



Nanostructure aspects of UV and low energy EB-cured materials: comparing free radical and cationic curing mechanisms

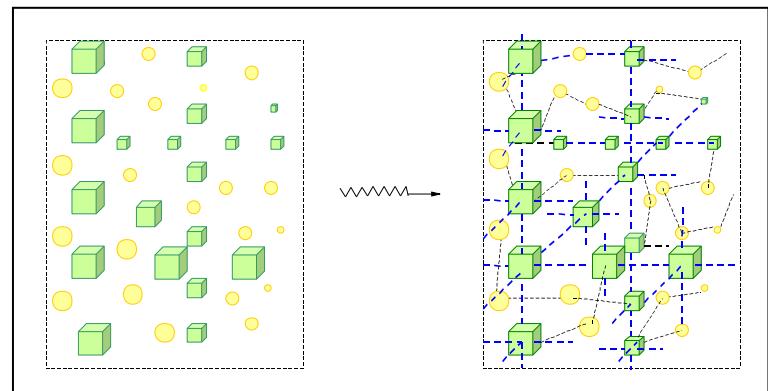
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- **Application domains**

- coatings: lacquers, paints, adhesives
- graphic arts: inks, microlithography
- functional coatings:
wear resistant, scratch resistant, matting, anti-adherent, sliding,
- some niches: rapid prototyping, composite materials, microsystems



- **Claimed advantages** 100% reactive formulations

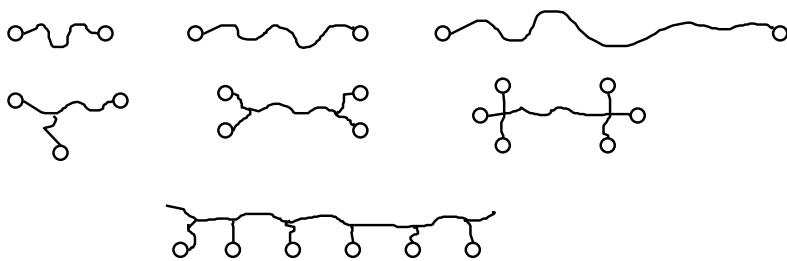
(solvent free, water based)

- fast and continuous treatment
- low energetic cost
- compactness of curing equipment
- bulk pieces and objects processed at « room temperature »



Cross-linking polymerization

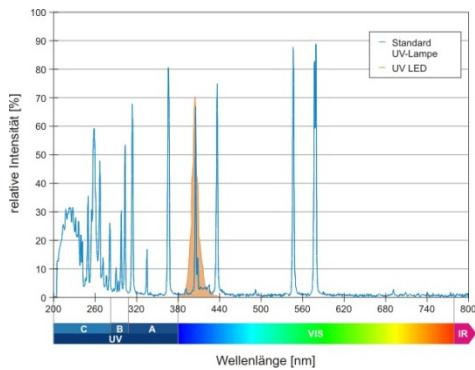
- Formulation
 - Prepolymer, reactive diluents
 - Initiator (UV, cationic EB)
 - Additives
 - Fillers, reinforcing agents
 - Pigments



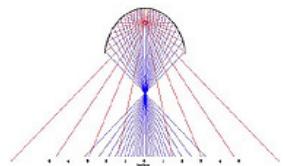
- Initial state
 - Solution
 - 100% reactive liquid
 - Aqueous dispersion
 - Powder
- Processing parameters
 - Radiation type
 - Dose (total, fractionated)
 - Intensity
 - Temperature, inertization

UV-visible radiation sources

Hg / Xe



LED UV



different irradiation systems

emission spectrum

light intensity

spatial distribution of energy



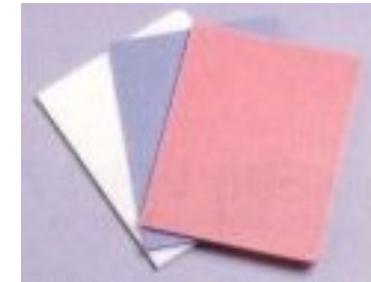
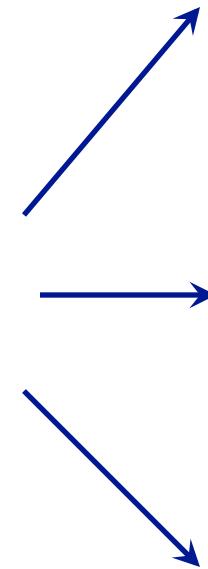
Un



EB: low energy electrons
for curing thin layers

A valuable alternative to UV technology for curing by XLinking polymerization :

- Inks
- Paints
- Coatings
- Adhesives



Short processing time and control of performances
by adjusting properties to specifications – migration issues lower for EB-cured coatings



Comparaison of UV-vis.-curing to EB curing

- By exposure to UV-vis. light
 - selective photon absorption by chromophores
 - light penetration limited by strong absorption, by scattering
 - associated IR radiation
 - **low capital cost**
 - «lamp» concept = simplicity
- Under ionizing radiation (EB, X-ray)
 - Random energy deposition essentially related to material density
 - High energy radiation (low LET) more penetrating
 - Induced chemistry less selective
 - ... and less documented
 - «cold » radiation
 - Capital cost, maintenance
 - Heavy regulatory constraints



UV vs EB curing of pigmented coatings

Reference : clear coat (resin + onium salt)

- UV : cured at 180 mJ.cm^{-2} (Hg MP)
- EB : cured at 120 kGy (175 kV)

Pigmented (20% TiO_2)

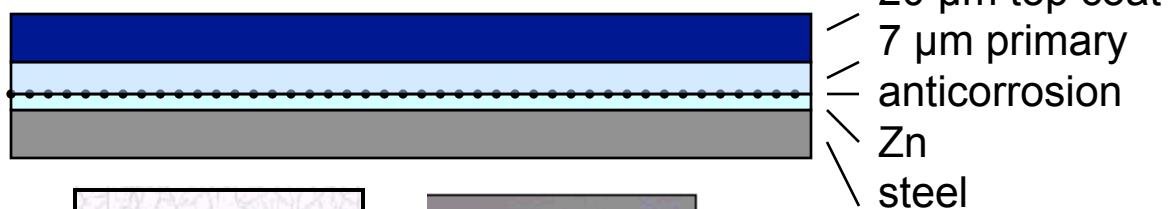


- UV : only surface curing,
even for doses of several J.cm^{-2}
- EB : complete
drying at 200 kGy

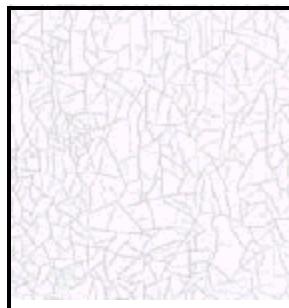


Applications currently tackled: coil coating

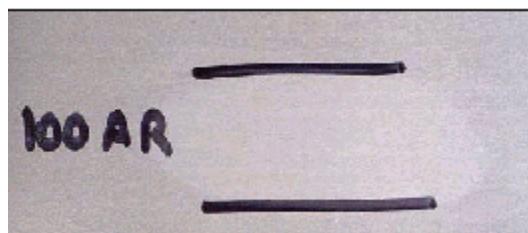
- Very demanding properties



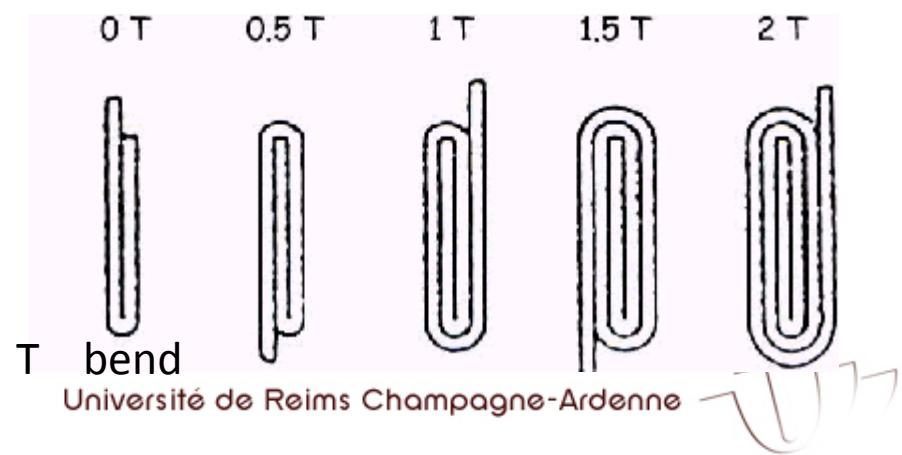
Salt fog
photo-ageing



RXN

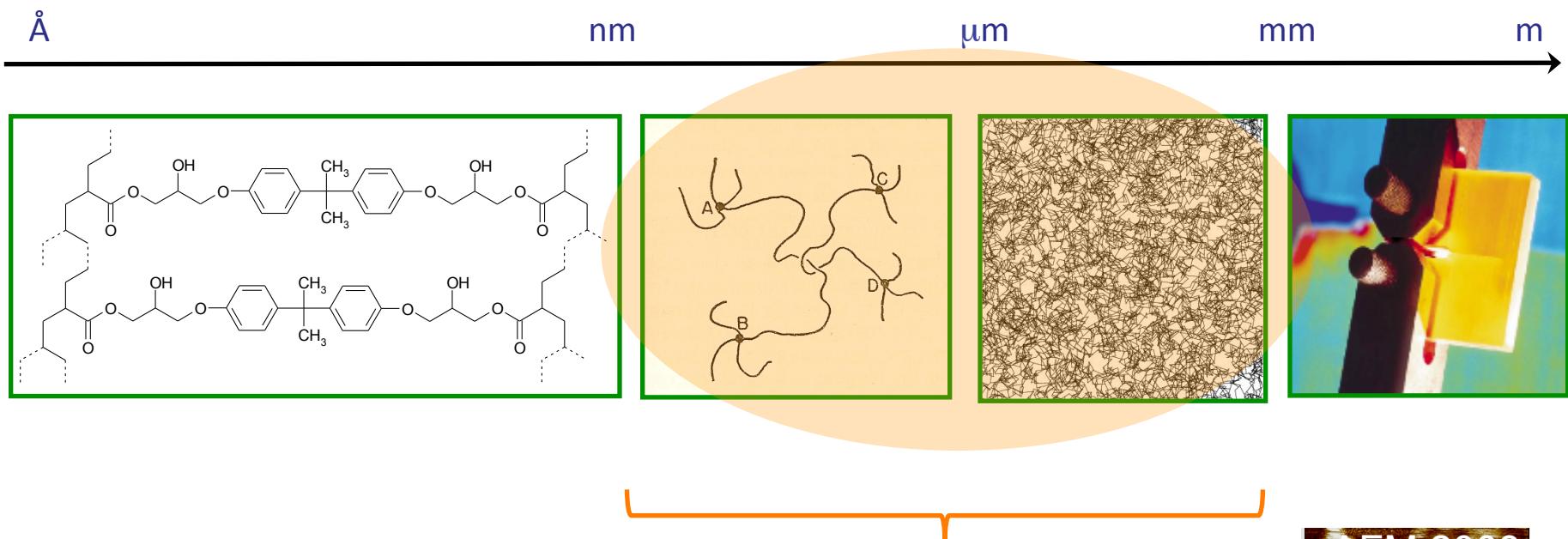


MEK rubs



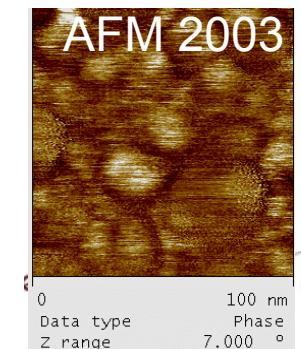
Basic aspects

Research in photopolymerization and radiation curing



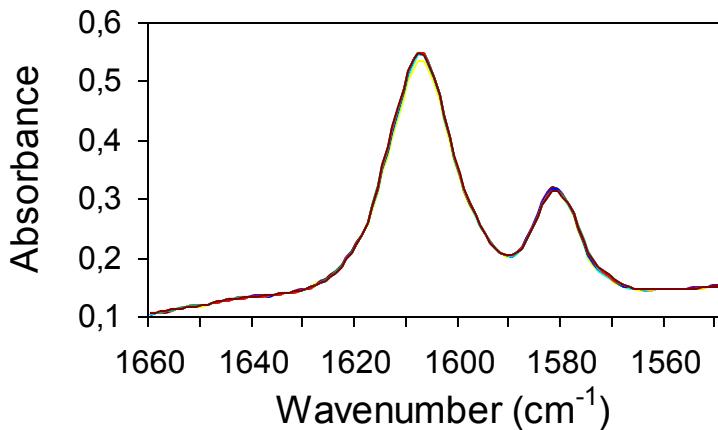
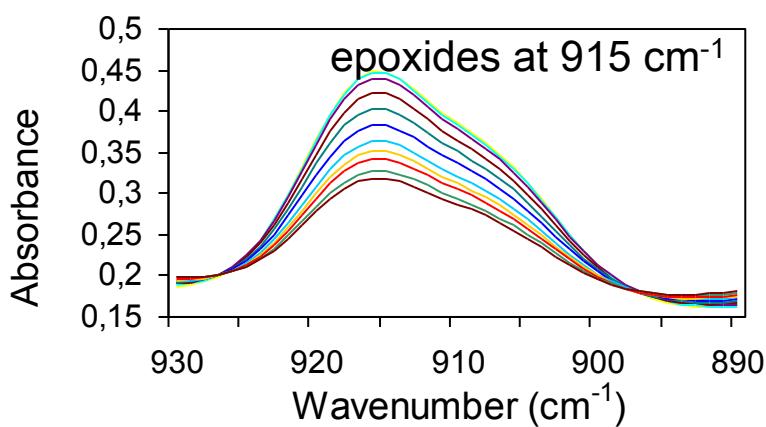
→ Microstructural characterization of model networks

- NMR relaxometry
- Temperature modulated differential scanning calorimetry
- AFM imaging

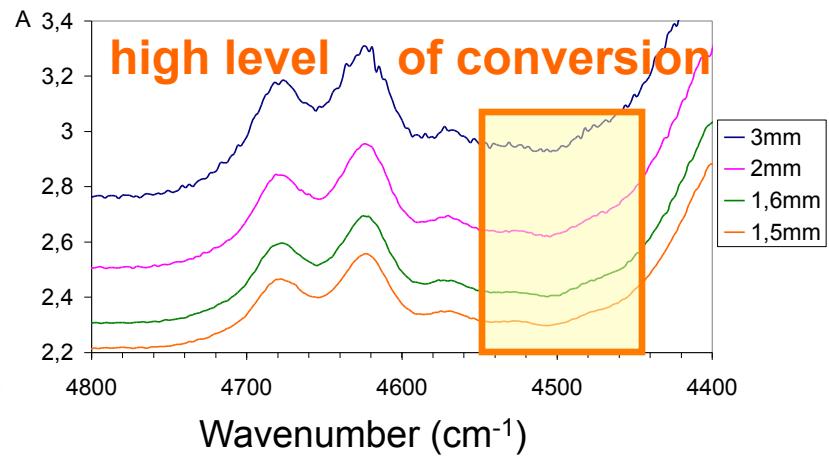
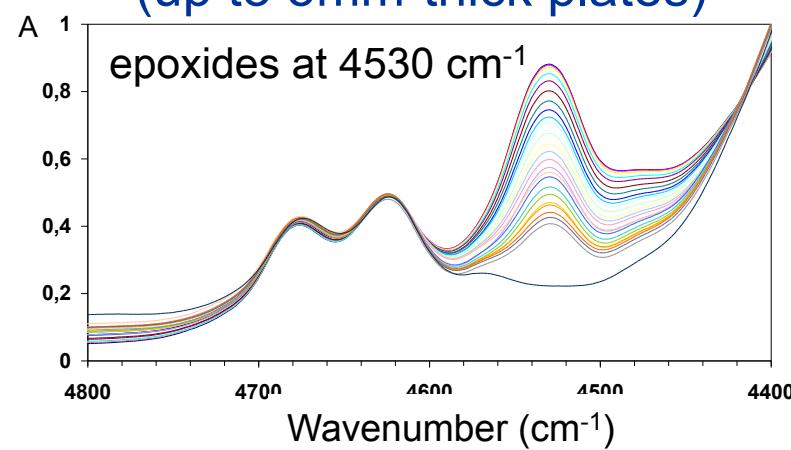


Determination of monomer (epoxide) conversion by FTIR

- MIR spectroscopy
(thin films, pellets)

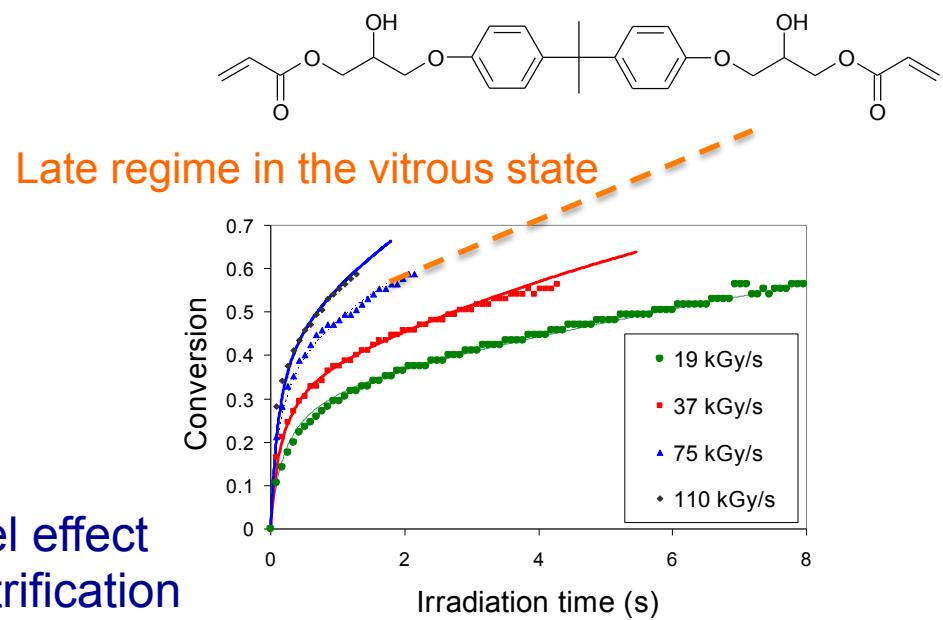
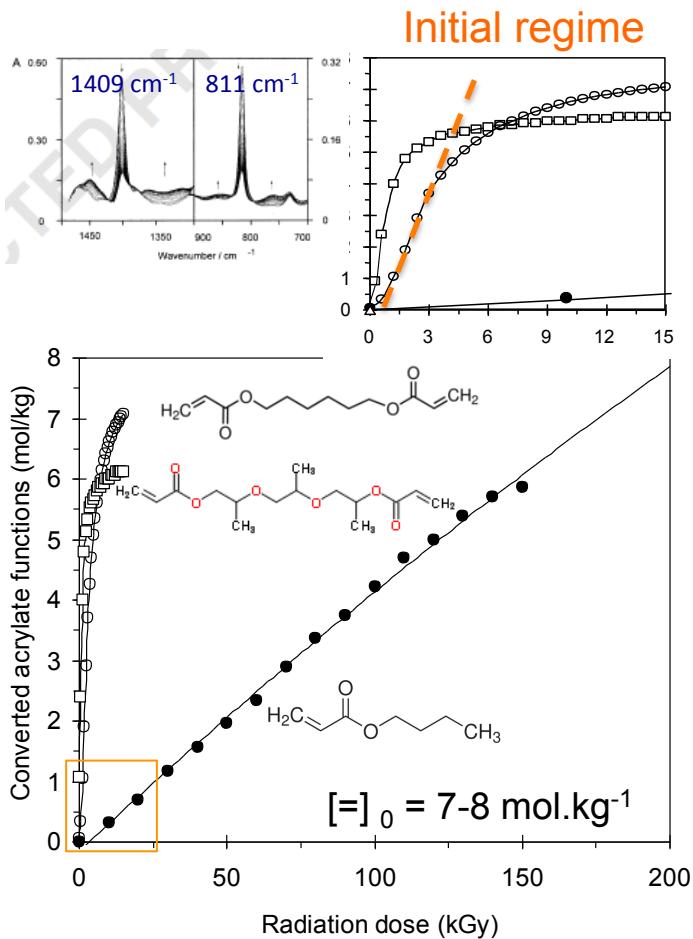


- NIR spectroscopy
(up to 5mm-thick plates)



Monitoring of radiation-initiated polymerization process

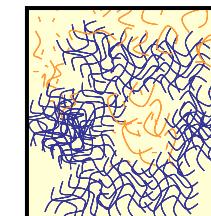
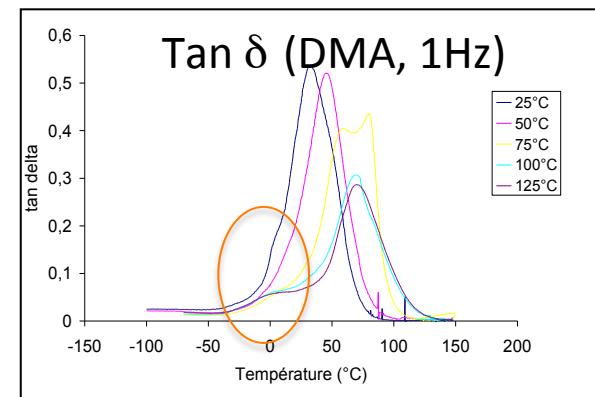
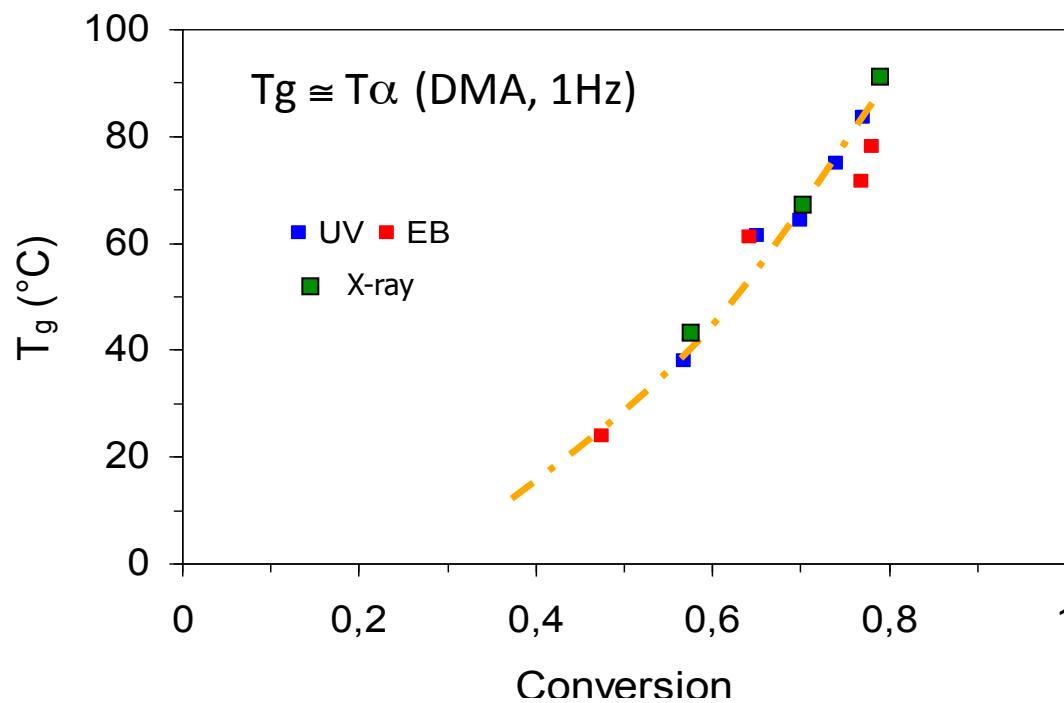
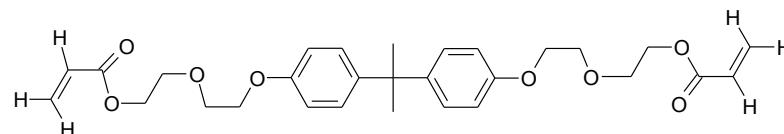
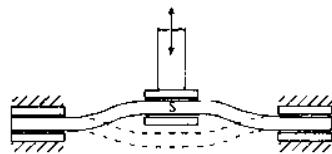
Representative examples: EB-polymerization of mono- and diacrylates monitored by FTIR



→ gel effect
→ vitrification

- Kinetic data dependent on
- Monomer type and prepolymer backbone
 - Initiator concentration
 - Temperature
 - Dose rate
 - Dose

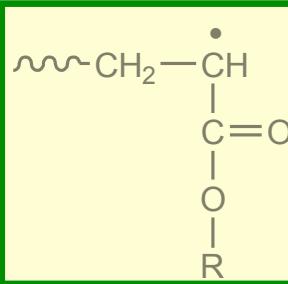
Unexpected uniform dependence of the glass transition temperature T_g on conversion



- Large relaxation domains for network segments: an evidence of the heterogeneous nature of radiation-cured networks
- No apparent influence of the nature of the initiation process and of its timescale on various macroscopic properties of the network

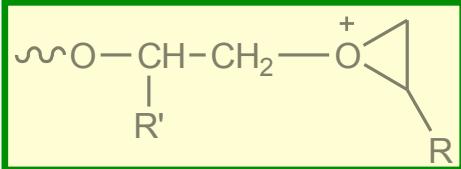
Comparison of cationic and free radical mechanisms

- Free radical
 - Acrylate monomers and prepolymers



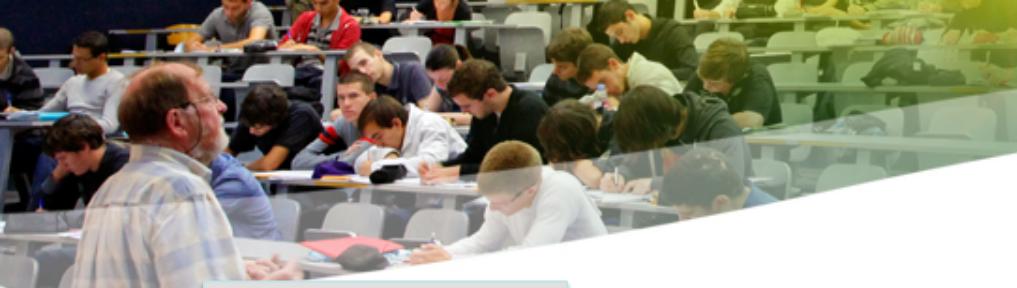
The diagram shows the chemical structure of an acrylate monomer radical. It consists of a polymer chain segment $\sim\sim\text{CH}_2-$ attached to a carbon atom. This carbon atom is bonded to a hydrogen atom with a radical dot above it, a double-bonded oxygen atom (part of the C=O group), and a single-bonded oxygen atom (part of the $\text{O}-\text{R}$ group). The entire structure is enclosed in a green rectangular box.

 - Initiator not needed for ionizing radiat.
 - Inhibition by oxygen
 - Fast termination
(steady state for free radical concentration)
 - Volume contraction
 - Large choice of monomers, prepolymers and initiators
- Cationic
 - Epoxies, vinyl ethers



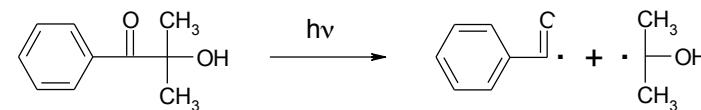
The diagram shows the chemical structure of a cationic polymer intermediate. It features a polymer chain segment $\sim\sim\text{O}-$ attached to a carbon atom. This carbon atom is bonded to a hydrogen atom (with a single bond) and a methyl group (CH_3). A double bond connects this carbon atom to another carbon atom, which is bonded to a positive charge ($+$) and an oxygen atom. This oxygen atom is further bonded to a methyl group (CH_3). The entire structure is enclosed in a green rectangular box.

 - Onium salt initiator required
 - Unsensitive to oxygen, but sensitive to humidity
 - Inhibition by nucleophiles
 - Living character
 - Low shrinkage
 - Polarity of the polymerized function
 - Limited number of monomers
 - Higher cost of raw products



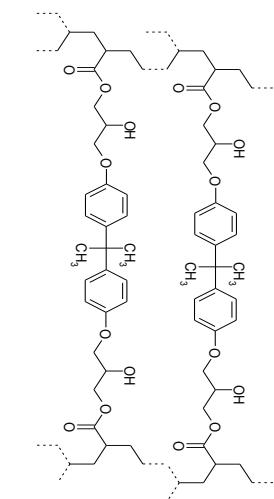
Initiation with radiation

UV (365 nm)

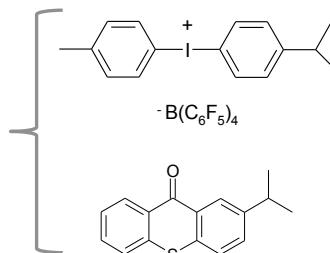


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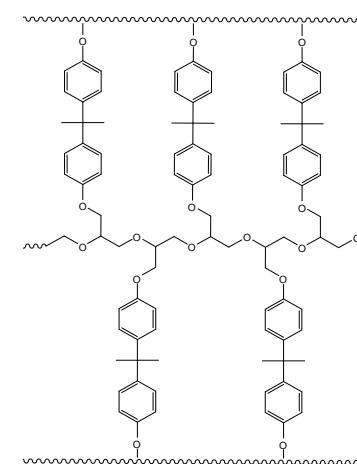
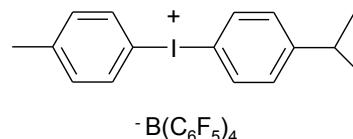
EB, X-ray

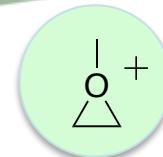


UV (385 nm)
or vis (LED)

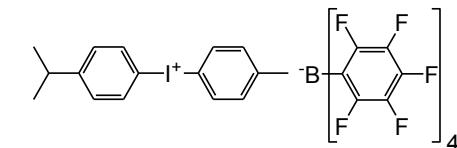


EB, X-ray

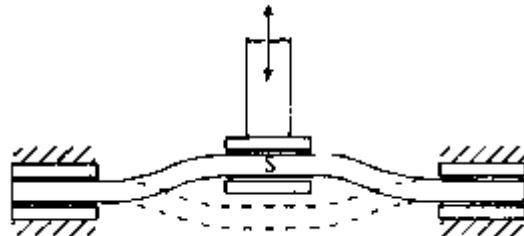




Relation between T_g and conversion

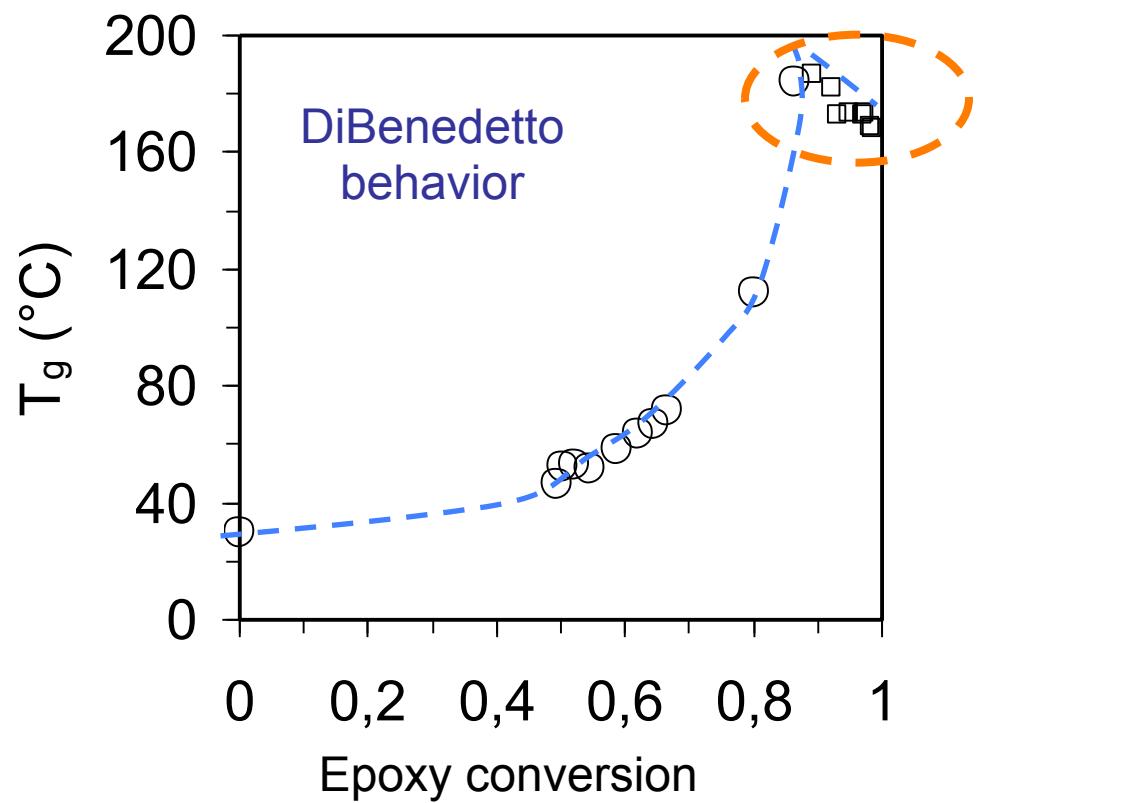


- Epoxy-aromatic resin DGEBA + 0.25 to 5 wt-% DAIS
- EB curing (10-50 kGy)



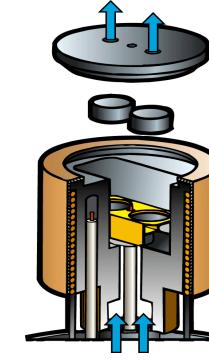
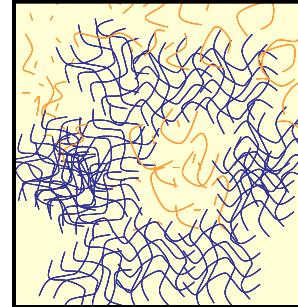
T_g from E''
second scan

+ Conversion measured

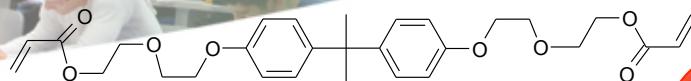




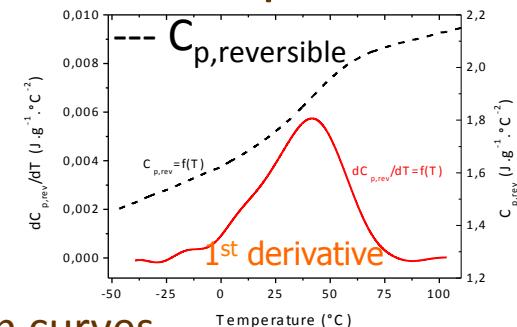
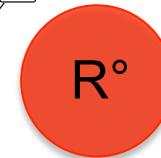
Calorimetric measurements temperature-modulated DSC



MDSC Technique – Results



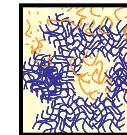
- Basis for interpreting MDSC experiments



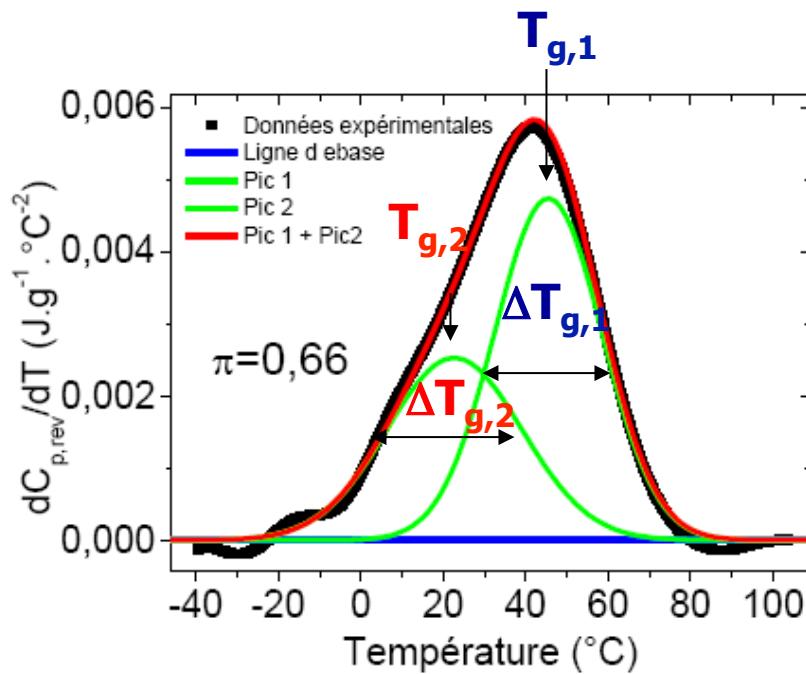
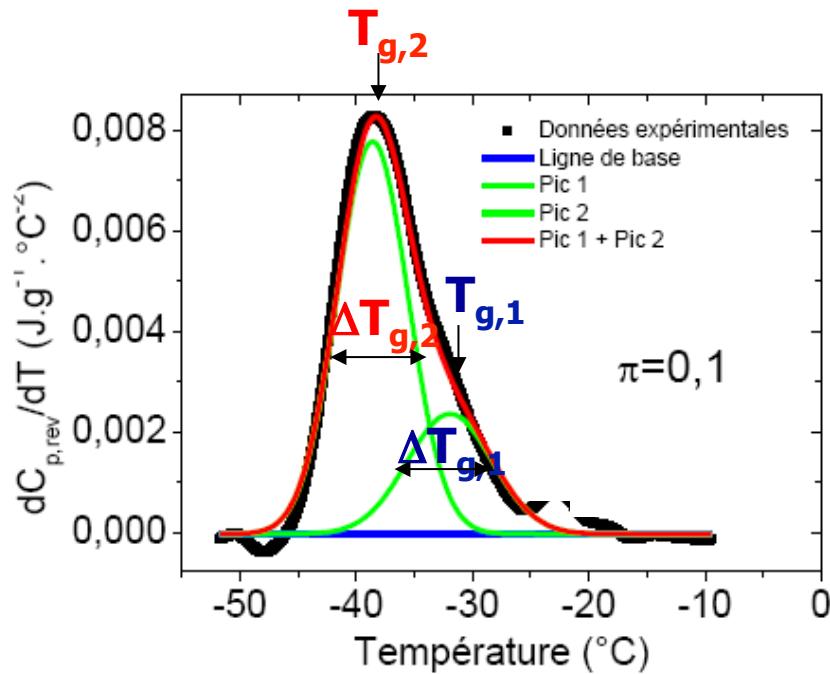
Modeling of $dC_{p,\text{rev}}/dT$ curves by a combination of 2 gaussian curves

$$\frac{dC_{p,\text{rev}}}{dT} = \sum_{i=1}^2 \frac{\Delta C_{p,i}}{\Delta T_{g,i} (\pi/2)} \exp\left(-\frac{2(T - T_{g,i})^2}{(\Delta T_{g,i})^2}\right)$$

Low T_g



High T_g





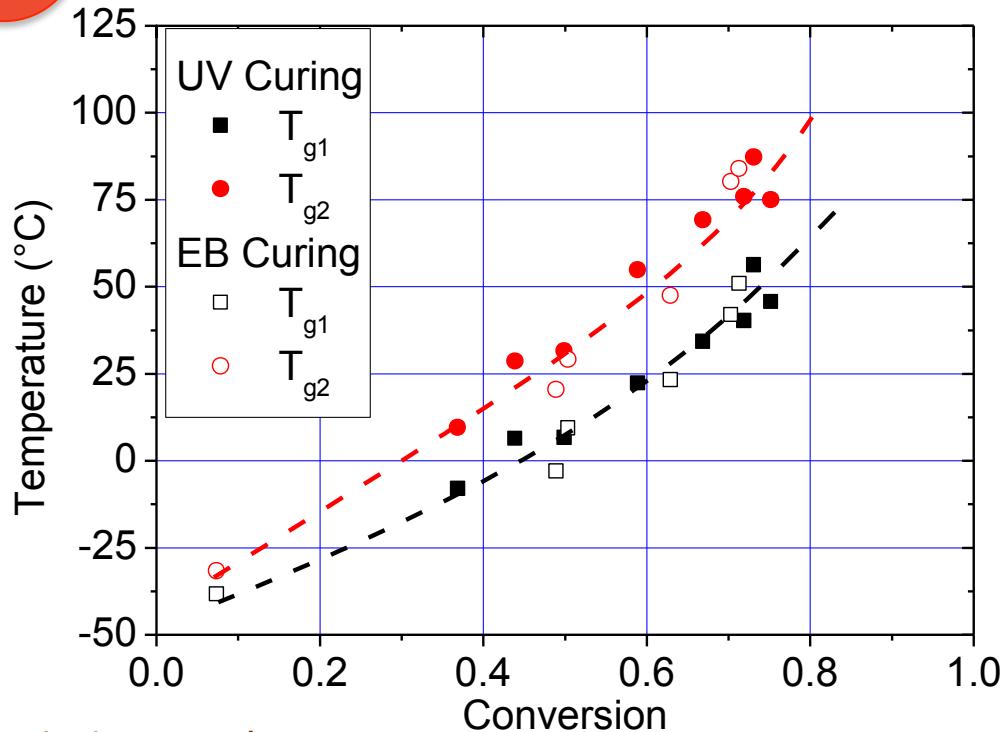
MDSC Technique – $T_{g,i} = f(\text{conversion})$

R°

- Two component model fit well the experimental data

Samples with conversion ratio ranging from $\pi = 0.1$ to $\pi \approx 0.8$

- Glass transition temperature
 - Parallel evolution of Tg's
 - No evidence of the influence of initiation mechanism
 - Tg values similar to those determined by DMA
 - ΔT_g as a function of conversion :



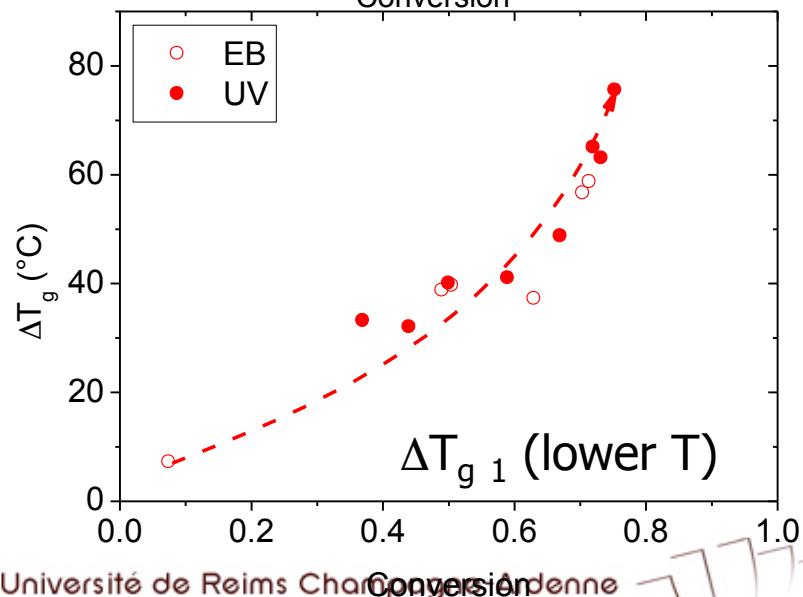
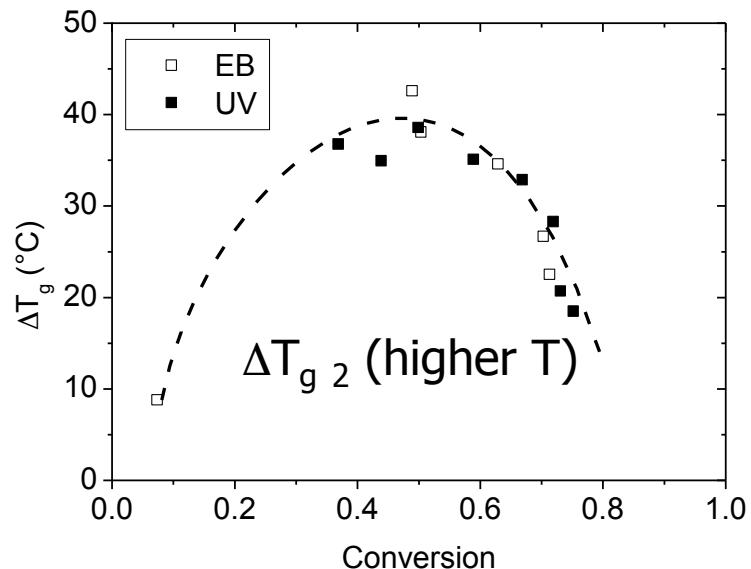
high Tg peak narrowing, low Tg peak broadening



MDSC Technique – Results

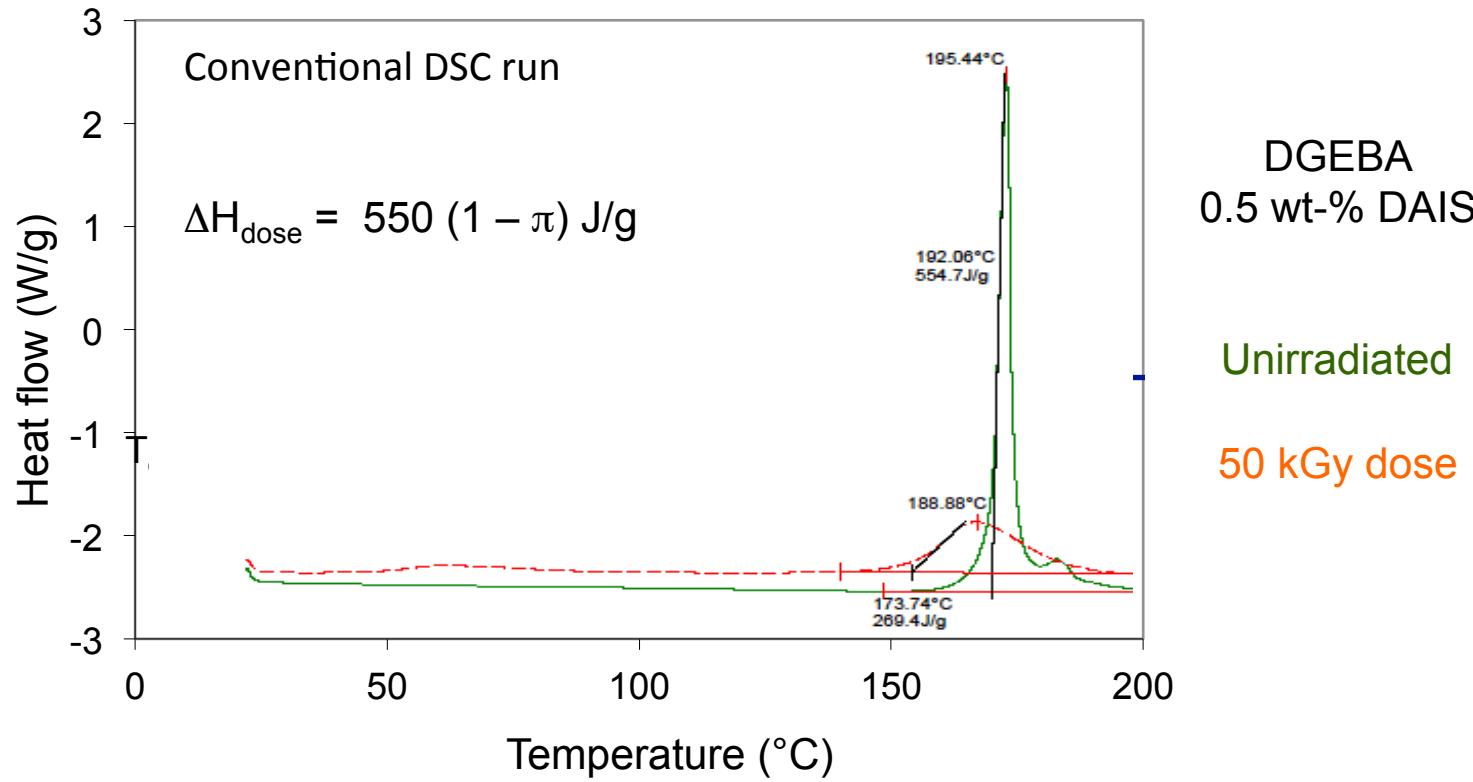
- Glass transition domain
 - Main relaxation Peak
 - Two evolution regimes
 - 1 Gradual nucleation and growth of microgels (broadening)
 - 2 Percolation and / or end of « densification » (sharpening)
 - Presence of a shoulder
 - Polymerization taking place in interstitial domains
 - Gradual increase of ΔT_g
 - Polymerization essentially progressing by defect creation at high conversion values ($p > 0.5$)
 - Difficulties to assess the weight fraction of each type of phase
(C_p unknown)

R°





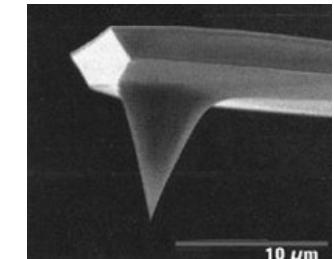
Conventional DSC of UV or EB cured DGEBA



- Thermal exchanges are dominated by post-polymerization (occluded cationic centres, and thermal decomposition of the onium salt)
- Good method for determining the residual monomer content



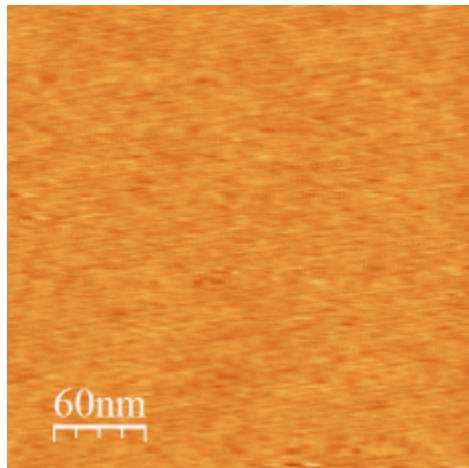
AFM imaging



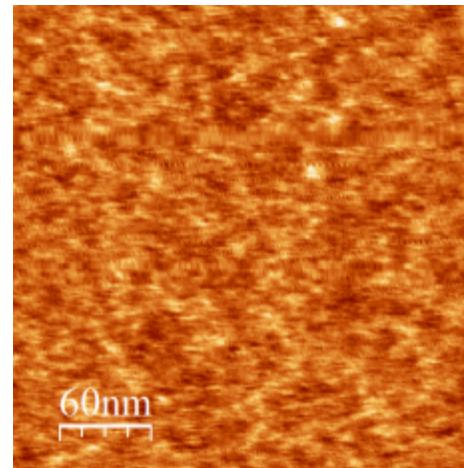
AFM Dimension setup equipped Nanoscope V controller (Veeco)

Silicon tip 450kHz – 200N.m⁻¹

Tapping mode (probed zone 300 x 300 nm²)



Height image
Rms roughness 0.32 nm



Phase image

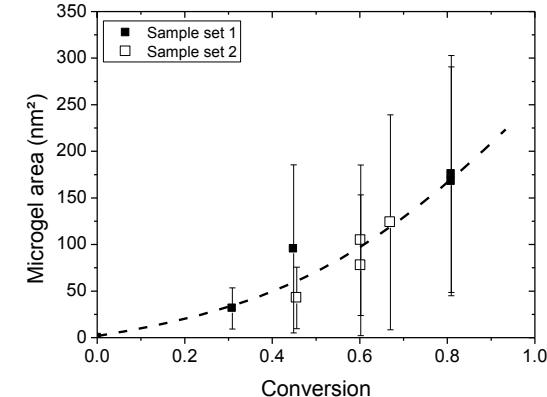
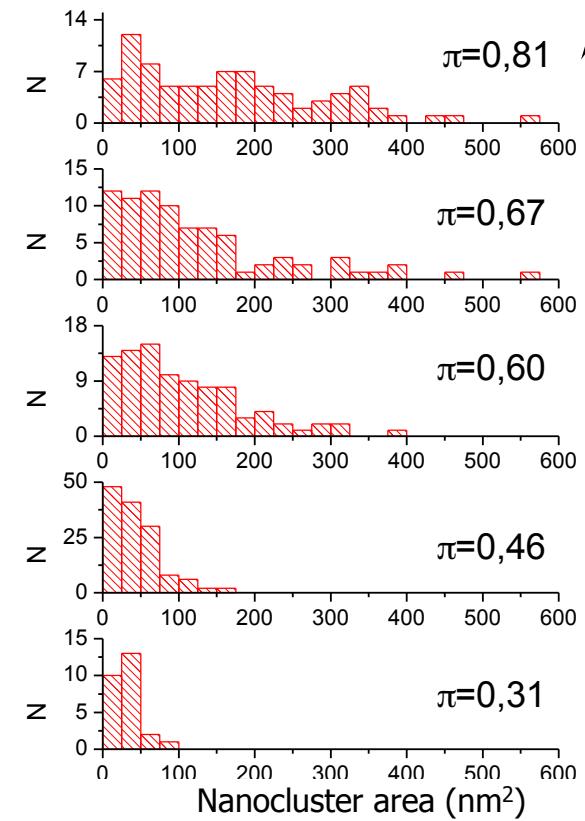
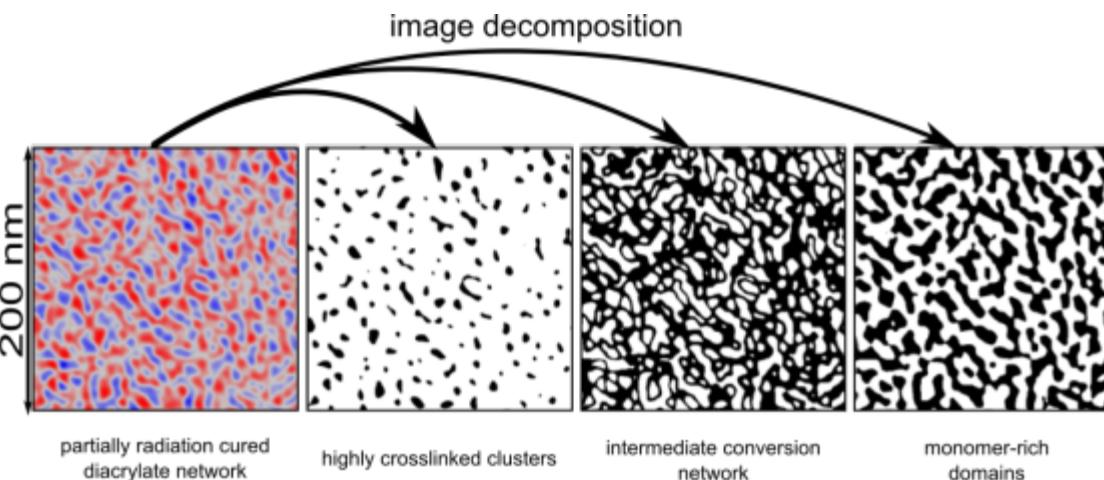
Phase-imaging
of local « viscoelasticity »

whiter zones
=
highly cross-linked clusters

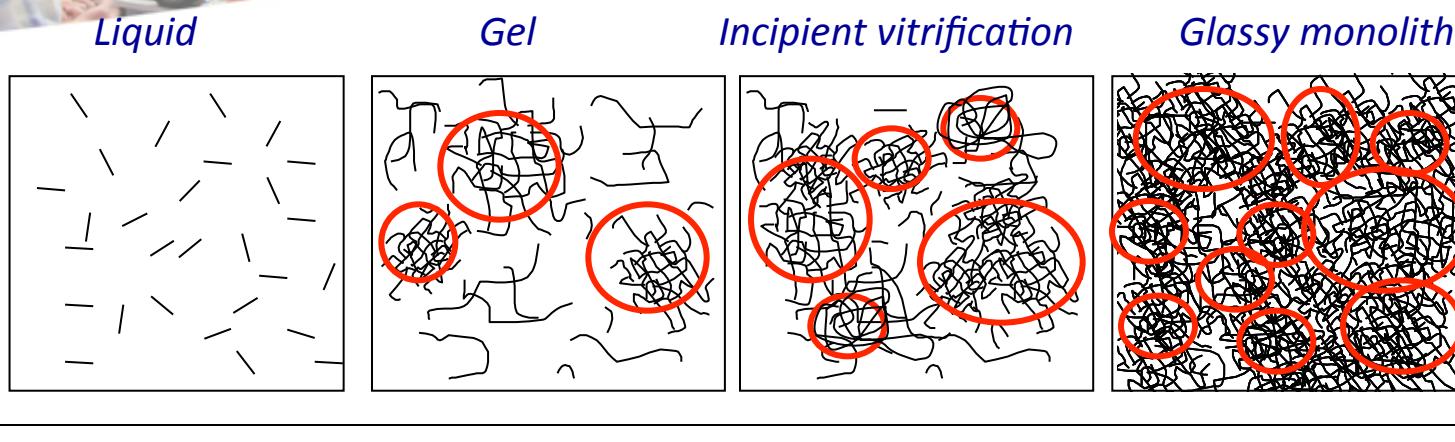


AFM observations Quantitative results

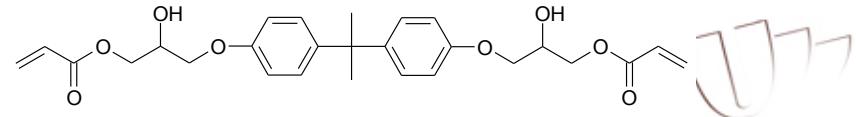
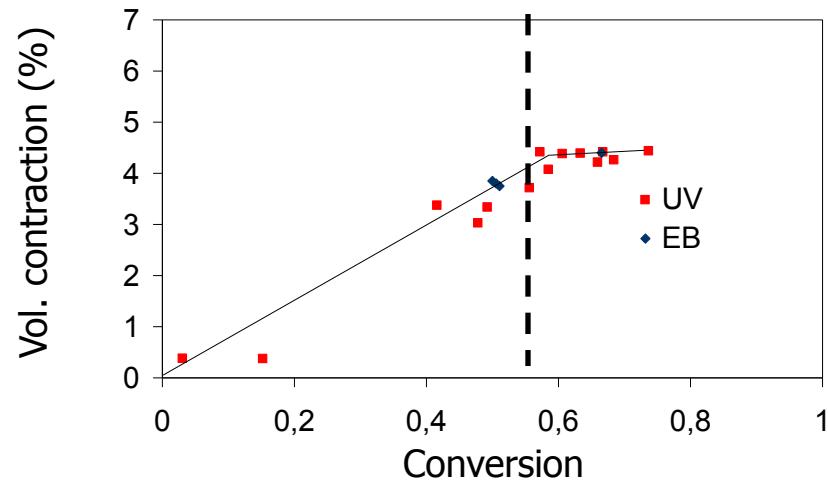
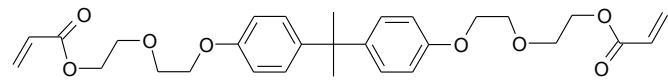
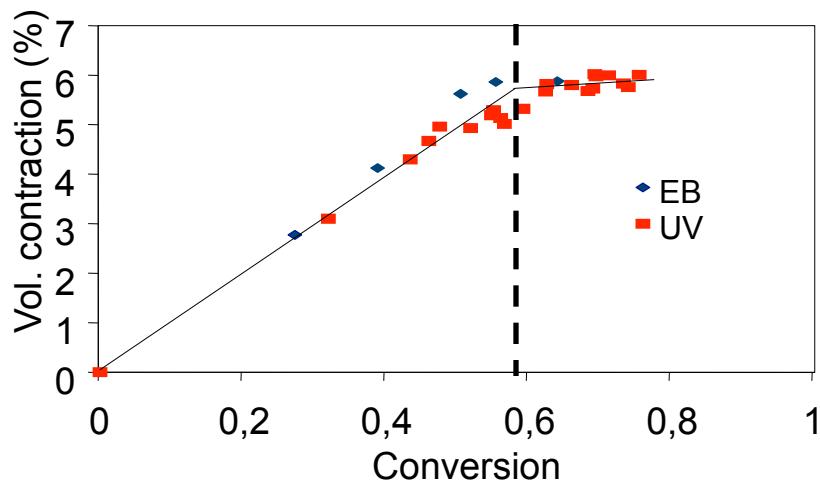
- Feret's diameter
- Circularity index
- Area of individual clusters
 - Broadening of size distribution
 - Nucleation of nanogels is the main process until $\pi \sim 0.5$
 - For $\pi > 0.5$ growth by aggregation seems the dominant process



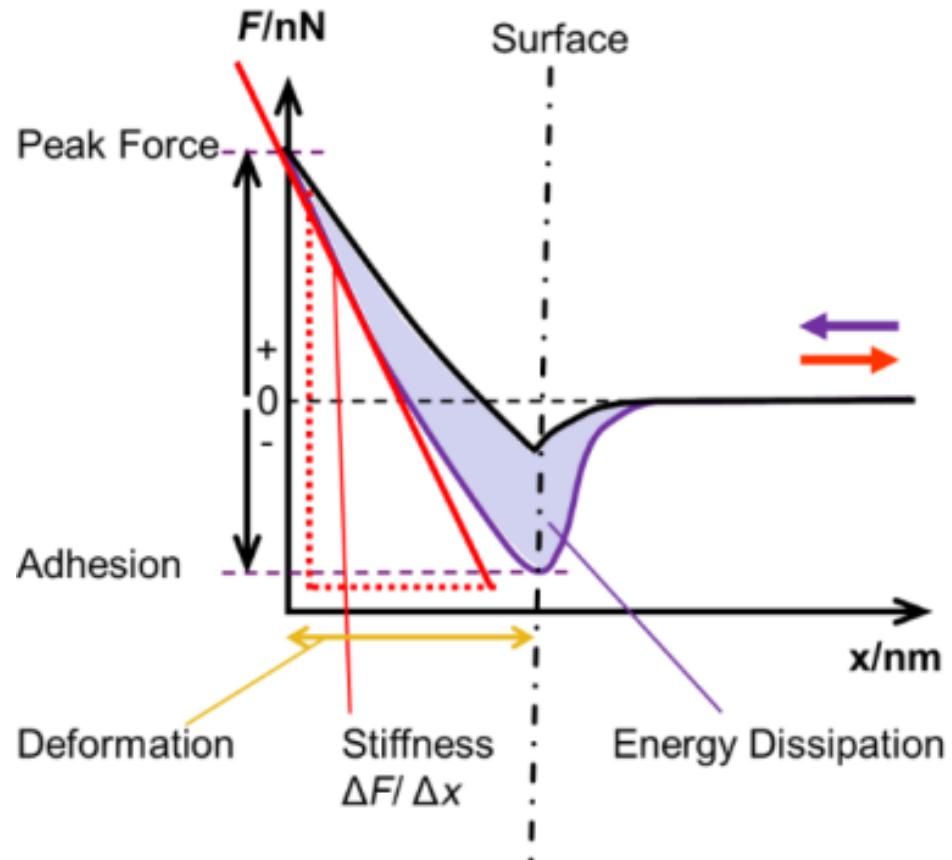
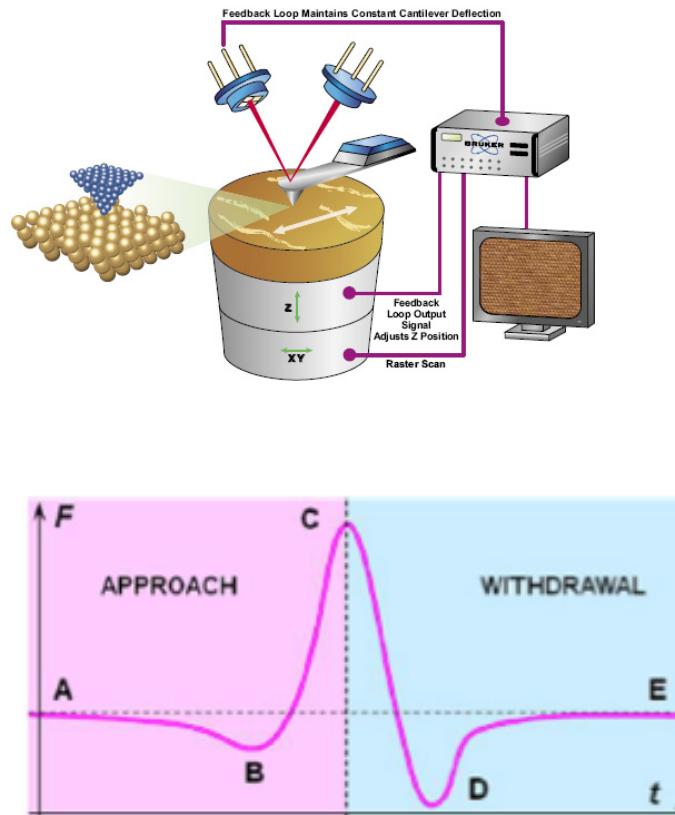
Proposed scenario for network formation



Progress of cross-linking polymerization

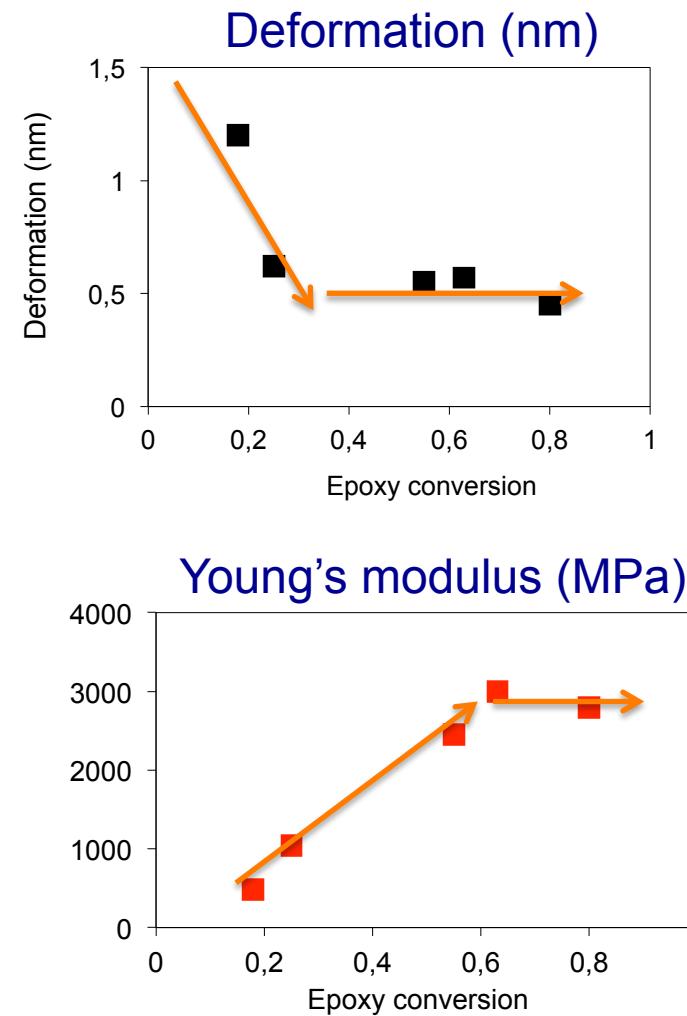
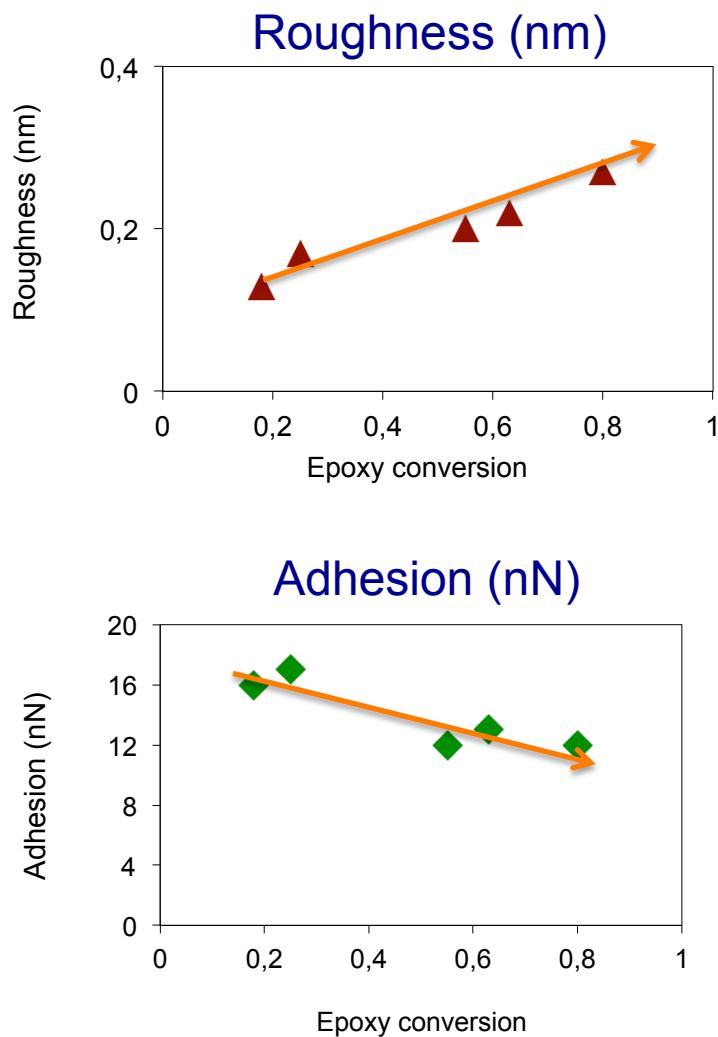


Quantitative Nano Mechanical AFM imaging

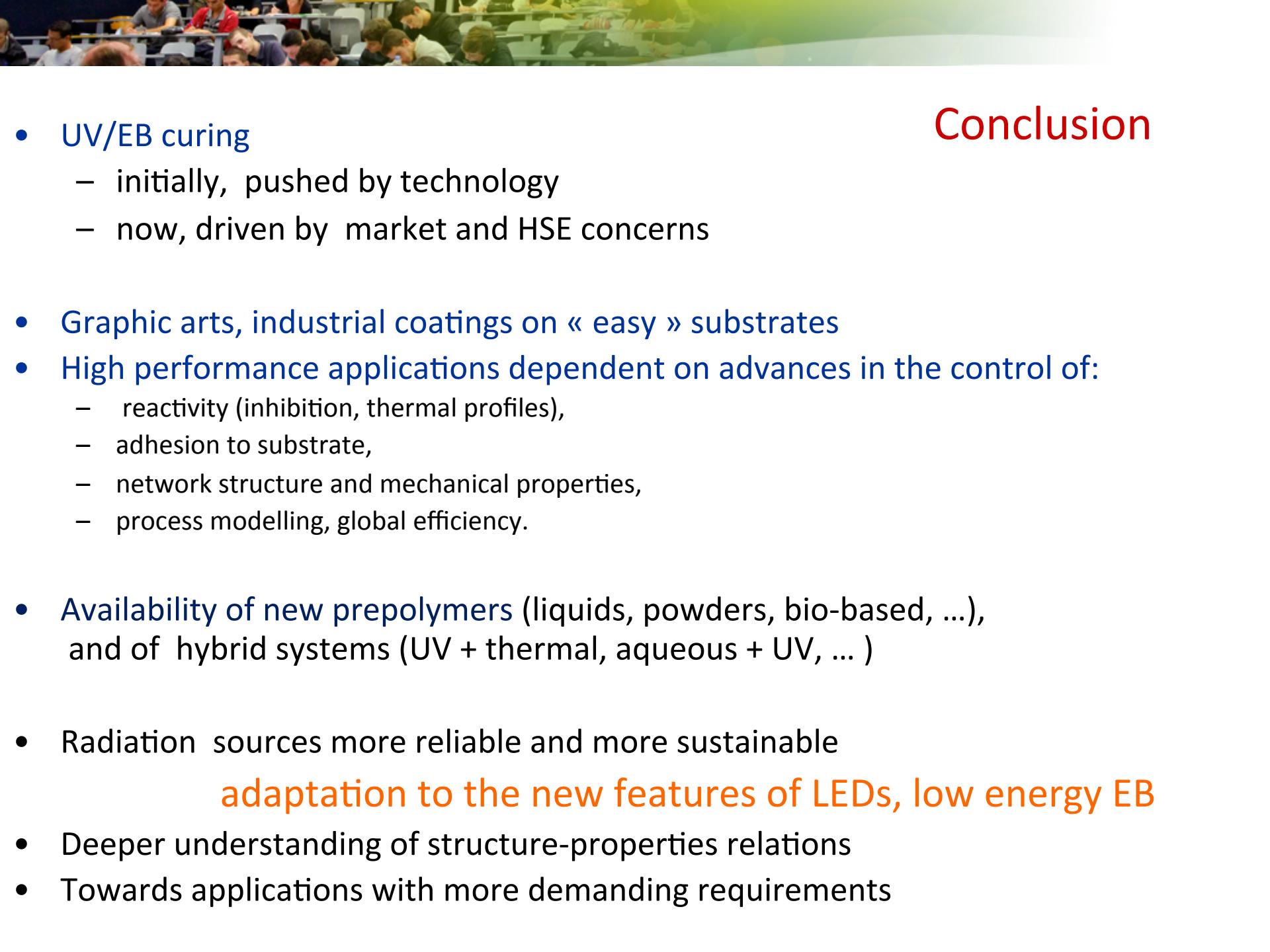




Local probing of EB-cured Epoxy novolac samples 1% DAIS



777



Conclusion

- UV/EB curing
 - initially, pushed by technology
 - now, driven by market and HSE concerns
- Graphic arts, industrial coatings on « easy » substrates
- High performance applications dependent on advances in the control of:
 - reactivity (inhibition, thermal profiles),
 - adhesion to substrate,
 - network structure and mechanical properties,
 - process modelling, global efficiency.
- Availability of new prepolymers (liquids, powders, bio-based, ...), and of hybrid systems (UV + thermal, aqueous + UV, ...)
- Radiation sources more reliable and more sustainable
 - adaptation to the new features of LEDs, low energy EB
- Deeper understanding of structure-properties relations
- Towards applications with more demanding requirements

Acknowledgements

- Hélène Degrand, Stéphane Robiani
- Jonathan Edgeworth, Freddy Bénard
- Roman Mahias, Dominique Lacour
- Thierry Bonnefond, Vincent Peypoudat
- European Space Agency
 - ULS contract 2004
 - POCS contract 2006
- ANR CP2D, Mat&Pro, EcoTech



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