to:
sensitivity;

coefficient.

tant especially for
materials.

High Energy Chemistry, 2006, Vol. 40, No. 3, pp. 131–141

Photopolymers: chemical amplification

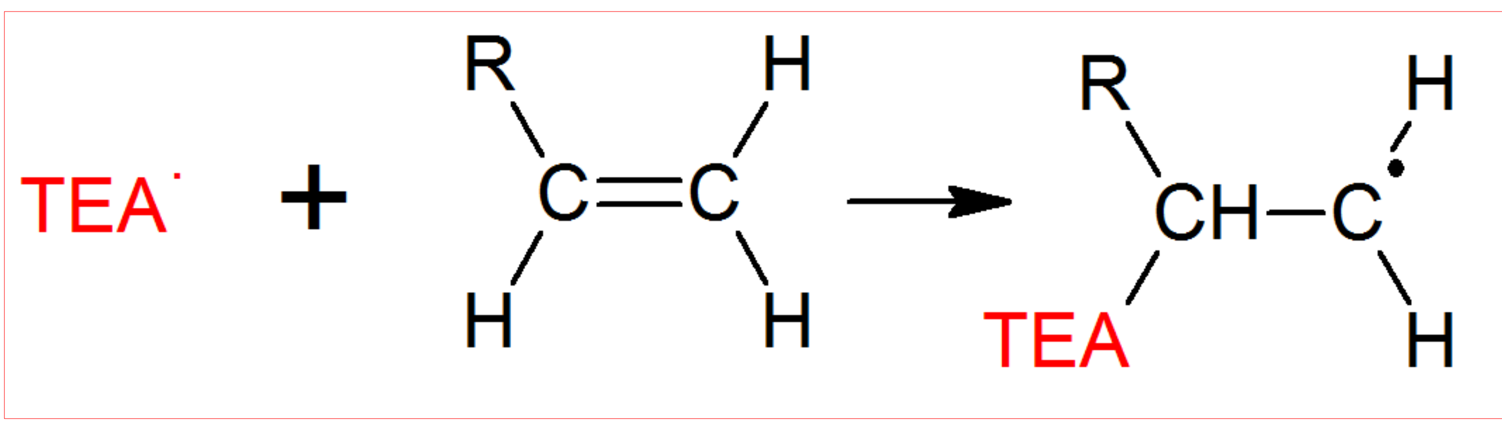
$$^{3}D^{*} + (\mathrm{HOCH_2CH_2})_3\mathrm{N}: \rightarrow D^{\cdot -} + (\mathrm{HOCH_2CH_2})_3\mathrm{N}^{\cdot +}.$$

Free radical (TEA)

$$(\mathrm{HOCH_2CH_2})_3\mathrm{N}^{\cdot +} \rightarrow (\mathrm{HOCH_2CH_2})_2\mathrm{NCH^{\cdot}CH_2OH} + \mathrm{H}^{+}.$$

This step is really dependent on the system used

Reaction with the monomer



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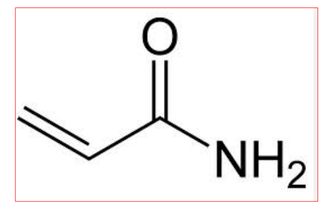
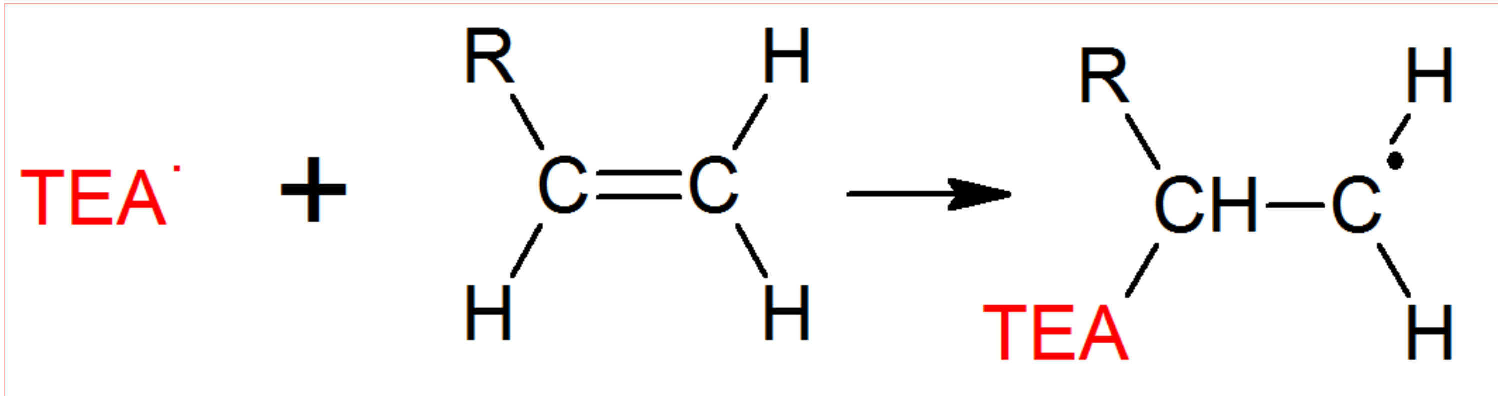
$$(\mathrm{HOCH_2CH_2})_3\mathrm{N}^{\cdot +} \rightarrow (\mathrm{HOCH_2CH_2})_2\mathrm{NCH^{\cdot}CH_2OH} + \mathrm{H}^{+}\,.$$

Acrylamide the most studied monomer

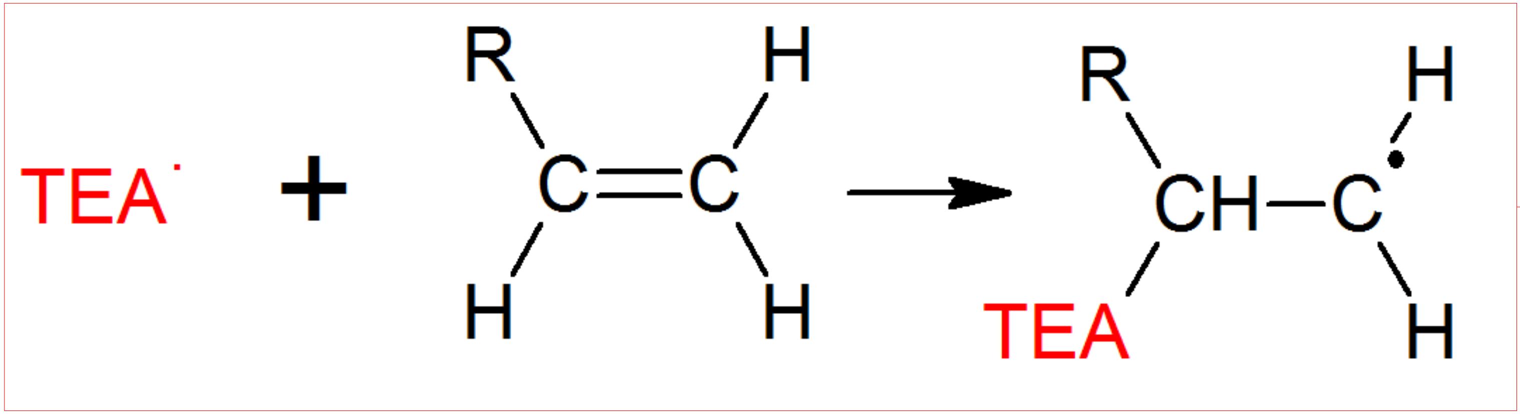


Reaction with the monomer

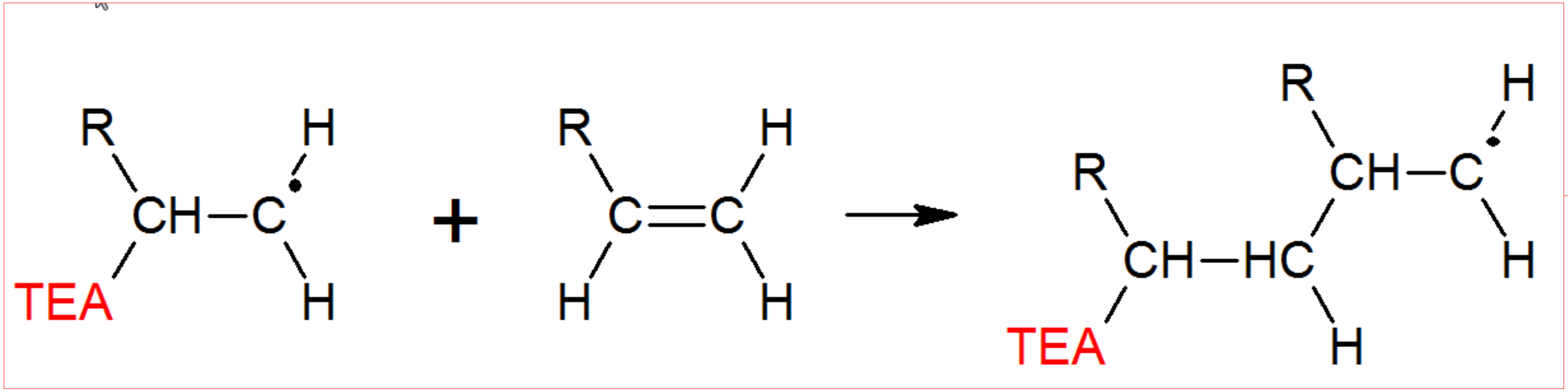


Photopolymers: chemical amplification

Reaction with the monomer: **INITIATION**

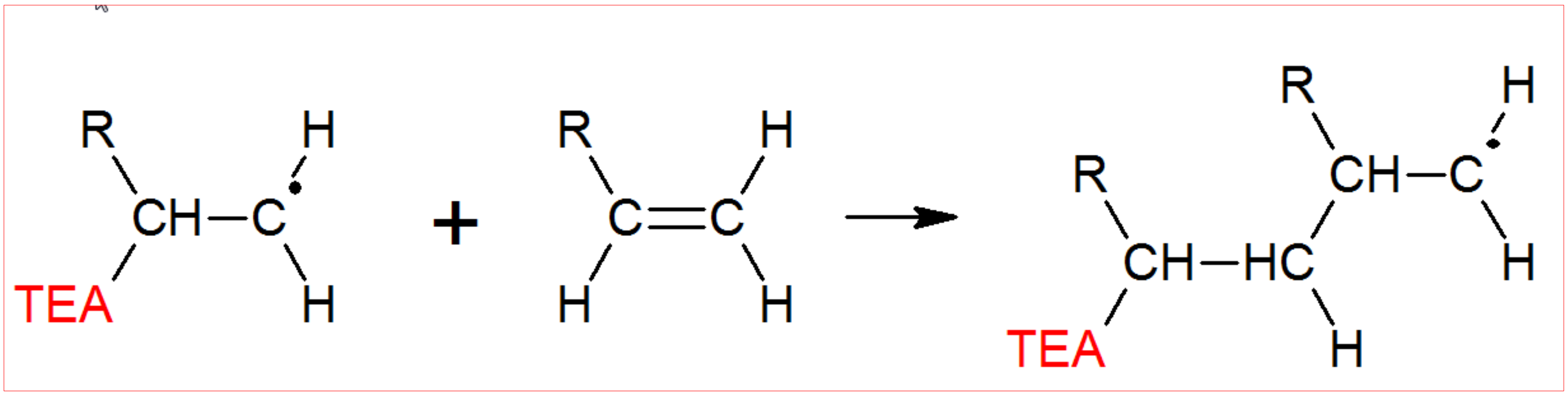


Reaction with another monomer: **PROPAGATION**

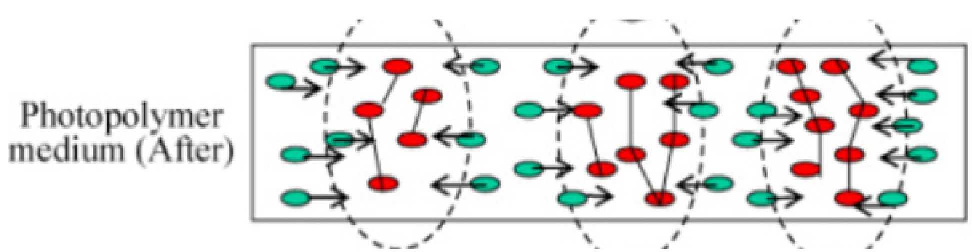


Photopolymers: chemical amplification

Reaction with another monomer: **PROPAGATION**



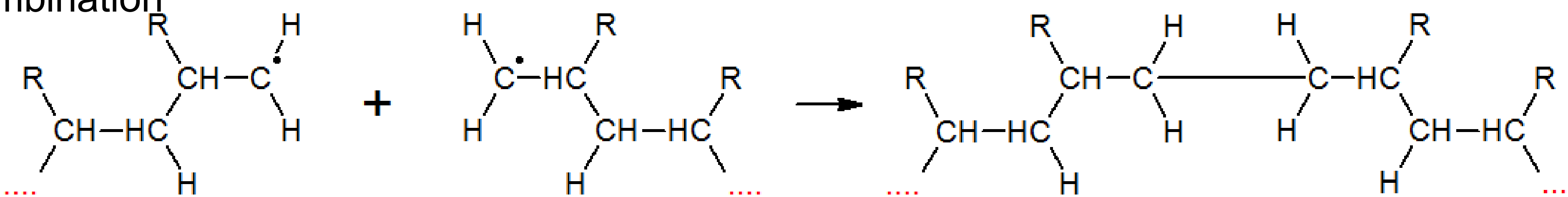
During the **PROPAGATION...**
- The concentration gradient occurs;
- Diffusion of monomers compensates the gradient;
- The viscosity of the medium increases and makes the diffusion more and more difficult.



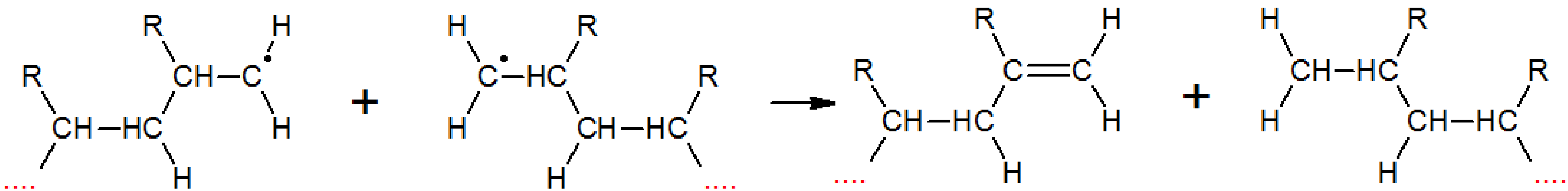
Photopolymers: chemical amplification

End of reaction: **TERMINATION**

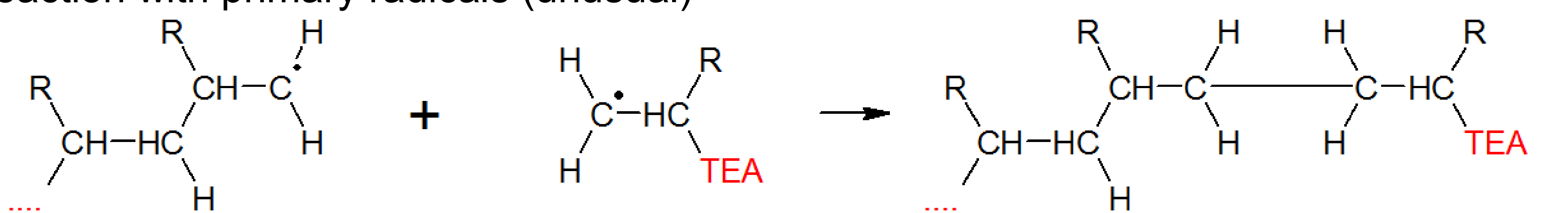
Combination



Disproportionation



Reaction with primary radicals (unusual)



Photopolymers: chemical amplification

In this way the radical reaction stops, but it is necessary that no other reactions can take place. Important to bleach all the dye in the photopolymer.

Dye bleaching: important step to stop the reaction and make the material transparent. No more dye is active.

$$(HOCH_2CH_2)_2NCH^{\cdot}CH_2OH + H^+ + D^{\cdot -}$$
$$\rightarrow (HOCH_2CH_2)_2NCH = CHOH + H_2D\,.$$

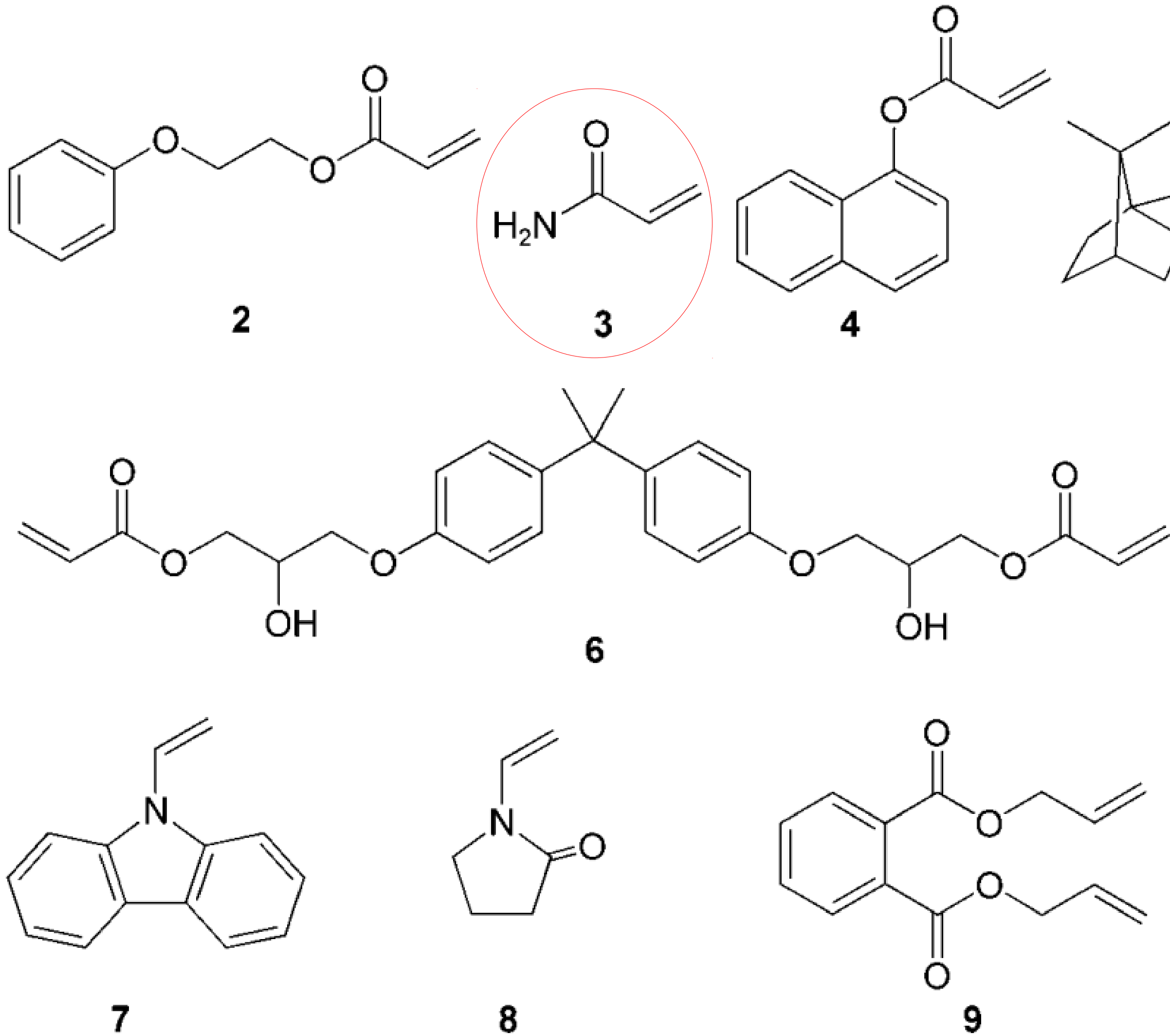
$$(HOCH_2CH_2)_2NCH$$
$$= CHOH \rightarrow (HOCH_2CH_2)_2NCH_2CHO\,.$$

This is usually achieved with an uniform illumination with incoherent visible light

Photopolymers: considerations

- The radical reaction is sensitive to oxygen: it inhibits the reaction;
- For effective phase hologram formation, the diffusion of monomer should be faster than its consumption by polymerization.
- The diffusion depends on hologram line density: low density longer path for the diffusion;
- For high line density, risk of growth of macroradicals in dark ares;
- The diffusion depends on the writing laser power: the higher the power, the lower the diffusion;
- The ratio of the two writing beams power affects the diffusion: no really dark areas, so uniform polymerization.

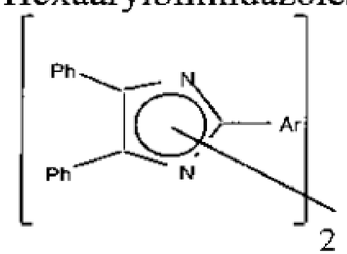
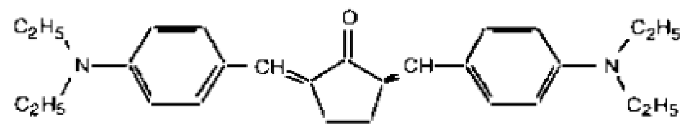
Photopolymers: monomers

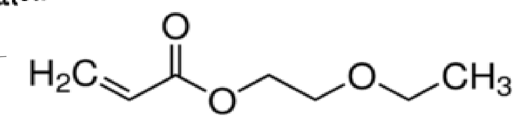


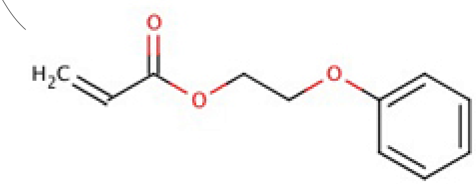
The main properties of the monomers are:
- Reactivity;
- Diffusivity;
- Polarizability;
- Compatibility;
- Number of reactive centers.

Photopolymers: DuPont

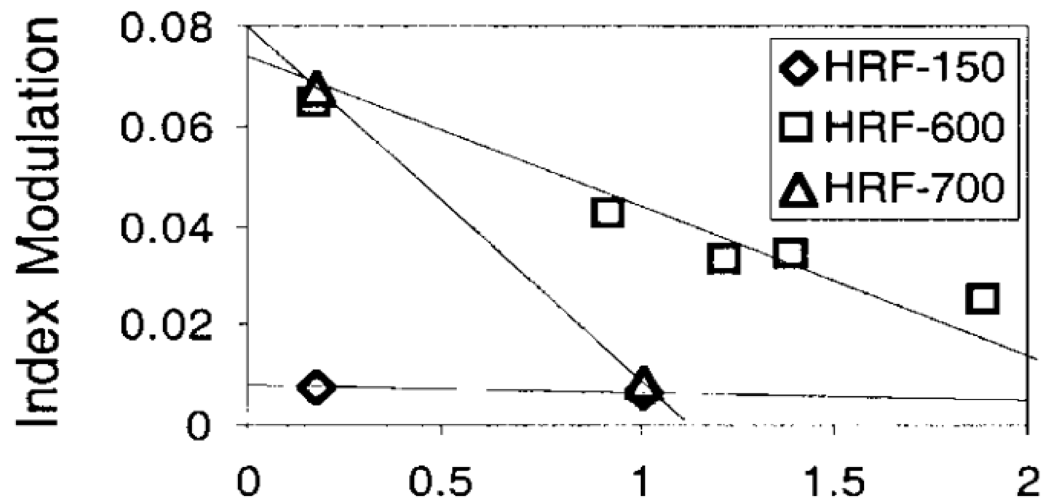
Table 2. Model components for DuPont holographics.

BINDERS:	Poly(vinyl acetate), poly(methyl methacrylate), cellulose acetate butyrate, poly(styrene–methyl methacrylate)	
MONOMERS:	2-Phenoxyethyl acrylate, 2-ethoxyethyl acrylate	
INITIATORS:	Hexaarylbiimidazoles  HABI	SENSITIZING DYES:  DEAW





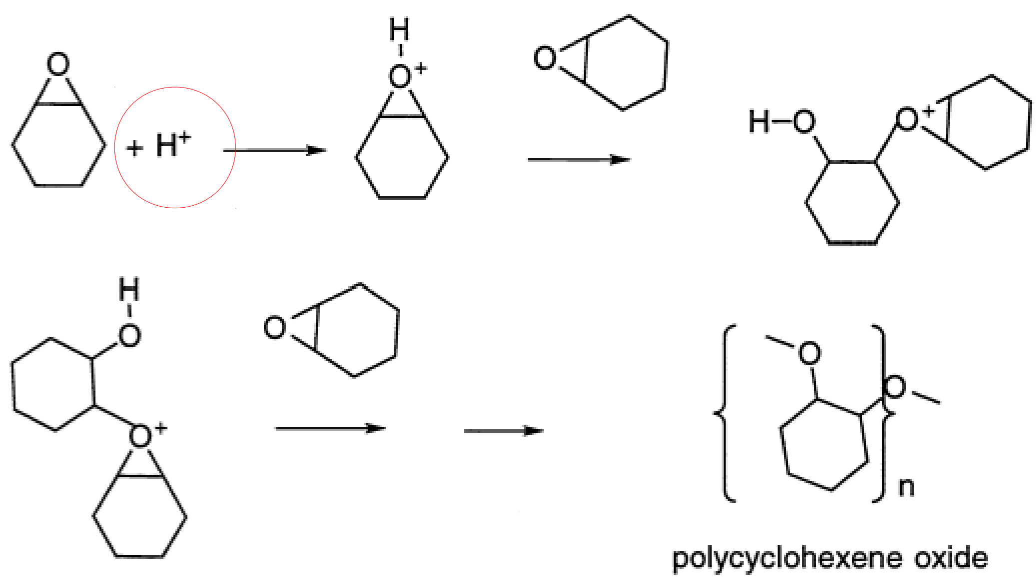
DuPont photopolymers were characterized by a large Δn, but large shrinkage;
A thermal treatment enhanced the Δn, promoting a further diffusion



Trout et al. Adv. Mater. 1998, 10, No. 15

Photopolymers: other reactions

Cationic Ring-Opening Reaction (CROP):
1) Fast (not often) initiation and propagation of cationic polymerization with low exposure energy is possible.
2) Cationic polymerization is not inhibited by oxygen.
3) Cationic ring-opening polymerization results in less shrinkage than free radical polymerization.

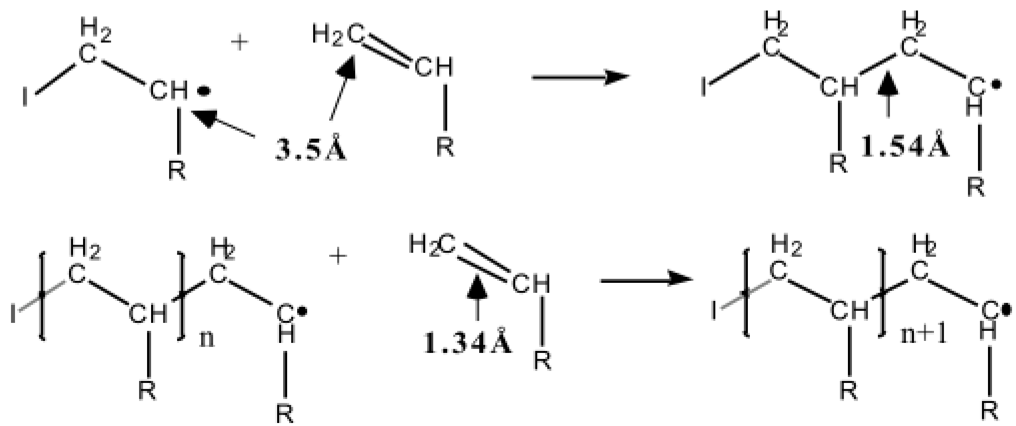


The reaction is catalyzed by acid, therefore it is necessary in the composition a Photoacid Generator. The presence of acid is, on the other hand, a drawback since it affects the time stability of the hologram.

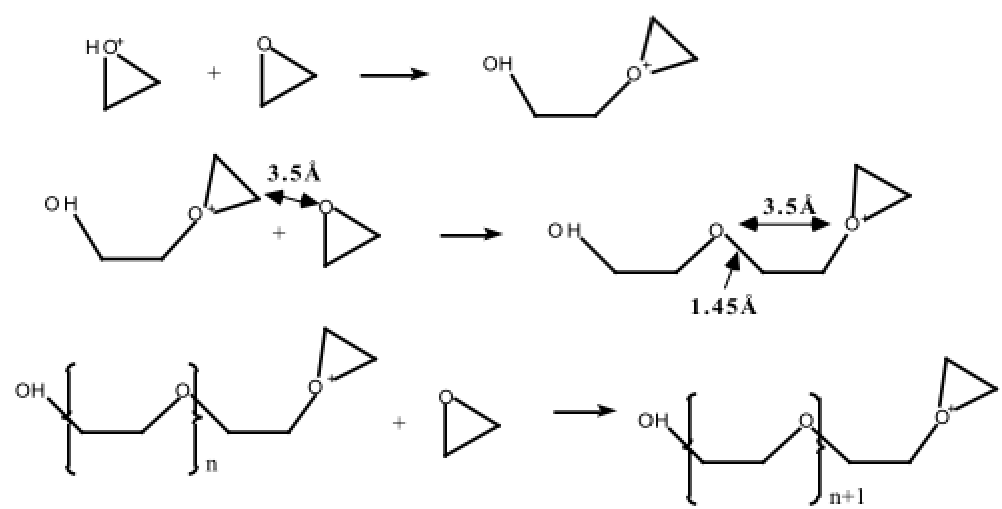
Photopolymers: other reactions

Low shrinkage:

Vinyl Free Radi cal



Cationic Ring Opening



Photopolymers: summary

Attractive systems thanks to the chemistry possibilities and the self-developing;

Many components have to be optimized (monomer, binder, initiator,...) at the same time;

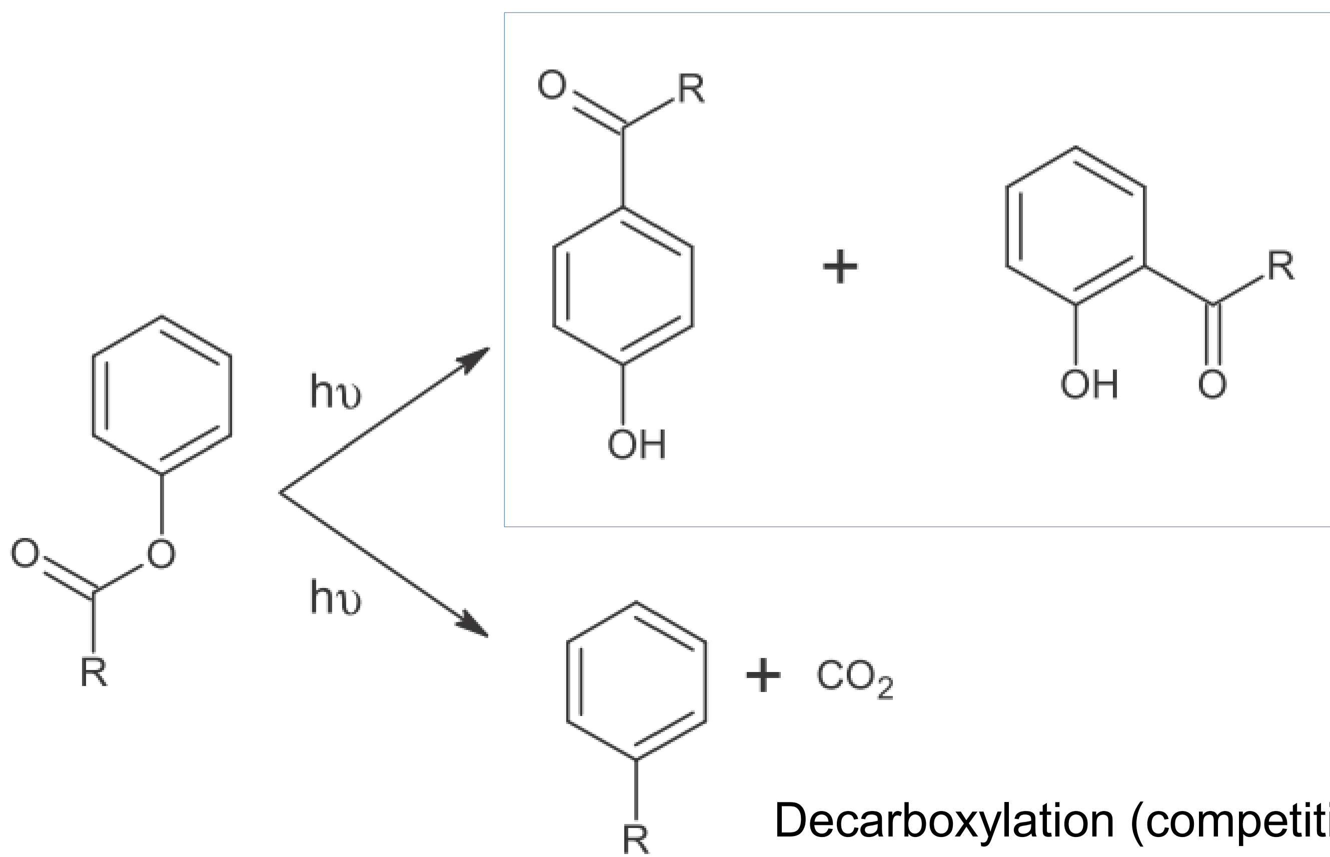
Important to have in mind the final use of the photopolymer;

New routes: cross-linkable binder with low shrinkage, multifunctional monomers, ROP reactions;

Modeling of the process as closer as possible to the real reaction (no approximations, all the variable considered such as oxygen quenching).

New approach: Photo-Fries reaction

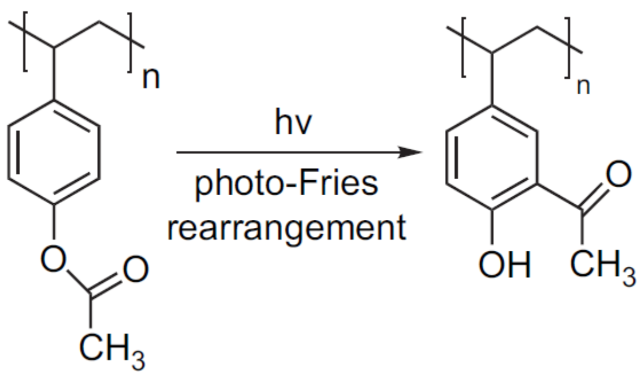
- Aromatic esters undergo to Photo-Fries rearrangement, when exposed to UV light. The result is an aromatic hydroxy-keton.
- Other paths are possible and in particular the decarboxylation.



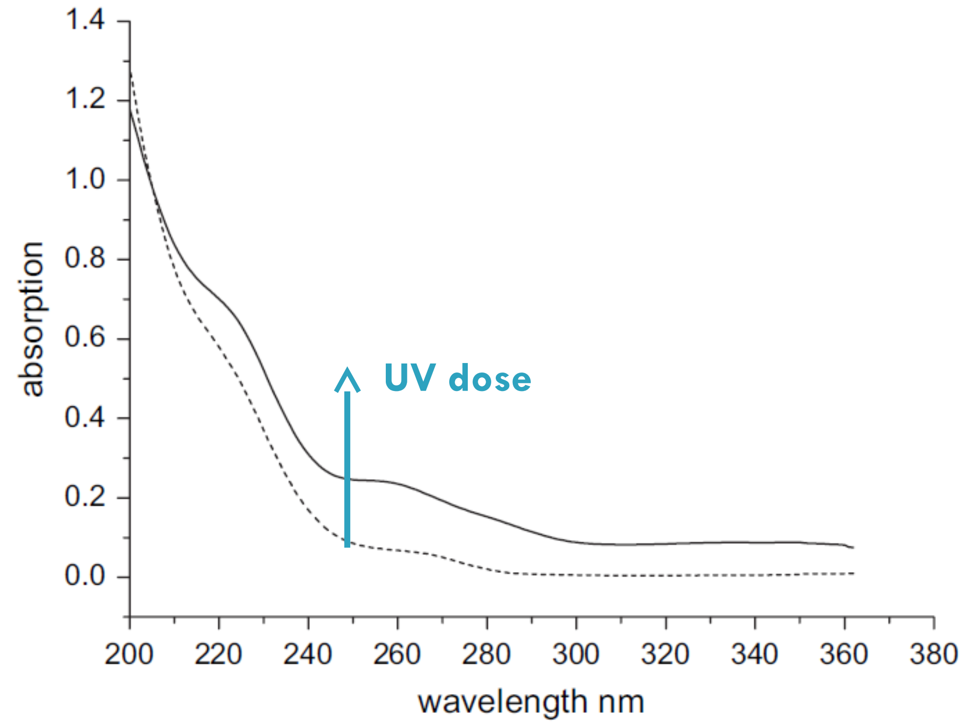
Decarboxylation (competitive reaction)

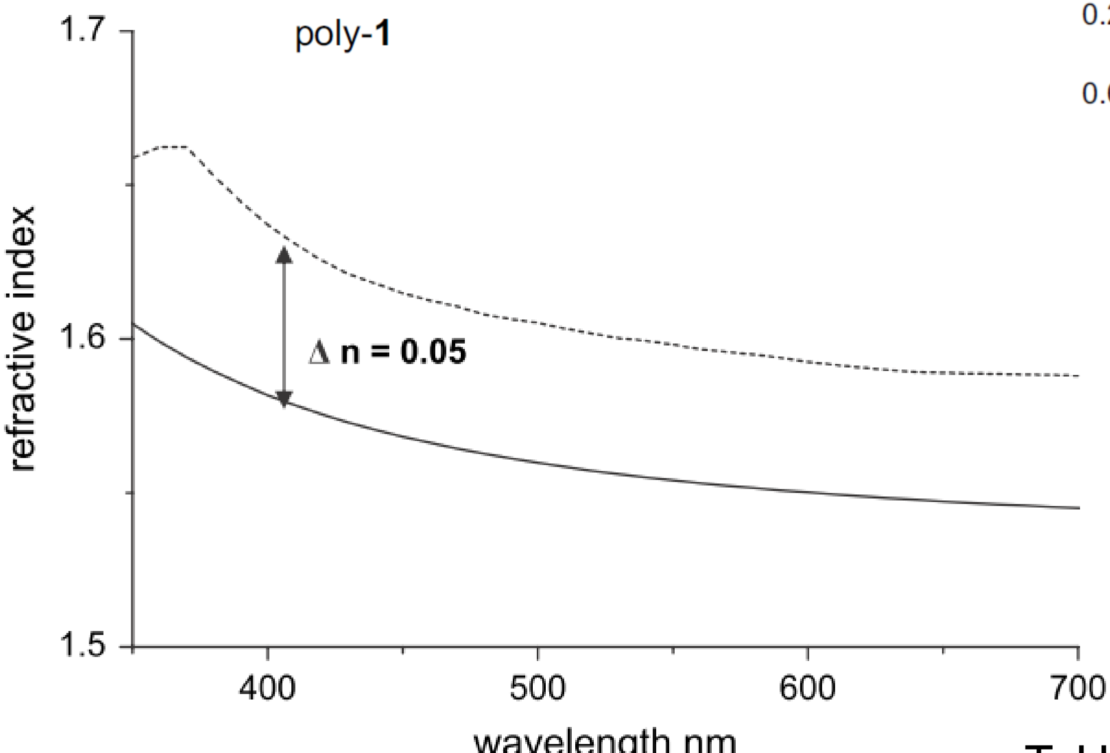
G. M. Coppinger, E. R. Bell, The Journal of Physical Chemistry, 70 (11) 1966

New approach: Photo-Fries reaction



poly-**1**



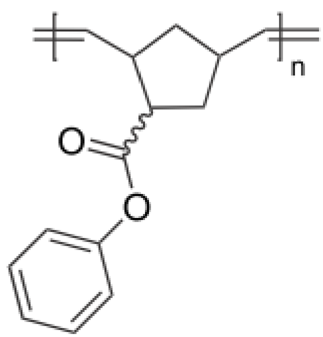


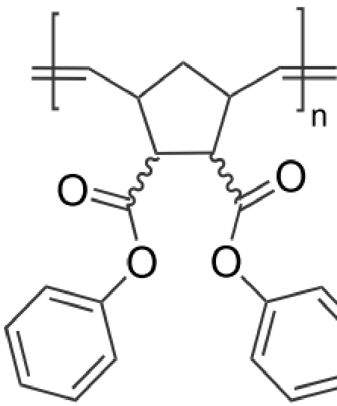
Thin films of **Polyacetoxystyrene (PAS)** show a remarkable change in the refractive index when exposed to UV light

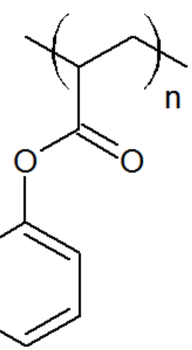
T. Hofler et al. / Polymer 48 (2007) 1930-1939

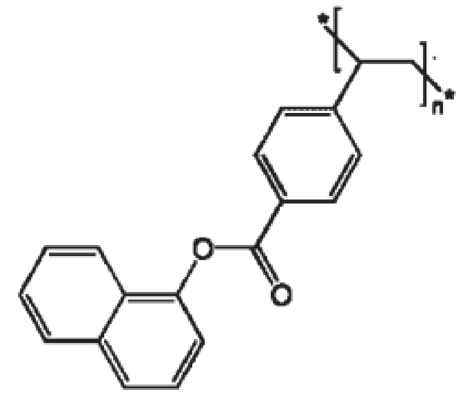
Photo-Fries reaction: systems

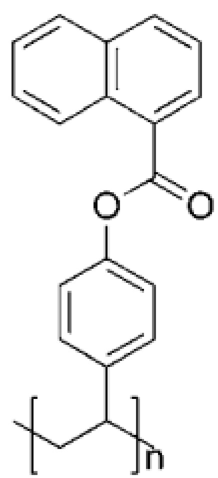
Some other examples...

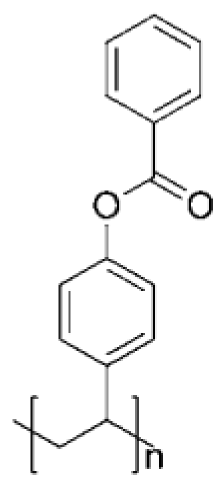


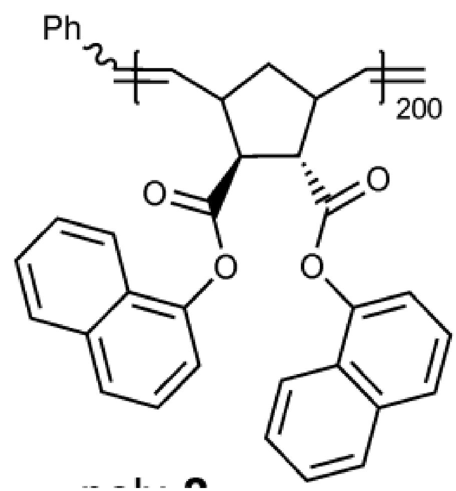










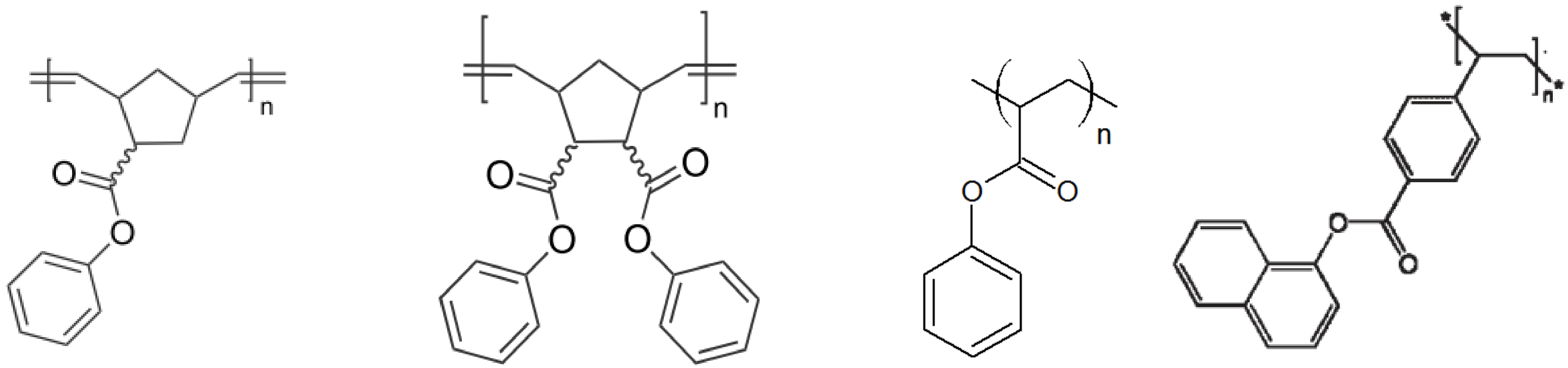


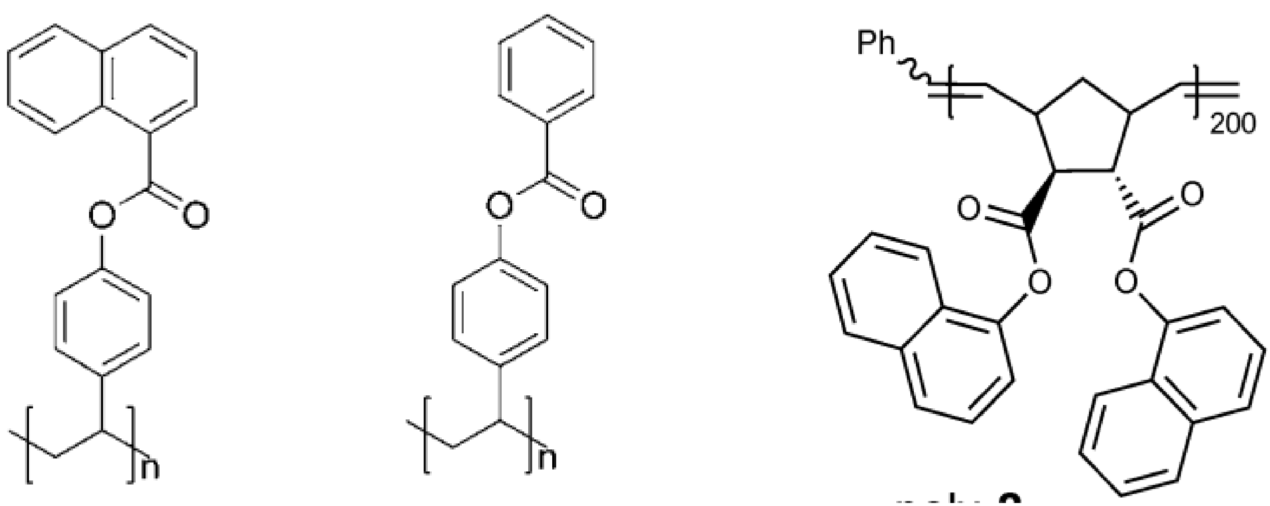
$\Delta n = 0.01 – 0.07$

Kopplmayr et al. *J. Mater. Chem.*, 2011, 21, 2965–2973
Daschiel, U. et al, *Macromol. Chem. Phys.* 2007, 208, 1190–1201
Griesser et al., *J. Mater. Chem.*, 2009, 19, 4557–4565
T. Ho¨fler et al. / *Polymer* 48 (2007) 1930-1939

Photo-Fries reaction: systems

Some other examples...





$\Delta n = 0.01 – 0.07$

Why?

$\Delta\alpha$ or $\Delta\rho$

Kopplmayr et al. *J. Mater. Chem.*, 2011, 21, 2965–2973
Daschiel, U. et al, *Macromol. Chem. Phys.* 2007, 208, 1190–1201

Griesser et al., *J. Mater. Chem.*, 2009, 19, 4557–4565
T. Ho¨fler et al. / *Polymer* 48 (2007) 1930-1939

Photo-Fries reaction: approach (1)

- Perform quantomechanical calculations (DFT, B3LYP, 6-31G**)

→ **Optimized geometry** of the model molecules

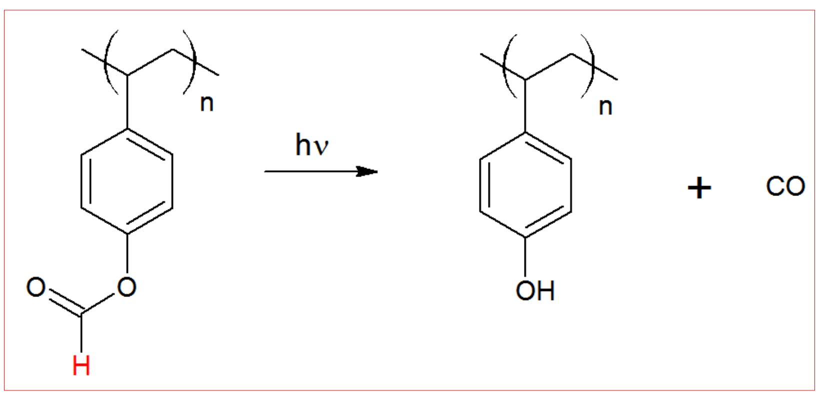
→ **Polarizability tensor (α)** at static electric field

→ **Refractive index (n)** applying the Lorentz-Lorenz model

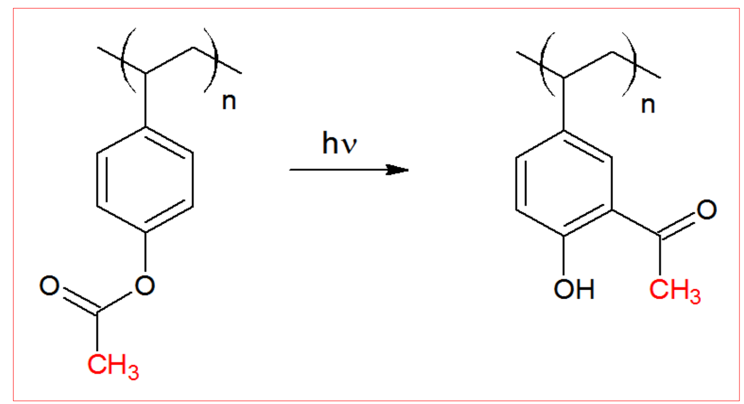
Photo-Fries reaction: approach (2)

- Polymer (1) and (2) have been synthesized and thin films have been spin-coated on Si substrate

Polymer (1)



Polymer (2)

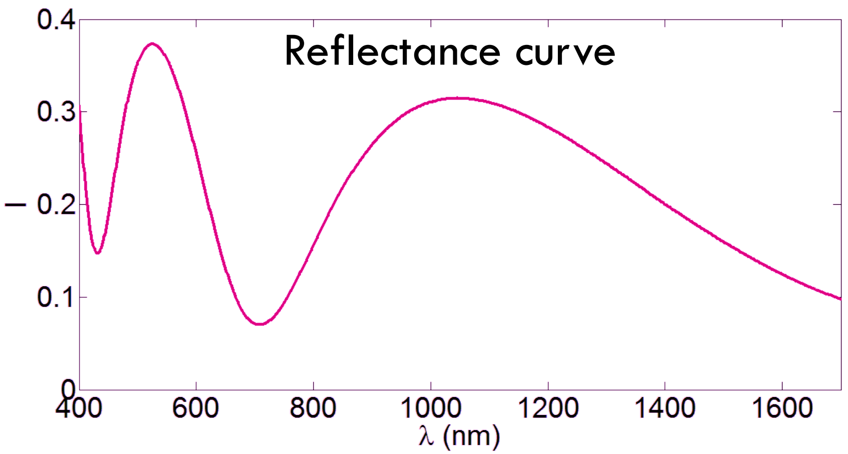


► **Spectral reflectance curves** as function of UV exposure @ 254 nm

Dispersion curves of n and film thickness (d) as function of UV exposure fitting with a Sellmeier 4-terms model.

Zanutta, A.; Colella, L.; Bertarelli, C.; Bianco, A. *Optical Materials* **2013**, *35*, 2283.

Photo-Fries reaction: approach (2)



fit

Thickness *d*

$$R = A + B\cos\left(\frac{4\pi n d}{\lambda}\right)$$

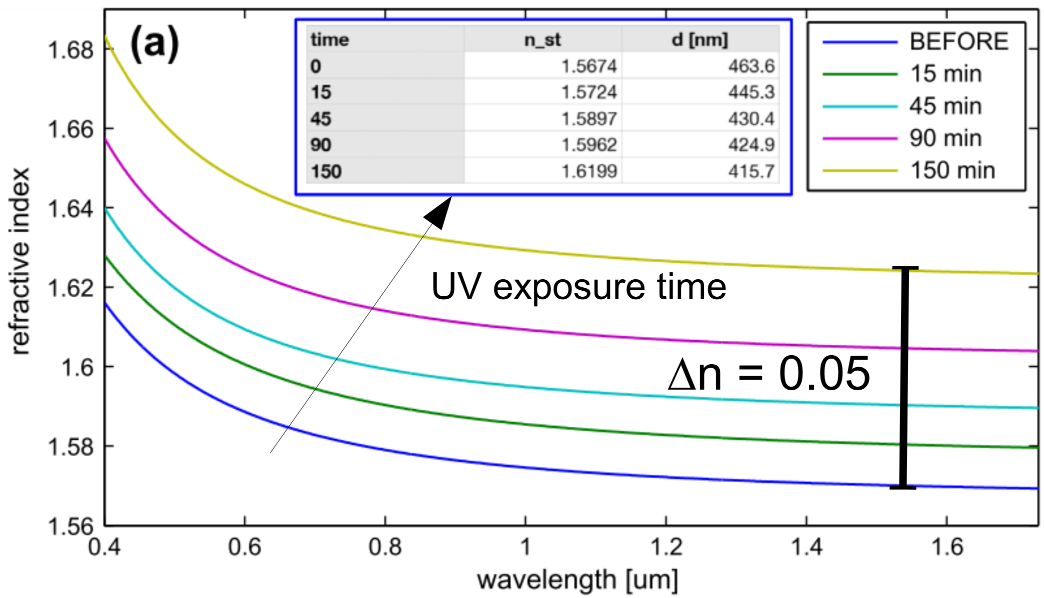
Dispersion curve *n(λ)*
and
Thickness *d*

$$n^2 = 1 + \frac{A_1.\lambda^2}{\lambda^2 - B_1} + \frac{A_2.\lambda^2}{\lambda^2 - B_2}$$

Sellmeier equation

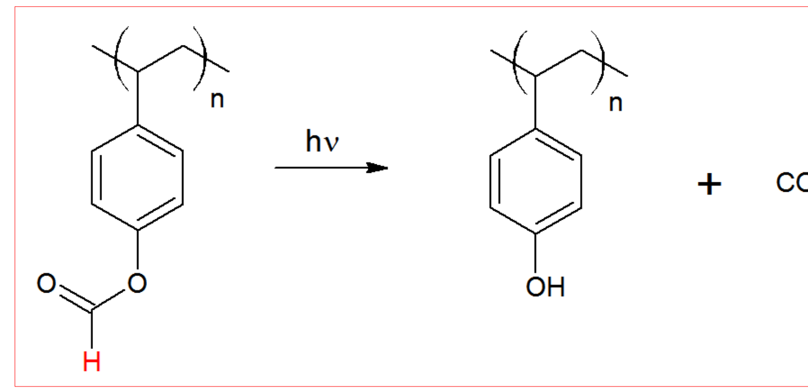
Static field refractive index $n_{st} = \sqrt{1 + A_1 + A_2}$

New approach: Photo-Fries reaction

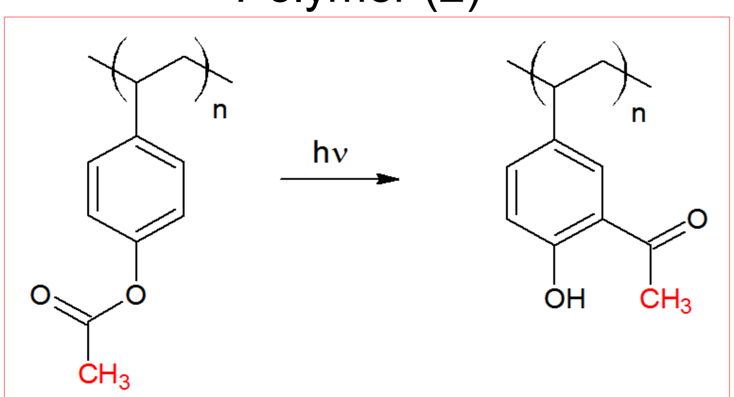


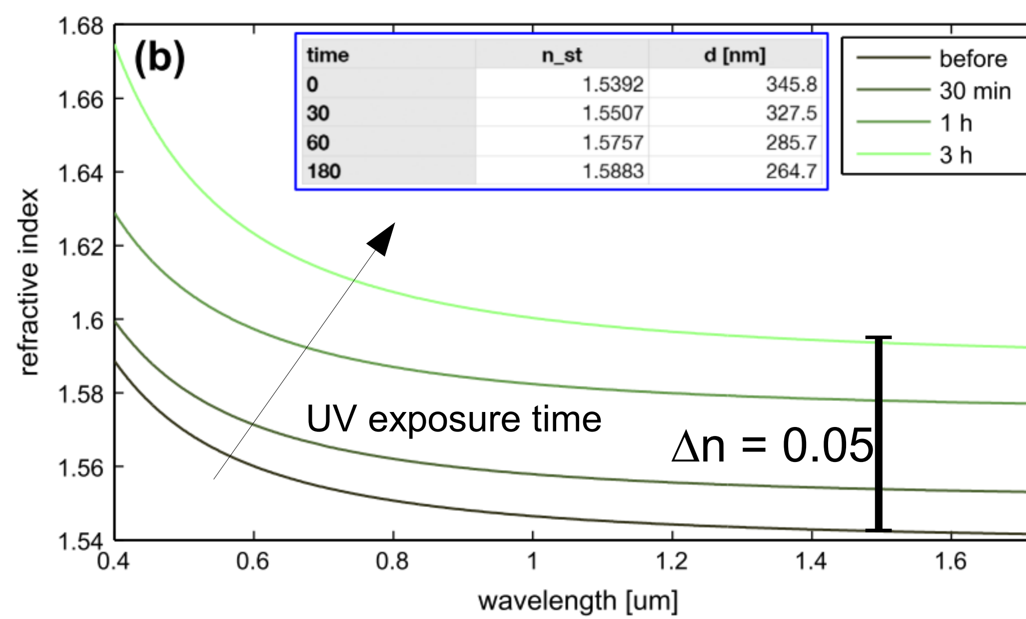
time	n_st	d [nm]
0	1.5674	463.6
15	1.5724	445.3
45	1.5897	430.4
90	1.5962	424.9
150	1.6199	415.7

Polymer (1)



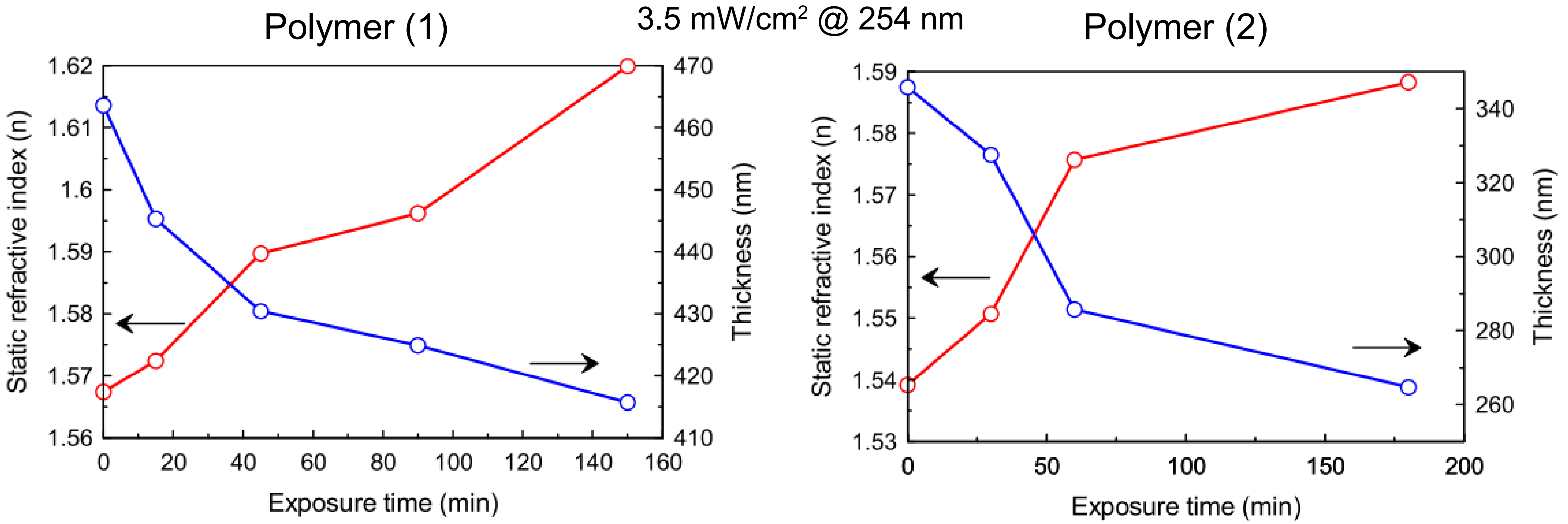
Polymer (2)





time	n_st	d [nm]
0	1.5392	345.8
30	1.5507	327.5
60	1.5757	285.7
180	1.5883	264.7

New approach: Photo-Fries reaction

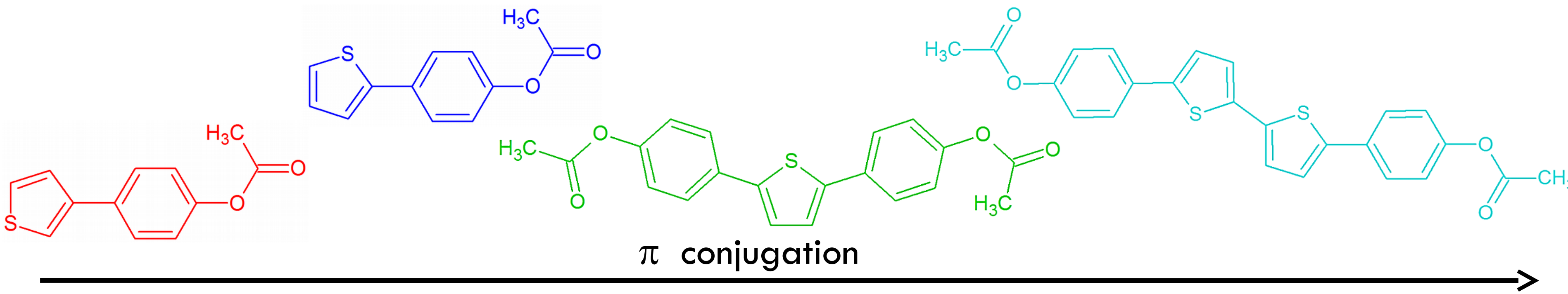


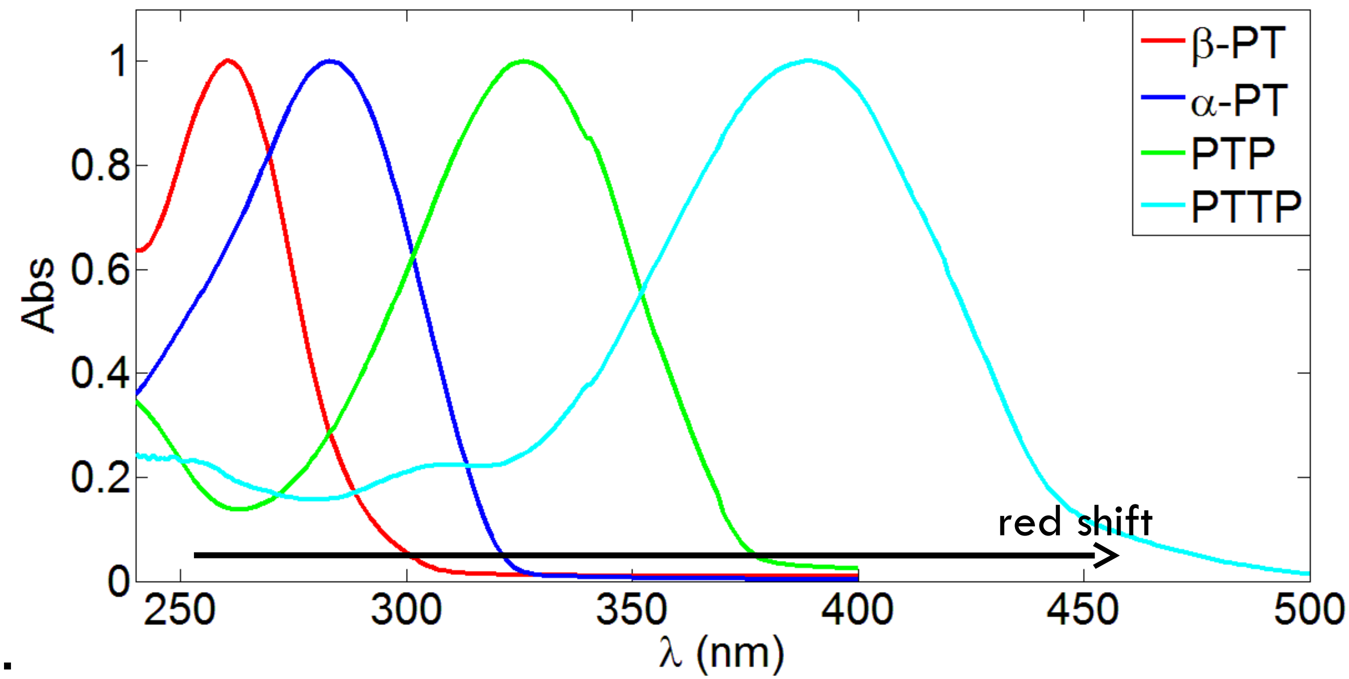
Increasing the exposure time to UV light:

n↑ d↓

There must be a change in **material density** that dominates the modulation of the refractive index

Photo-Fries reaction: new trends





IDEA:

Shift the peak at longer λ;

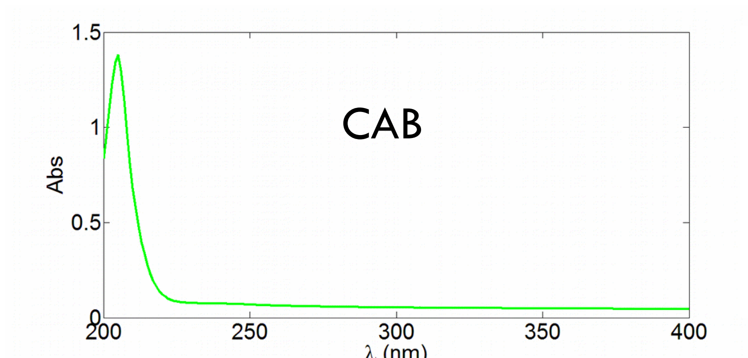
Make the system more transparent during the reaction.

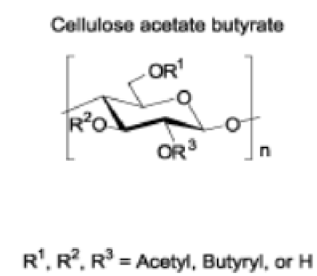
Photo-Fries reaction: new trend

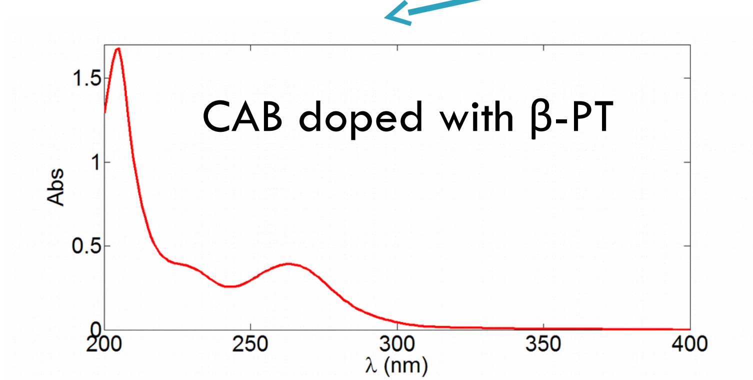
We have to find a suitable polymer matrix

Longer molecules show a low solubility = low concentration

Thin films were prepared by spin coating using as polymer matrix CAB (cellulose acetate butyrate)







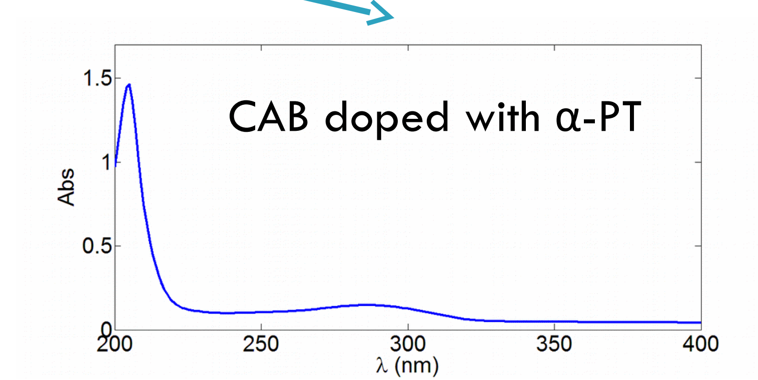


Photo-Fries reaction: new trend

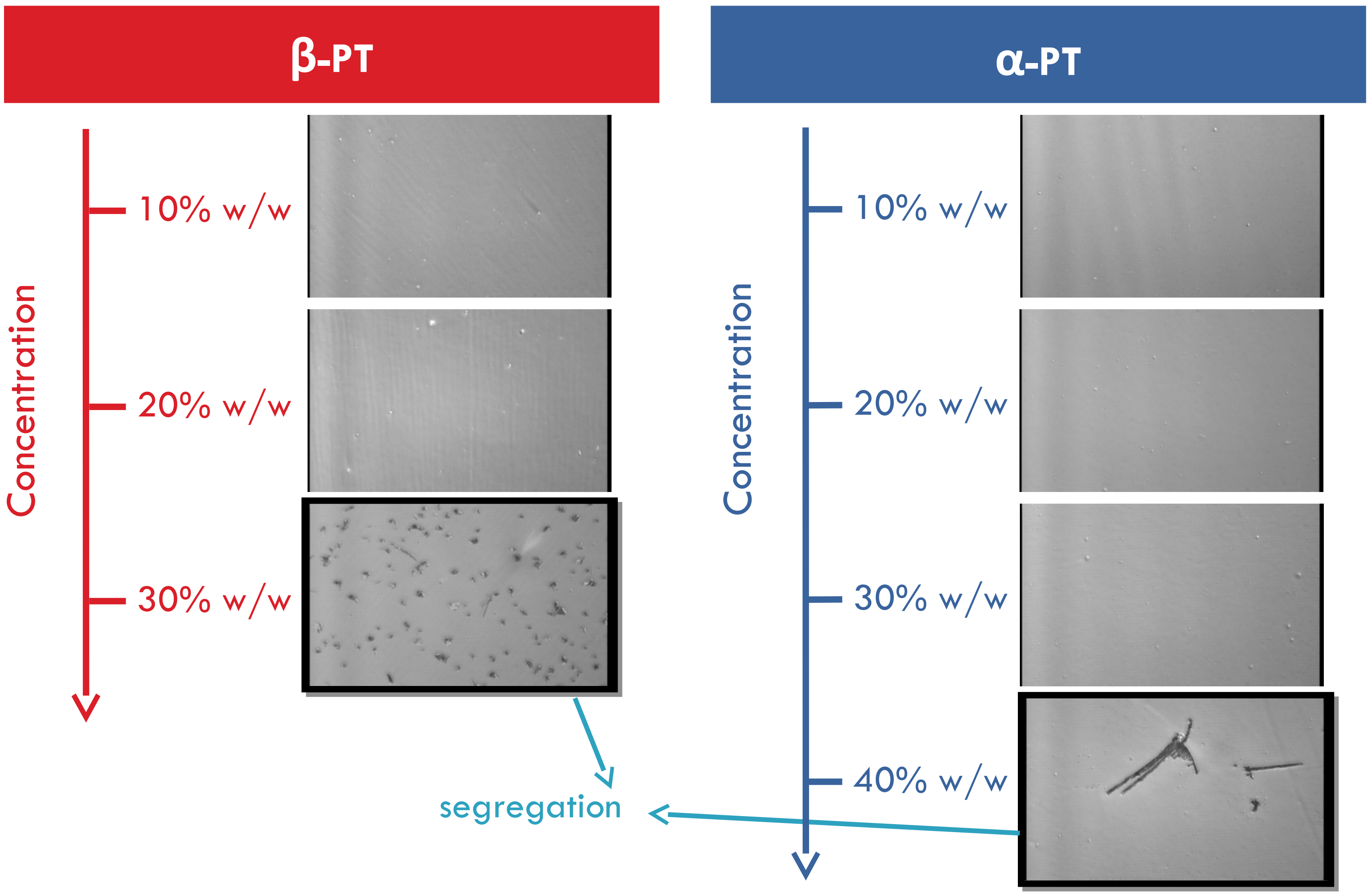
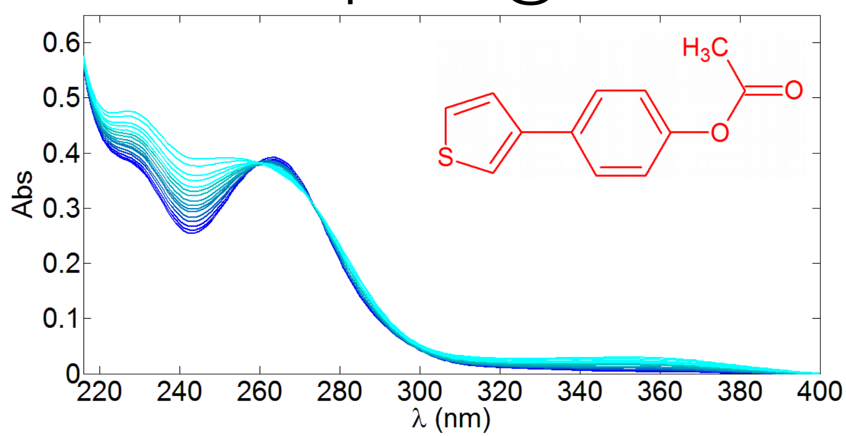


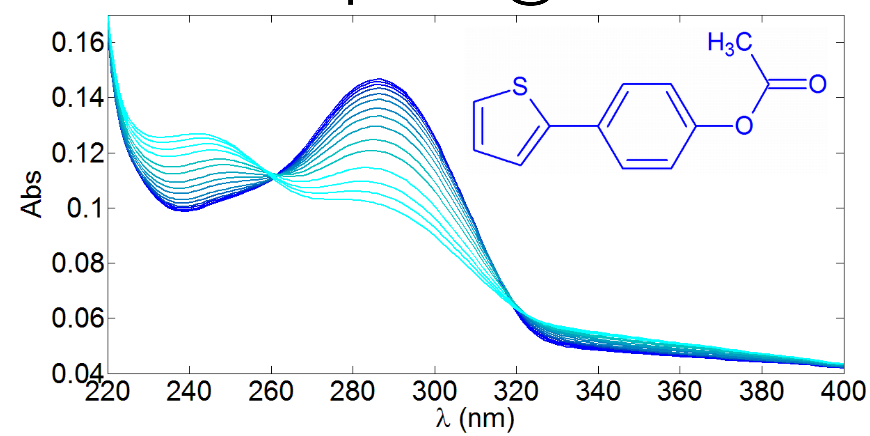
Photo-Fries reaction: new trends

Thin films were prepared by spin coating using as polymer matrix CAB (cellulose acetate butyrate)

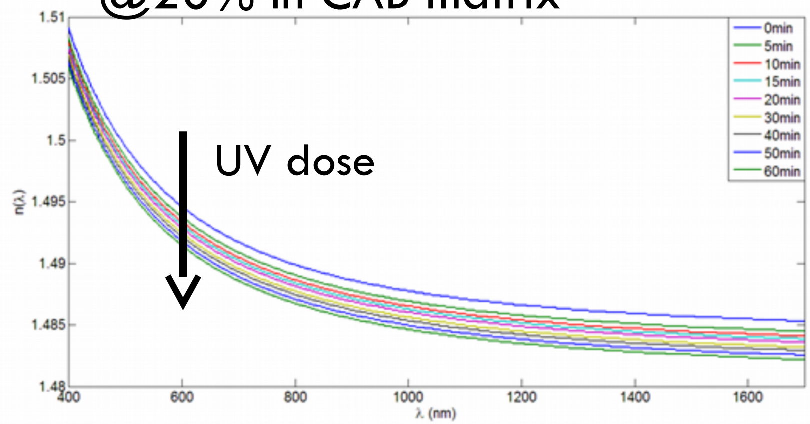
UV-exposure @ 254 nm



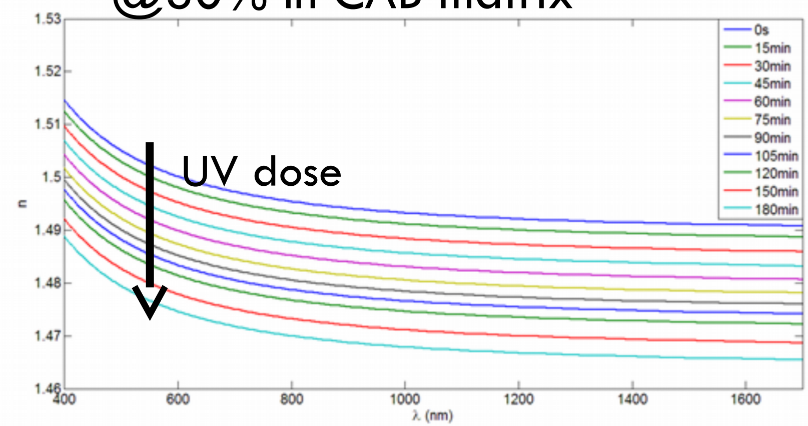
UV-exposure @ 311 nm



Change of the refractive index @20% in CAB matrix



Change of the refractive index @30% in CAB matrix

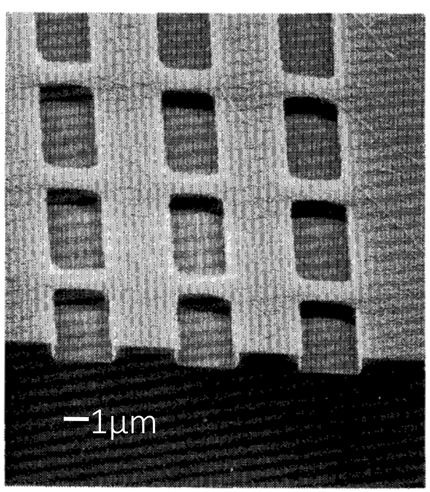


New approach: Diazo Meldrum's acid

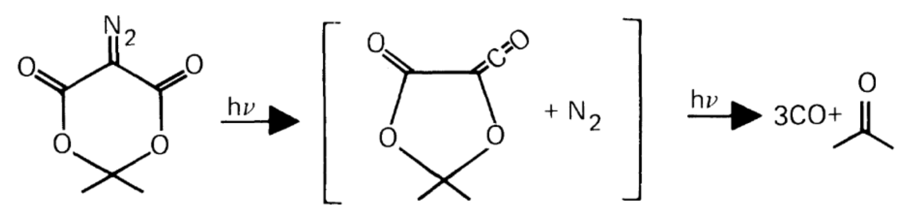
Our strategy: development of new materials with combination of properties ➡ From DCGs: high Δn by microvoids formation through light exposure ➕ From photopolymers: self-developing process easy processability

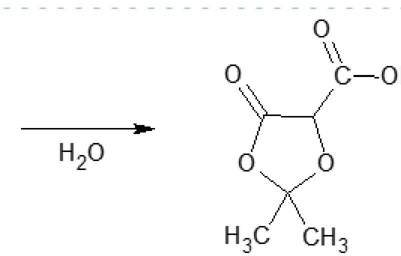
➢ Possible candidate: diazo Meldrum's acid (DMA):

- In the past used in photoresist formulations at 254nm (UV light) for microlithography



- photoreaction of DMA:





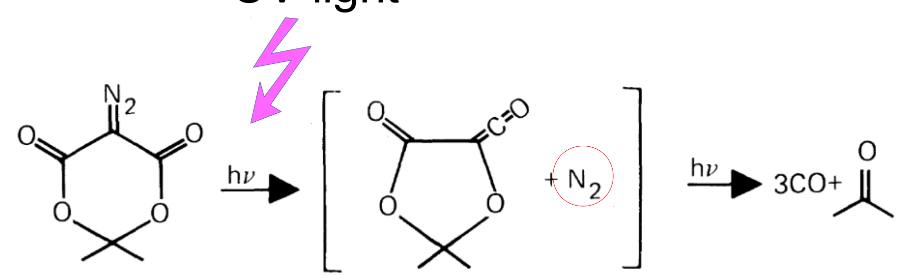
New approach: Diazo Meldrum's acid

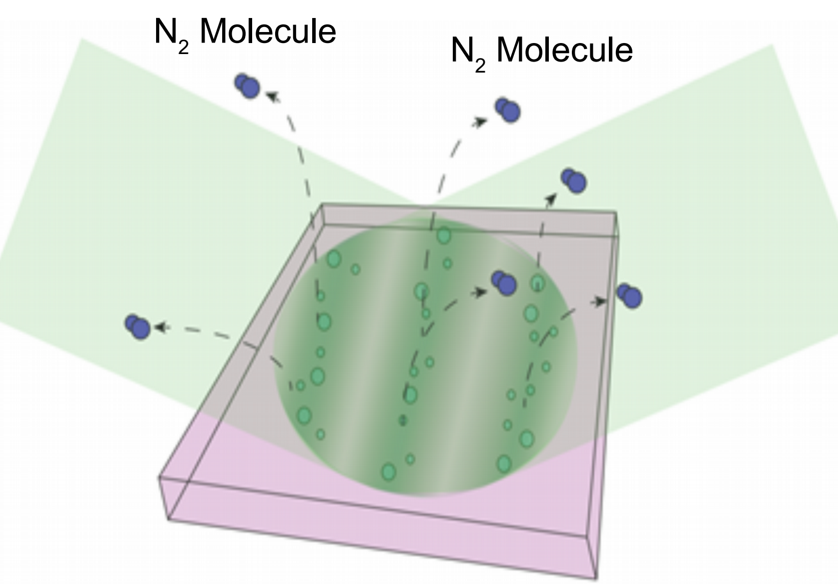
Our strategy: development of new materials with combination of properties

From DCGs: high Δn by microvoids formation through light exposure

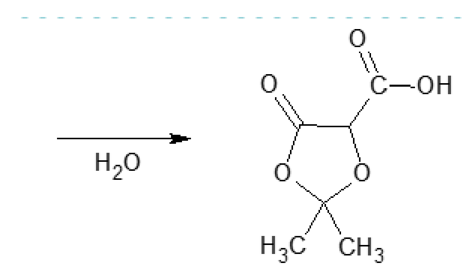
From photopolymers: self-developing process easy processability

- Possible candidate: diazo Meldrum's acid (DMA):



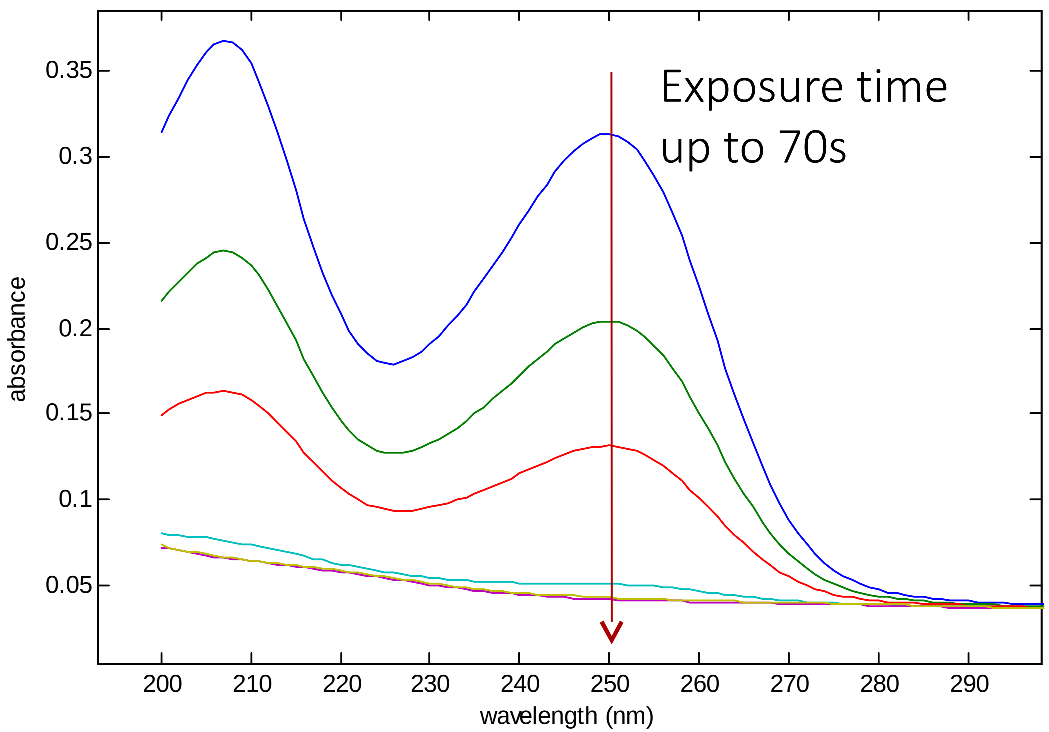


We could suppose that DMA, embedded in polymer matrix, creates microvoids and so Δn only upon light exposure

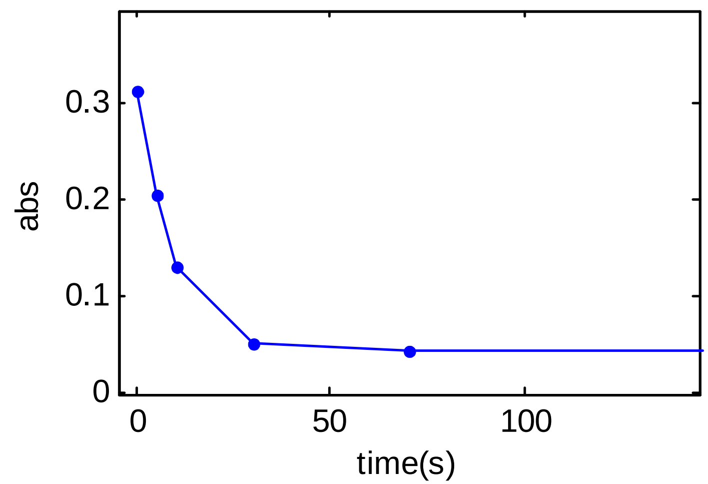


New approach: Diazo Meldrum’s acid

UV absorption spectra of a 40% DMA doped CAB film from 0s to 70s of exposition at 254nm UV light, 11.8 mW/cm^2



- DMA peaks totally disappear;



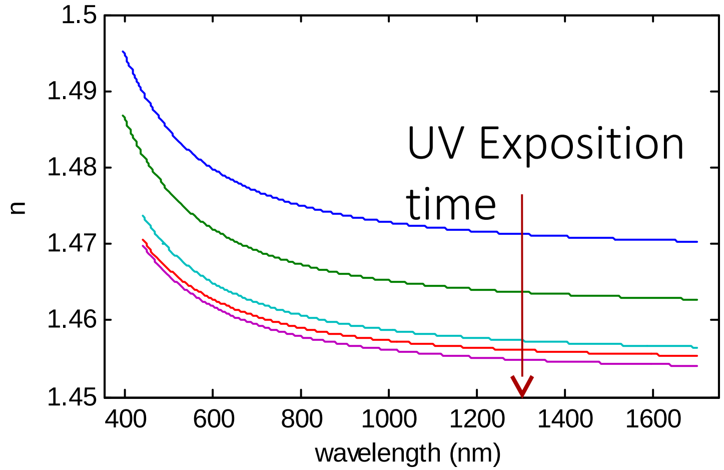
trend of the value of maximum peak at 248nm during time

Zanutta et al, Opt,. Mater, 2016

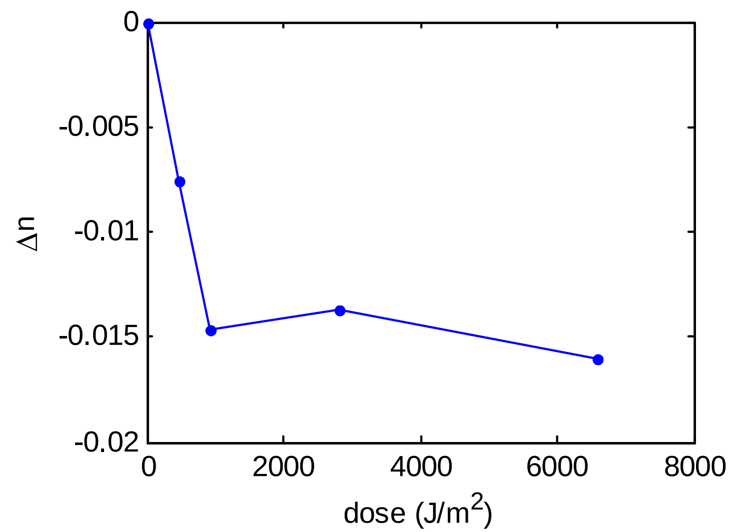
New approach: Diazo Meldrum's acid

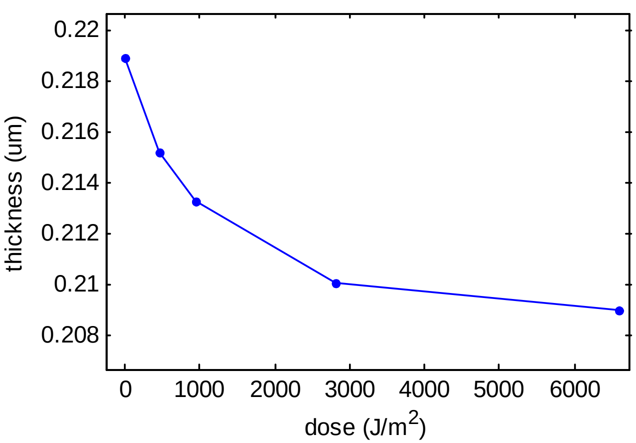
Film CAB+DMA 40% on Si wafer → Acquisition of spectral reflectance after UV light exposition 254nm → Reliable dispersion of the refractive index with wavelength by Sellmeier equation fit

refractive index dispersion curves



Δn as function of the UV dose





- Fast process, curves are shifted at lower values suddenly after UV exposition
- Δn reaches a plateau after 70s of UV exposition with a value of 0.015
- Small shrinkage of film thickness (-4.6%)

Zanutta et al, Opt,. Mater, 2016

Conclusions

Δn as a result of $\Delta\alpha$ and/or $\Delta\rho$;

Selection of the photoreaction;

Optimization at the molecular level is necessary but not enough;

Also the material has to be optimized (concentration, optical quality,...)