ANALYTICAL METHODS

STATE OF THE ART and NEW DEVELOPMENTS

THE PHOTOPOLYMERIZATION PROCESS IS A RAPID TRANSFORMATION OF A LIQUID MONOMER INTO A SOLID POLYMER INDUCED BY LIGHT.

WHEN M RE USED AS START WORK IS FORMED.

BUT...
what does
SOLID POLYMER
mean?

FROM MONOMERS TO POLYMERS

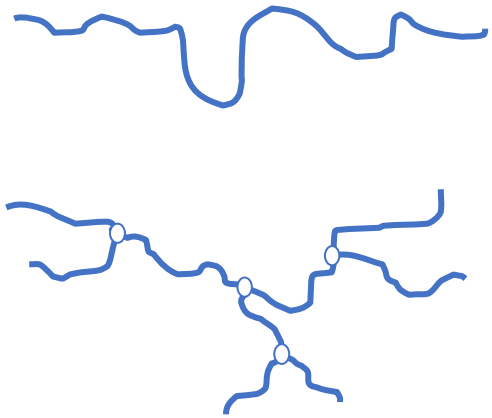
MONOMERS/OLIGOMERS

- Low M_w
- Viscous liquid
- Soluble
- Formable
- Amorphous, low T_g

monofunctional

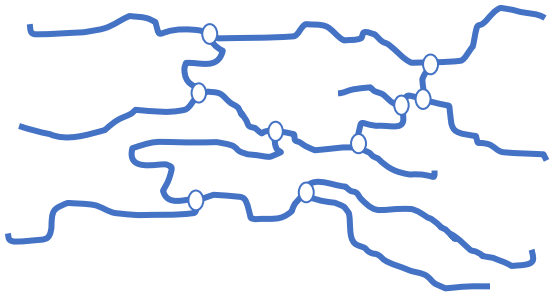
polyfunctional

LINEAR/BRANCHED THERMOPLASTIC POLYMERS



- High M_w
- Solid (or liquid)
- Semicrystalline (T_m) or amorphous, high(er) T_g
- Mostly soluble
- Formable (heat)

CROSSLINKED POLYMER (Thermoset)

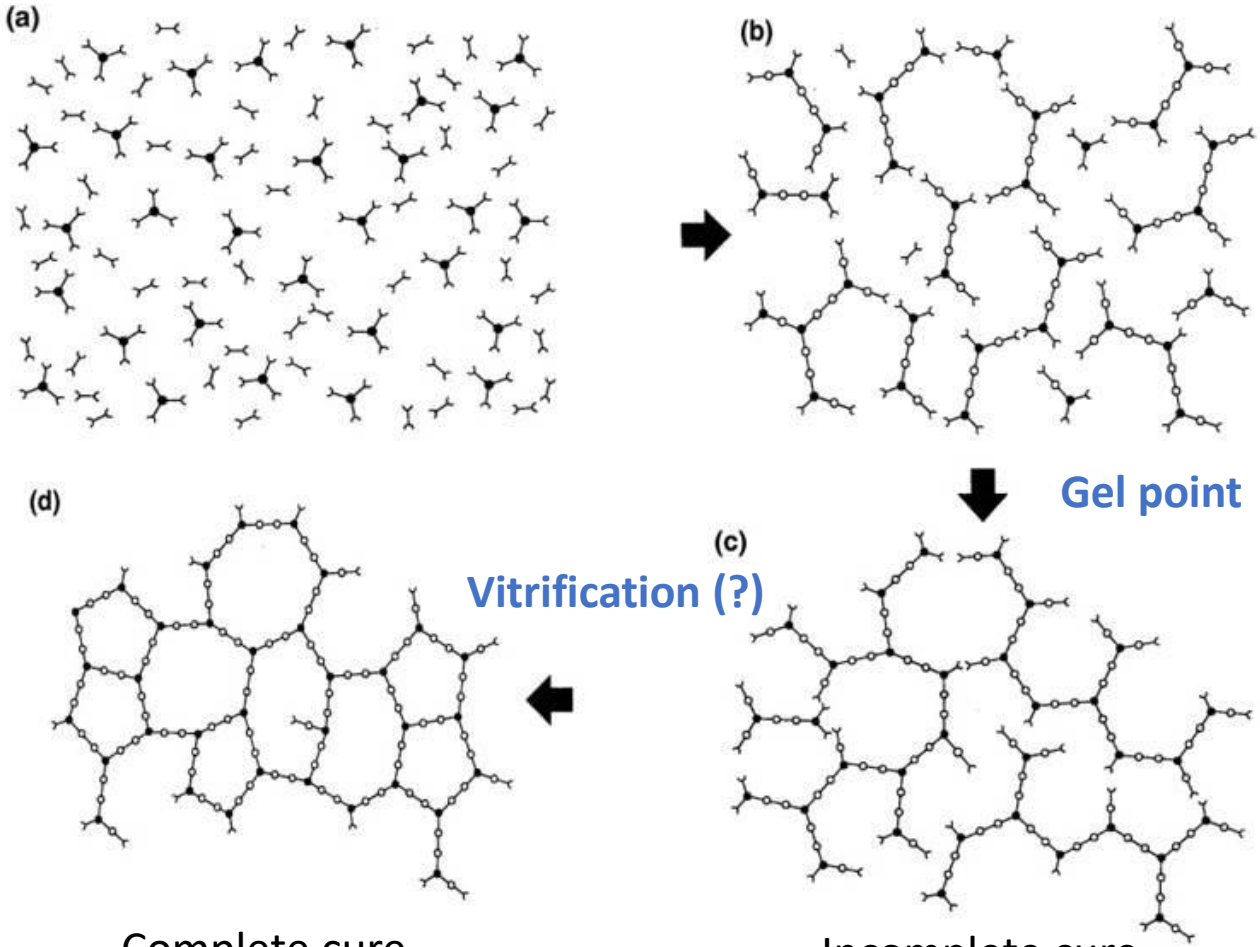


- Infinite M_w
- Solid
- Amorphous, high(er) T_g
- Not soluble
- Not formable

THERMOSET POLYMER (PHOTO)CURING PROCESS

Monomers/oligomers

Linear growth and branching (before gel)



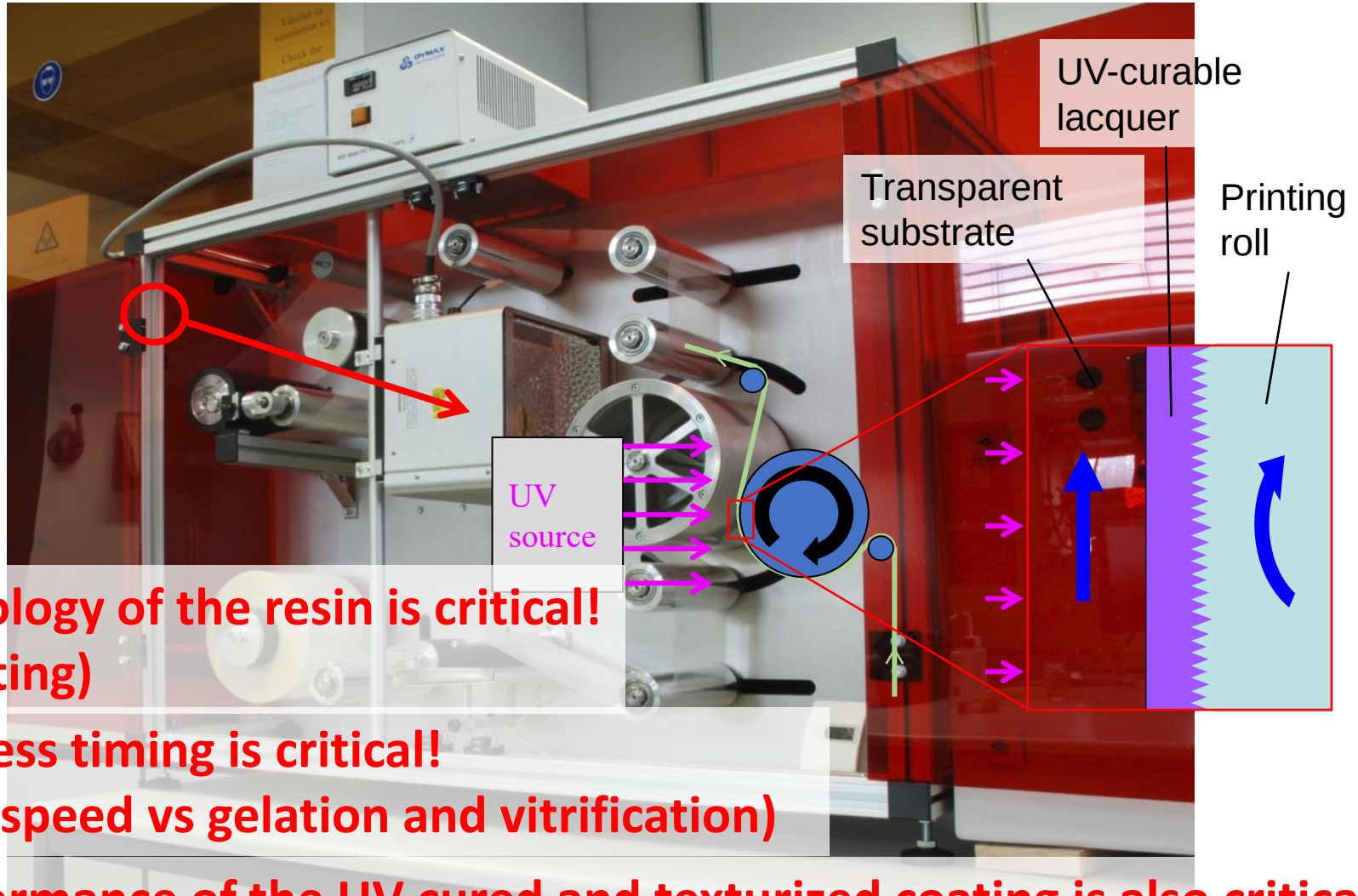
Complete cure

Incomplete cure (after gel)

CHARACTERIZATION METHODS: WHY?

- Goal → obtain a material/final product with specific characteristics:
  - Properties of the precursors
  - Processing aspects
  - Properties of the final product:
    - Degree of cure/insoluble content
    - Thermo-mechanical properties
    - Other functional properties

ROLL-TO-ROLL UVNIL



Rheology of the resin is critical! (coating)

Process timing is critical! (line speed vs gelation and vitrification)

Performance of the UV cured and texturized coating is also critical! (replication fidelity vs shrinkage and stress)

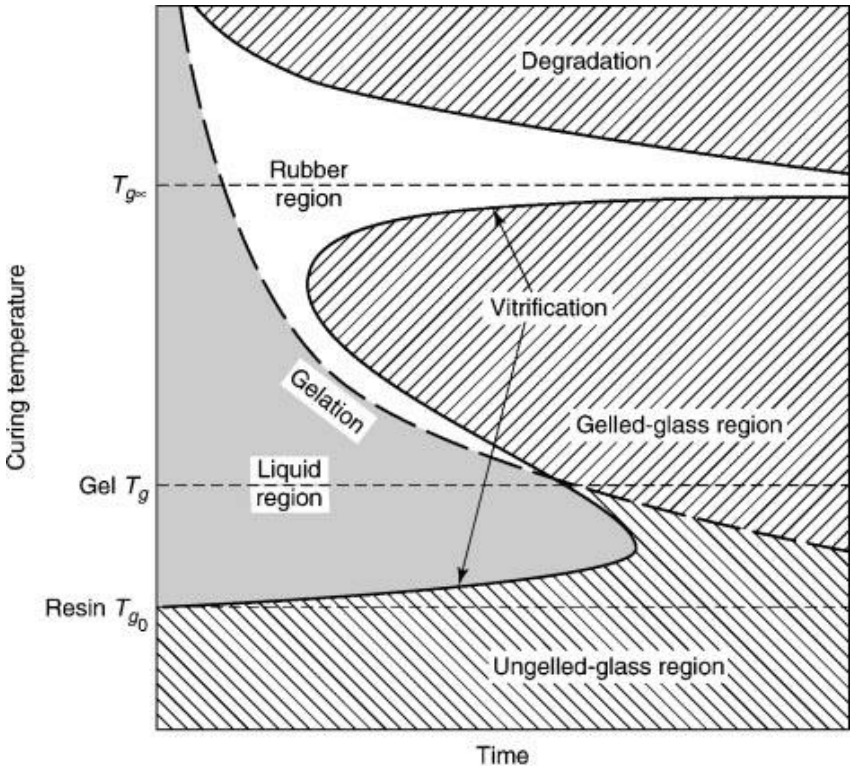
CHARACTERIZATION METHODS: WHY?

- Did we obtain the product (polymer) we wanted?
  - Degree of cure/insoluble content
  - Thermo-mechanical properties
  - Other functional properties
- Relationships between polymerization reaction and processing?
  - How fast? Reaction kinetics
  - Real-time analysis of structure development during photopolymerization:

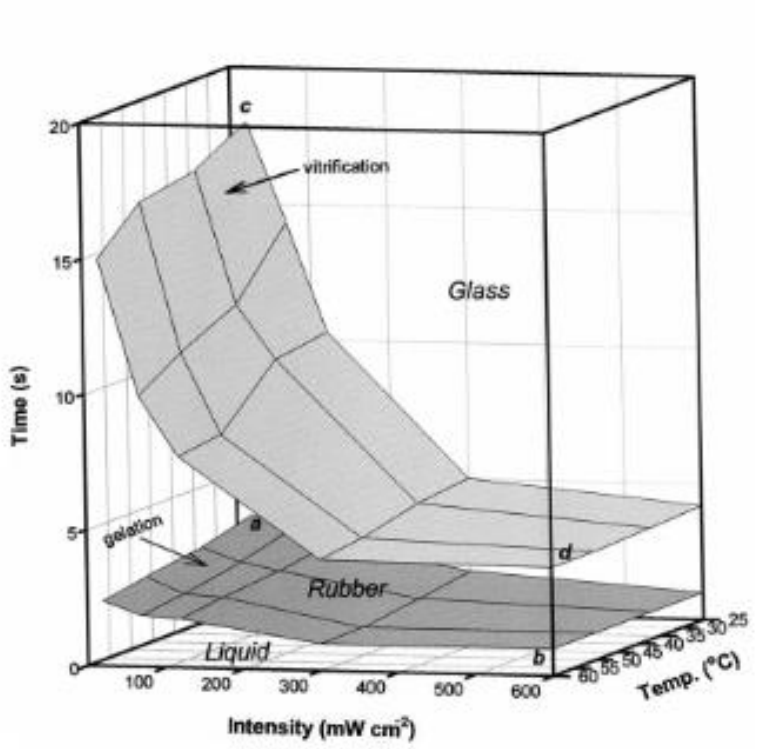
– gelation – vitrification	*in relation to*	– viscosity/modulus – shrinkage – stress

  - Determination of time-intensity-transformation diagrams

TTT DIAGRAMS FOR THERMOSETS

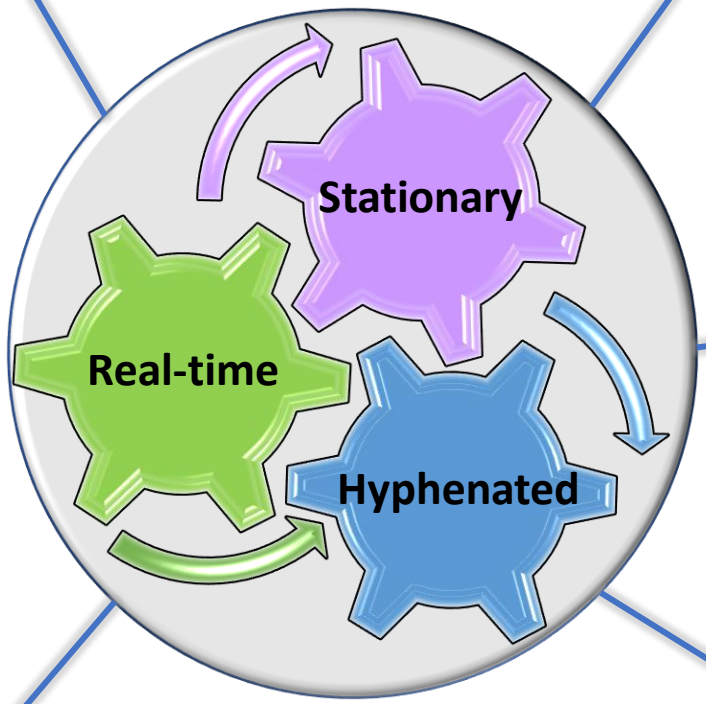


Gillham & co-workers, J Appl Polym Sci (1983)



Lee et al., Polymer Journal, Vol. 35, No. 10, pp 778—784 (2003)

Monitoring techniques:



Physical properties

- **DSC (T_g)**
- DMA (T_g, E'…)
- TGA (thermal stability)
- M_w (GPC)
- Dielectric spectroscopy
- Photoacoustic spectroscopy
- …

Thermal effects

- **Photo-DSC**
- **Optical pyrometry**

Gel% or extractables

- **Gravimetry**
- HPLC
- GC, GC-MS

Mechanical properties

- **Photo-rheometry**
- **Interferometry**

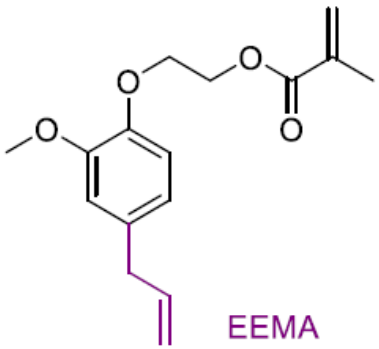
Functional groups

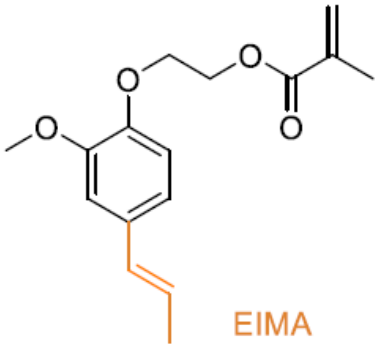
- **FTIR**
- NIR
- Raman
- UV-Vis
- NMR

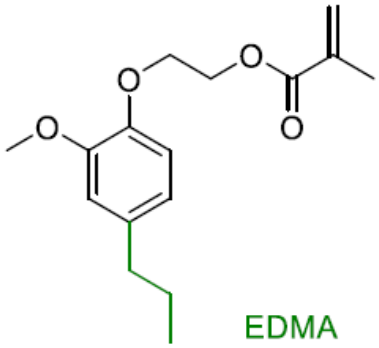
GEL or INSOLUBLE CONTENT

The polymer is weighed (W_i), wrapped in a fine mesh, soaked in the solvent for a given time, rinsed, dried and weighed again (W_f).

$$Gel\% = 100 \times \frac{W_f}{W_i}$$





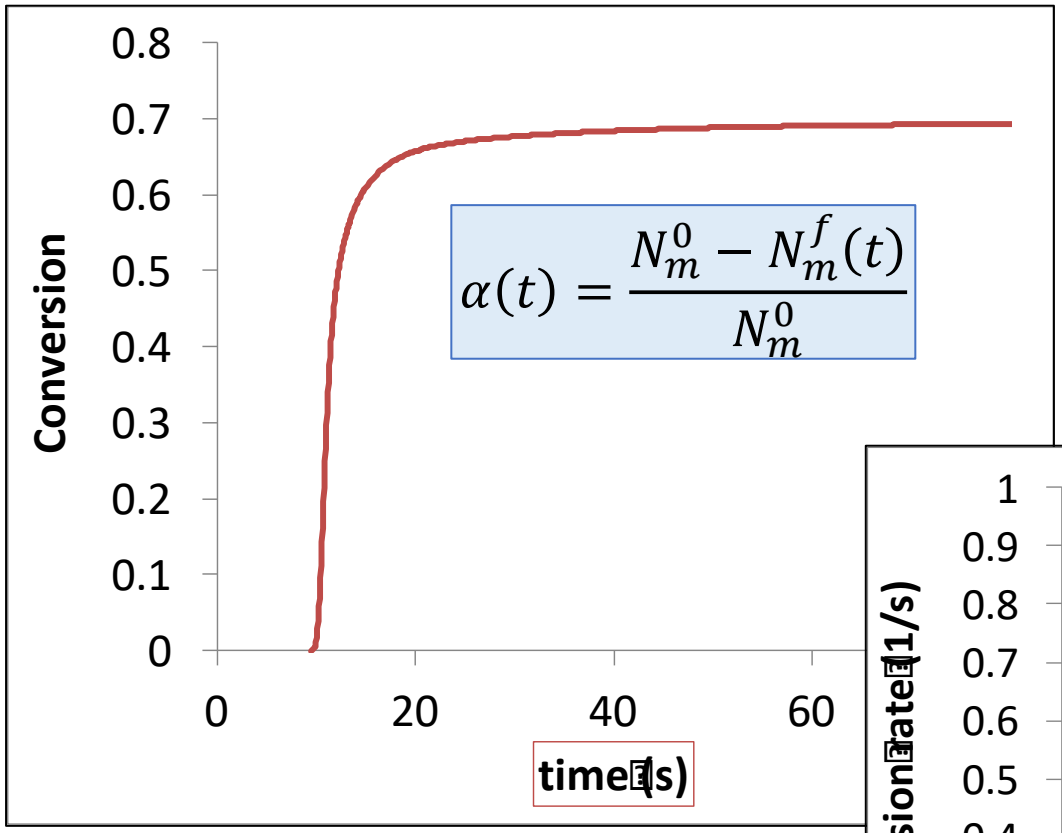


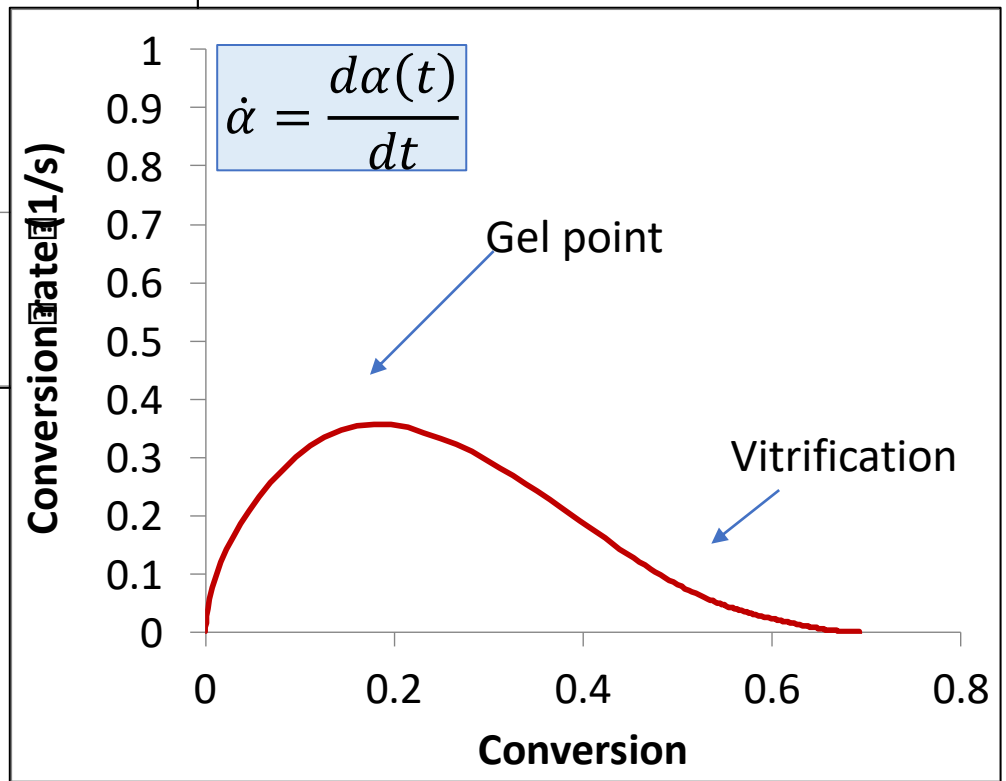
Monomer	Polymerization Condition	Gel Content (%)
EDMA	with air	2
	no air	3
EEMA	with air	100
	no air	98
EIMA	with air	100
	no air	100

MDB conversion by FTIR > 80%

Molina-Gutiérrez et al. Molecules **2020**, 25, 3444

Kinetics





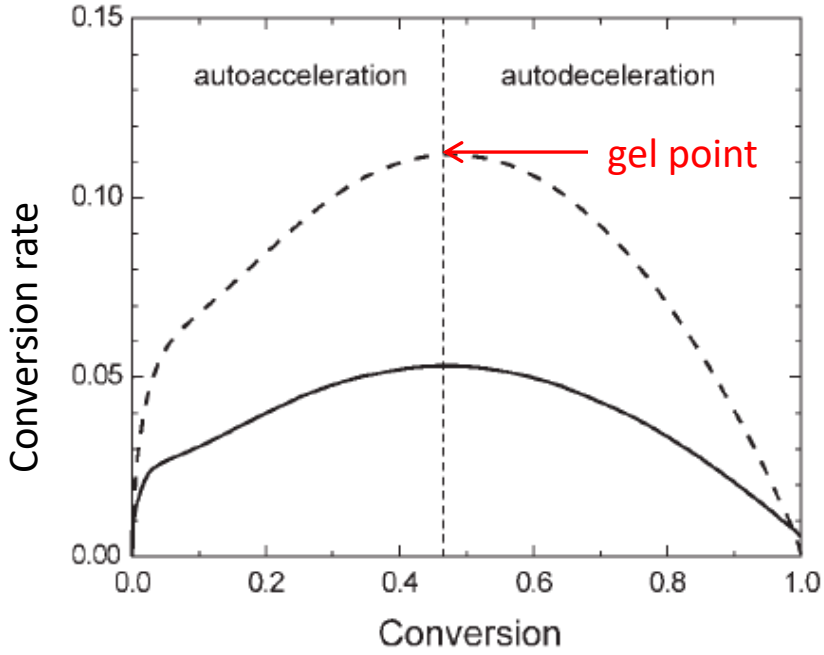
N_m = number (mols, concentration) of monomers or reacting groups

KINETICS: AUTOCATALYTIC MODEL

Photoinduced reactions are autoaccelerated and are well described by the autocatalytic model.

Two polymerization regimes:

- Autoacceleration
- Autodeceleration



Autocatalytic model:

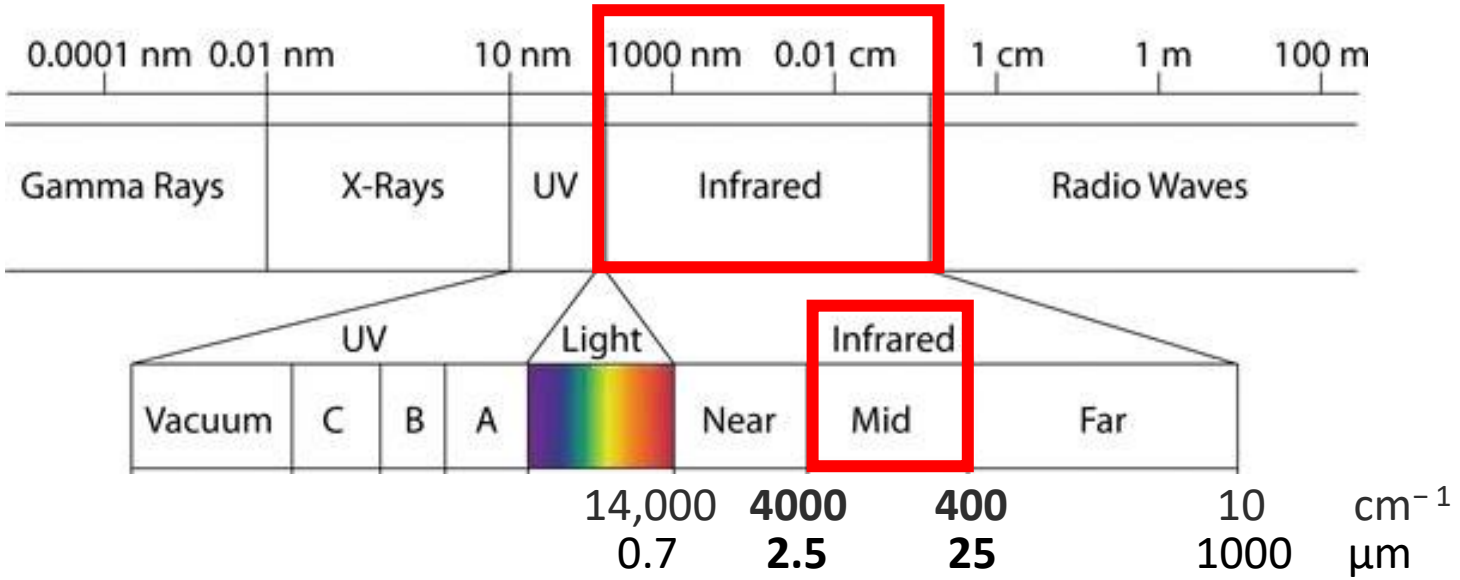
$$\frac{d\alpha}{dt} = k(I)\left(1 - \frac{\alpha}{\alpha_{max}(I)}\right)^{n}\left(\frac{\alpha}{\alpha_{max}(I)}\right)^{m}$$

k = kinetic constant
m = autocatalytic exponent
n = reaction order

Bowman and Kloxin, Toward an Enhanced Understanding and Implementation of Photopolymerization Reactions, AIChE (2008)

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared spectroscopy is a technique based on the interaction of infrared light with matter



Wavenumber [cm^{-1}]

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Velocity of light

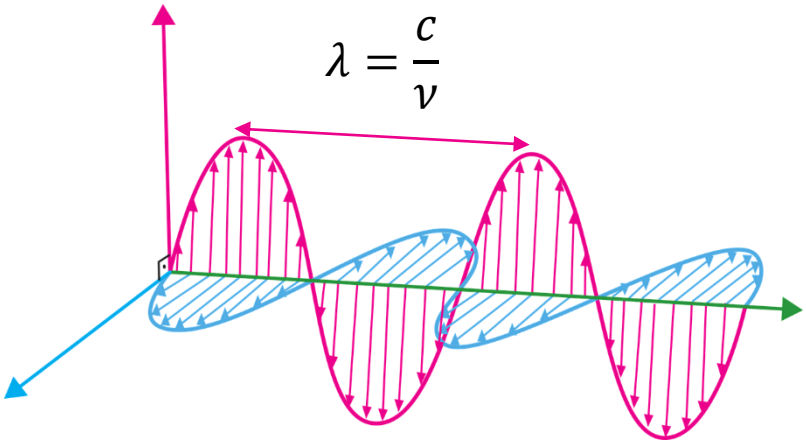
$$c = \lambda \cdot \nu \cong 3 \times 10^{8} m\, s^{-1}$$

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

- According to the electromagnetic radiation theory the energy of a photon is:

$$E = h \cdot \nu$$

Plank equation



- Energy of a mol of photons in the IR range:

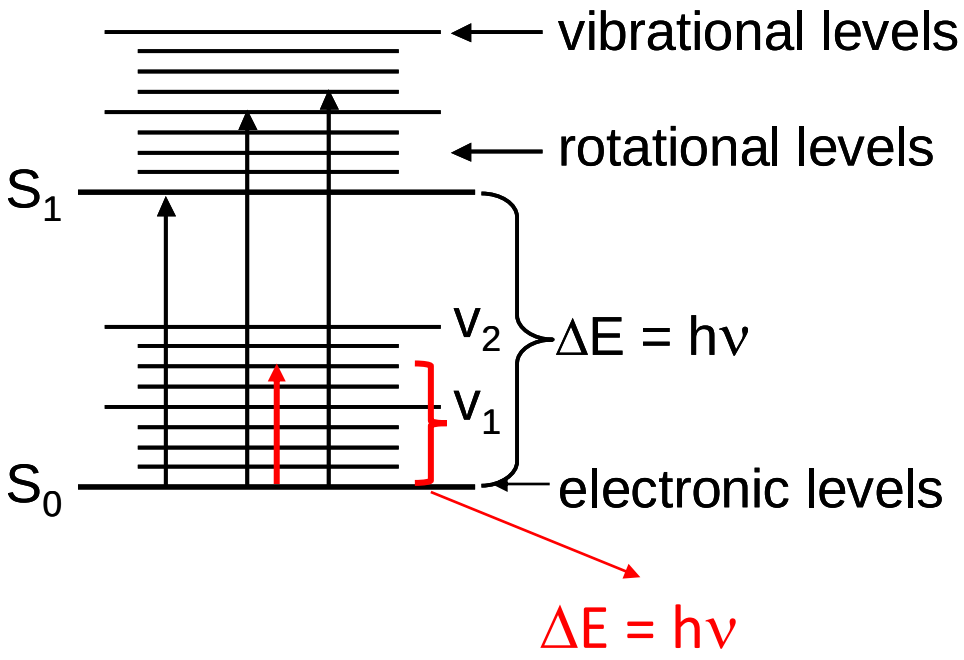
$$E \cdot N_A = h \cdot \frac{c}{\lambda} N_A = \frac{2.86 \times 10^{-3} (kcal\ cm\ mol^{-1})}{\lambda (cm)}$$

$\sim 1\ kcal\ mol^{-1} \quad (\bar{\nu} = 400\ cm^{-1})$

$\sim 11\ kcal\ mol^{-1} \quad (\bar{\nu} = 4000\ cm^{-1})$

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

- Each atom or molecule in a system must exist in quantized discrete energy levels. Atomic or molecular processes are associated with these states and can be represented in terms of E_0, E_1, E_2, etc
- Whenever a molecule interacts with radiation, a quantum of energy (or photon) is either emitted or absorbed. In each case, the energy E of the quantum of radiation must exactly fit the energy gap $E_f - E_i$.



$$E_f - E_i = E = h \cdot \nu$$

$$\frac{E_f - E_i}{h} = \nu$$

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

- Infrared spectroscopy (IR) relies on the fact that most molecules absorb IR light, converting it to molecular vibration.
- This absorption is characteristic of the nature of the chemical bonds present in a sample.
- To show infrared absorptions the electric dipole moment of molecule must change during the vibration.

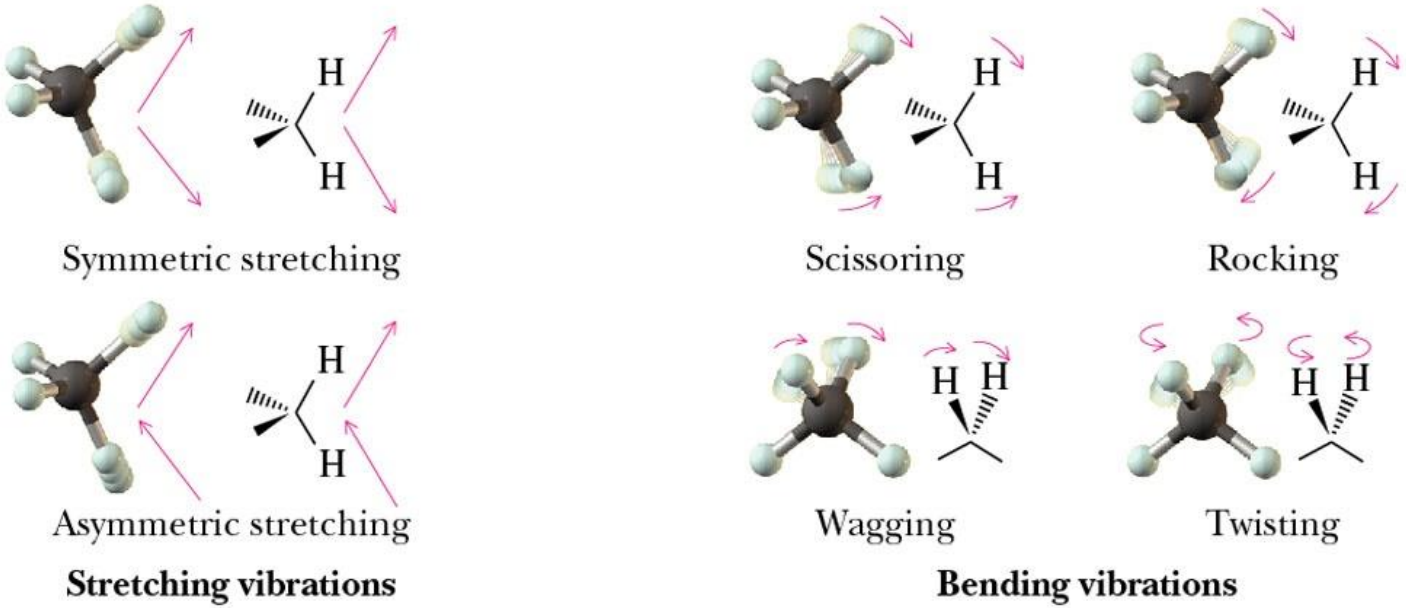
FTIR: vibrations in molecules

Stretching and bending movements (i.e. vibrations): bond lengths and bond angles can vary.

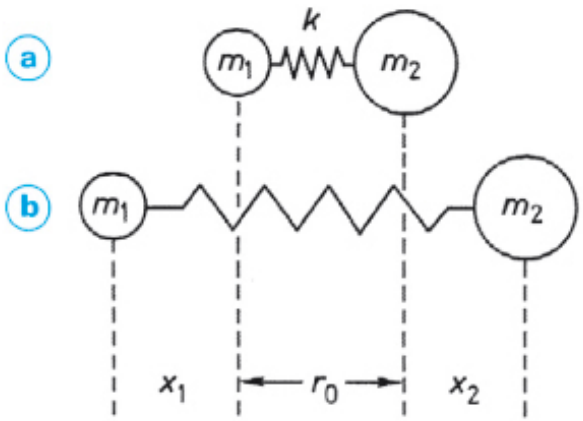
- Diatomic molecule: only bond length can change (stretching)

$$C \overset{\longleftrightarrow}{=} O$$
$$\delta^+ \quad \delta^-$$

- Poliatomic molecules: stretching and bending



Molecular vibrations (stretching)



k = a force constant, which is a measure of the bonds' strength; force constants for single, double, and triple bonds are approximately 5, 10, and 15 x 10^5 mN/m

m = reduced mass of the two atoms = $(m_1 m_2)/(m_1 + m_2)$

$F = -k\,x \qquad F = ma = m d^2x/dt^2$

$-kx = m\, d^2x/dt^2$

$\varpi^2 = k/m \qquad \rightarrow -\varpi^2\, x = d^2x/dt^2$

$d^2x/dt^2 + \varpi^2 x = 0$

$$x = A\cos(\varpi t + \varphi_0)$$

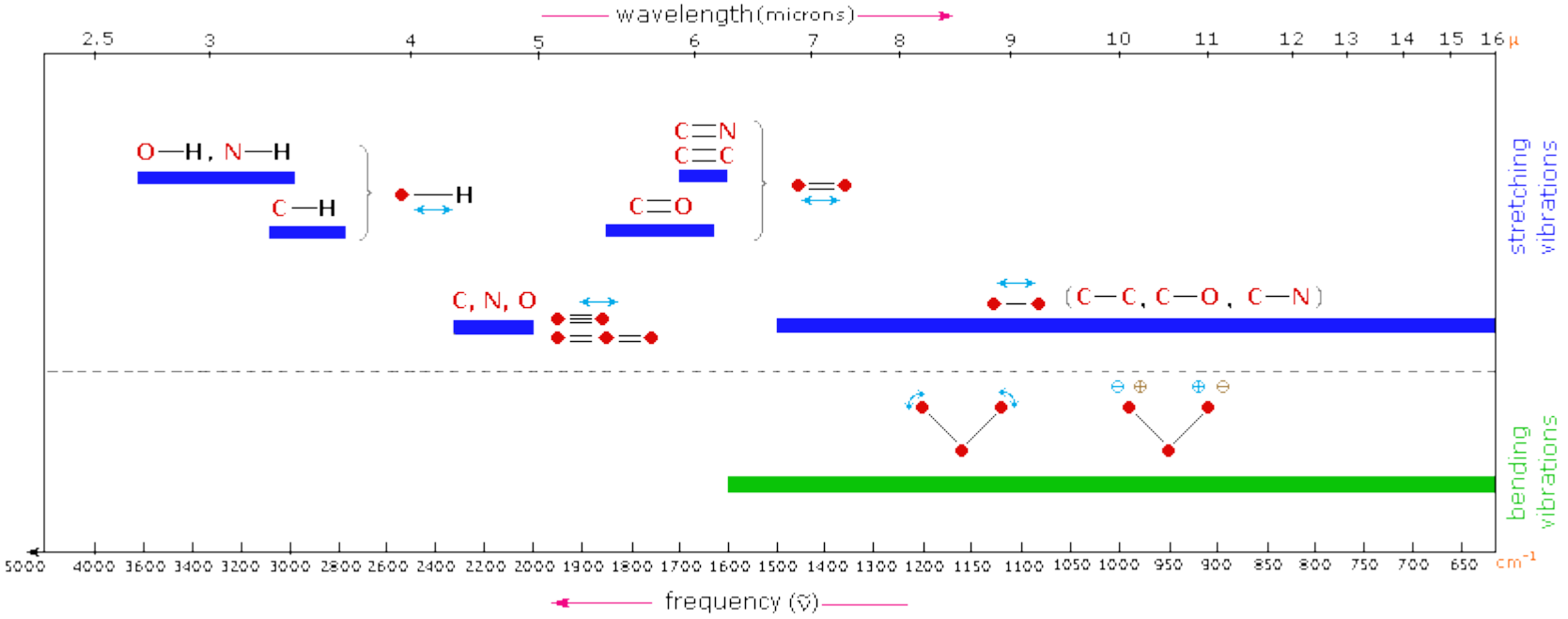
$$F = -\frac{dE_p}{dx} = -k\,x$$

$$dE_p = k\,x\,dx \quad \Rightarrow \quad \int_0^{E_p} dE_p = \int_0^{x} k\,x\,dx$$

$$E_p = \frac{1}{2}k\,x^2 = \frac{1}{2}m\,\varpi^2\,x^2$$

Approximate Infrared Stretching Frequencies

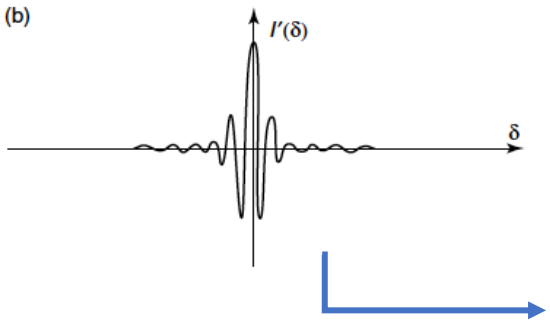
B-H 2400 cm^{-1}	C-H 3000 cm^{-1}	N-H 3400 cm^{-1}	O-H 3600 cm^{-1}	F-H 4000 cm^{-1}
Al-H 1750	Si-H 2150	P-H 2350	S-H 2570	Cl-H 2890
	Ge-H 2070	As-H 2150	Se-H 2300	Br-H 2650

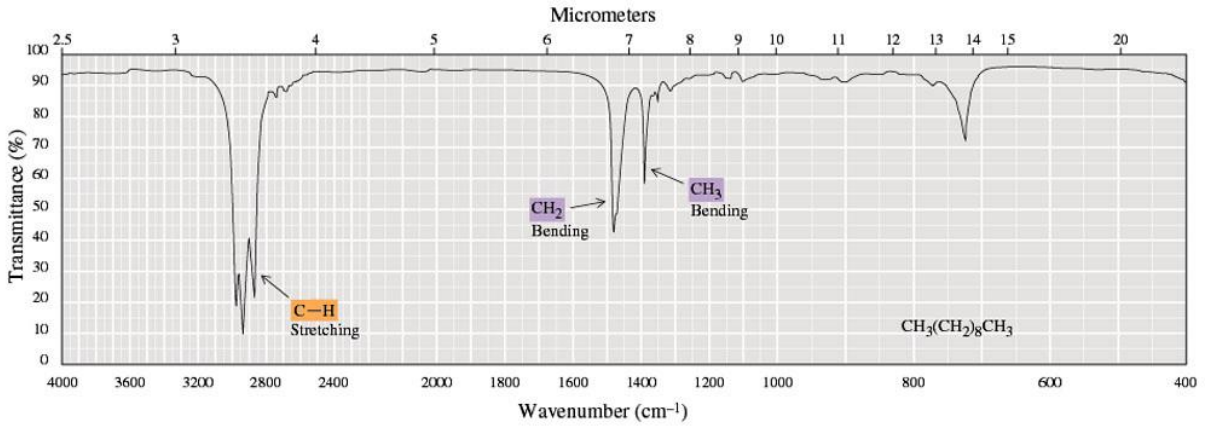


https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm

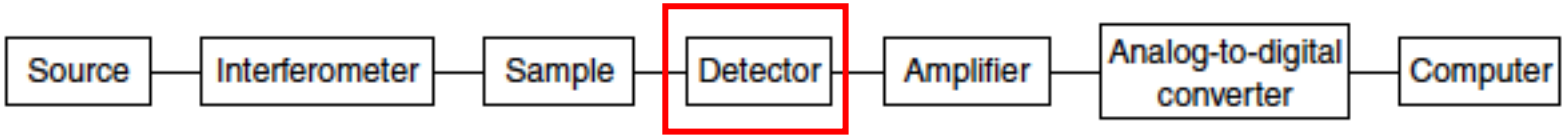
FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

- An infrared spectrum is obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at each particular wavelength.
- FTIR is based on the interference of radiation between two beams giving an interferogram. Fourier transformation converts the interferogram into a spectrum.
- Peaks in absorption spectra appear at wavelengths corresponding to the frequency of vibration of a part of a sample molecule.





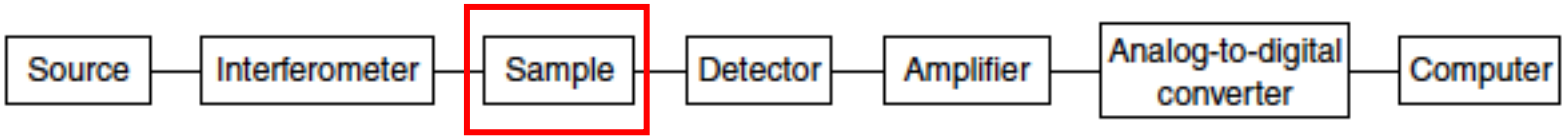
FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)



- DTGS →routine detector (pyroelectric: deuterium tryglycine sulfate in a alkali-halide window)

- MCT →more sensitive (mercury cadmium telluride, needs liquid nitrogen cooling), necessary for real time measurements (kinetics)

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)



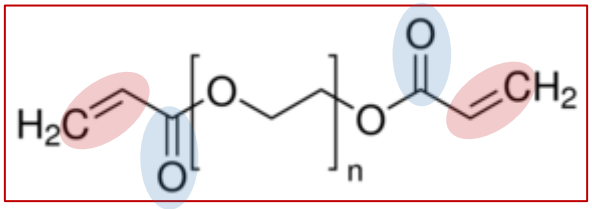
- Transmission:
  - Thin film
  - KBr pellet
  - Coating on IR transparent substrate (e.g. silicon wafer)
  - cells for fluids
  - …
- Reflectance:
  - **Attenuated Total Reflectance (ATR):** uses a high refractive index crystal to obtain total internal reflection
  - Specular Reflectance: for surfaces (reflective or attached to a reflective substrate)
  - Diffuse Reflectance (DRIFT): for powders or fibers

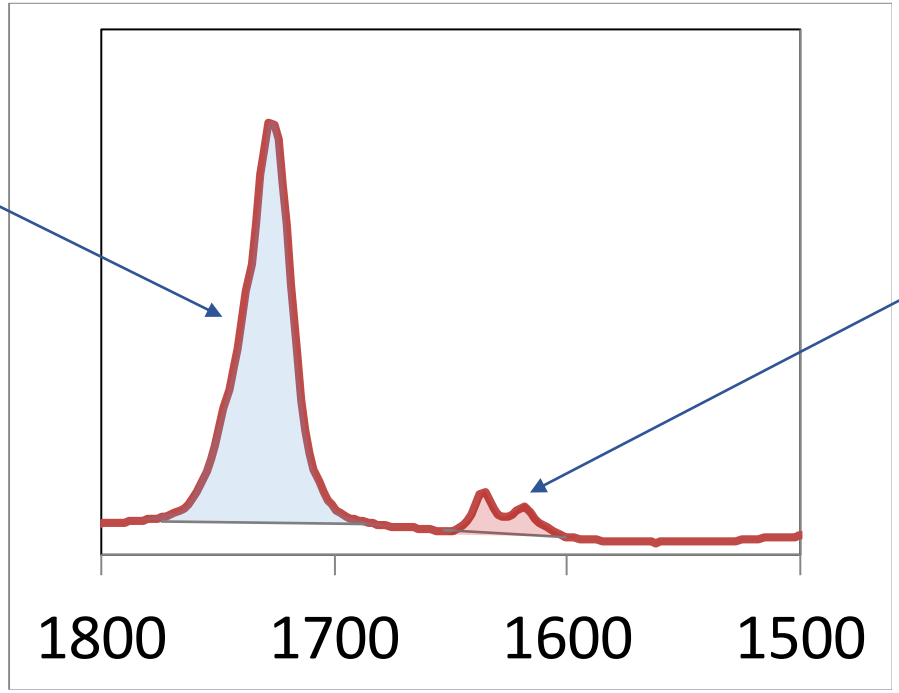
e.g. see ThermoFisher Scientific at https://tinyurl.com/rvxq7zy

FTIR: monitoring a reaction

- Beer-Lambert law: $A = \varepsilon l c$ (c = concentration)
- The area of the peak of the group undergoing polymerization A_F (and that of a reference peak, A_R) are calculated before polymerization, and after a time *t* from the beginning of the reaction
- Conversion (α) is calculated as:

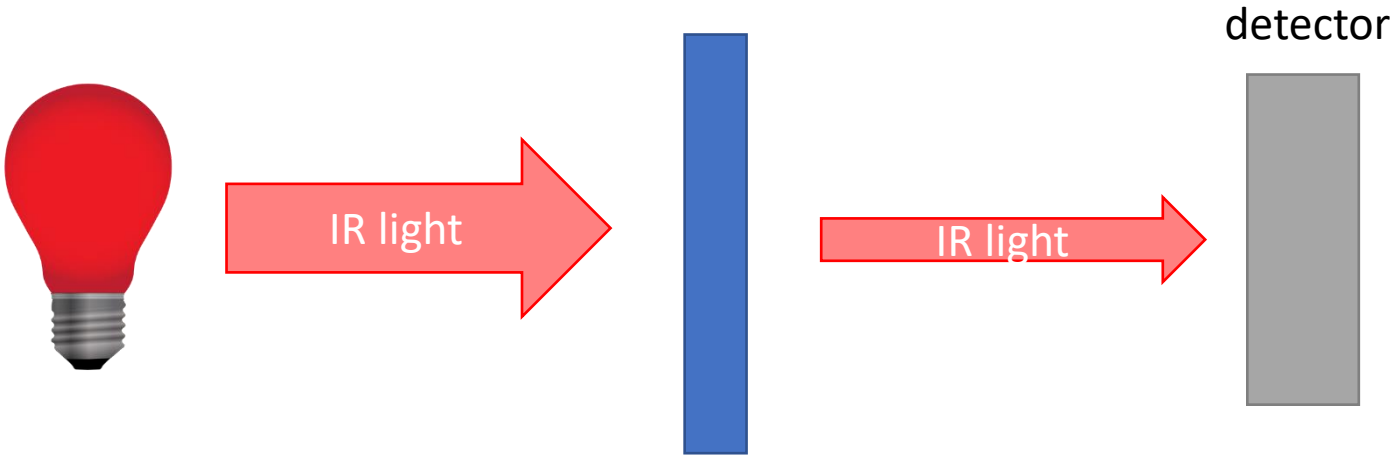
$$\alpha = \left(1 - \frac{A_F/A_R}{A_F^0/A_R^0}\right)$$





FTIR in transmission mode

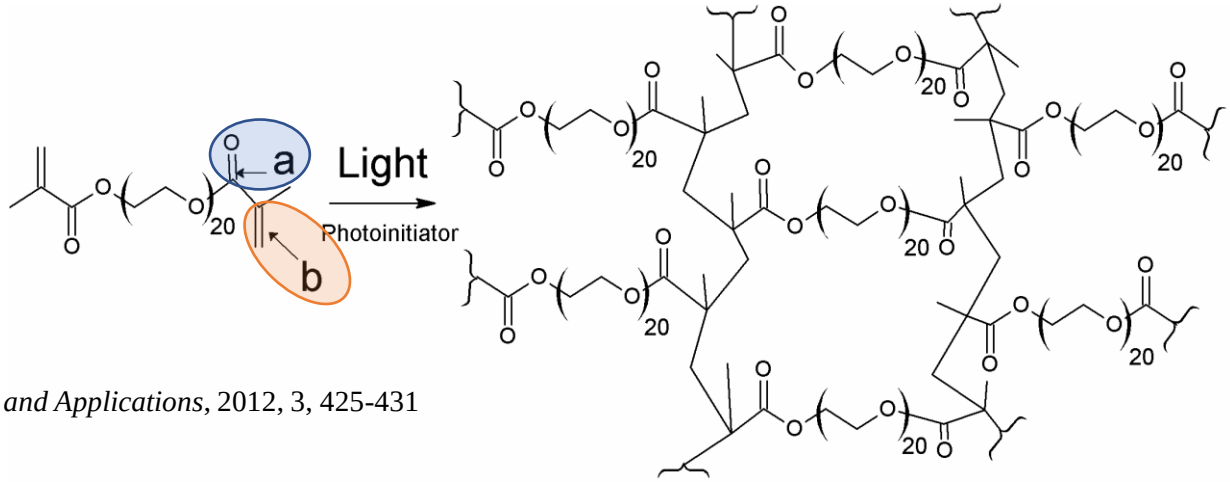
Polymer sample: usually in the form of thin films or thin coatings on IR transparent substrates



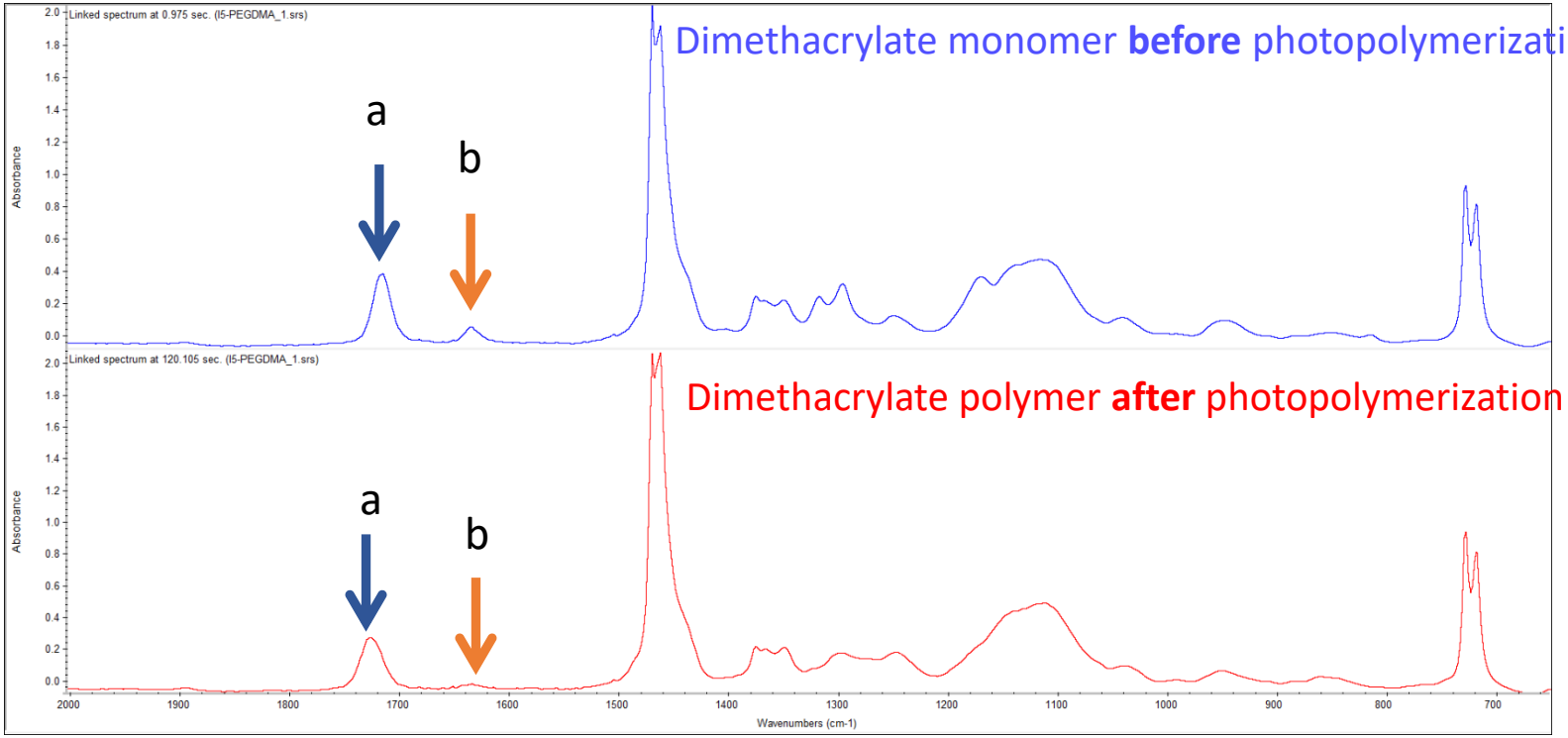
Absorption of UV light
(at specific wavelengths)

Bulk measurement: average of through-thickness composition

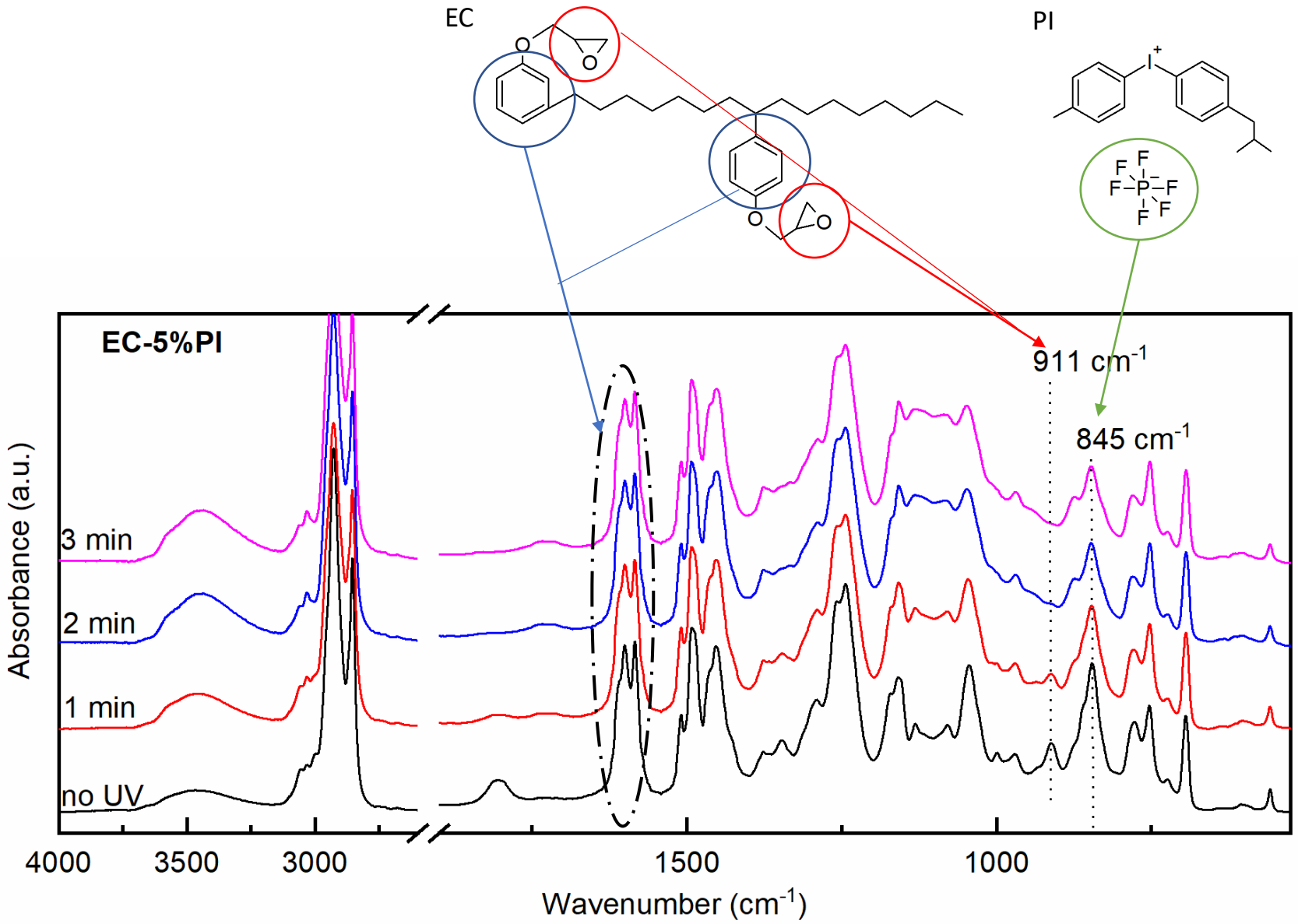
FTIR in transmission mode: example 1



Materials Sciences and Applications, 2012, 3, 425-431

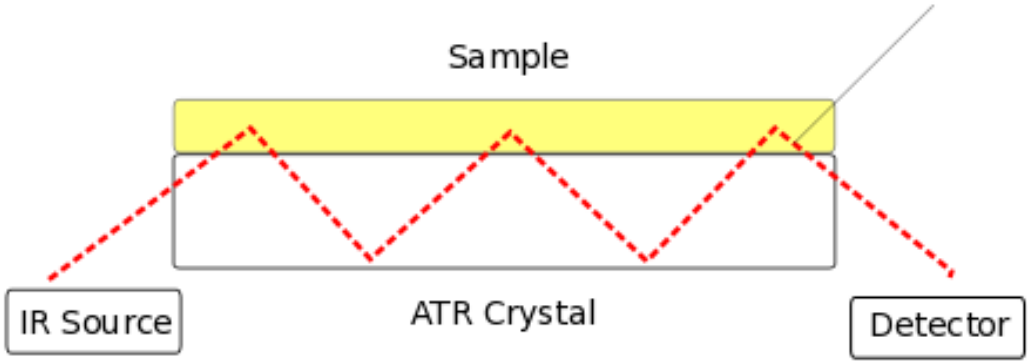


FTIR in transmission mode: example 2



FTIR in ATR mode

- The IR wave slightly penetrates into the less optically dense sample
- Evanescent field that interacts with sample (few microns)

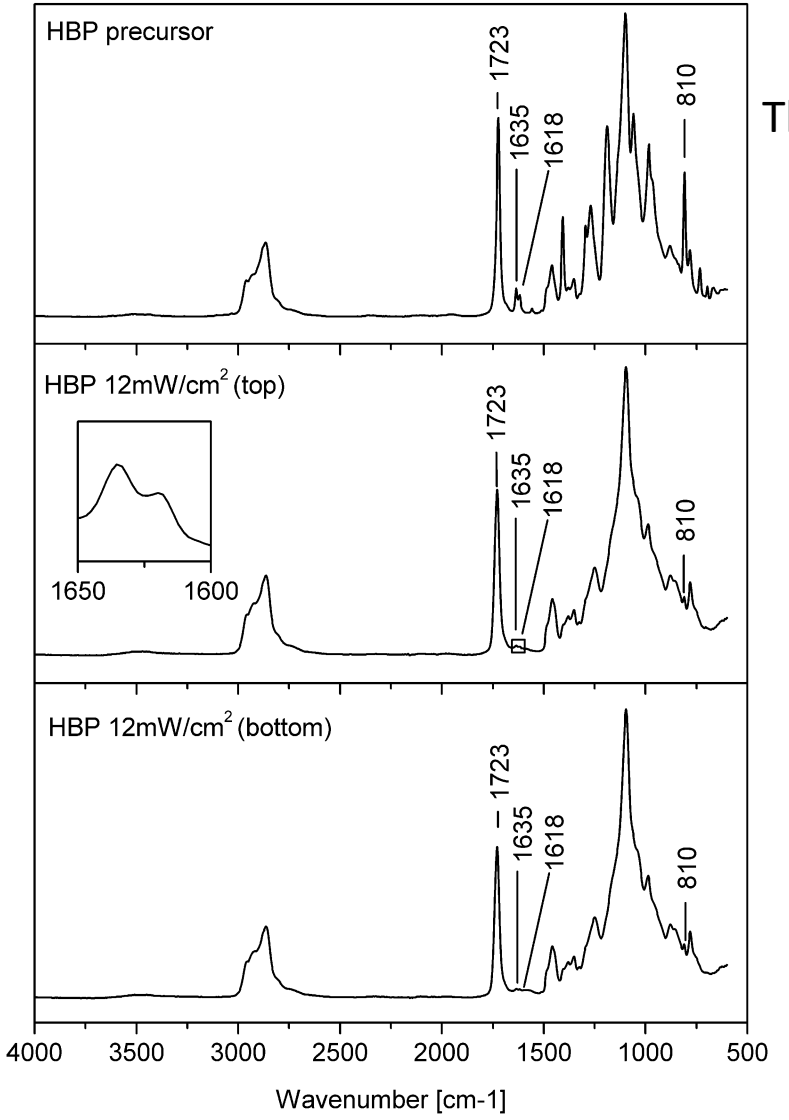


Surface measurement: composition of a thin layer

S. Dalle Vacche et al. Polymer 51 (2010) 334–341

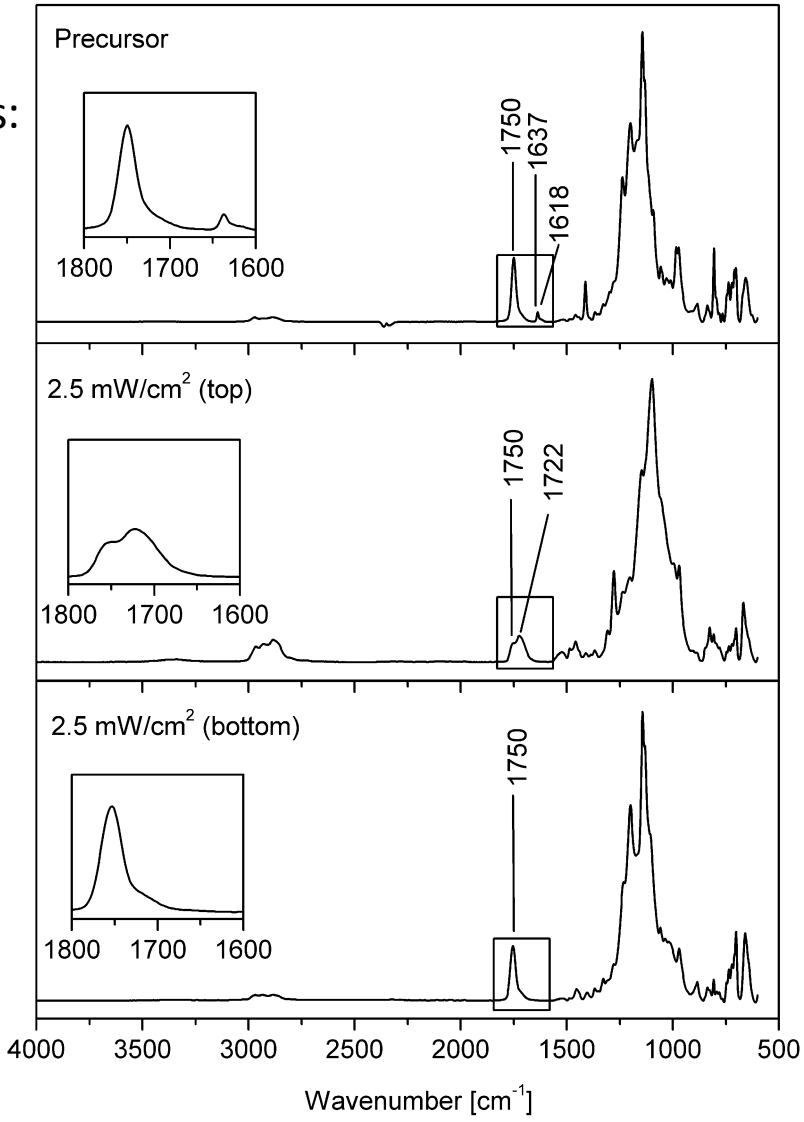
ATR-FTIR

Hyperbranched polyether acrylate (HBP)



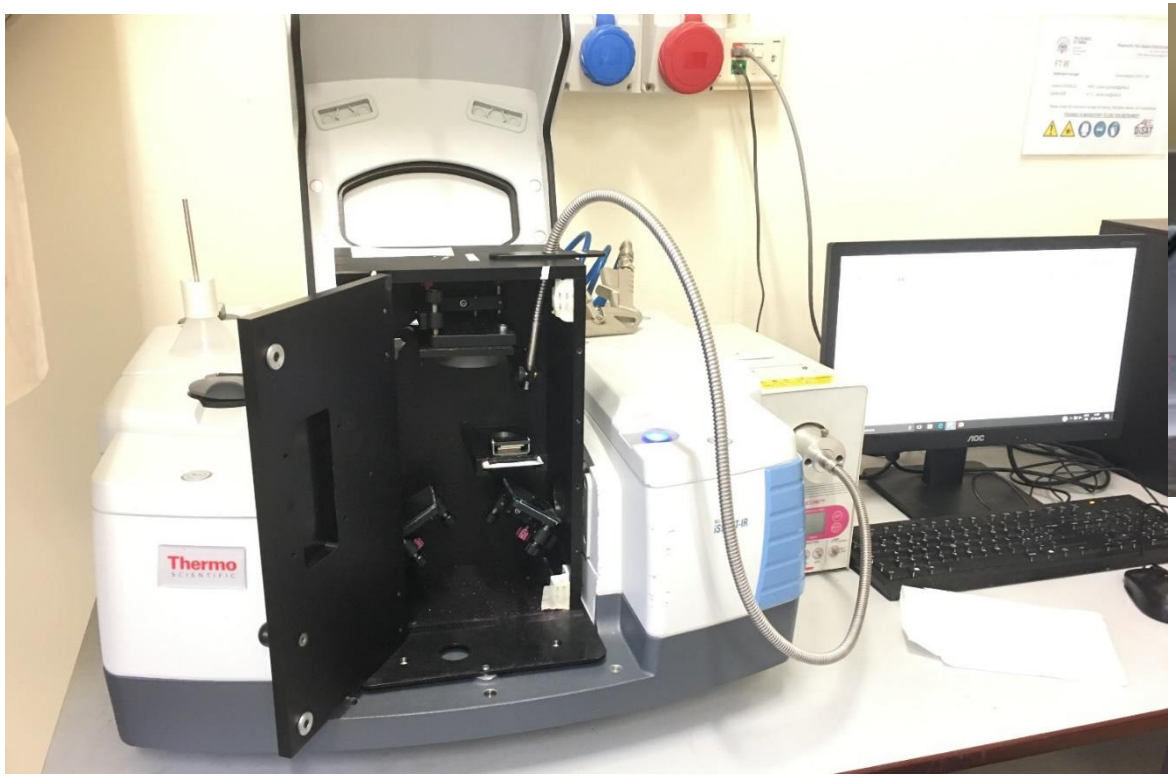
Thickness:
500 μm

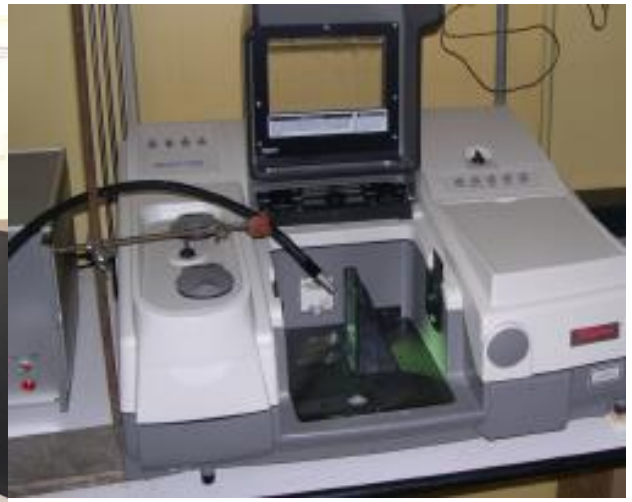
Perfluorooctyl acrylate + silica particles



Real time FTIR (rt-FTIR)

- A series of IR spectra are recorded while UV light irradiates the sample.
- Transmission (vertical or horizontal films) or ATR

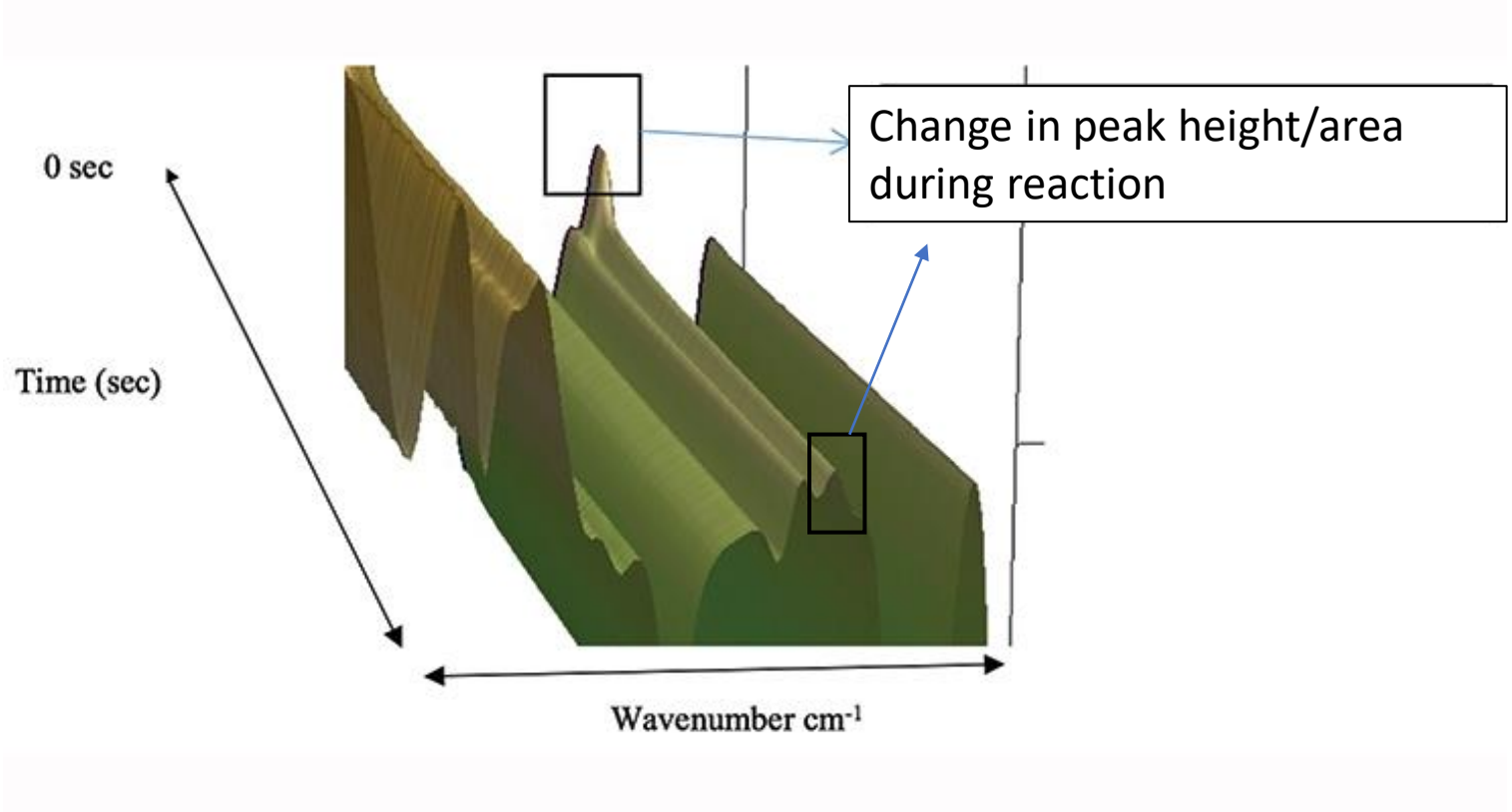




Decker, C.; Moussa, K. Eur Polym J 1990, 26, 393.
6. Decker, C.; Moussa, K. Makromol Chem 1990, 191, 963.
7. Decker, C. J Polym Sci Part A: Polym Chem 1992, 30, 913.

Real time FTIR

- Continuous monitoring of the growth or disappearance of the IR band corresponding to the functional group undergoing polymerization

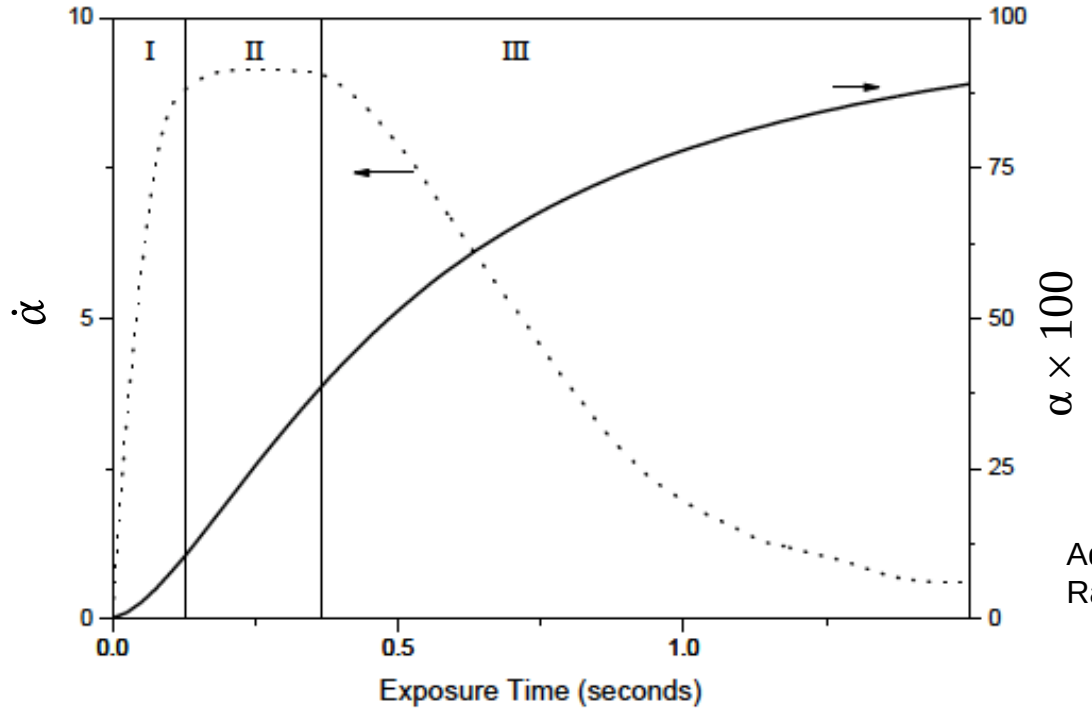


www.coatingsworld.com

REAL-TIME INFRARED SPECTROSCOPY (rt-FTIR)

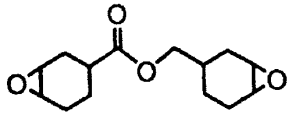
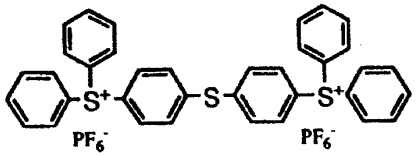
- Conversion as a function of time → $\alpha(t) = \left(1 - \frac{A_F(t)/A_R(t)}{A_F^0/A_R^0}\right)$

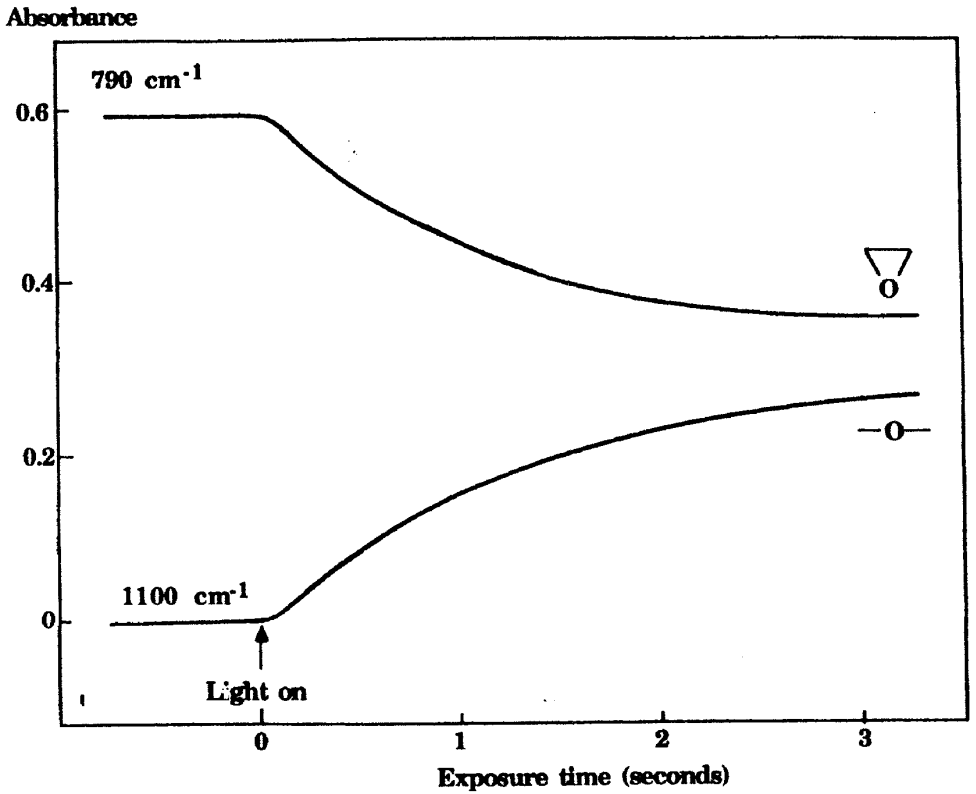
- Conversion rate → $\dot{\alpha} = \frac{d\alpha(t)}{dt}$



Adapted from Fouassier, J.P., Rabek J.F. (1993). Radiation Curing in Polym. Sci. Tech.

rt-FTIR: EXAMPLES

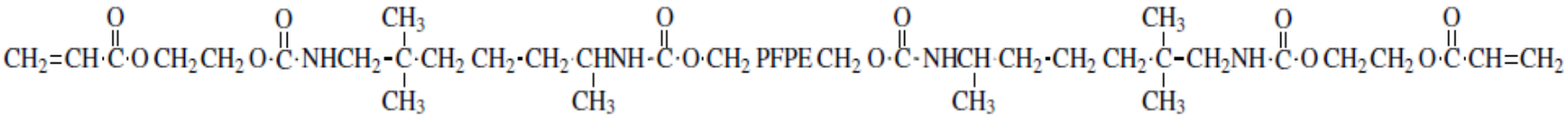
Photopolymerization of  with 



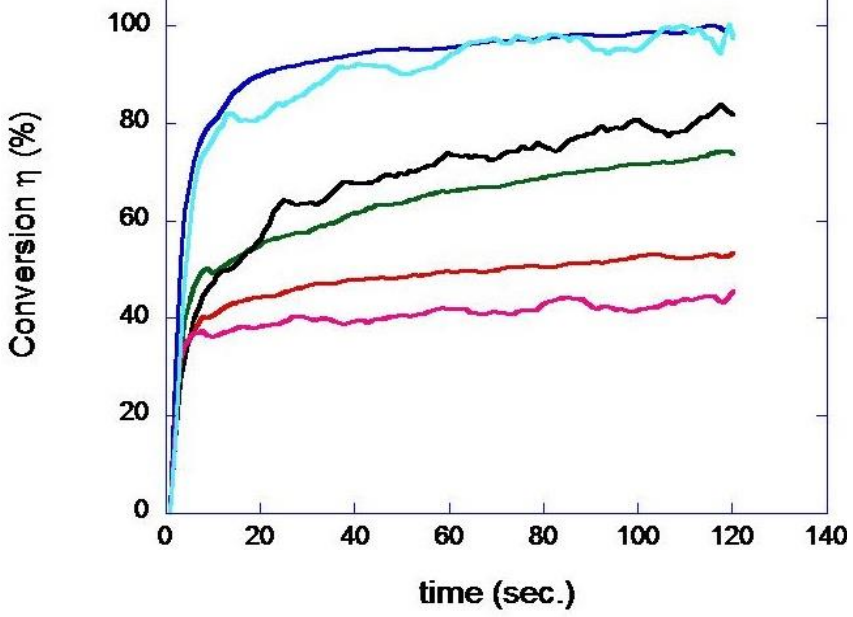
C. Decker and K. Moussa, J. Polymer Sci.: Part A: Polym. Chem., 28, 3429, (1990).

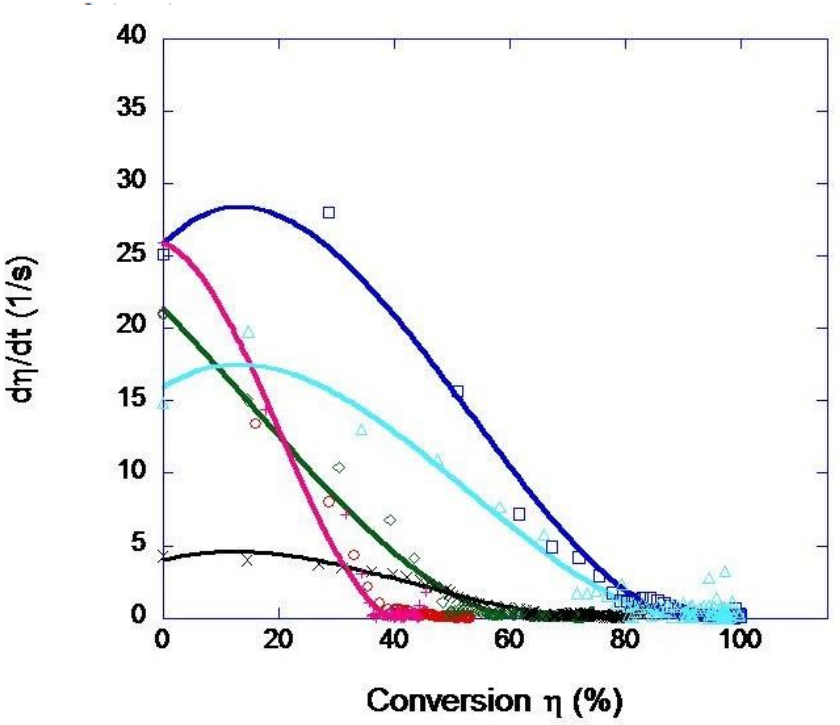
rt-FTIR: EXAMPLES

R. Bongiovanni et al, Polym Int, 2012;61:65–73



$$\eta = 1 - \frac{A_{1636\ cm^{-1}}(t)/A_{1735\ cm^{-1}}}{A_{1636\ cm^{-1}}(t=0)/A_{1735\ cm^{-1}}} = 1 - \frac{[M]}{[M_0]}$$



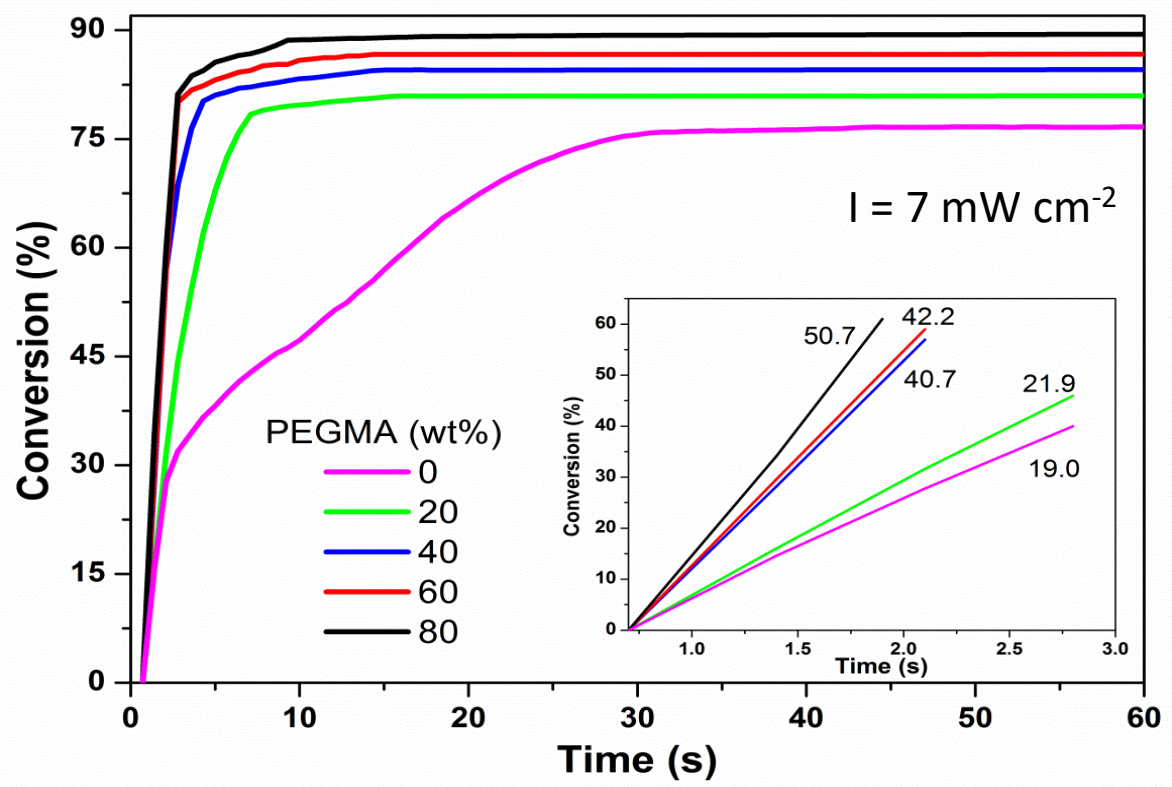


Photoinitiator	Mechanism
P1 DAROCUR BP® (Ciba)	Norrish II
P2 DAROCUR BP®/ SARTOMER CN 386® 5:4 w/w	Norrish II(amine-synergist)
P3 IRGACURE 500® (Ciba)	Norrish II
P4 DAROCUR 1173® (Ciba)	Norrish I
P5 IRGACURE 819® (Ciba)	Norrish I
P6 DAROCUR 1173®/IRGACURE 819® 4/1 w:w	Norrish I

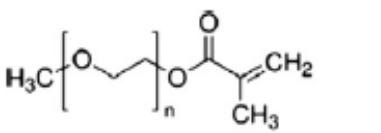
rt-FTIR: examples

The addition of a monofunctional reactive diluent (PEGMA) increases the conversion rate of PEGDA:

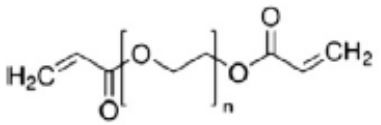
- Decrease of viscosity: higher chain mobility
- Decrease of T_g: delayed vitrification



(n = 9)



PEGMA



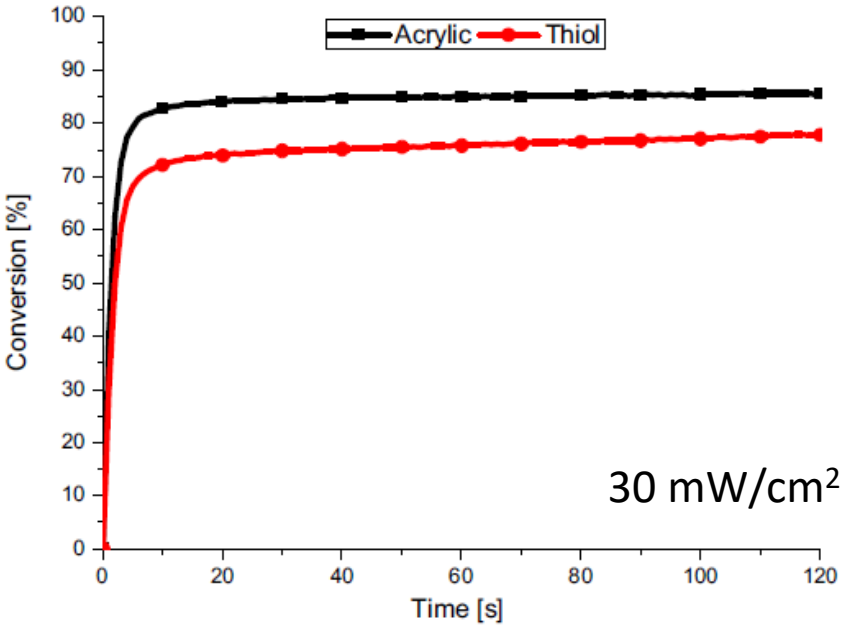
PEGDA

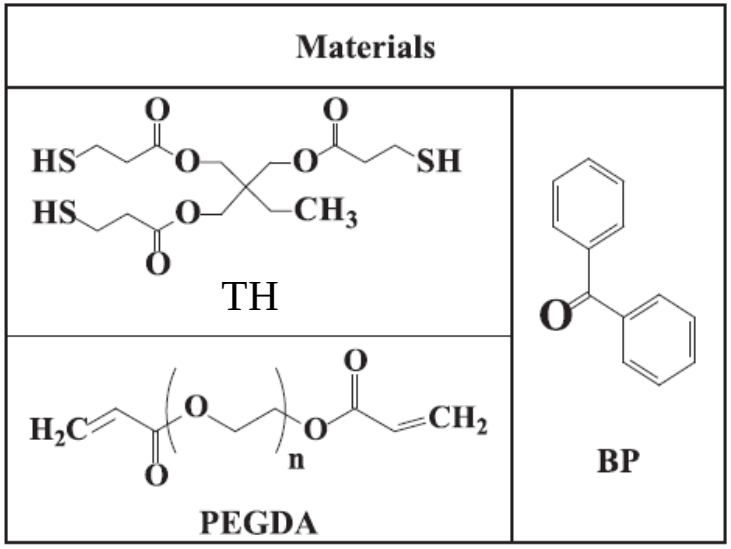
(n = 3)

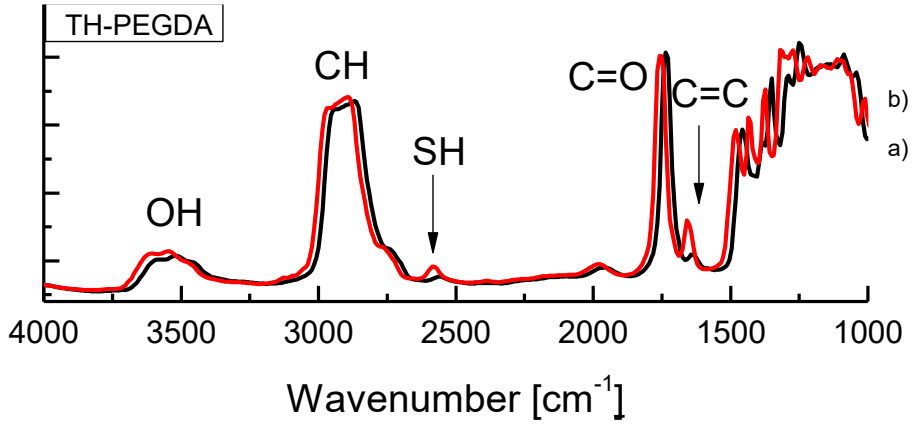
rt-FTIR: examples

Thiol-ene reaction→ reactive functionalities: thiol SH band at 2570 cm^{-1} and acrylate C=C band at 1640 cm^{-1}.

Area normalized by a constant signal in the spectra (C=O peak at 1730 cm^{-1}).

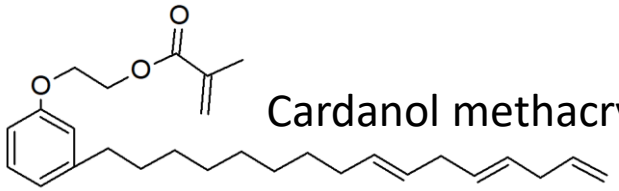






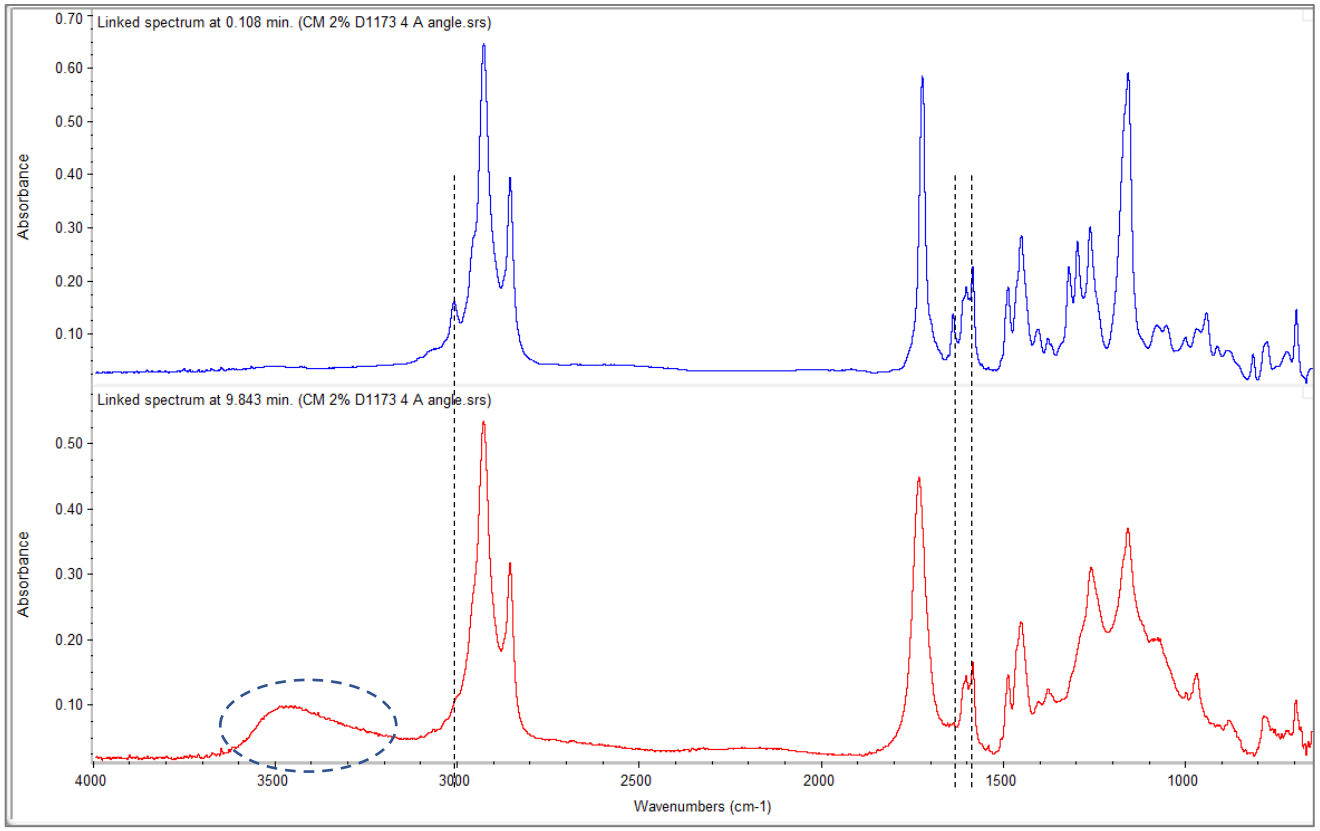
Colucci, Progress in Organic Coatings 77 (2014) 1104

rt-FTIR



Cardanol methacrylate

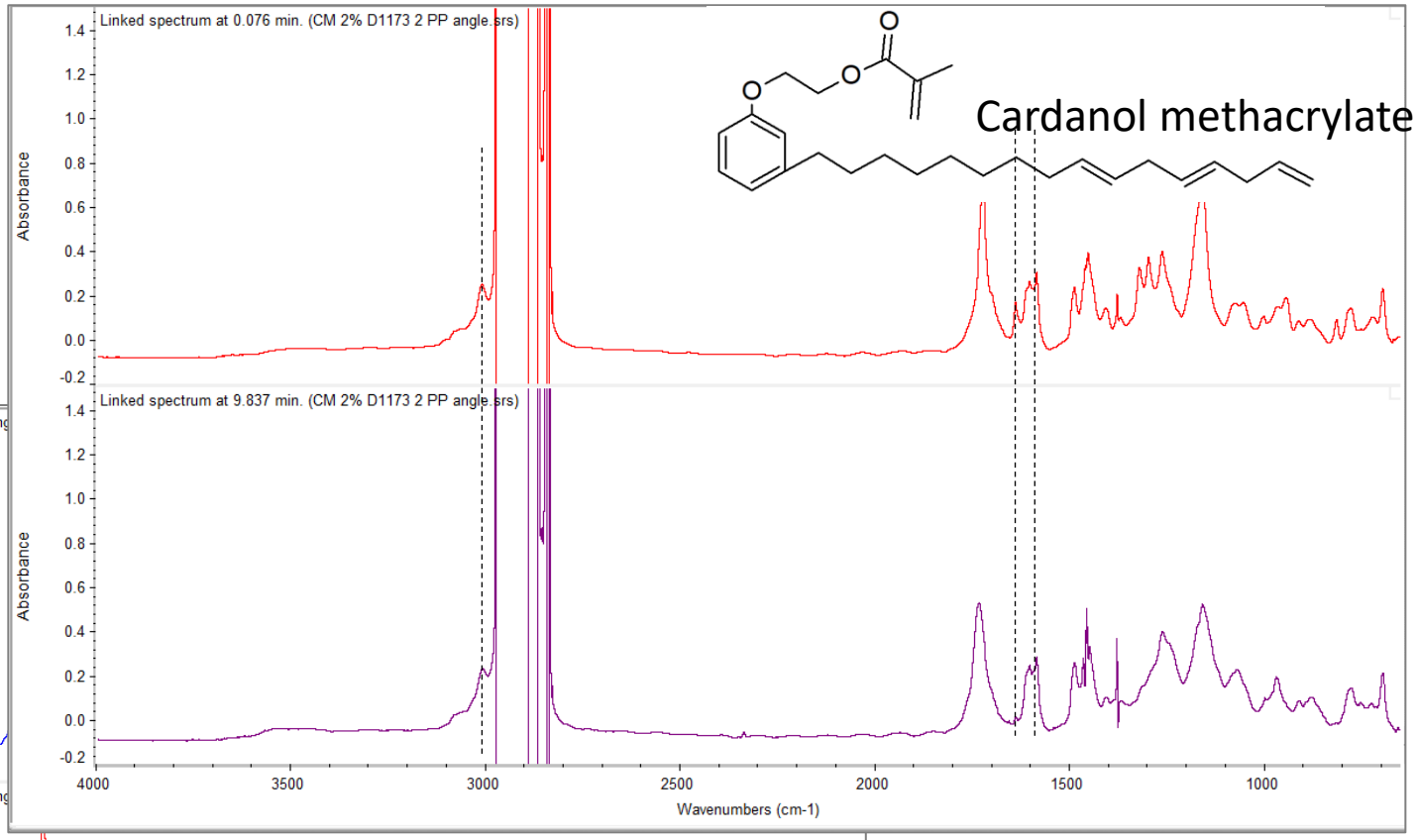
In air



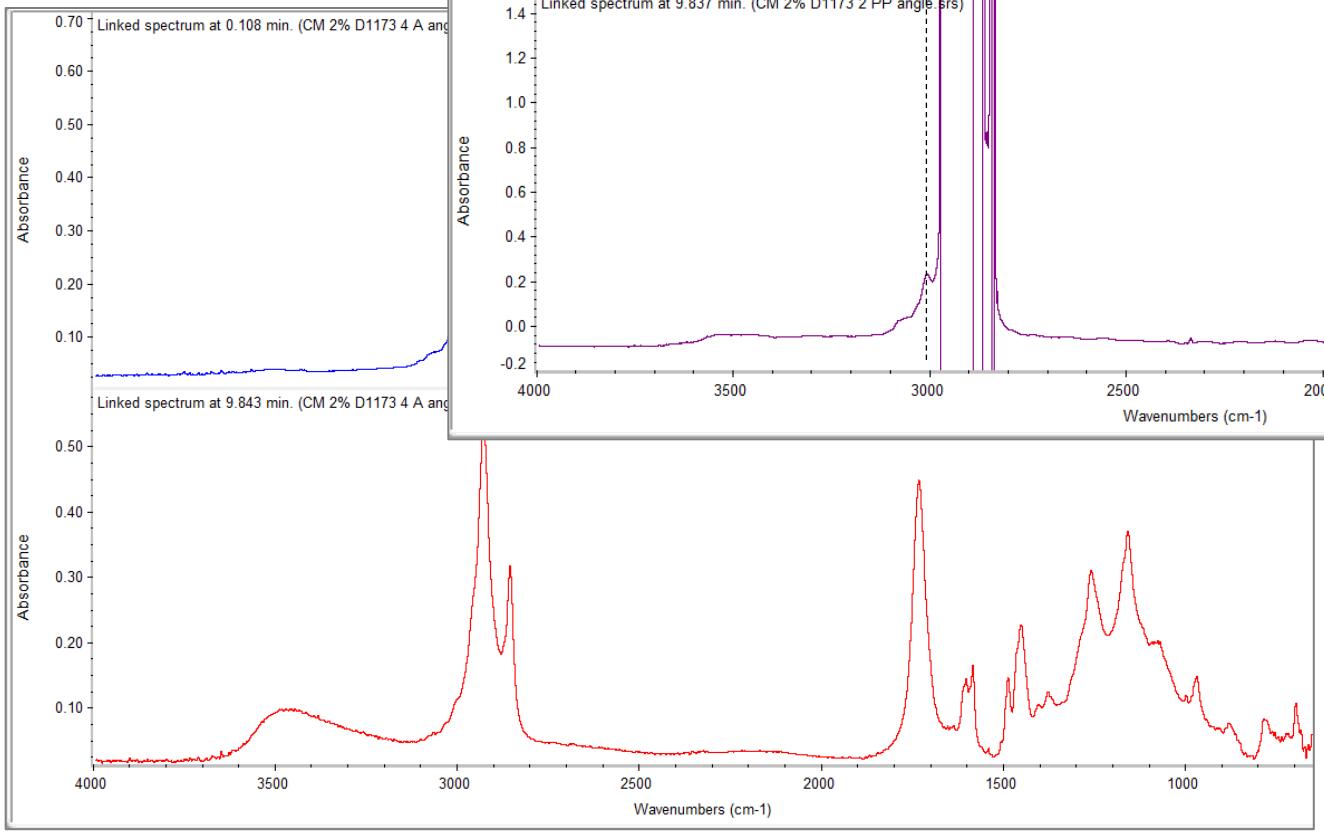
rt-FTIR

Covered by PP

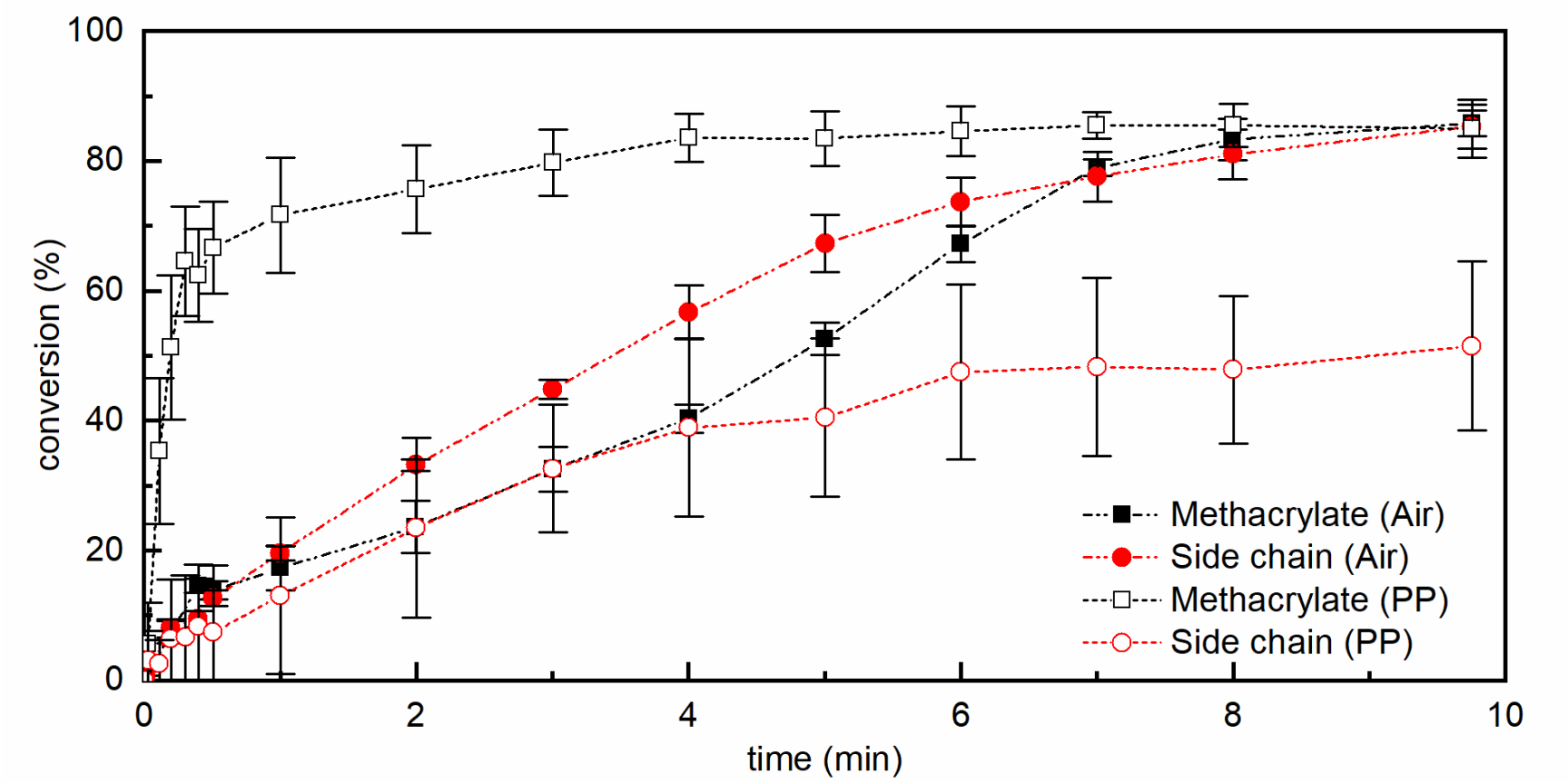
In air



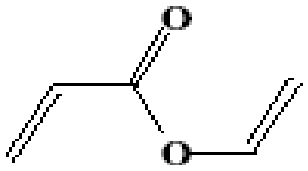
Cardanol methacrylate



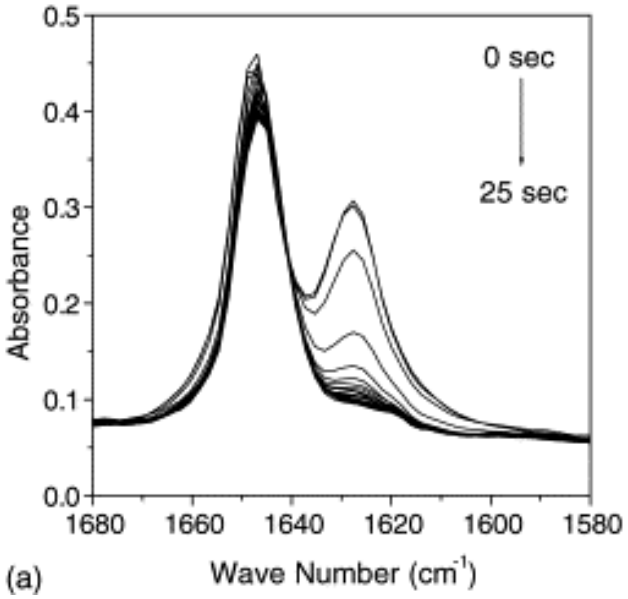
Rt-FTIR

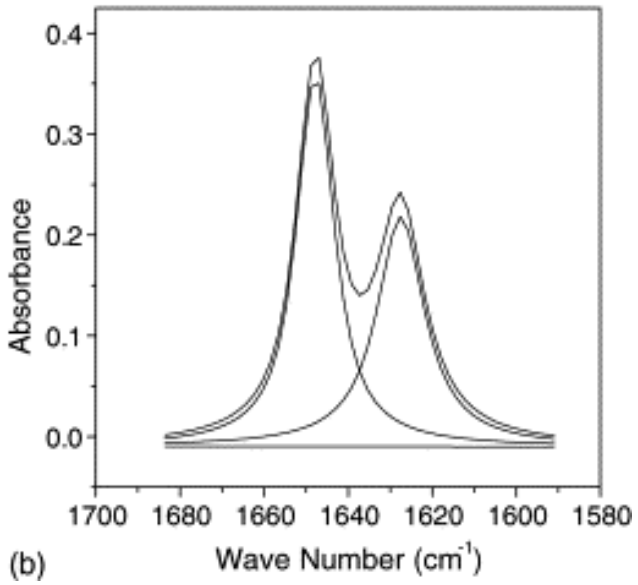

100
80
60
40
20
0
conversion (%)
0
2
4
6
8
10
time (min)
Methacrylate (Air)
Side chain (Air)
Methacrylate (PP)
Side chain (PP)

Example: peak deconvolution

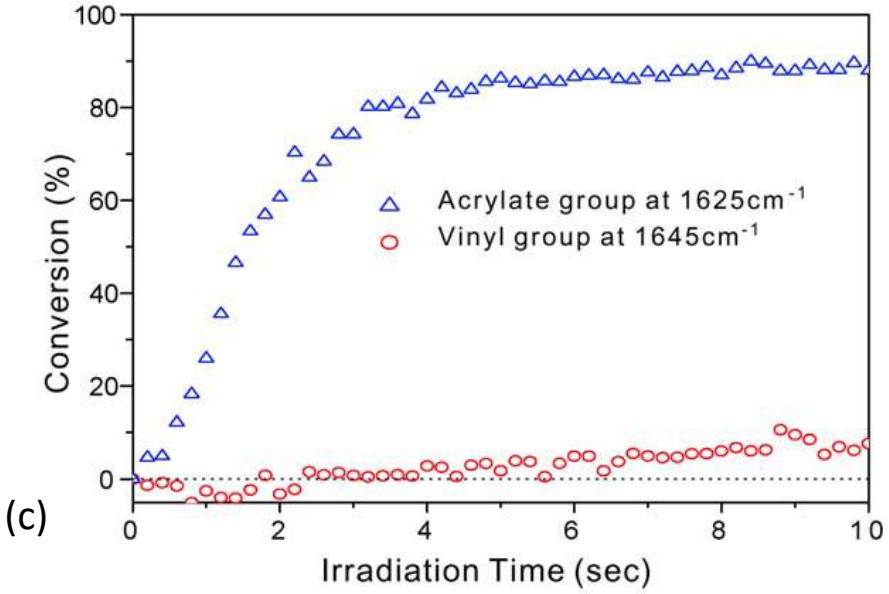


Vinylacrylate
(VA)





(a) The IR absorbance change of acrylate and vinyl ester during vinyl acrylate polymerization
(b) Deconvolution of 1625 and 1645 cm^{-1} bands
(c) Conversion of acrylate and vinyl groups during irradiation



Progress in Organic Coatings, 52 (1), 2005, 63-72

Real time FTIR

Pros

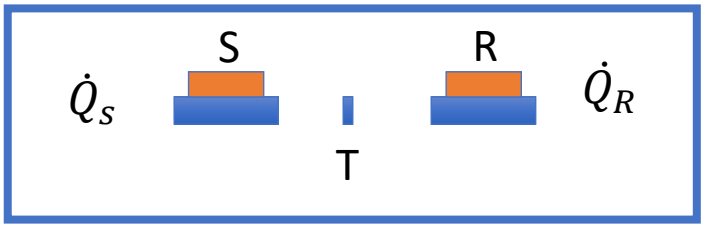
- Follows functional group evolution (specific to reaction)
- Close to real life conditions for coatings

Cons

- Transmission : only thin films (saturation of signal)
- ATR: non-sticking films, surface only
- Usually no temperature control and in air (oxygen inhibition)
- Overlapping peaks
- Composites may be difficult to analyse
- Substrate must be transparent to IR

DIFFERENTIAL SCANNING CALORIMETRY

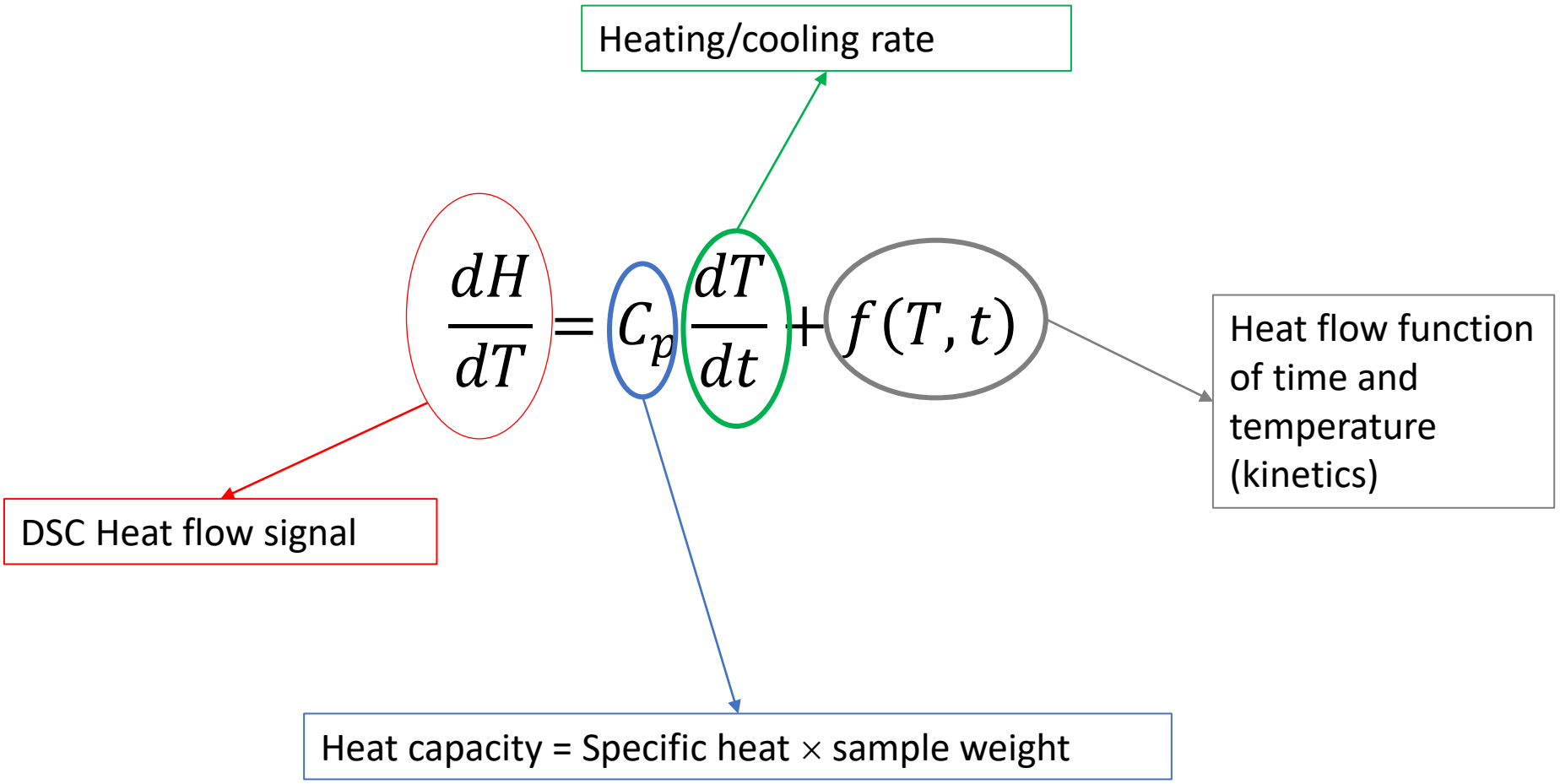
- DSC measures the heat flow rate difference (mW = mJ/sec) between a sample and an inert reference as a function of time and temperature in a controlled atmosphere



$$\Delta\dot{Q} = \dot{Q}_s - \dot{Q}_R$$

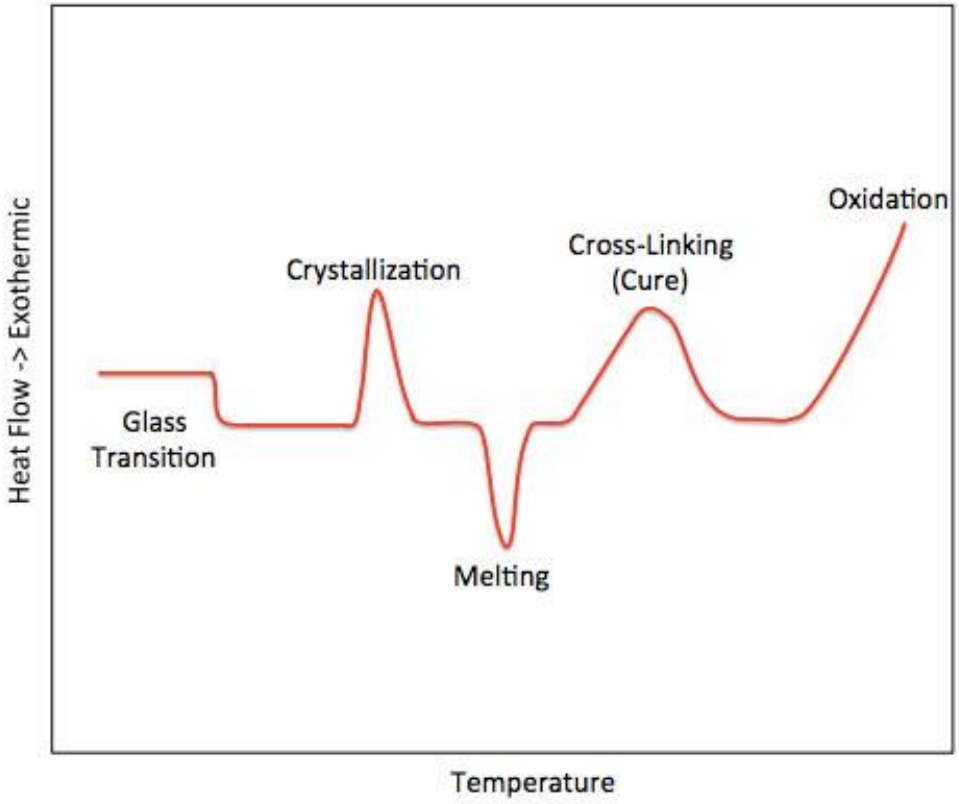
- Qualitative and quantitative information about physical or chemical transformations in the sample that determine endothermic or exothermic heat exchanges or variations in the heat capacity

HEAT FLOW IN DSC



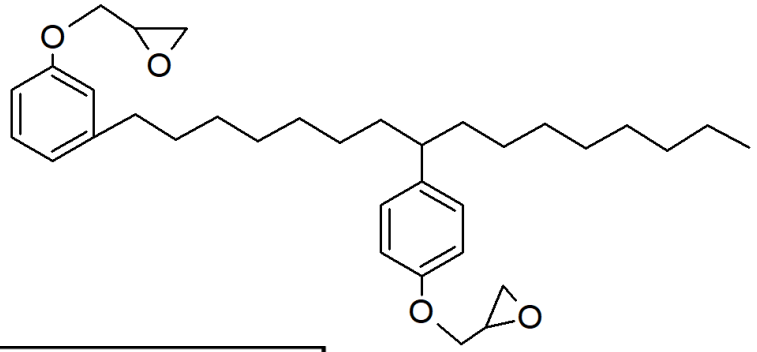
INFORMATION THAT CAN BE OBTAINED BY DSC

- Specific heat and heat capacity
- **Glass transition**
- Melting point and boiling point
- Crystallization temperature/time
- Enthalpic relaxation
- Crystallinity
- Heat of fusion
- **Enthalpy of reaction**
- **Reaction rate and kinetics**
- …

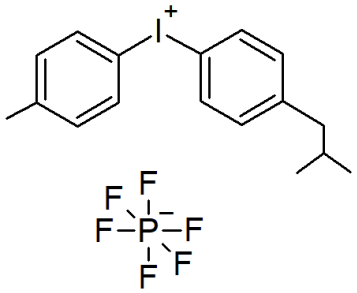


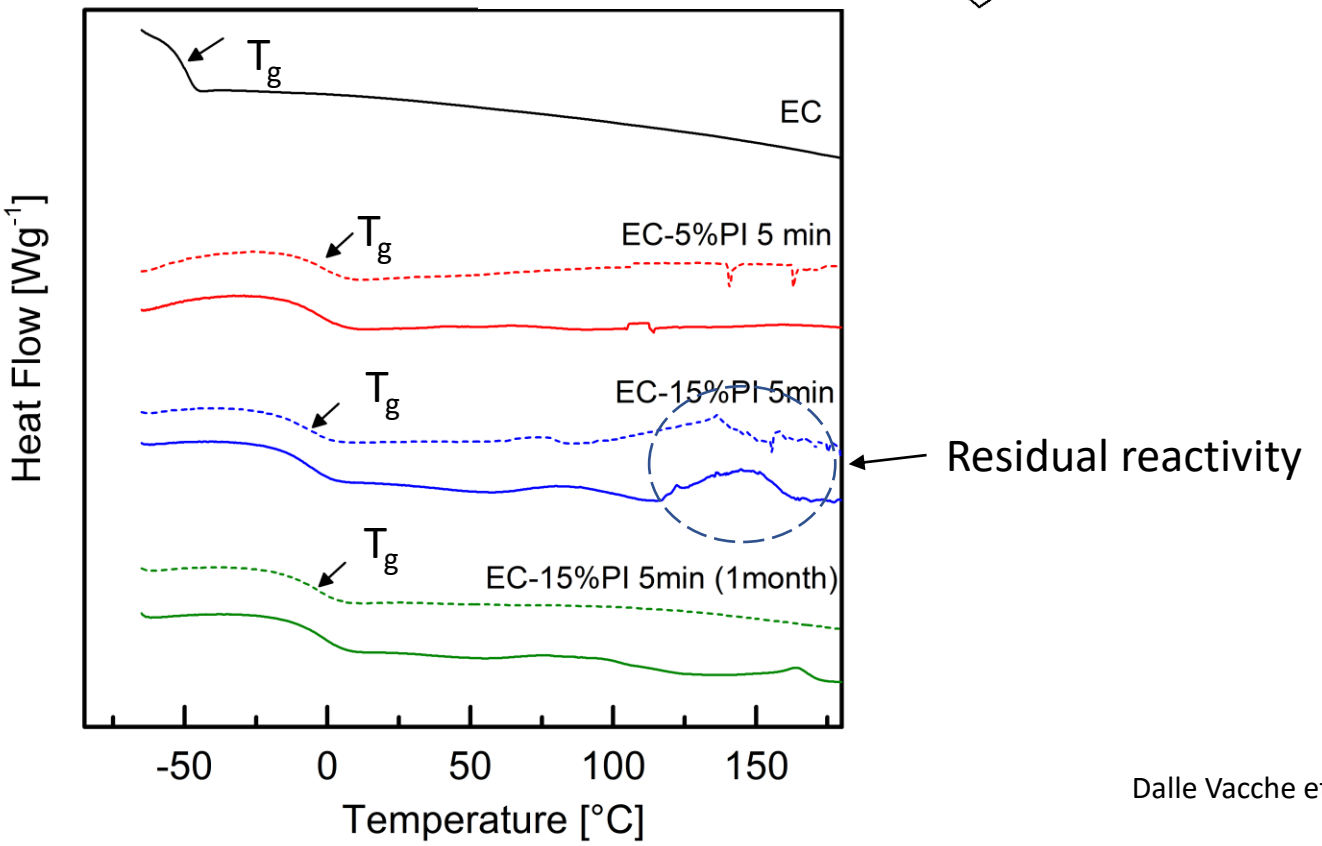
DSC: MONOMER VS CURED POLYMER

EC



PI



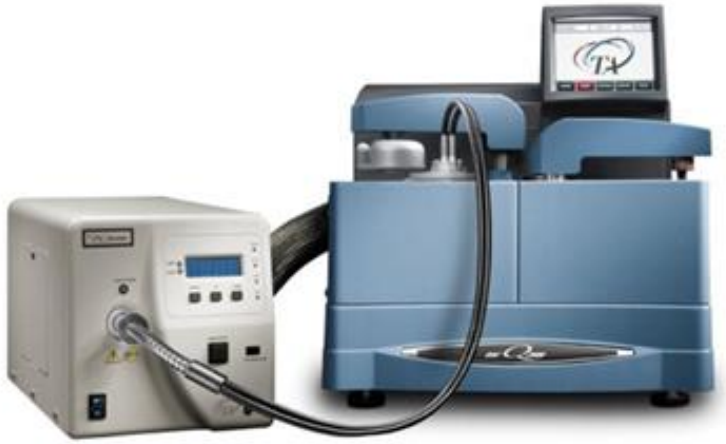


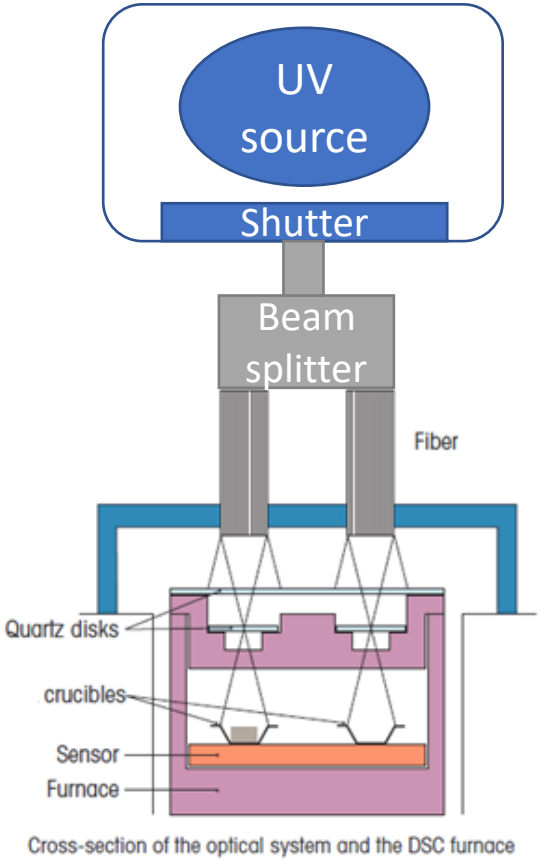
Residual reactivity

Dalle Vacche et al. Molecules **2019**, 24, 3858

PHOTOCALORIMETRY (Photo-DSC)

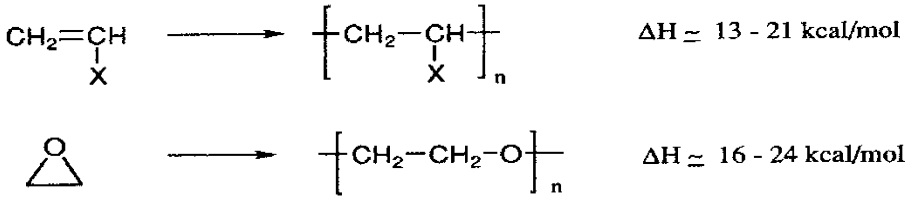
- Continuous monitoring with time of the heat of polymerization during a photoinduced polymerization (UV cure)





Cross-section of the optical system and the DSC furnace

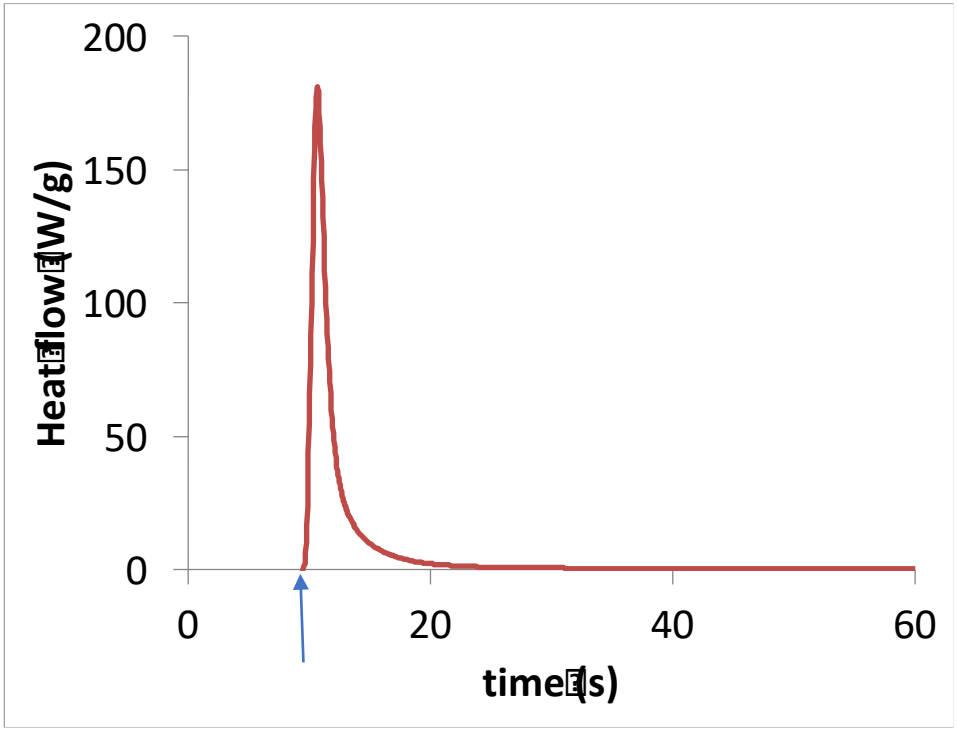
Heats of Polymerization:



PHOTOCALORIMETRY (Photo-DSC)

- The DSC chamber is kept at constant temperature
- UV light irradiates sample and reference
- The heat flow is measured as a function of time

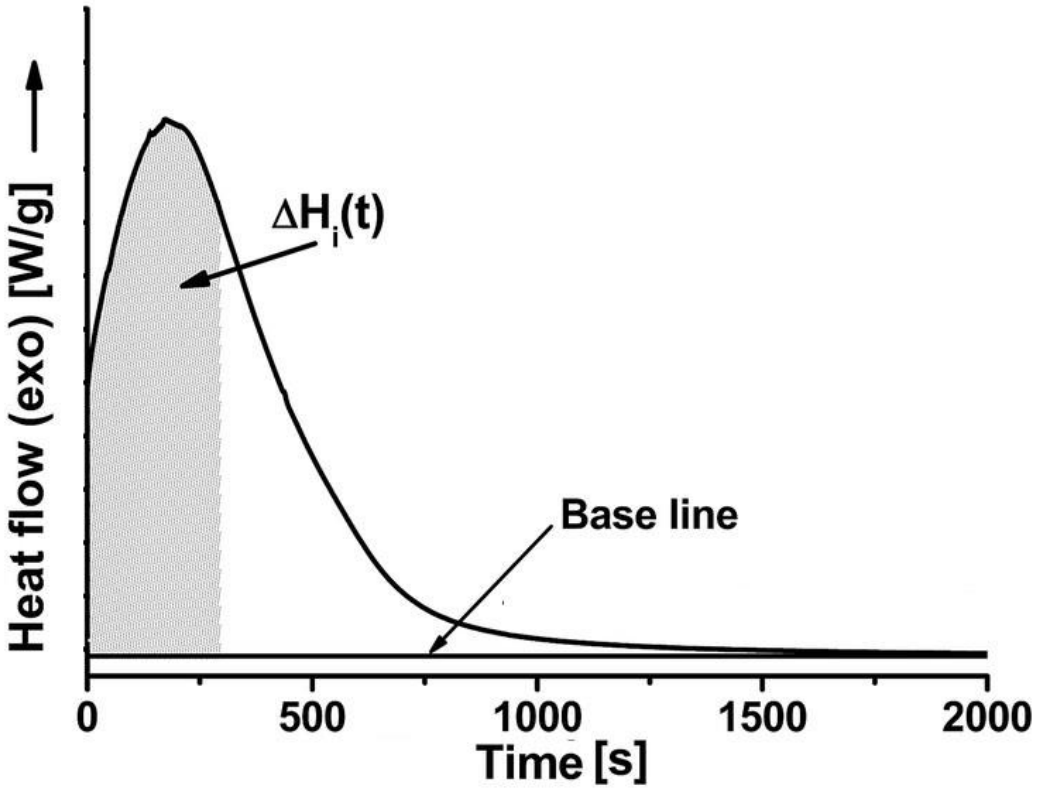
Typical heat flow curve from a photo-DSC run
The arrow indicates start of irradiation



N.B. A second scan at the same conditions of the first one may need to be performed on the cured sample and subtracted from the first scan (baseline)

FROM HEAT FLOW TO ENTHALPY

- The integral of the heat flow curve (until the time t) gives the enthalpy of reaction at t ➔ ΔH(t)



FROM ENTHALPY TO CONVERSION

To obtain conversion → $\alpha = \frac{\Delta H(t)}{\Delta H_{tot}}$

ΔH_{tot} → theoretical heat of reaction developed if all the reactive groups react = ΔH_r × mols of reactive groups

ΔH_r = heat developed by the reaction of one mol of reactive groups

Table 6 Molar Heat of Polymerisation of Reactive Groups

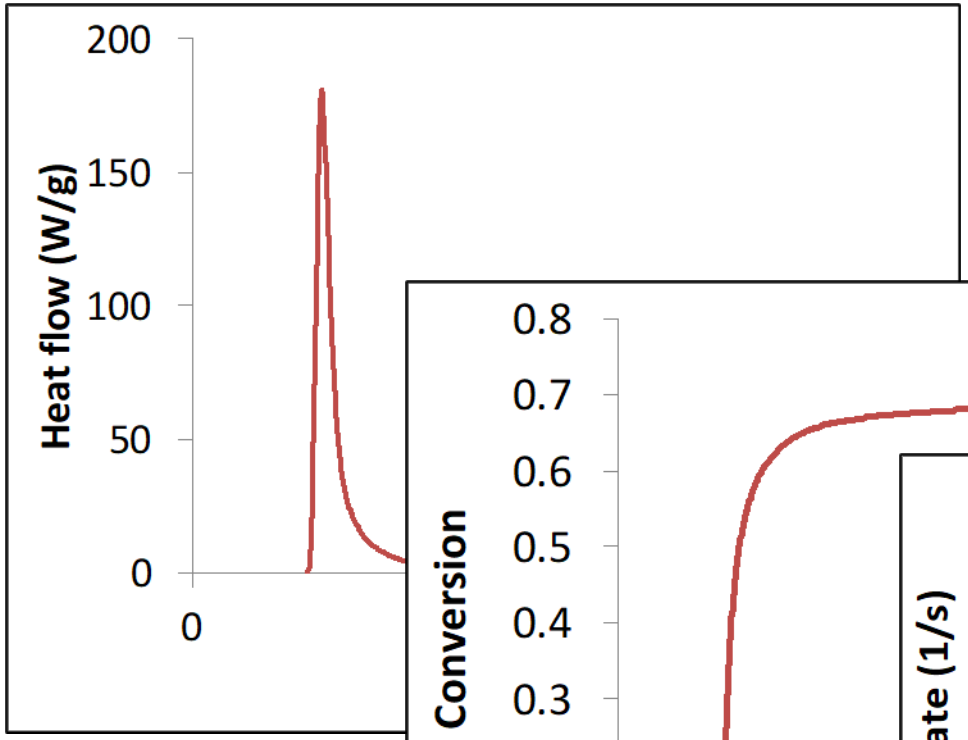
Reactive group	Heat of polymerisation ($kJmol^{-1}$)
Acrylate	78 - 86
Methacrylate	57
Vinyl ether	60
Oxirane ring	88
Vinyl acetate	80

Note:

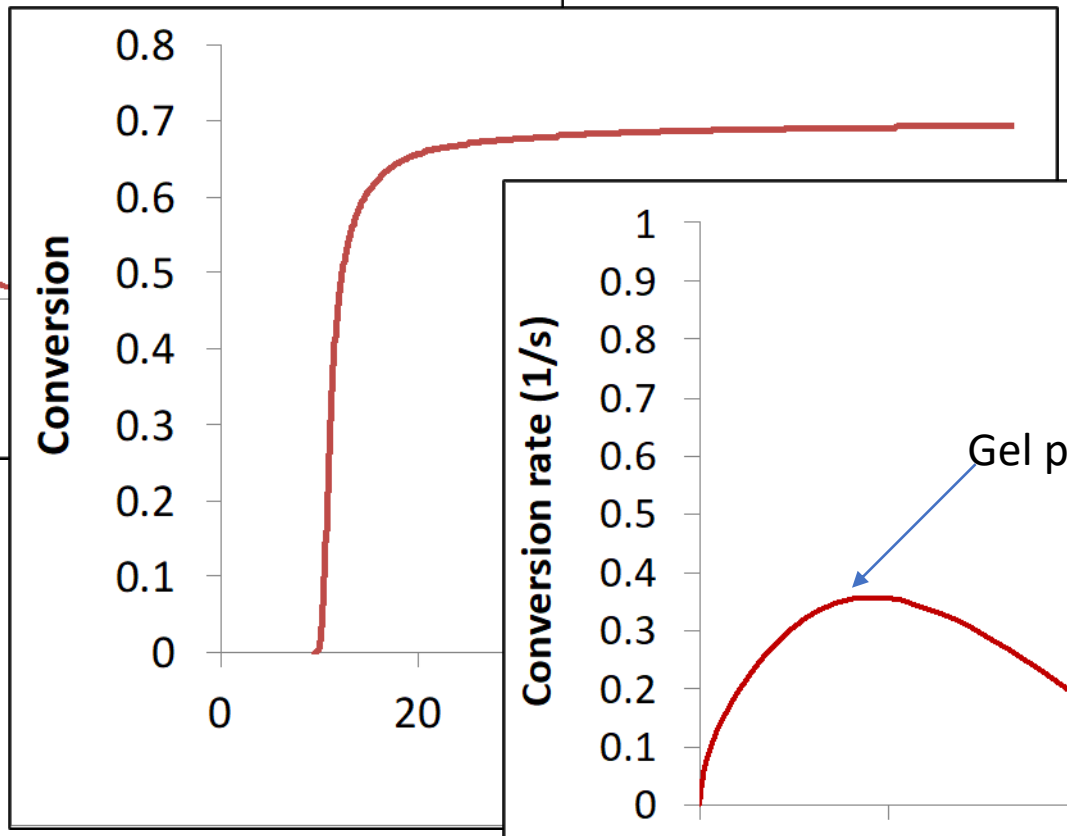
ΔH_{tot} → could also be the max

heat of reaction measured if one knows that the reaction is complete

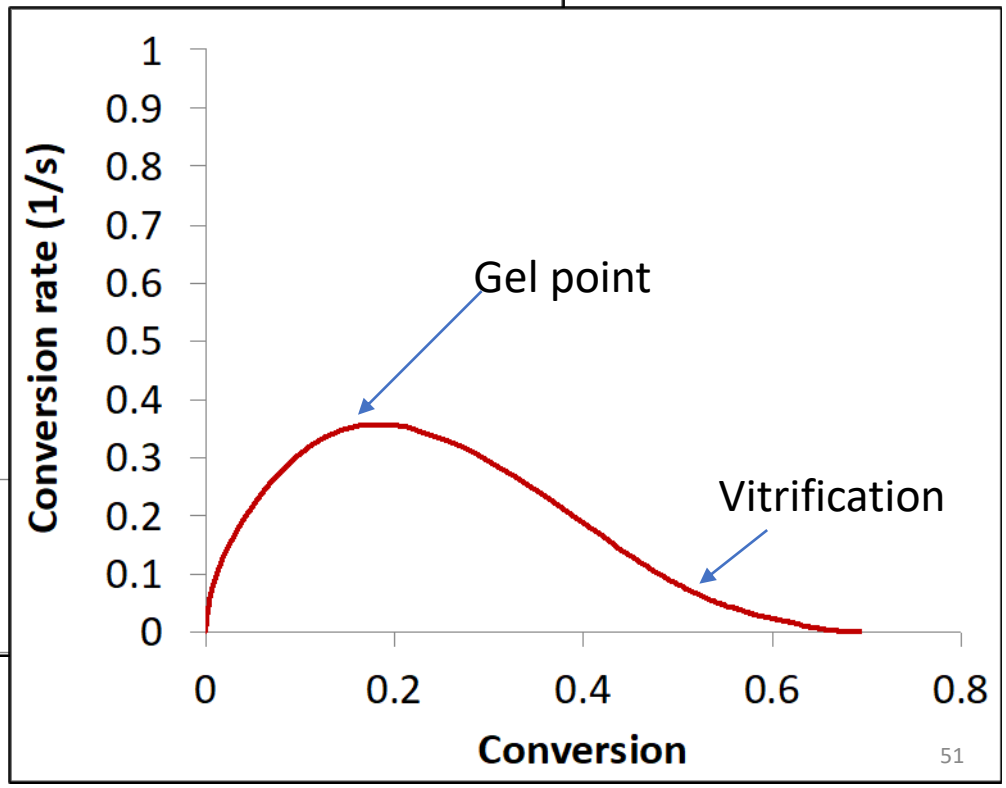
FROM HEAT FLOW TO CONVERSION



$$\alpha = \frac{\Delta H(t)}{\Delta H_{tot}}$$

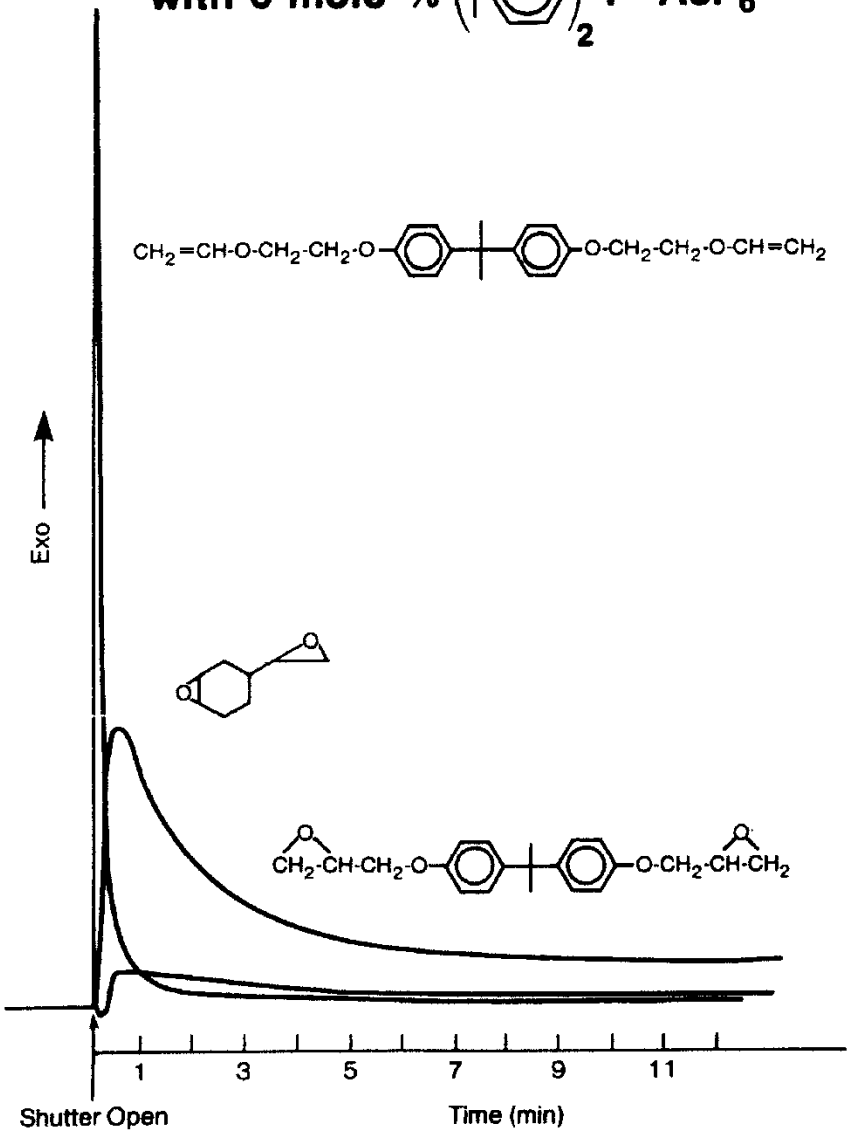


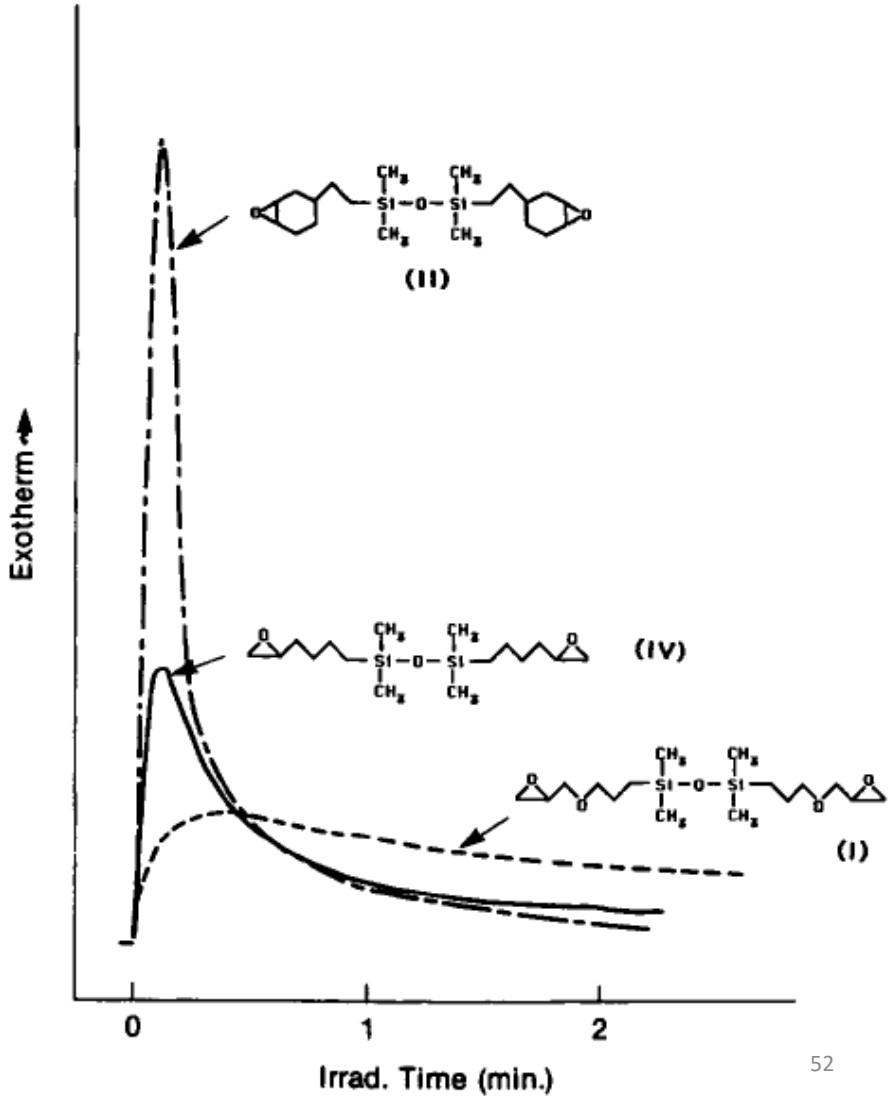
$$\dot{\alpha} = \frac{d\alpha(t)}{dt}$$



DSC STUDY PHOTOPOLYMERIZATIONS

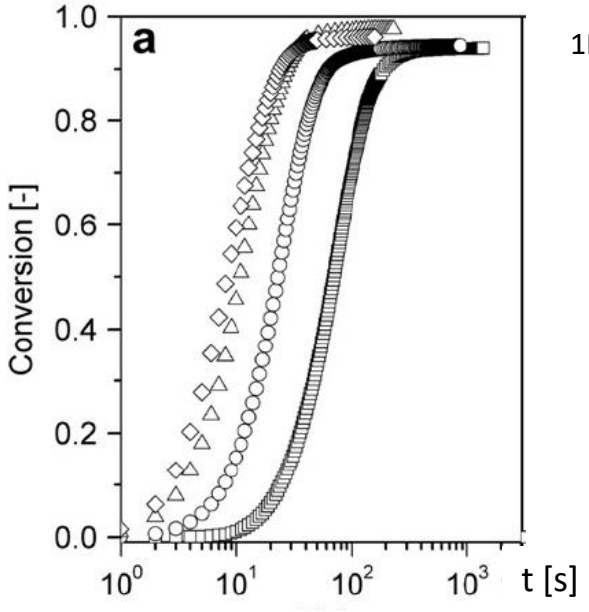
with 3 mole % $\left(\text{+}\bigcirc\right)_2\text{I}^+\text{AsF}_6^-$

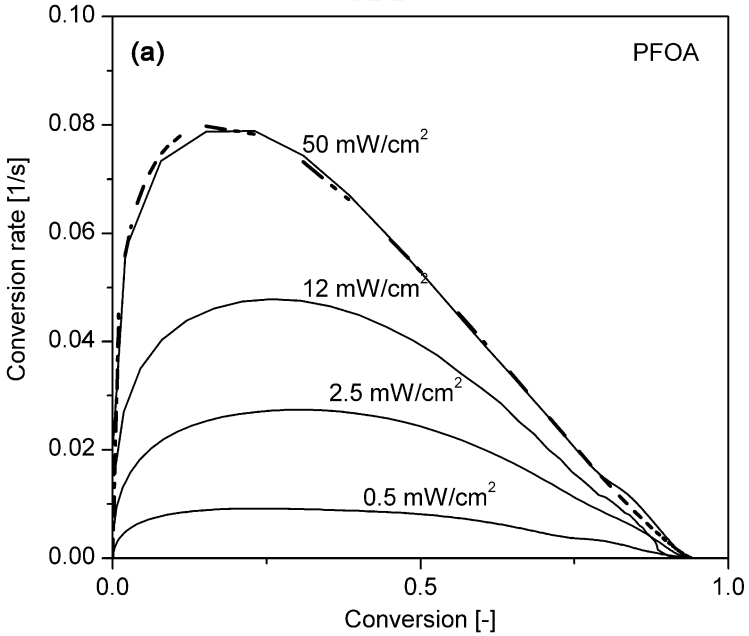




Kinetic study: PFOA + nanosilica

1H-1H perfluoro-n-octyl acrylate (PFOA)





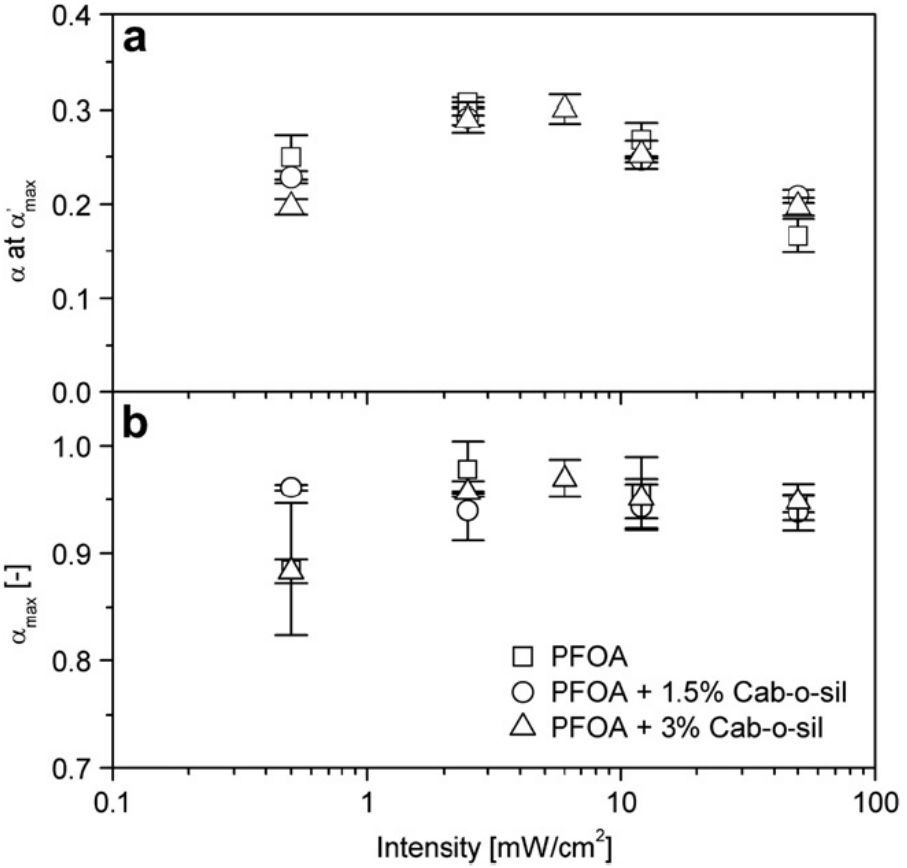
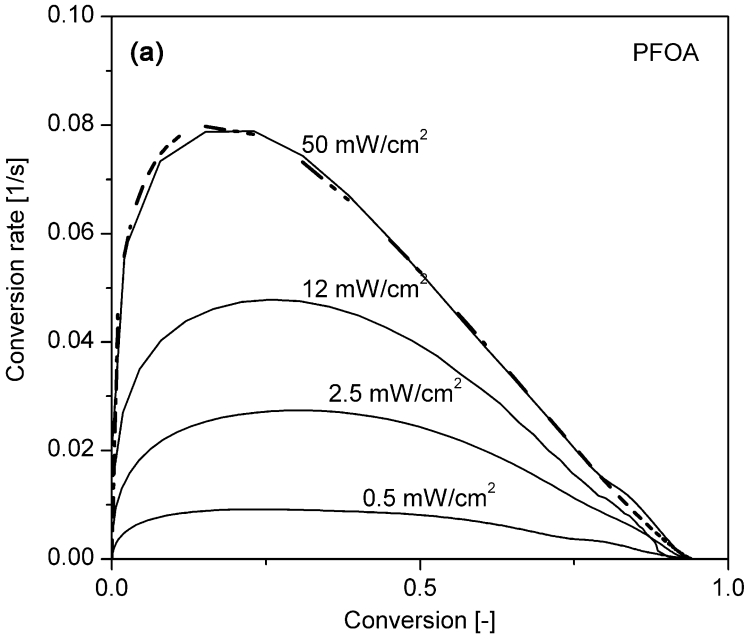
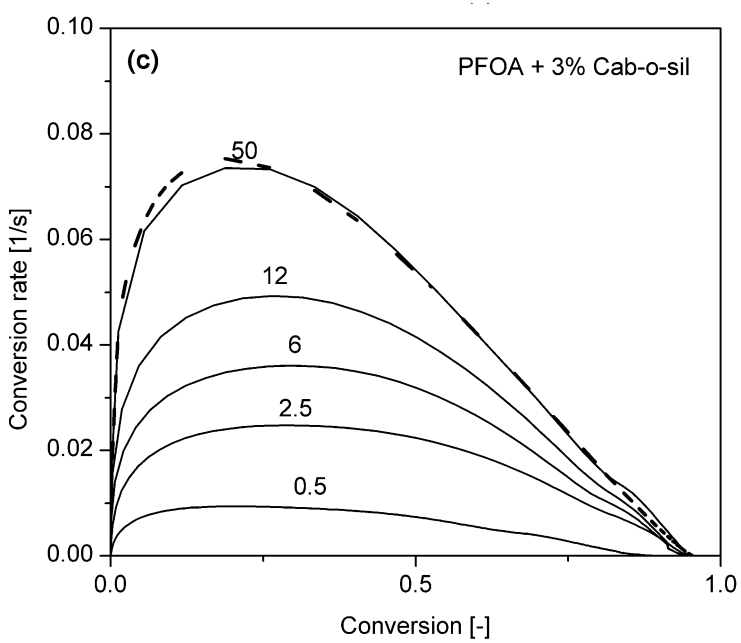


Photo-DSC: AUTOACCELERATED REACTION MODELLING

1H-1H perfluoro-n-octyl acrylate (PFOA)



PFOA + silica particles



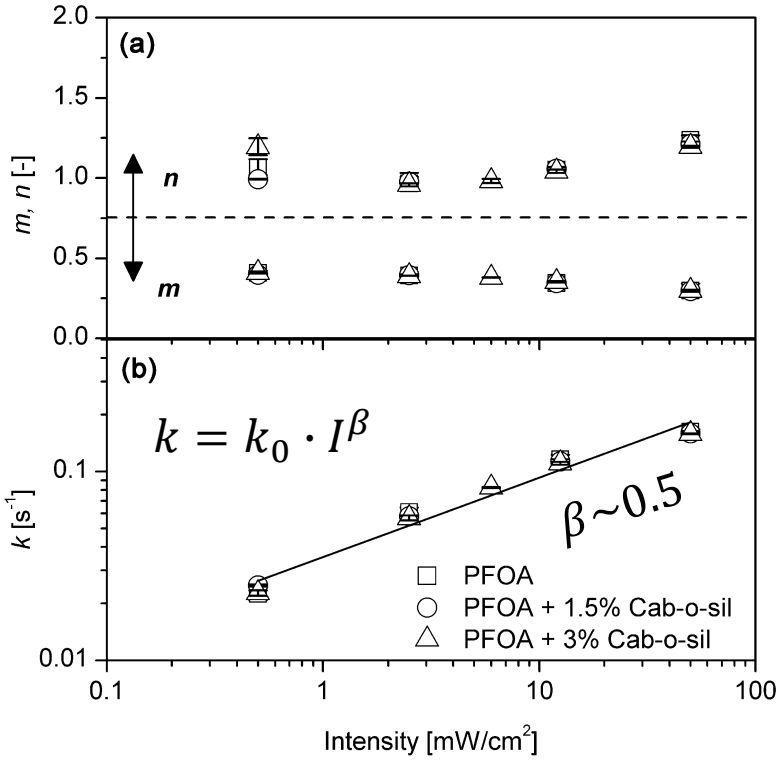
$$\frac{d\alpha}{dt} = k(I)\left(1 - \frac{\alpha}{\alpha_v(I)}\right)^n \left(\frac{\alpha}{\alpha_v(I)}\right)^m$$

➡ Prediction of conversion as a function of time, intensity and composition

S. Dalle Vacche et al. Polymer 51 (2010) 334–341

Photo-DSC: AUTOACCELERATED REACTION MODELLING

$$\frac{d\alpha}{dt} = k(I)\left(1 - \frac{\alpha}{\alpha_v(I)}\right)^n \left(\frac{\alpha}{\alpha_v(I)}\right)^m$$



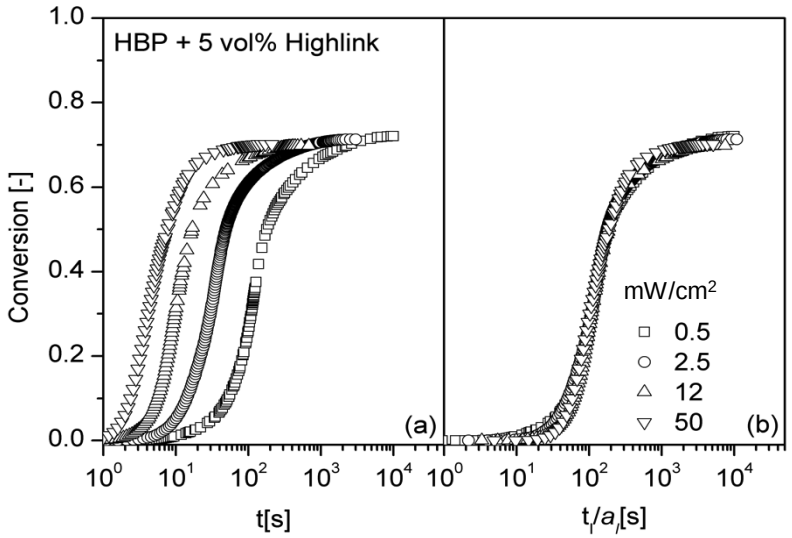
In free-radical systems:

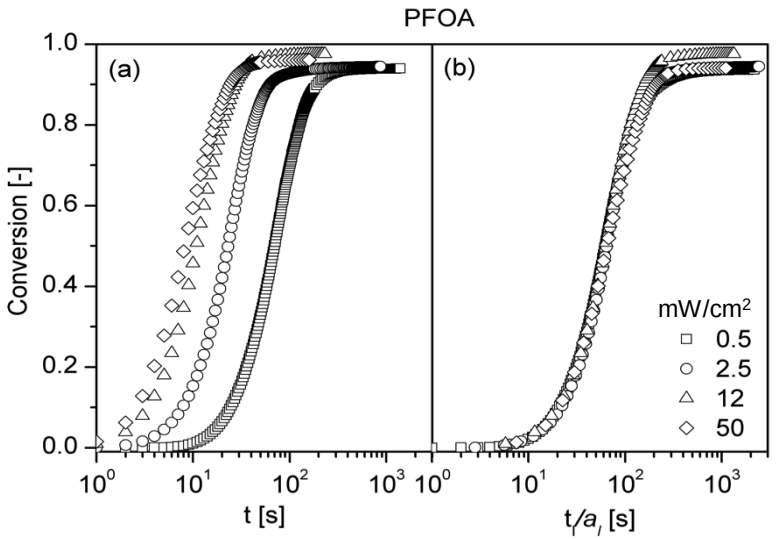
- power law intensity dependence for rate constant *k*
- weak intensity dependence of the conversion at vitrification α_v (polymerization shrinkage lags behind conversion)
- Reaction order exponent *n* and autocatalytic exponent *m* are independent of intensity

➡ Prediction of conversion as a function of time, intensity and composition

Andrzejewska, Prog Polym Sci 2001
Dalle Vacche et al., Polymer (2010)

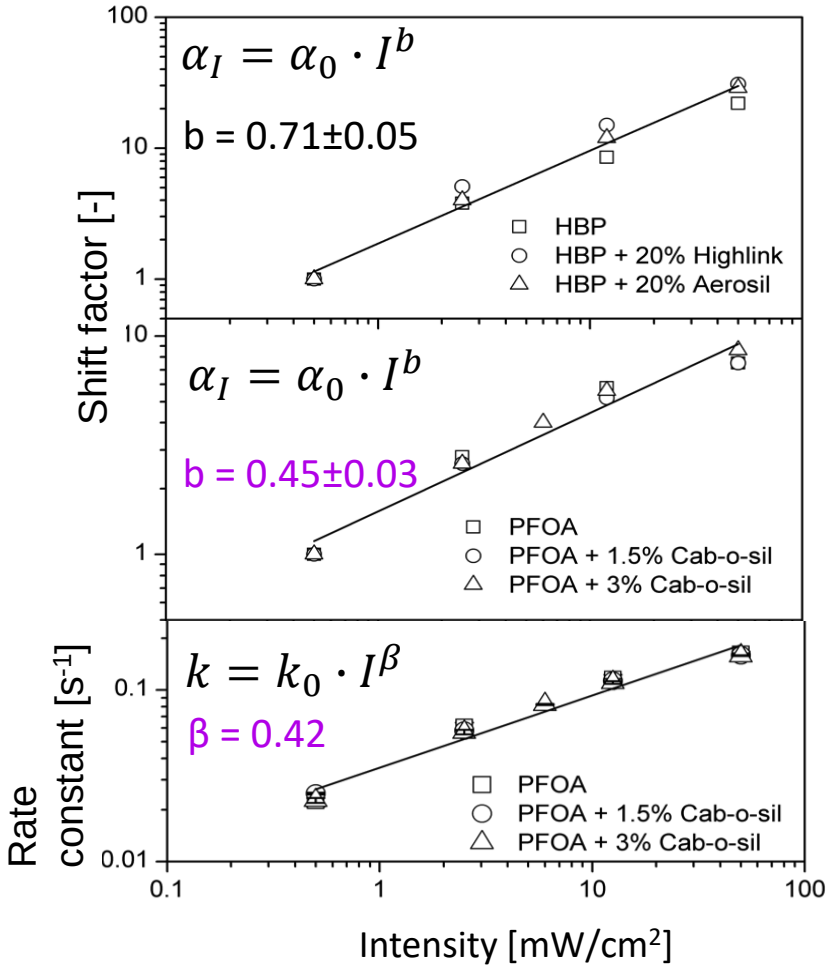
Time intensity superposition





$$a\left(t_1, I_1\right) = a\left(t_0, I_0\right) \Leftrightarrow t_1 = \frac{t_0}{a_I}$$

$$t_1 = t_0 \left(\frac{I_0}{I_1}\right)^b$$



Dalle Vacche et al., Polymer (2010)

Photo-DSC

- **Pros**

- Easy to use
- Controlled temperature and atmosphere
- Composites

- **Cons**

- Side reactions, overlapping transitions
- Very fast reactions (heat flow at beginning of reactions)
- Thickness of the layer in the pan poorly controlled: influences kinetics

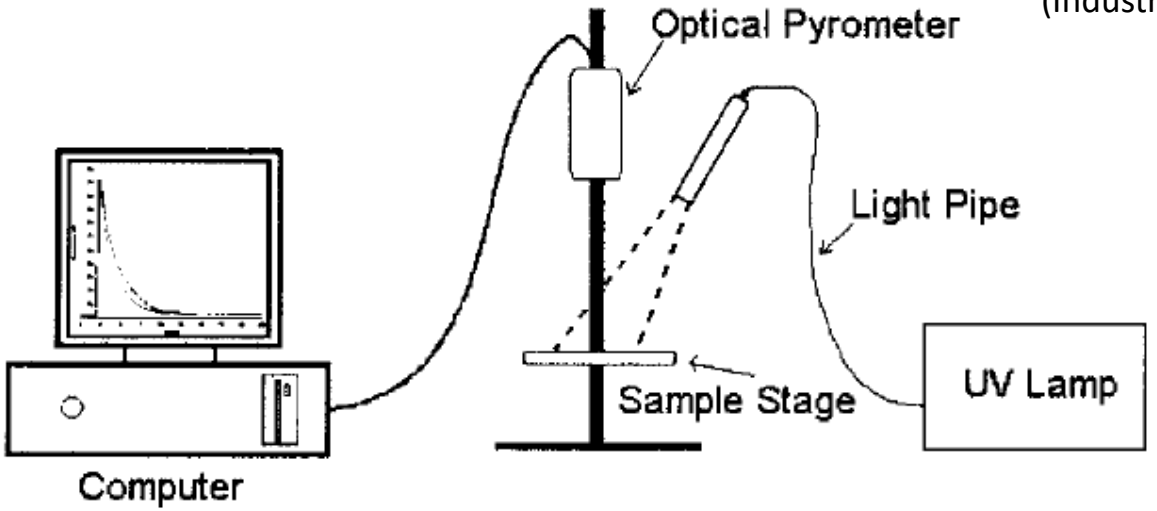
OPTICAL PYROMETRY

Monitoring Photopolymerization Reactions with Optical Pyrometry

BENJAMIN FALK, SANTIAGO M. VALLINAS, JAMES V. CRIVELLO

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 579–596 (2003)

(Industrial Infrared Thermometer)



Optical pyrometry

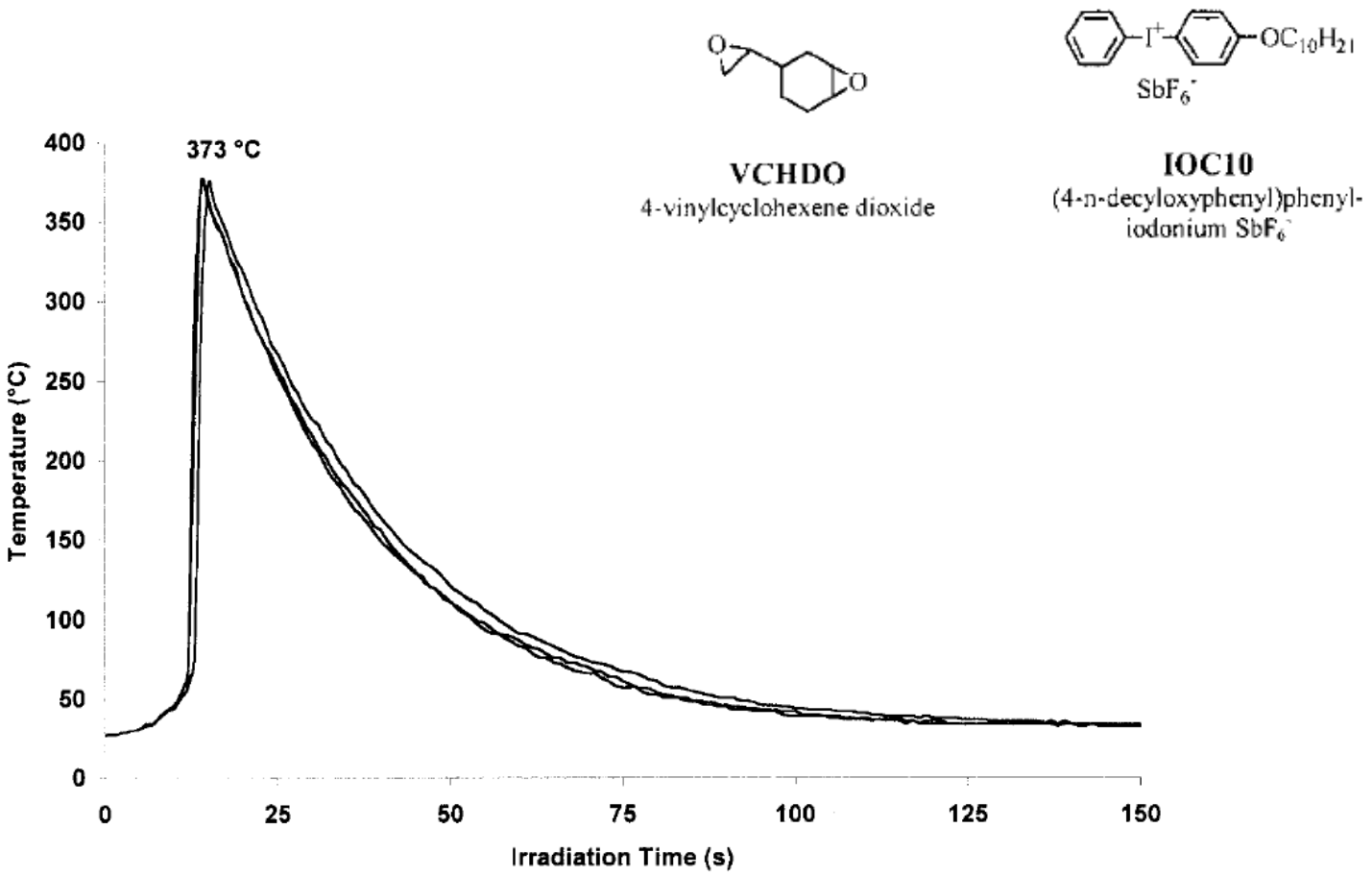


Figure 2. Temperature profiles for the cationic photopolymerization of VCHDO with 1.0 mol % IOC 10 as photoinitiator (light intensity: 395 mJ/cm^2 min).

Optical pyrometry

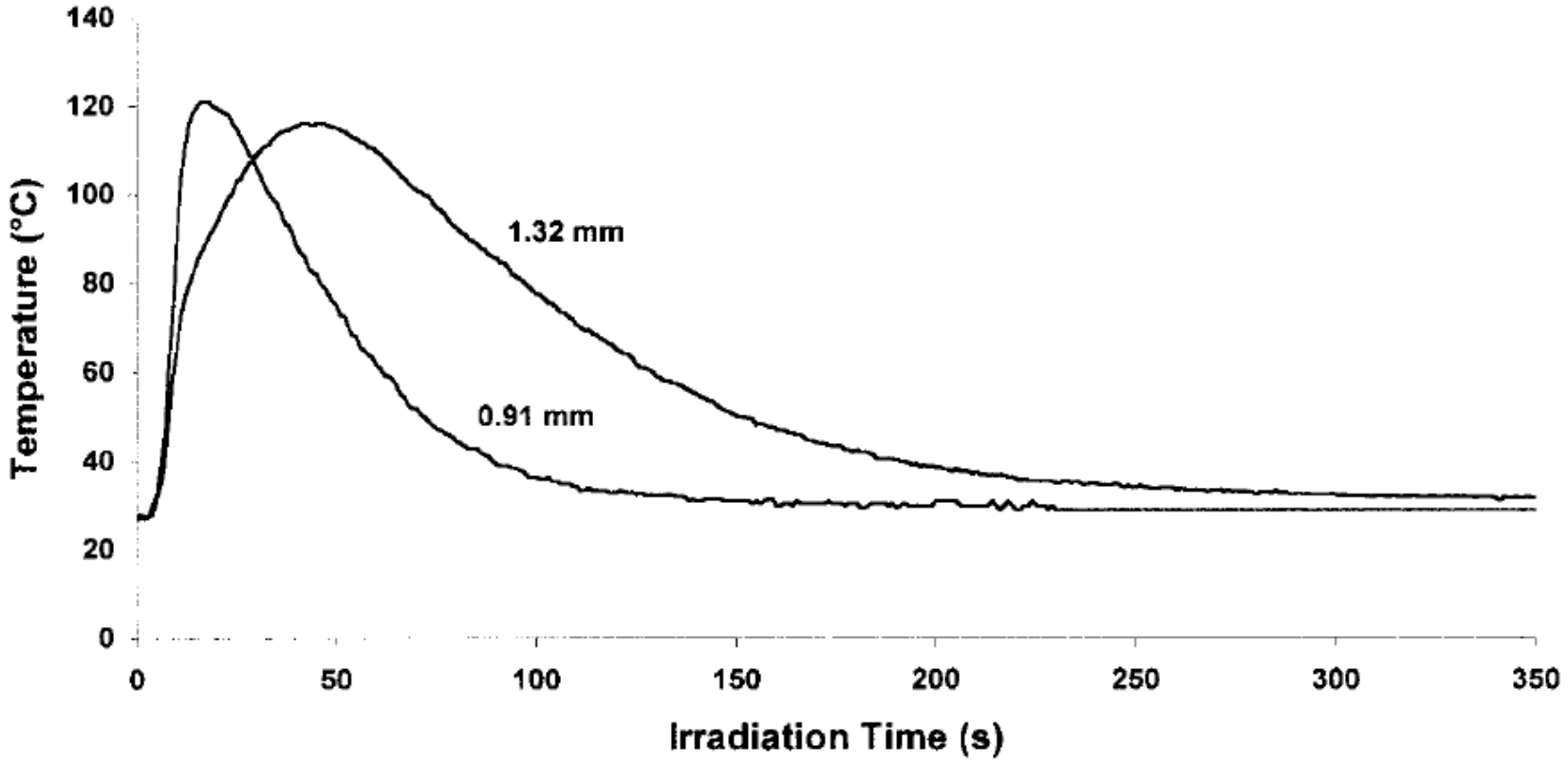


Figure 3. Effect of sample thickness on the temperature during the cationic photopolymerization of PC-1000 with 0.25 mol % IOC 10 as photoinitiator (light intensity: 404 mJ/cm^2 min).

Optical pyrometry

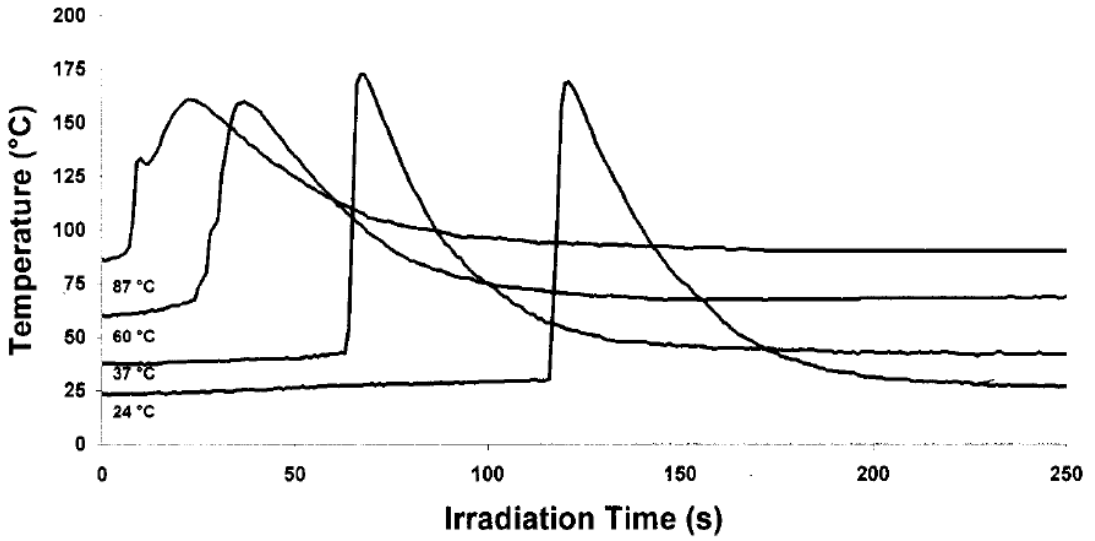


Figure 15. Temperature effects on the photopolymerization POX with 1 mol % IOC 10 (light intensity: 403 mJ/cm^2 min).

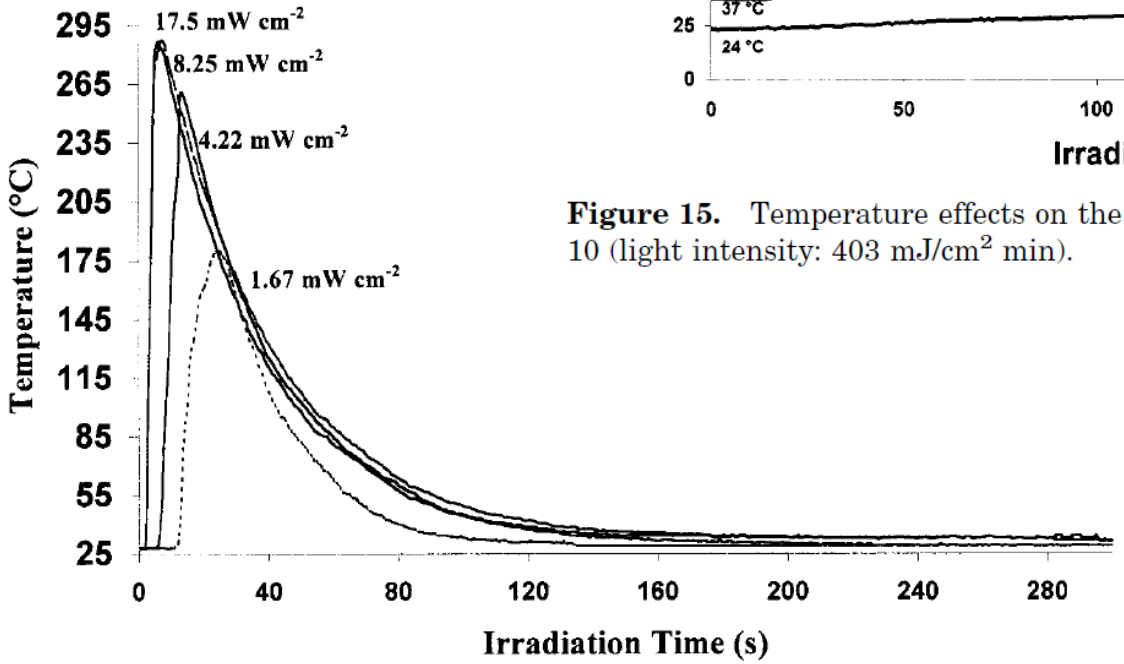
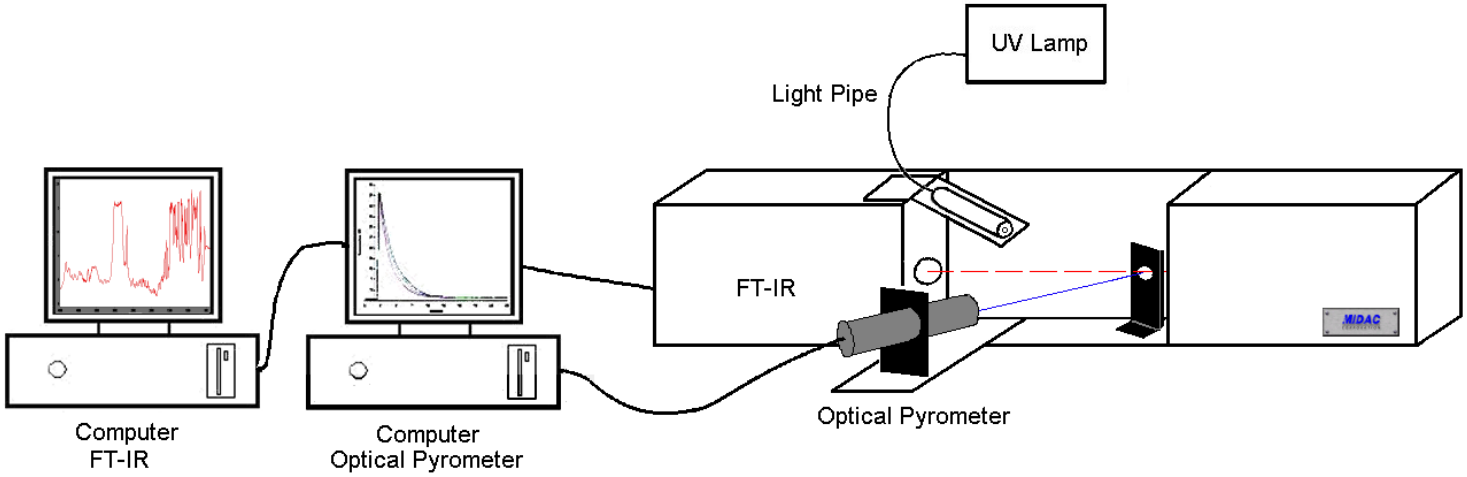


Figure 14. Effect of light intensity on the photoinitiated polymerization of DEGDA (1.0 mol % Irgacure 184® as photoinitiator).

OP + rt-FTIR



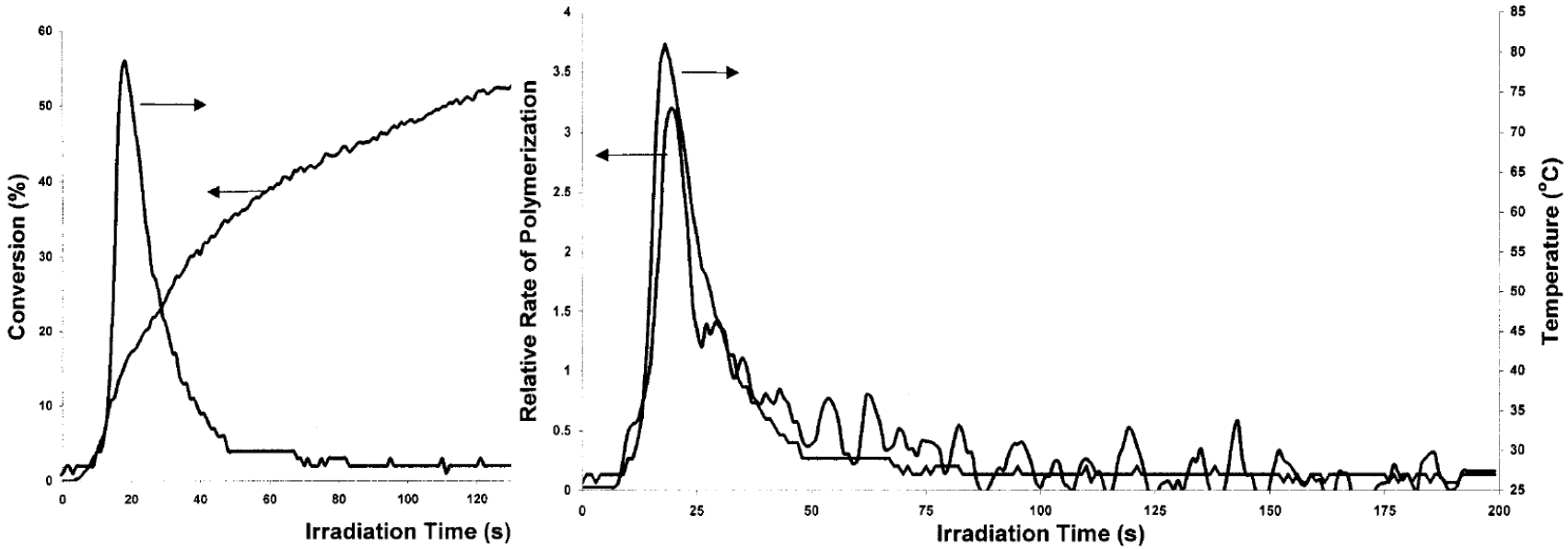
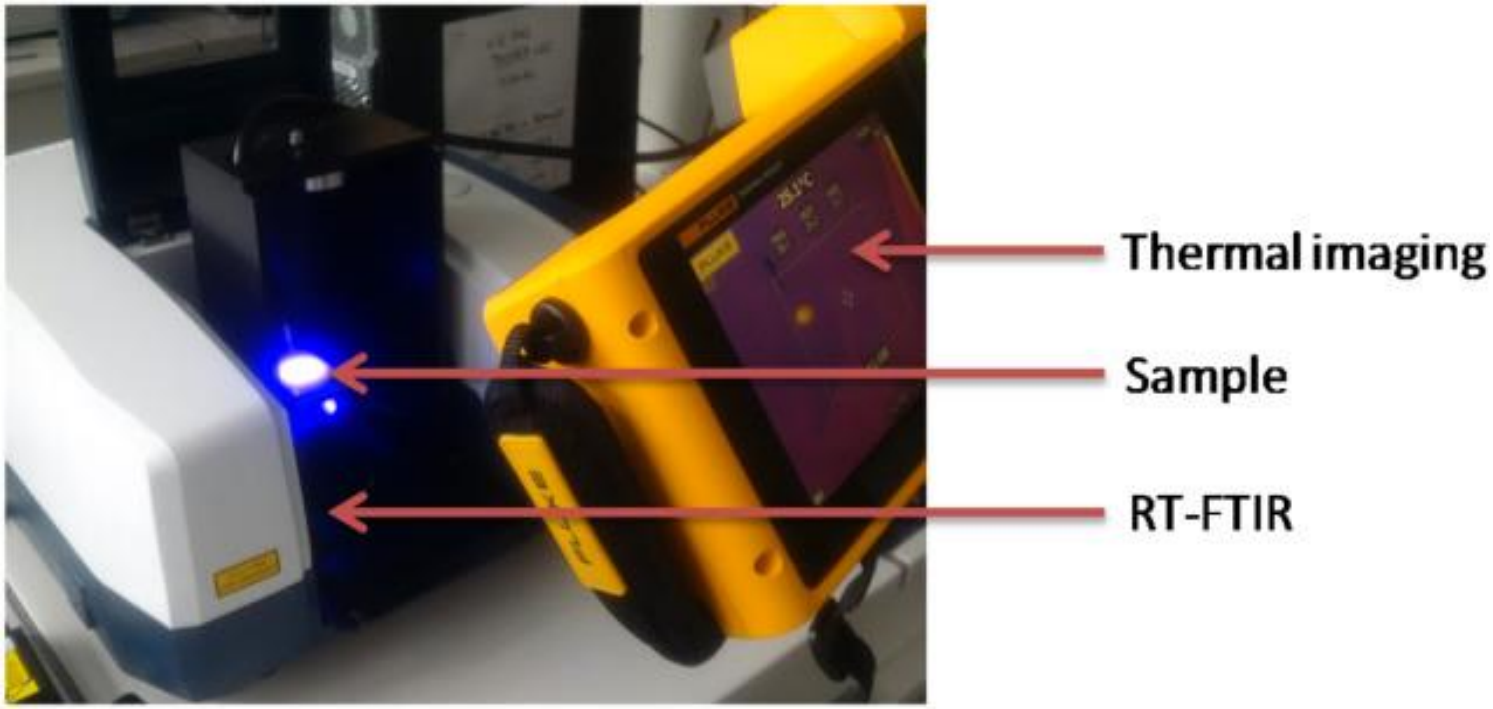


Figure 4. Combined OP/FT-RTIR study of the photopolymerization of HDODA carried out in the presence of 1.0 mol % Irgacure 184® (light intensity: 350 mJ/cm^2 min; IR band: 1626–1649 cm^{-1}).

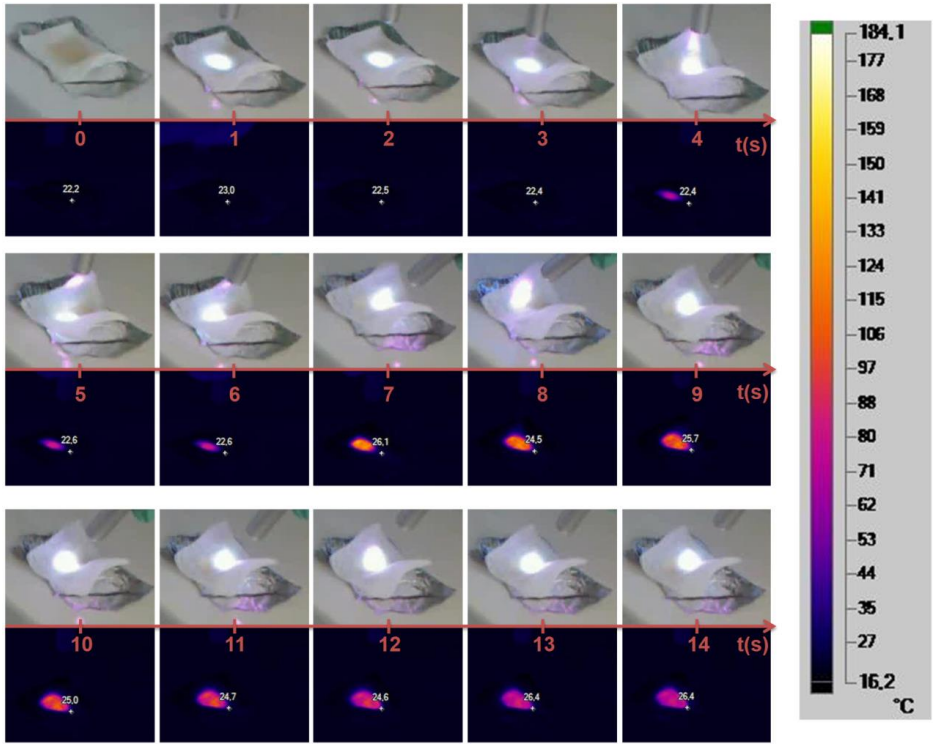
Thermal imaging

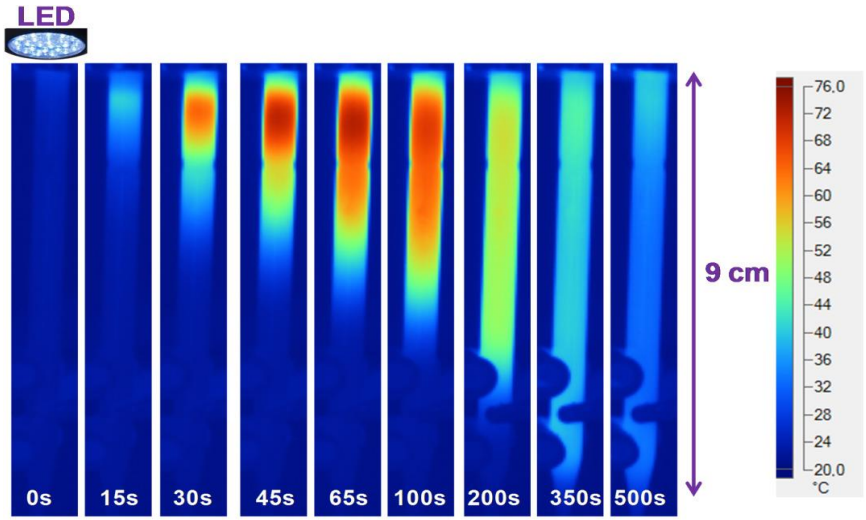


Monitoring photopolymerization reactions through thermal imaging: A unique tool for the real-time follow-up of thick samples, 3D printing, and composites

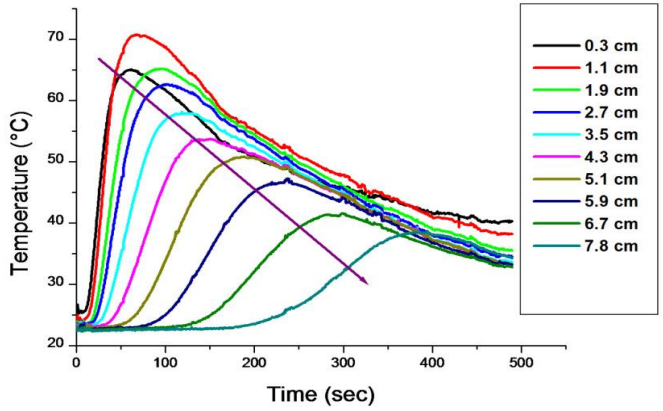
Journal of Polymer Science Part A: Polymer Chemistry, Volume: 56, Issue: 8, Pages: 889-899, First published: 30 January 2018, DOI: (10.1002/pola.28965)

Thermal imaging



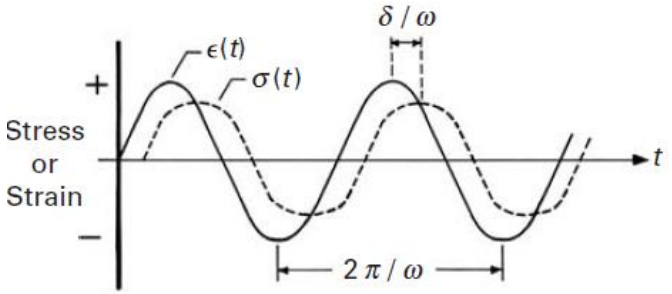


Temperatures of a formulation of surgical sealants deposited on a gauze



RHEOLOGICAL ANALYSIS

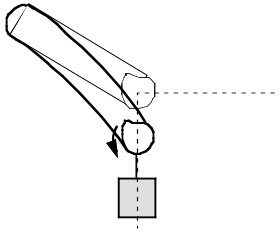
If a sinusoidal strain with frequency ω is imposed to the sample ($\gamma = \gamma_o \sin \omega t$), a sinusoidal change in stress will result



Elastic material

$\sigma = G\gamma = G\,\gamma_0 \sin \omega t$

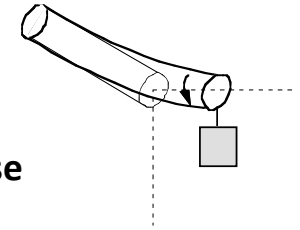
Stress and strain **in phase** (phase shift = 0)

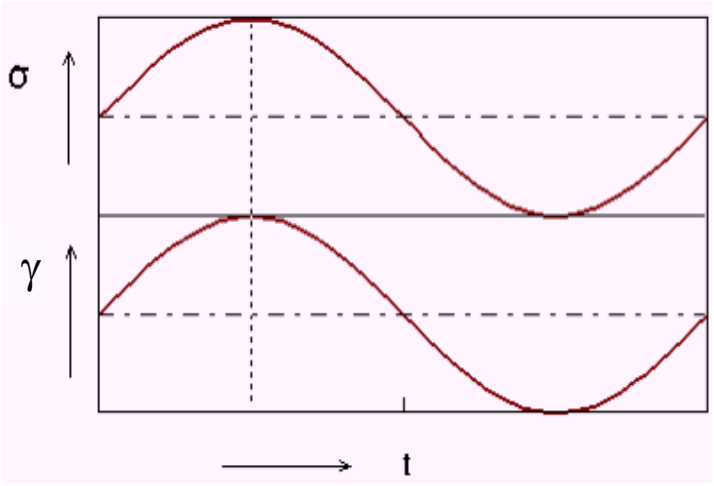


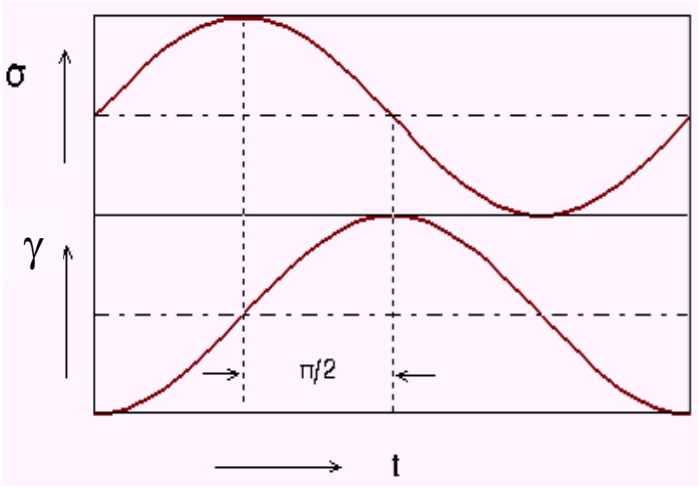
Viscous fluid

$\sigma = \eta\dot{\gamma} = \eta\omega\,\gamma_0 \cos \omega t$

Stress and strain **out of phase** (phase shift = $\pi/2$)





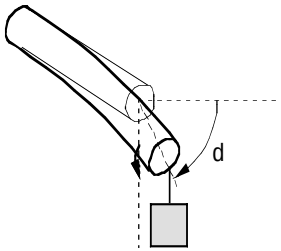


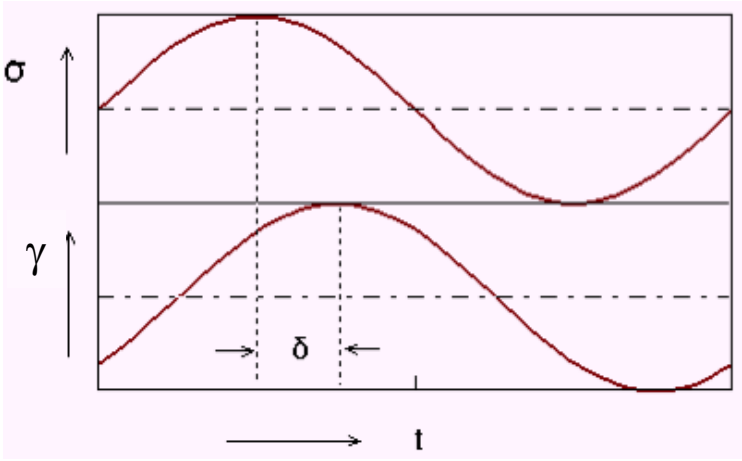
RHEOLOGICAL ANALYSIS

Viscoelastic material

$$\sigma = \gamma_0 \{G' \sin \omega t + G'' \cos \omega t\}$$
$$= \sigma_0 \sin(\omega t + \delta)$$

Stress and strain **dephased**
(phase shift = δ)

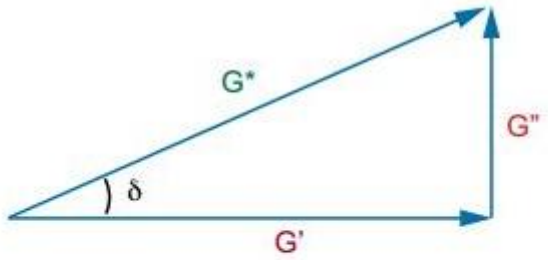




Storage modulus: $G'(\omega) = \frac{\sigma_0}{\gamma_0} \cos \delta$

Loss modulus: $G''(\omega) = \frac{\sigma_0}{\gamma_0} \sin \delta$

Loss factor (damping factor): $\frac{G''}{G'} = \tan \delta$



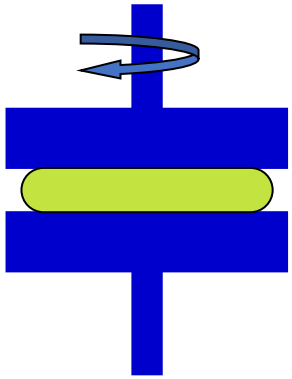
Rheological Parameters
- G* = Stress*/Strain
- G' = G* • cosδ
- G" = G* • sinδ
- tan δ = G"/G'

Criterion for gelation: tan(δ) = 1
Winter & Chambon, J. Rheol 1986

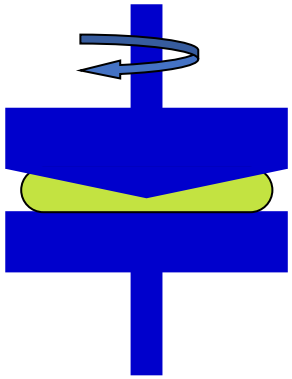
Criterion for vitrification: local maximum in tan(δ)
Schmidt et al, Macromol Mater Eng 2005

RHEOLOGICAL ANALYSIS

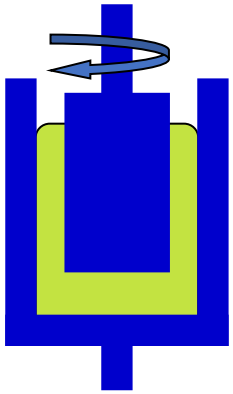
plate-plate



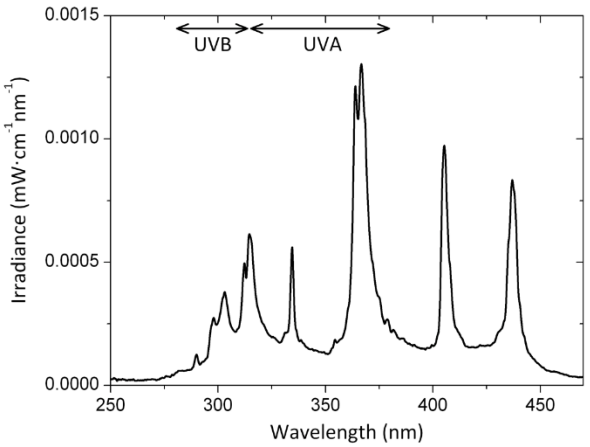
cone-plate



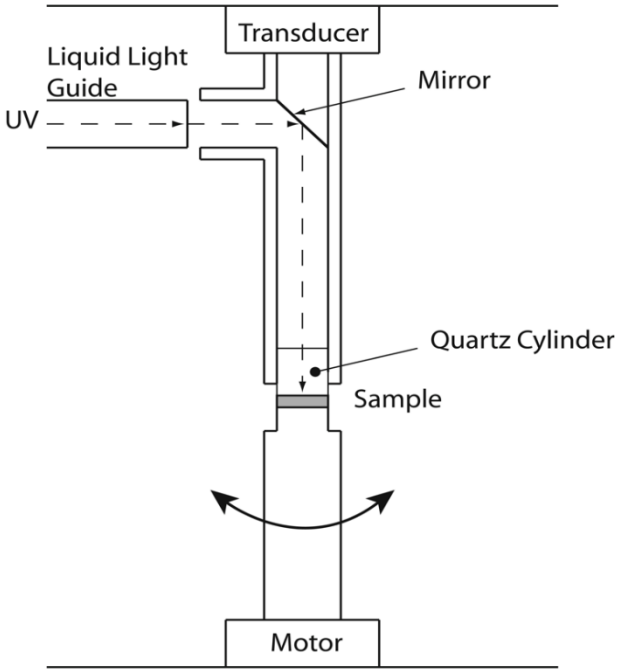
Couette



PHOTORHEOLOGY APPARATUS



200 W high pressure Hg source
0.2 – 30 W/cm^2
Liquid light guide



Main features of standard oscillatory rheological apparatus (ARES):

- time: maximum strain frequency 15 Hz (extension through dielectric measurements)
- acquisition 1 Hz
- stress: 200 Pa sensitivity, 80 MPa maximum shear modulus

Omnicure S2000

Lee et al., Prog Org Coat (2000)
Yu et al., J. Mater. Sci. (2001)
Schmidt et al., Macromol. Mater. Eng. (2005)

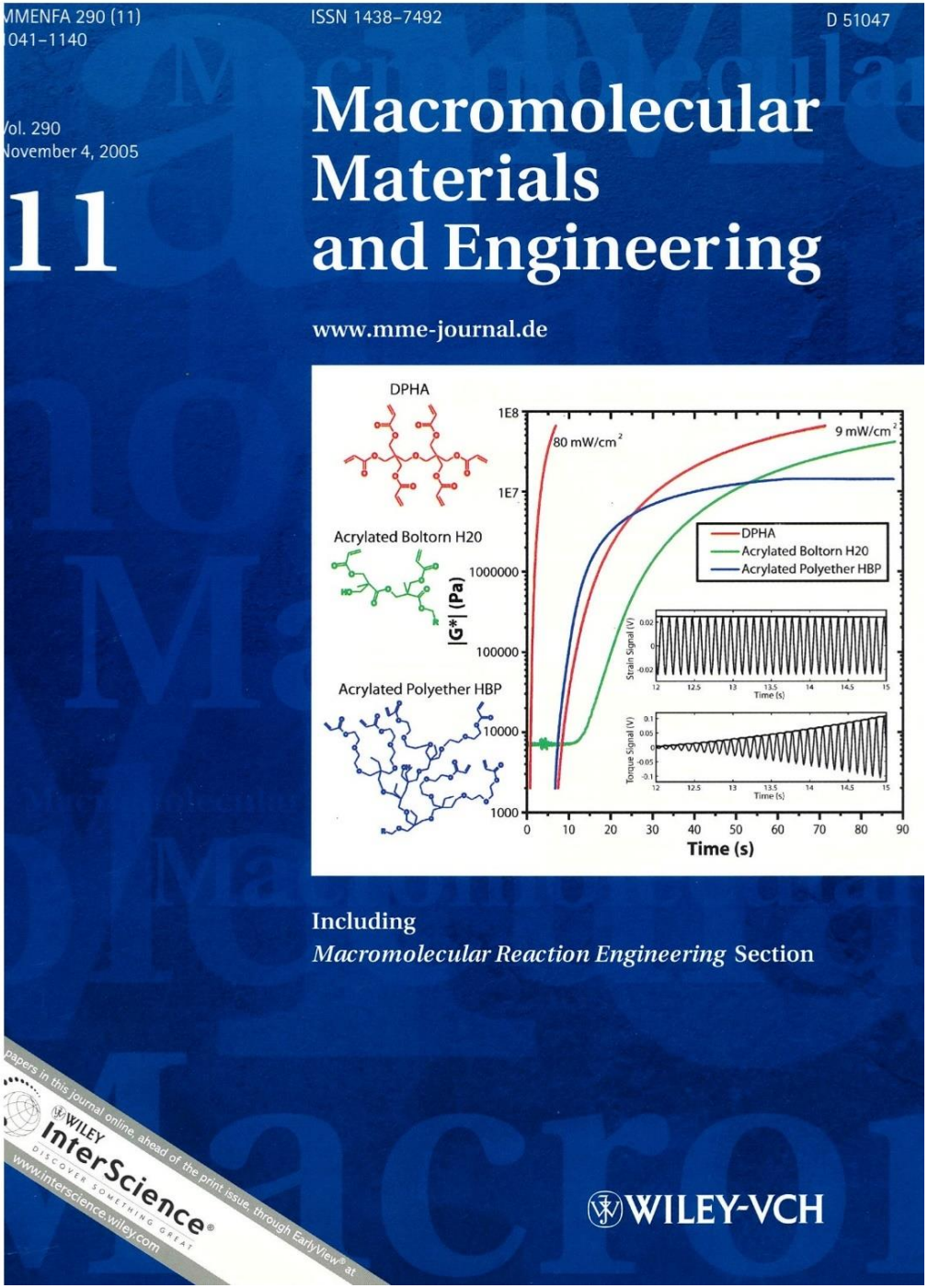
EVOLUTION OF PHOTO-RHEOLOGY

Feature	Unit	Standard oscillatory rheology	Bell Labs [1]	EPFL [2]	DSM Research [3]	INSA-Lyon [4]	EPFL [5]
Year			1992	2000	2004	2004	2005
time resolution	s	1	1	0.02	0.12	7	0.001
UV intensity	mW cm^{-2}	NA	pulses	15	28	0.15-1.36	9-80
stiffness increase	orders of magnitude	5	4	4	3	3	5
FTIR		no	no	no	yes	yes	no

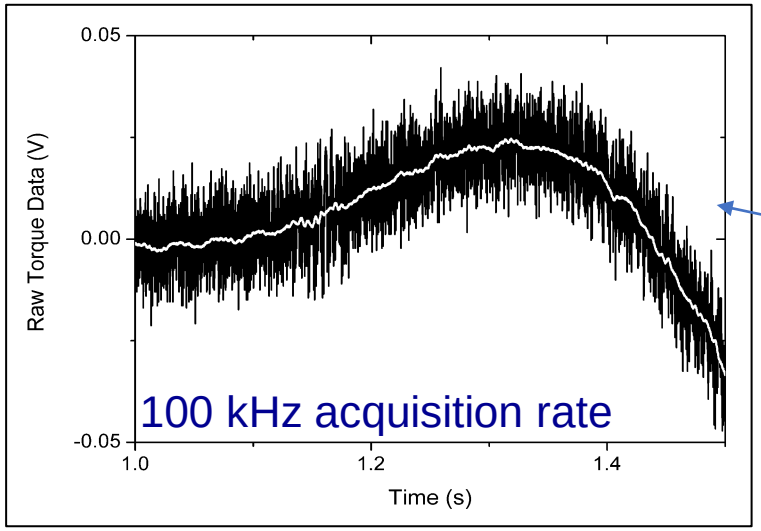
[1] Khan et al, Rheol Acta 1992
[2] Lee, Luciani, Månson, Prog. Org. Coat. 2000
[3] Steeman et al, Macromol 2004
[4] Botella et al, Macromol Rapid Comm 2004
[5] Schmidt et al, Macromol Mater Eng 2005

PHOTO-RHEOLOGY

Schmidt et al, Macromol Mater Eng 2005



PHOTORHEOLOGY: SIGNAL PROCESSING



Data Acquisition and Simultaneous Oversampling $d(t)$

Adaptive Denoising $y(t)$

Hilbert Transform

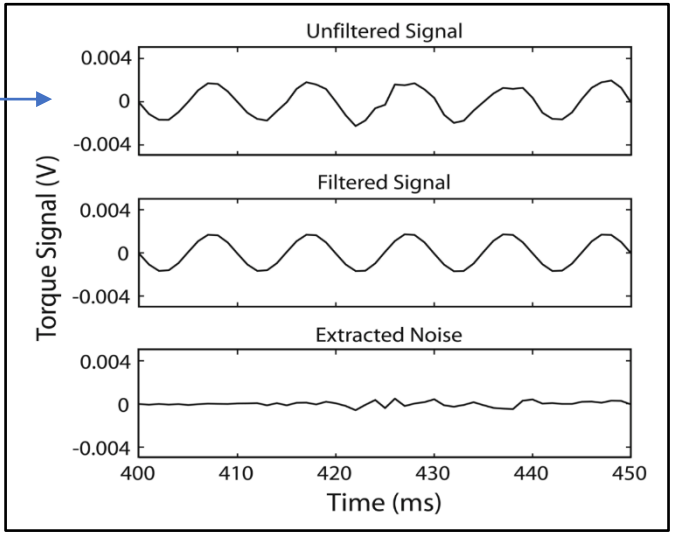
$$Y_{Hi}(t) = -\frac{1}{\pi t} \otimes y(t)$$

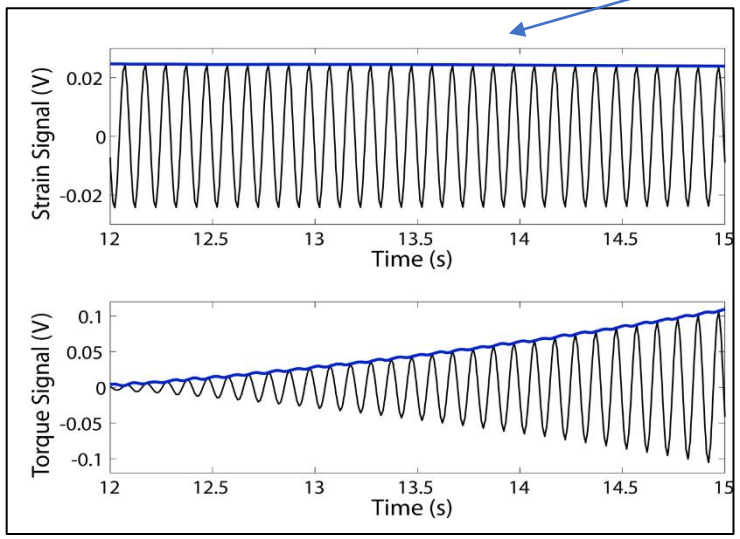
Analytical Signal

$$\hat{y}(t) = y(t) + iY_{Hi}(t)$$

Absolute Value $\Rightarrow$ Envelope $|\hat{y}(t)|$

Phase $\Phi(\hat{y}(t))$

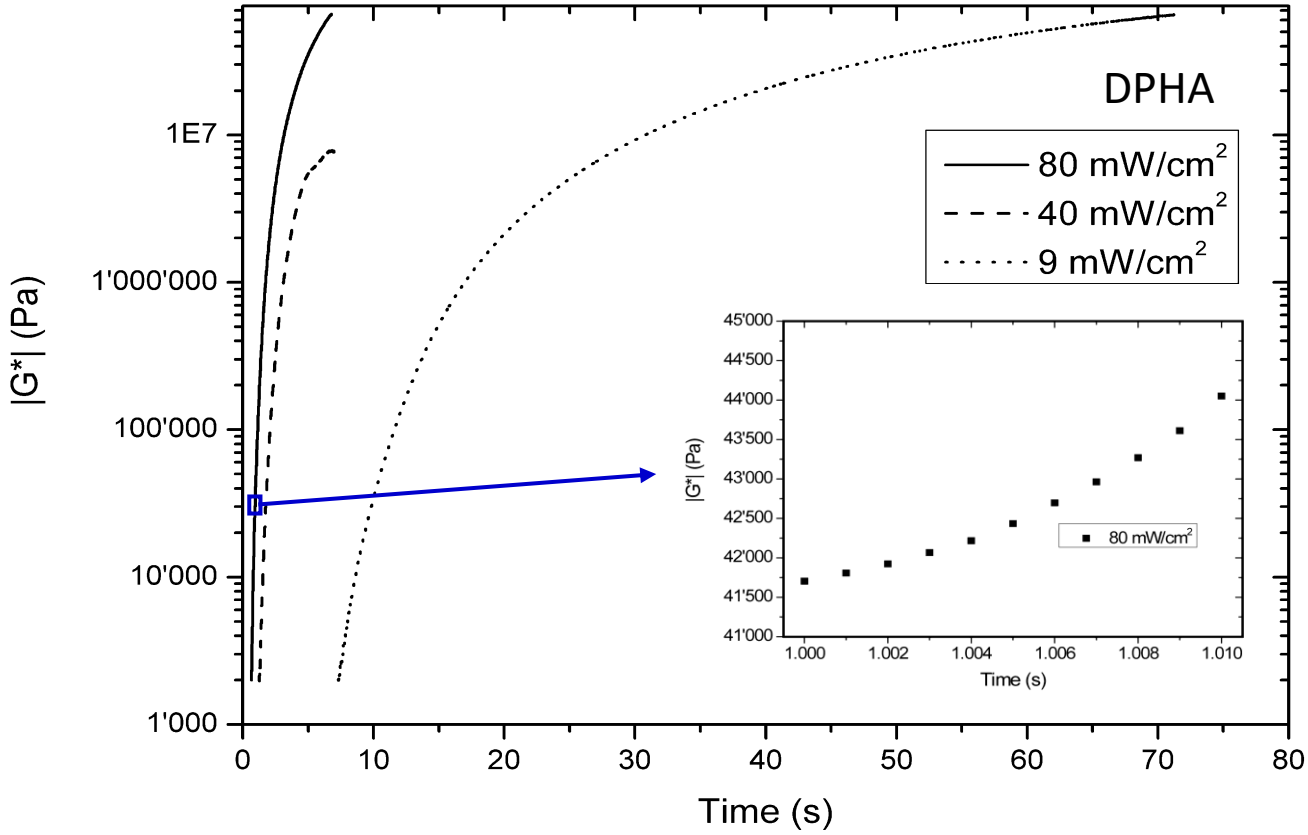




REAL-TIME STIFFNESS BUILD-UP

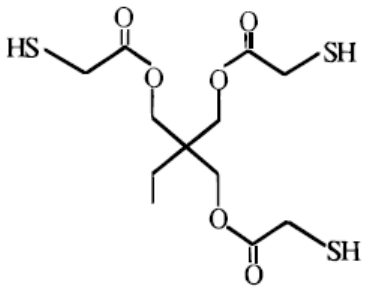
5-orders of magnitude increase of modulus

1 ms time resolution

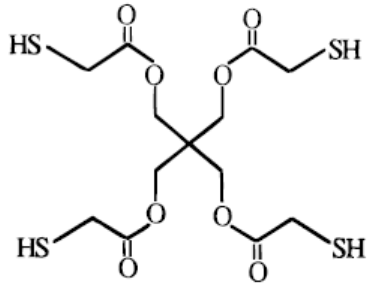


Schmidt et al., Macromol. Mater. Eng. (2005)
Schmidt, Schmäh, Leterrier, Månson, Rheol. Acta, 46, 693-701 (2007)
Schmidt, Leterrier, et al, J. Appl. Polym. Sci., 104, 2366-2376 (2007)

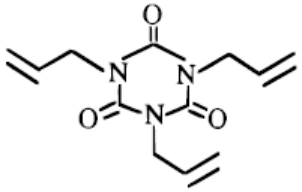
Photo-rheology examples: stiffness build-up



Trimethylolpropane tris(2-mercaptoacetate)



Pentaerythritol tetrakis(2-mercaptoacetate)



Triallyl Isocyanurate

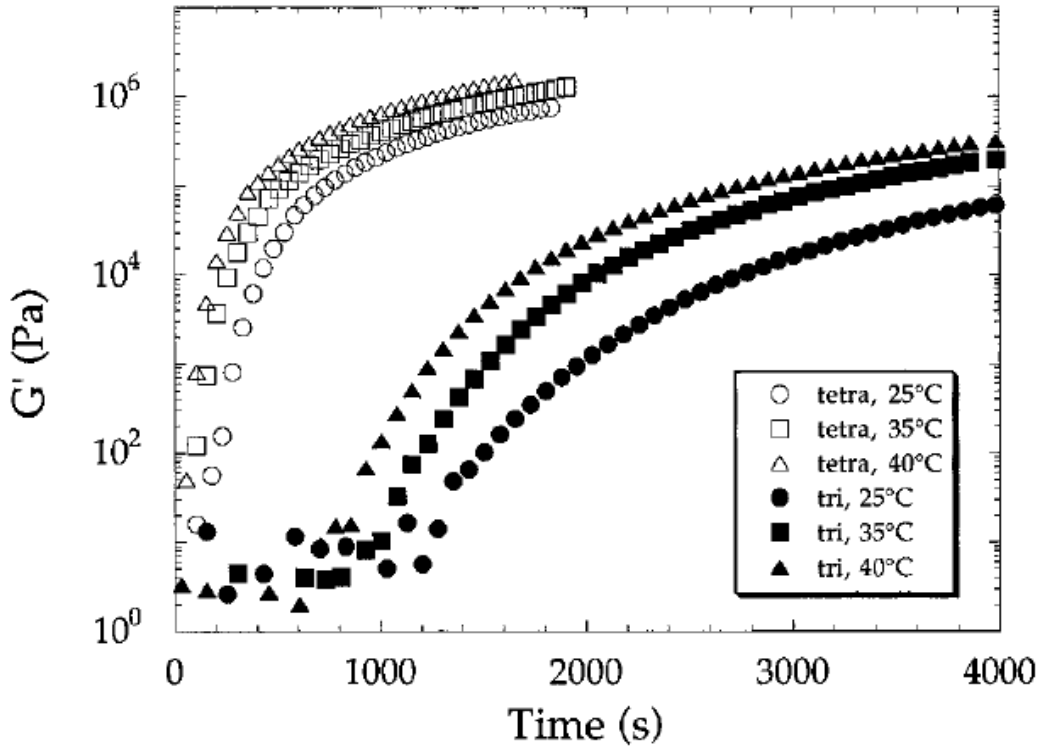


Figure 6. Comparison of the elastic modulus of the tri- and tetrafunctional thiol systems at different temperatures. The tetrafunctional thiol system cross-links much faster than the trifunctional thiol system for the temperatures studied. For both systems, increasing the temperature increases the cross-linking rate. Here, the frequency of oscillation is 10 rad/s.

Bor-Sen Chiou et al. *Macromolecules, Vol. 29, No. 16, 1996*

Photo-rheology examples: gel point

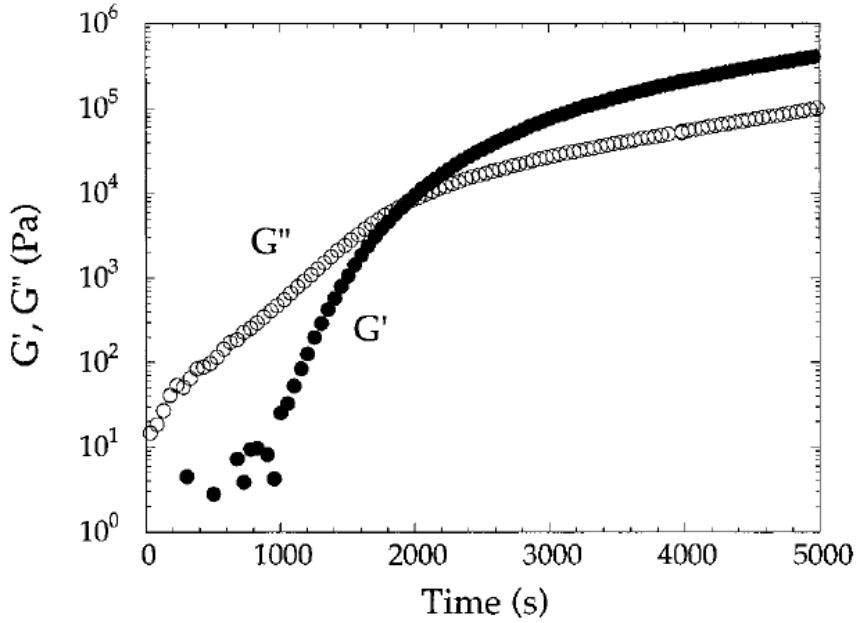


Figure 5. Evolution of the elastic (G') and viscous (G'') moduli as a function of exposure time for the trifunctional thiol system. The experimental temperature is 35 °C, and the frequency of oscillation is 10 rad/s. G'' is initially larger than G', but as the photo-cross-linking progresses, G' supercedes G''.

I = 0.1 mW cm^{-2}

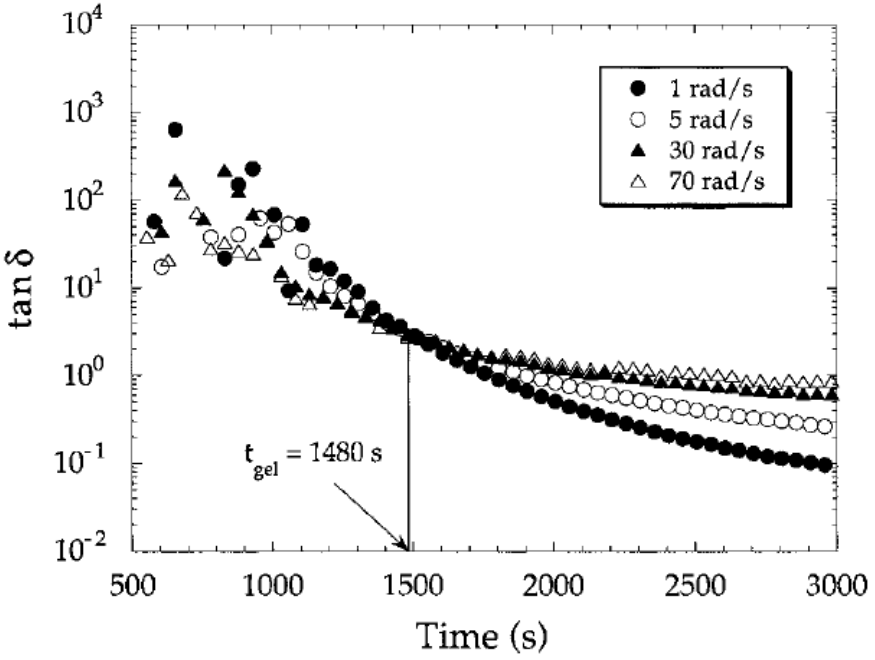


Figure 7. Loss tangent, tan δ, of the trifunctional thiol system plotted as a function of UV exposure time for different frequencies (as labeled in the figure). The intersection of tan δ at a single point ($t = 1480$ s) determines the gel point. Here, $T = 35$ °C.

Bor-Sen Chiou et al. *Macromolecules, Vol. 29, No. 16, 1996*

Photo-rheology

- **Pros**

- Information on properties of materials (processing)

- **Cons**

- Does not distinguish specific reactions
- No conversion can be calculated
- Difficult to find good conditions for beginning and end of curve for low viscosity resins
- Sampling rate

NIR-Photorheology

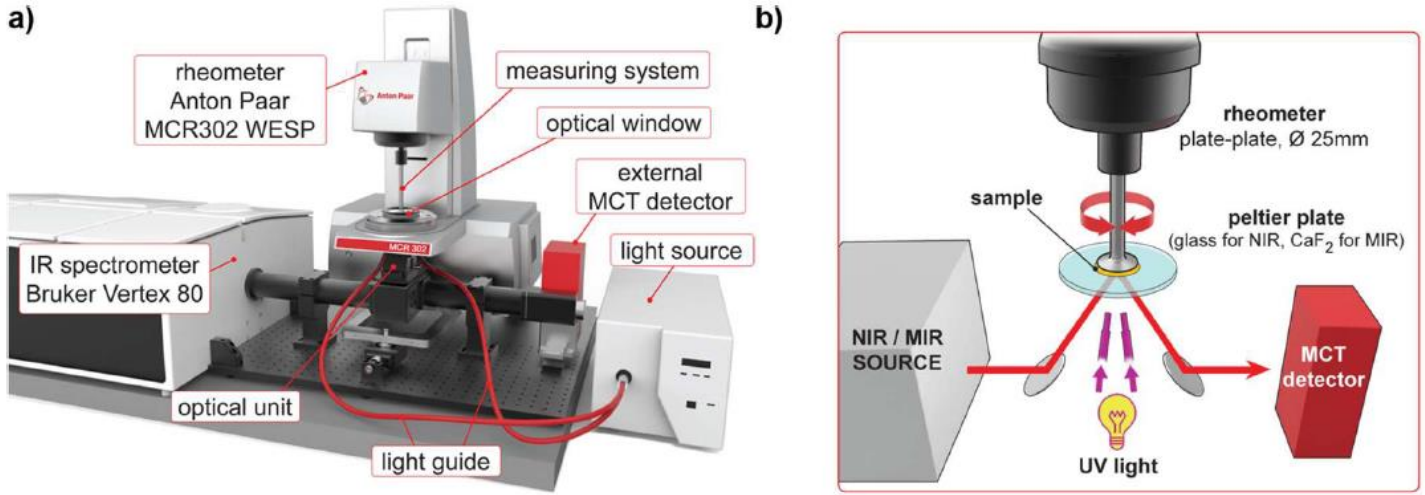
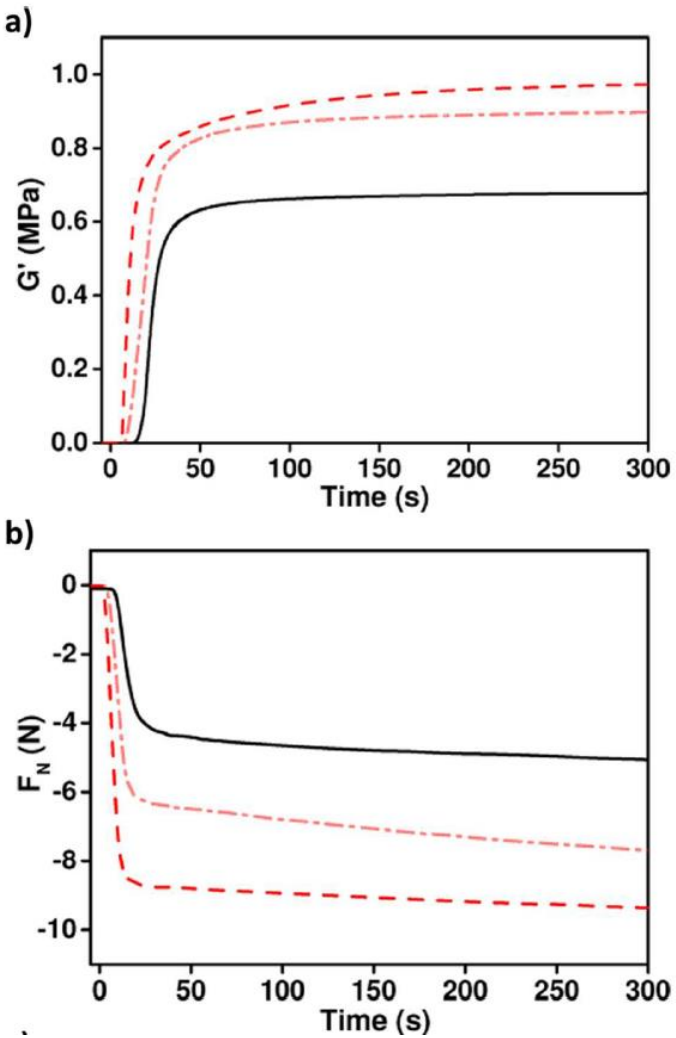


Figure 1. (a) RT-IR-Photorheology setup: Bruker Vertex 80 FTIR spectrometer coupled with an Anton Paar MCR302 WESP rheometer using an optical channel with integrated parabolic mirrors, an external MCT detector, and an Omnicure UV-light source; (b) Schematic illustration of the IR beam path.

Gorsche et al. Anal. Chem. 2017, 89, 4958−4968

Schmidt C. and Scherzer T., JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS 2015, 53, 729–739

NIR-Photorheology



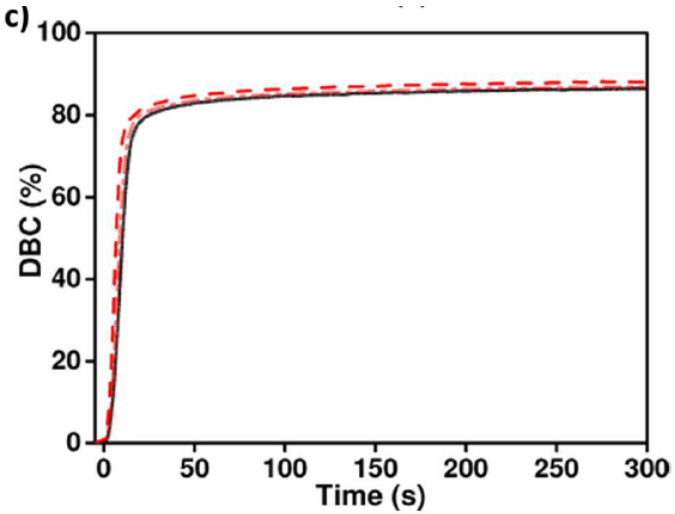
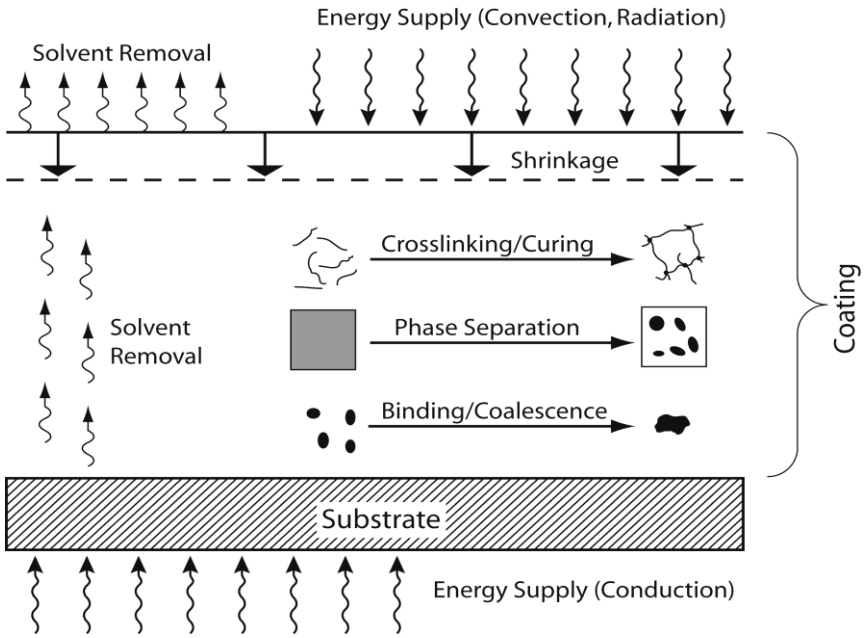


Figure 2. RT-NIR-Photorheology study of IBoA (—) and formulations with 10 wt % (-.-) and 50 wt % (- - -) HDDA: (a) storage modulus G'; (b) normal force F_N; (c) double bond conversion DBC.

Gorsche et al. Anal. Chem. 2017, 89, 4958−4968

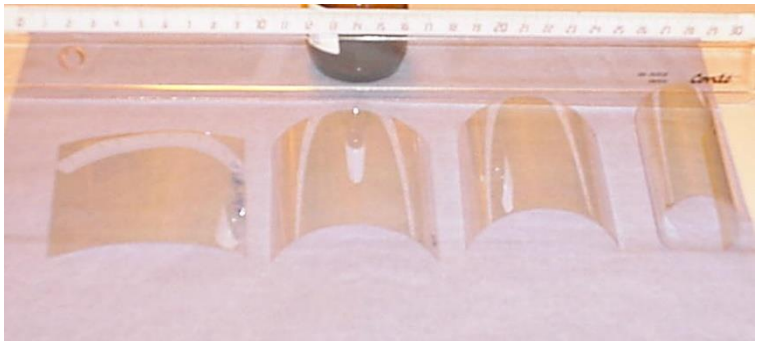
SHRINKAGE AND INTERNAL STRESSES



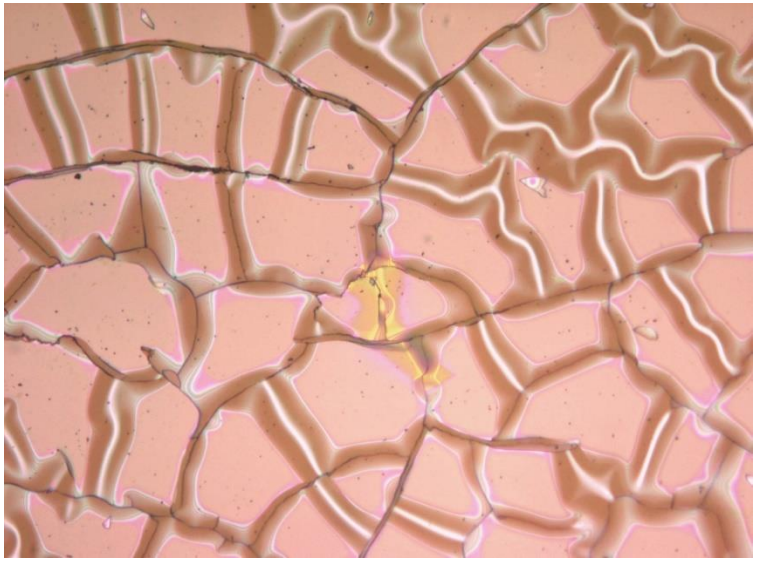
$$s(t) = 2\int_0^t G(t)\frac{\partial c}{\partial t}dt + 2\int_{T_c}^{T_f} G(a_s + \frac{\partial c}{\partial T})dT$$

Cure shrinkage stress

Thermal stress *(small for UV-curable polymers)*



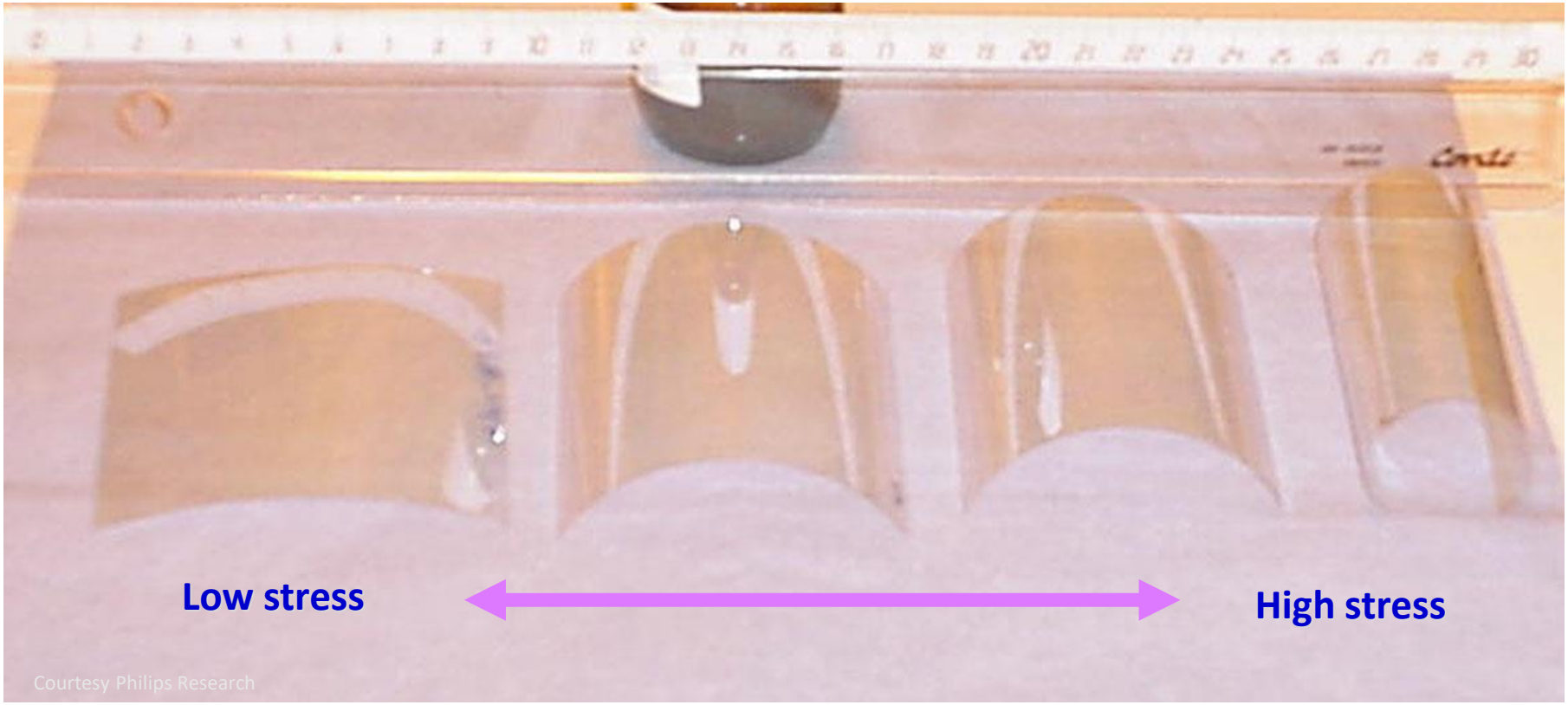
… Lack of dimensional stability



… Buckling and cracking

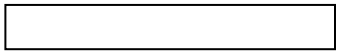
Lange, Månson et al., Polymer (1995, 1997); Payne et al., J Appl Polym Sci (1998, 2001)

STRESS ANALYSIS IN COATINGS



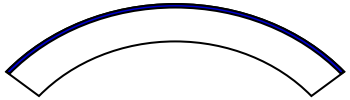
STRESS ANALYSIS IN COATINGS

Substrate, initially flat



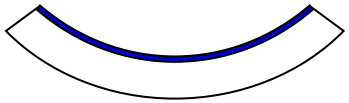
A thin substrate (< 1 mm) is preferable for reliable stress analysis based on curvature measurement

Coated substrate curved <-> internal stress



Compressive internal stresses "-"

Favorable if coating loaded in tension during service



Tensile internal stresses "+"

Favorable if coating loaded in compression during service

STRESS ANALYSIS IN COATINGS

Sato, Prog Org Coat (1980)
Francis et al., J Mater Sci (2002)

If coating (i.e. acrylate) modulus is unknown:

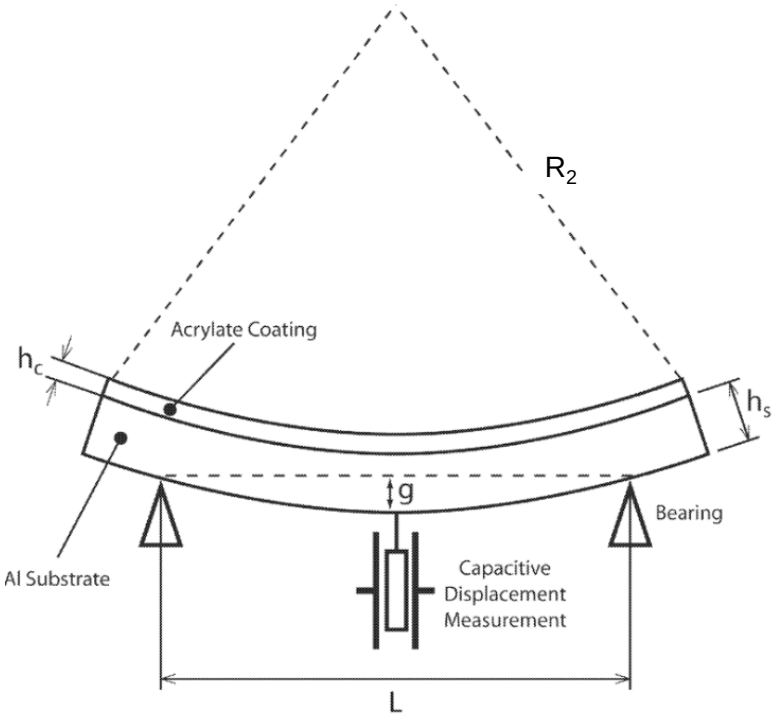
$$\sigma_i = -\frac{E_s h_s^2}{6h_c} \cdot \left(\frac{1}{R_2} - \frac{1}{R_1}\right)$$

Stoney, *Proc. Roy. Soc. London* 1909

If coating (i.e. acrylate) modulus is known:

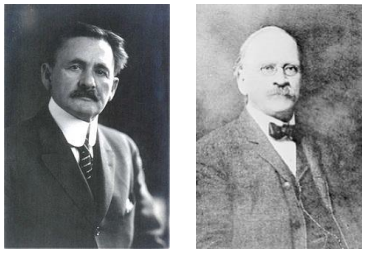
$$\sigma_i = -\frac{E_s h_s^2}{6h_c} \cdot \left(1 + \frac{h_c}{h_s} \cdot \left(4\frac{E_c}{E_s} - 1\right)\right)\left(\frac{1}{R_2} - \frac{1}{R_1}\right)$$

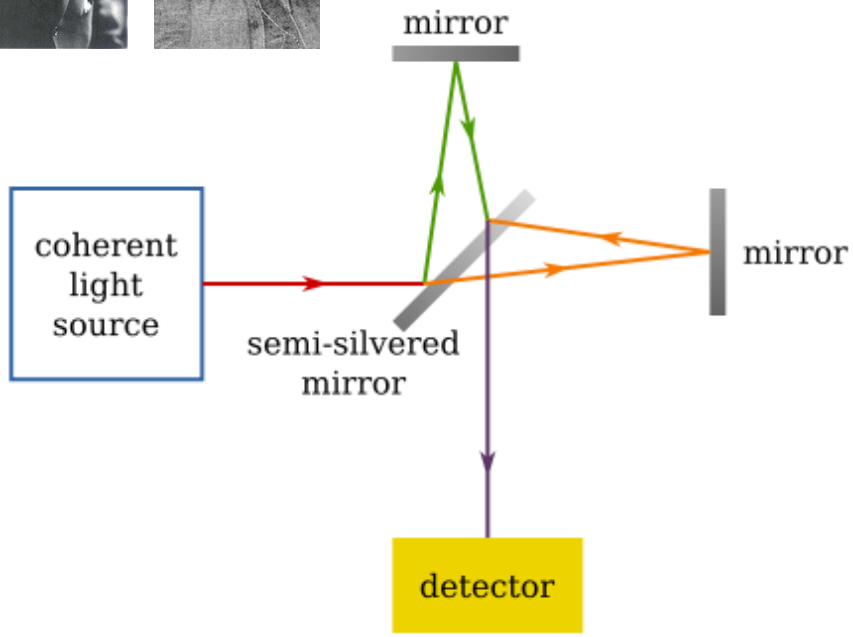
Röll, *J. Appl. Phys* 1976



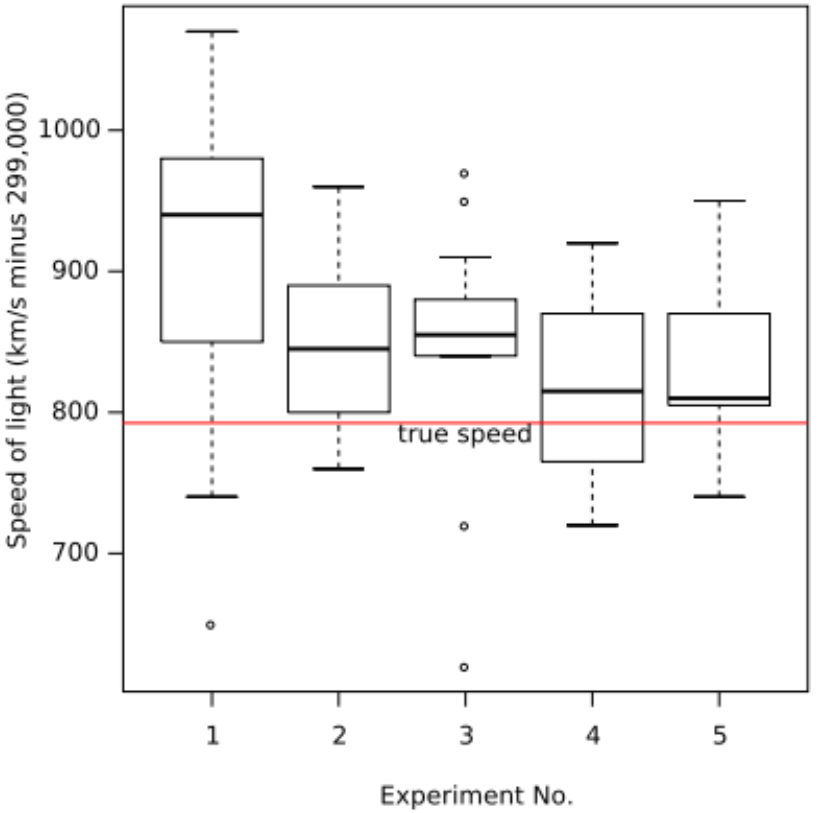
σ_i In-plane coating internal stress
h_c Coating thickness
h_s Substrate thickness
E_c Coating Young's modulus
E_s Substrate Young's modulus
R_1 Radius of curvature of uncoated substrate
R_2 Radius of curvature of coated substrate

PHOTO-INTERFEROMETRY (MICHELSON)



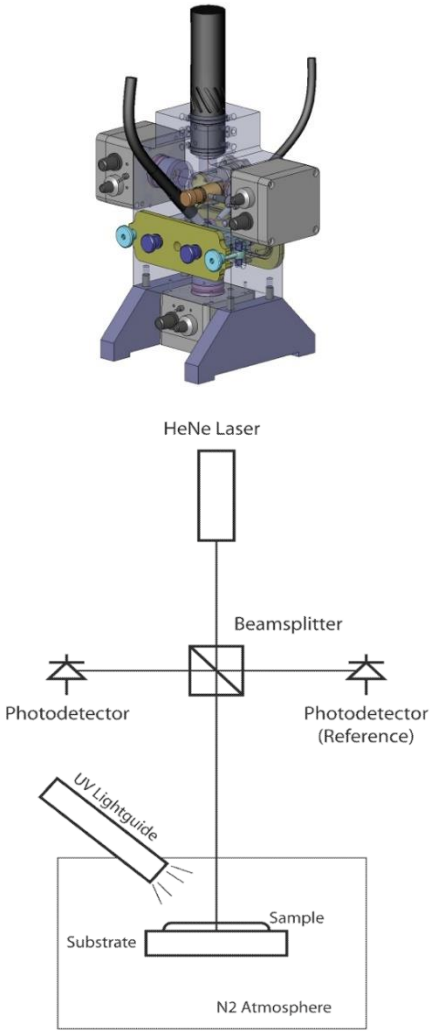


Michelson–Morley experiment, 1887



Michelson AA & Morley EW, 'On the Relative Motion of the Earth and the Luminiferous Ether' American Journal of Science 34: 333–345 (1887).

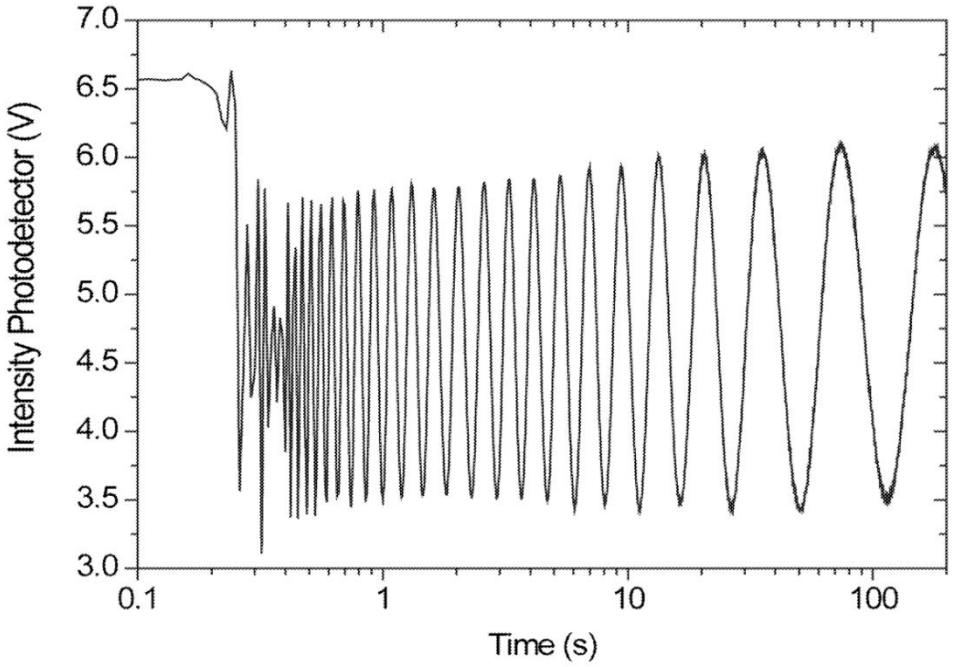
PHOTO-INTERFEROMETRY (MICHELSON)



Superposition of two reflected waves having a phase difference of:

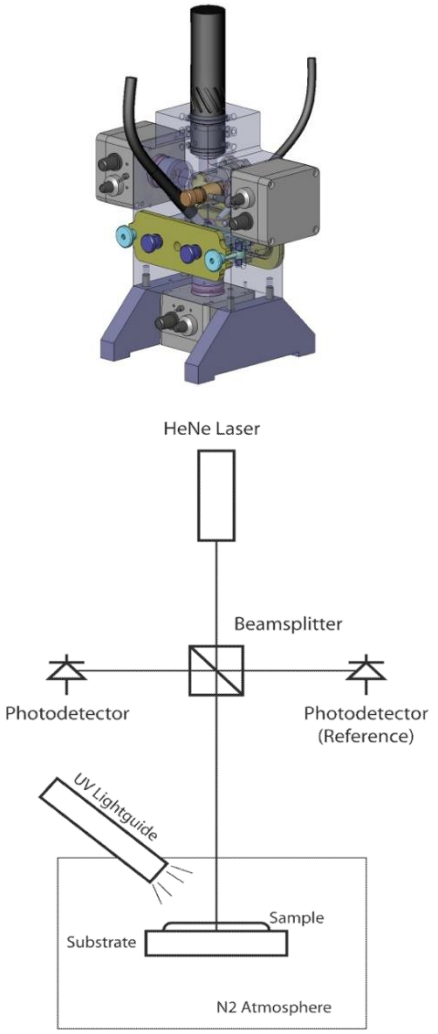
$$\Delta\phi = \frac{2\pi 2 h_c(t) n_c(t)}{\lambda_L}$$

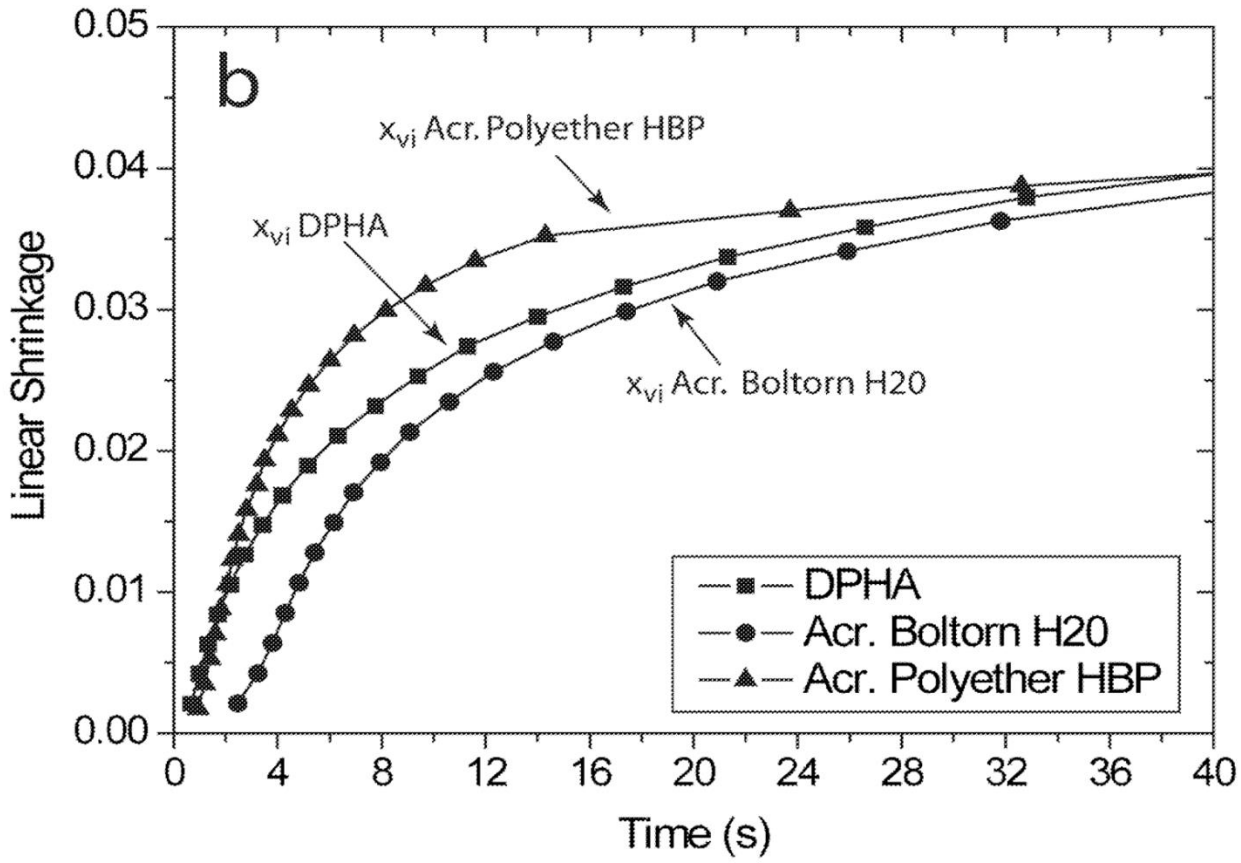
n_c refractive index
h_c thickness
λ_L laser wavelength (632.8 nm)



de Boer et al. Polymer (1992)
Schmidt et al., J. Appl. Polym. Sci. (2007)

PHOTO-INTERFEROMETRY (MICHELSON)





de Boer et al. Polymer (1992)
Schmidt et al., J. Appl. Polym. Sci. (2007)

STRESS ANALYSIS IN COATINGS

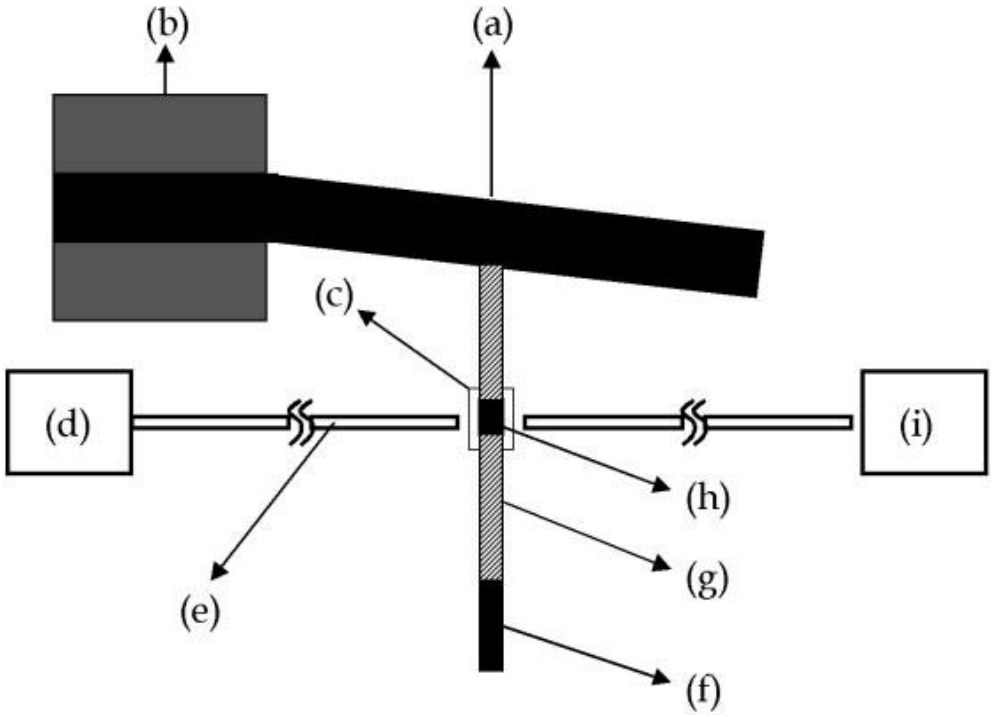
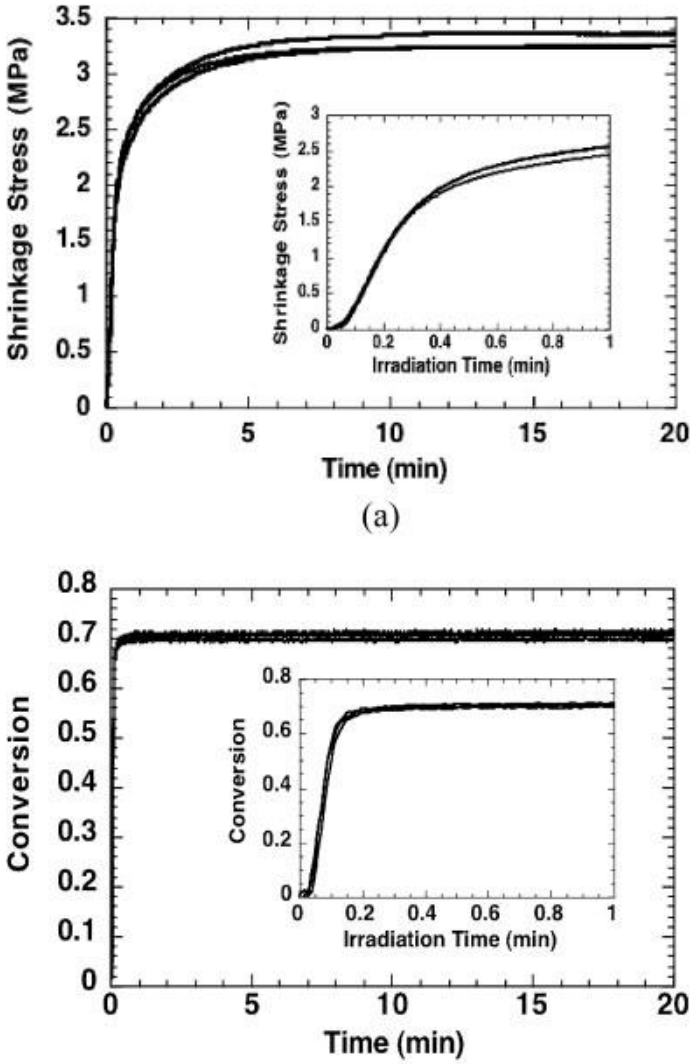


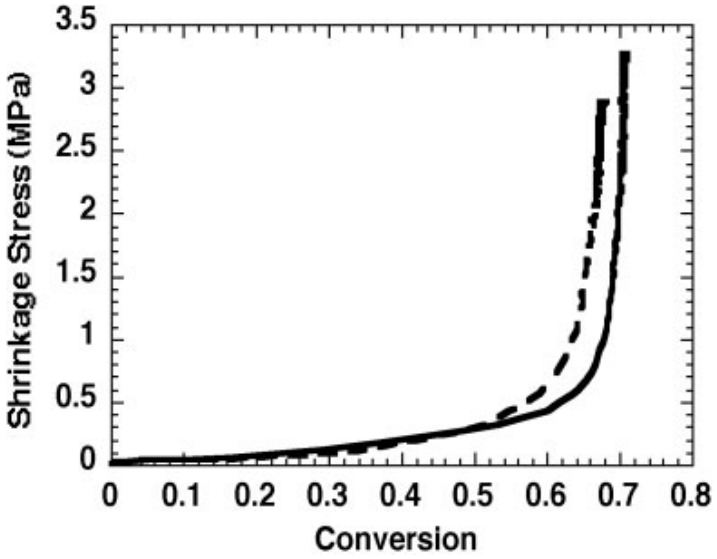
Figure 1. Schematic diagram of the simultaneous shrinkage stress and polymerization kinetics measurement setup (FTIR and NIR fiber port not shown): (a) cantilever beam, (b) cantilever beam holder, (c) PTFE sleeve, (d) NIR source, (e) NIR optical fiber, (f) curing light guide, (g) quartz rod, (h) sample, (i) NIR detector.

Lu et al., J Biomed Mater Res Part B: Appl Biomater (2004)

STRESS ANALYSIS IN COATINGS

Bis-GMA/TEGDMA





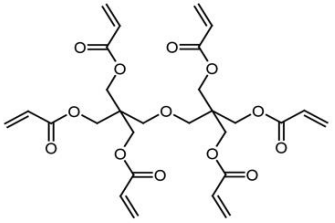
Shrinkage stress development as a function of double-bond conversion for Bis-GMA/TEGDMA (mass ratio, 70:30) (solid line) and Bis-GMA/TEGDMA/BG (mass ratio, 49:21:30) (dashed line), cured with 450 mW/cm^2 visible light for 60 s.

Lu et al., J Biomed Mater Res Part B: Appl Biomater (2004)

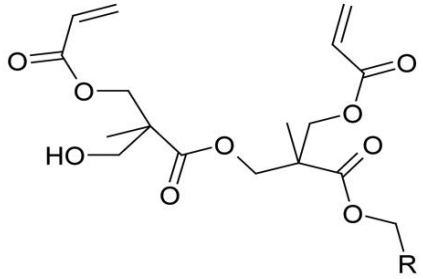
EXAMPLE: HYPERBRANCHED ACRYLATES (HBP)

a) Di-Pentaerythritol Hexaacrylate (DPHA)

DPHA
(T_g: 68° C)

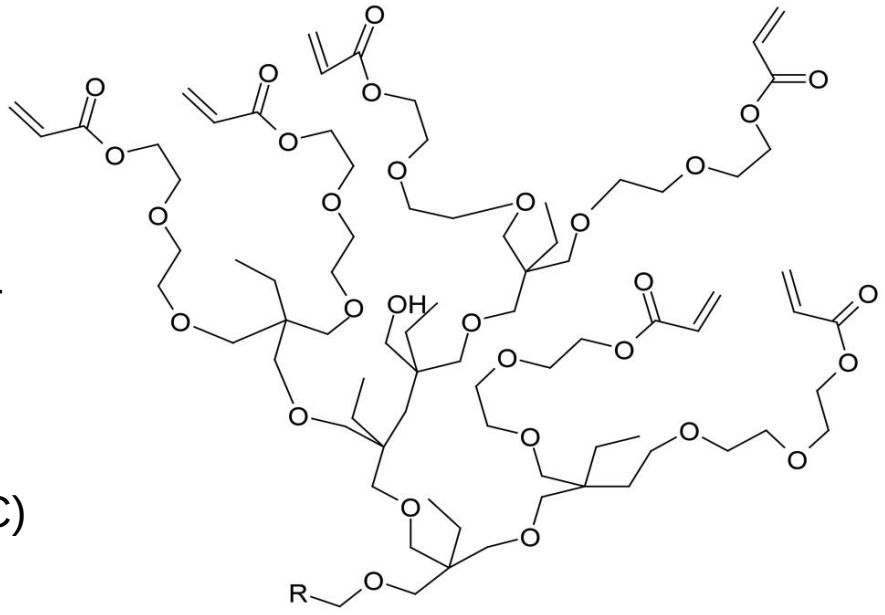


b) Segment of Acrylated Boltorn H20



Acrylated
Boltorn H20
(stiff polyester
T_g: 126° C)

c) Segment of Acrylated Polyether HBP



Acrylated
Polyether
HBP
(flexible
polyether
T_g: 28° C)

Photoinitiators

1-Hydroxy-cyclohexyl-phenyl-ketone

1:1 blend of 1-Hydroxy-cyclohexyl-phenyl-ketone and benzophenone

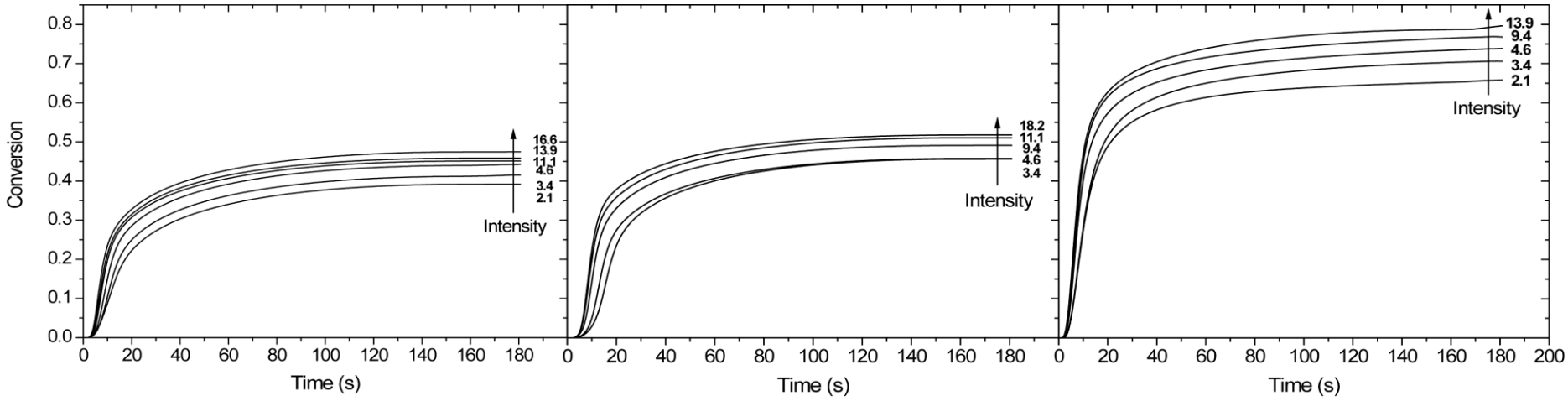
Hult & coworkers, J Coat Technol (1995), Adv Polym Sci (1999)
Klee et al., Polym Adv Technol (2001)

EXAMPLE: HYPERBRANCHED ACRYLATES (HBP)

DPHA

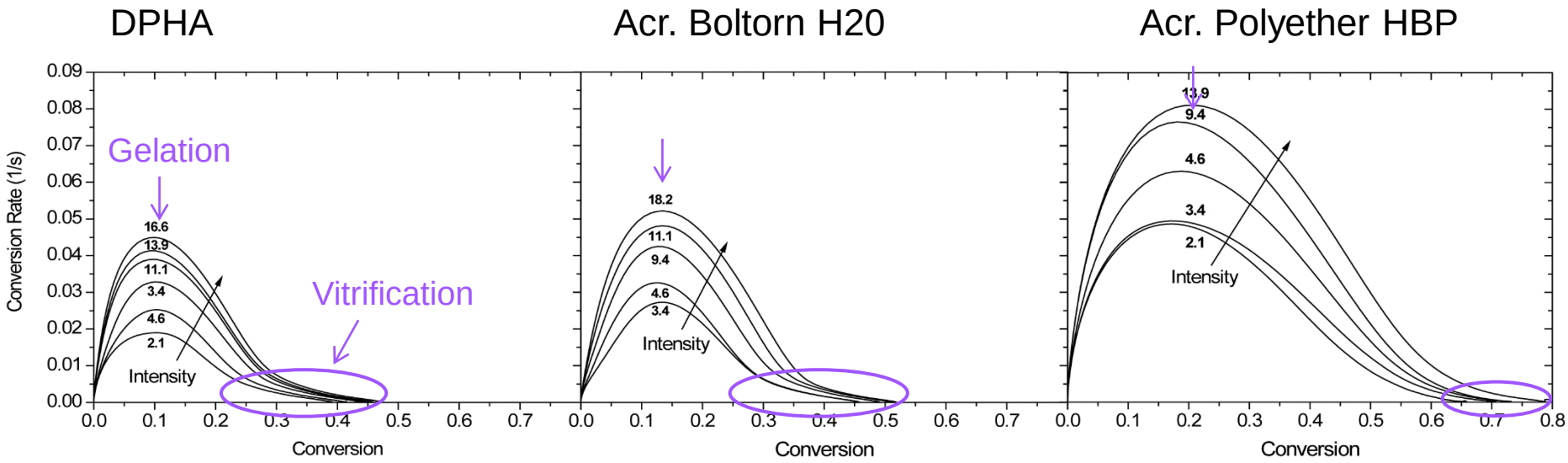
Acr. Boltorn H20

Acr. Polyether HBP

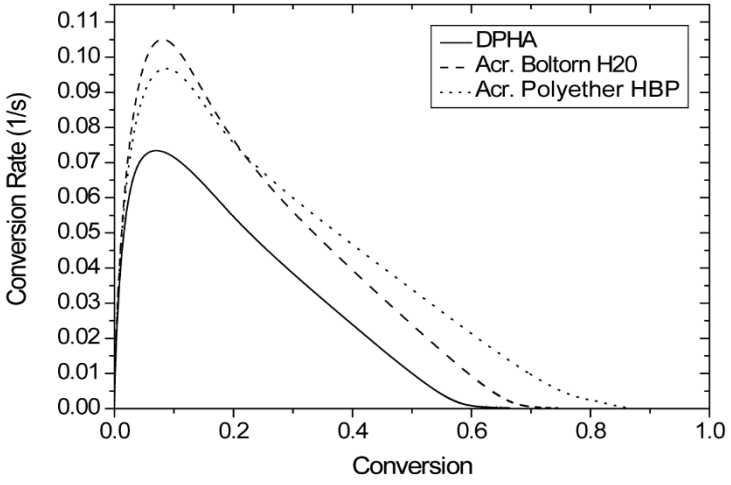


Bowman & Peppas, Macromol 1991
Yu et al., J. Mater. Sci. 2001

EXAMPLE: HYPERBRANCHED ACRYLATES (HBP)



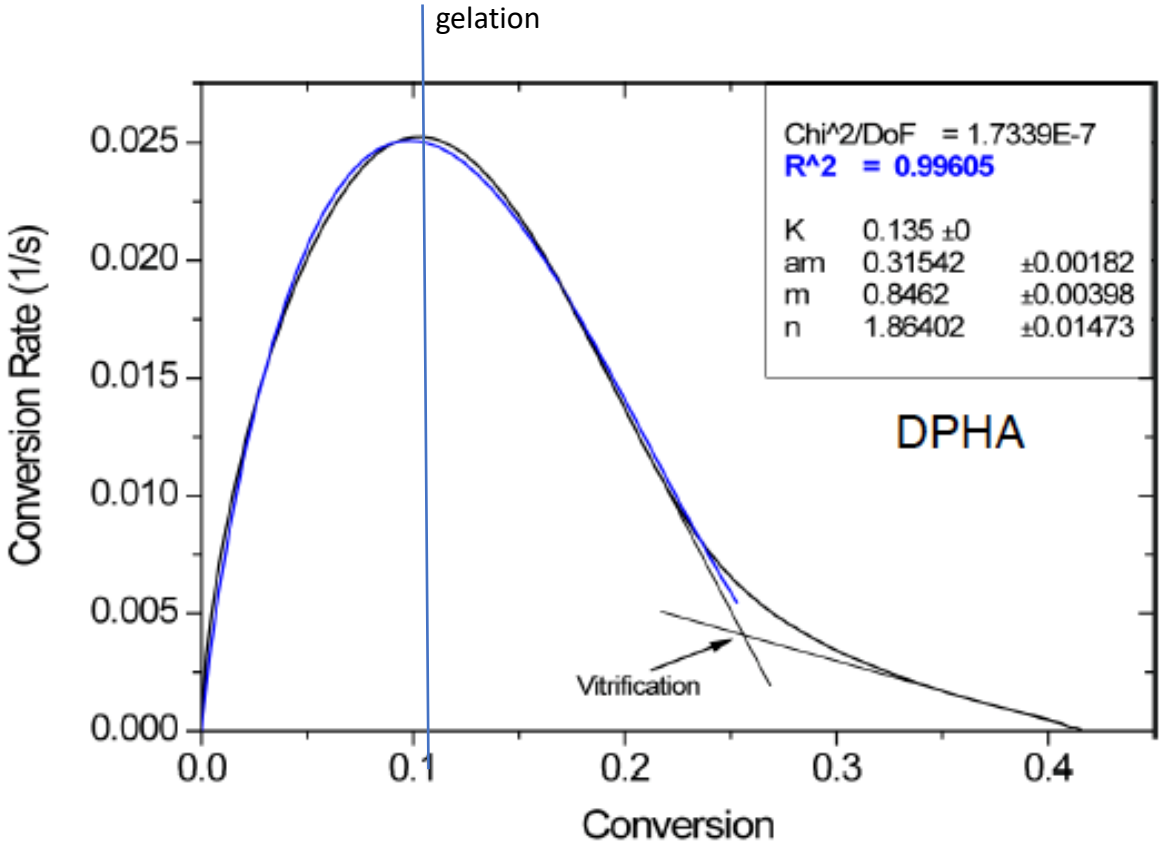
- Strong intensity dependence due to retarded volume relaxation.
- Higher conversion of the Acr. Polyether HBP due to later vitrification.
- 3rd stage in case of vitrifying systems



Bowman & Peppas, Macromol 1991
Yu et al., J. Mater. Sci. 2001

EXAMPLE

Kloosterboer 1988
Andrzejewska, Prog Polym Sci 2001
Schmidt et al., JAPS 2007

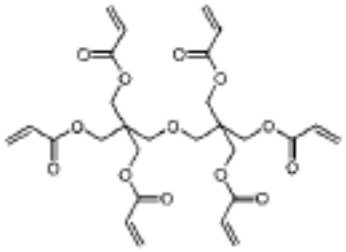


$$\frac{d\alpha}{dt} = k(I)\left(1 - \frac{\alpha}{\alpha_v(I)}\right)^n \left(\frac{\alpha}{\alpha_v(I)}\right)^m$$

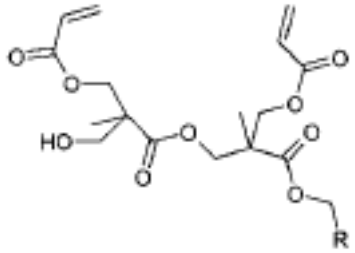
Adapted from Schmidt, Journal of Applied Polymer Science, Vol. 104, 2366–2376 (2007)

EXAMPLE

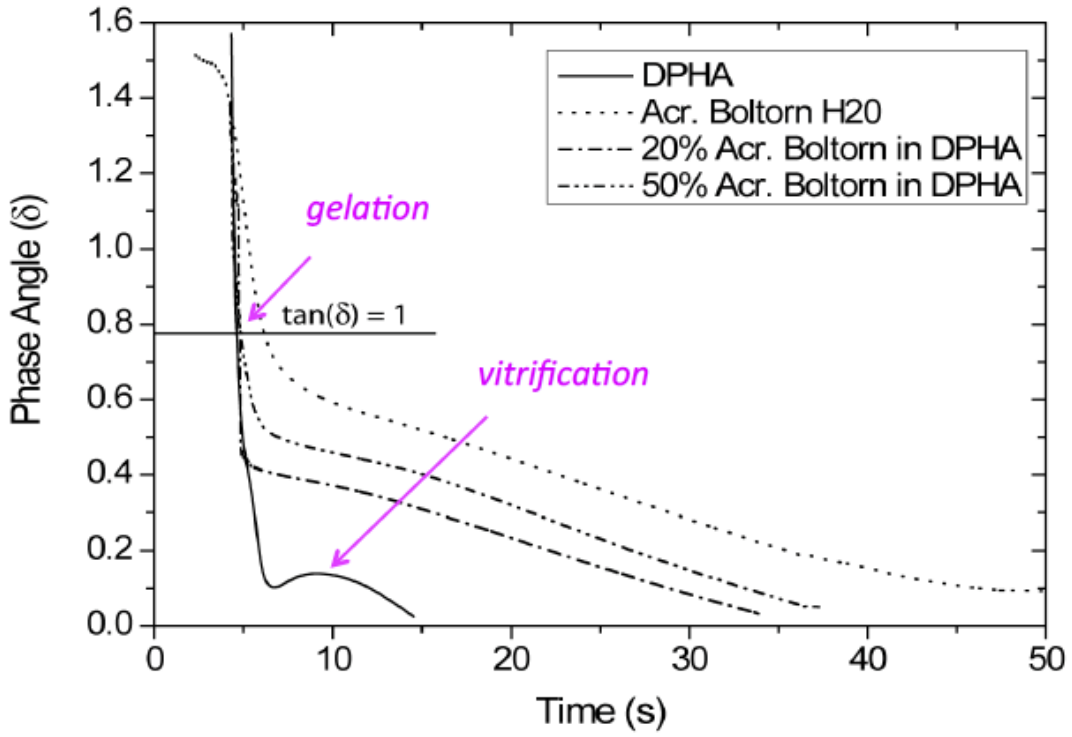
- Gel time and vitrification for different acrylic polymer mixtures by photo-rheology



DPHA



Acr. Boltorn



Schmidt et al., Macromol. Mater. Eng. (2005)
Schmidt, Schmäh, Leterrier, Månson, Rheol. Acta, 46, 693-701 (2007)
Schmidt, Leterrier, et al, J. Appl. Polym. Sci., 104, 2366-2376 (2007)

GELATION

Photo-Calorimetry
Conversion at maximum conversion rate

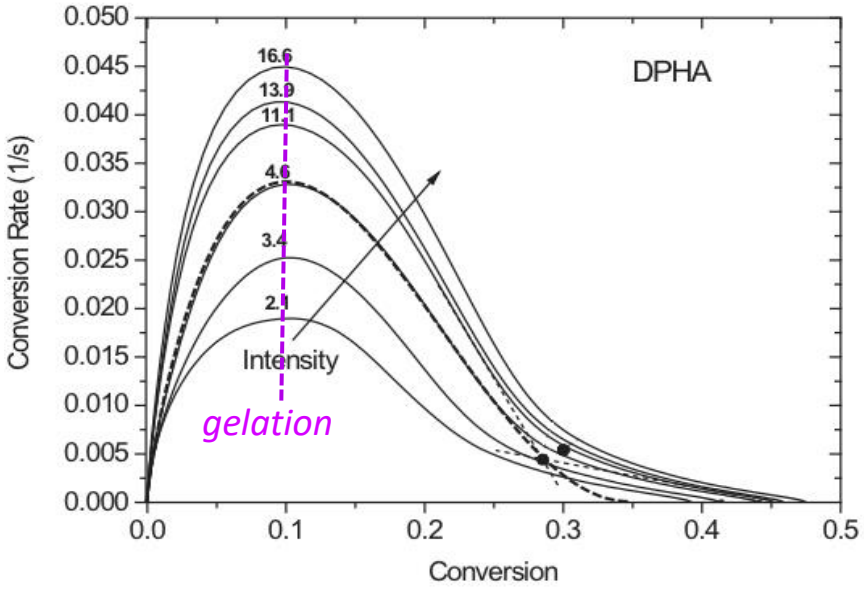
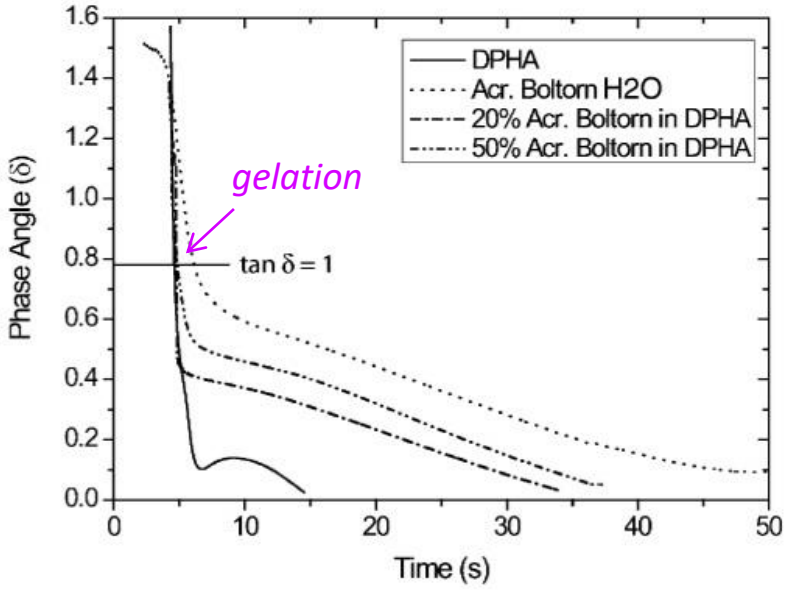


Photo-Rheology
G‘ = G‘‘



Geiser et al., J Appl Polym Sci, 114 (3), 1954, 2009
Schmidt et al., Macromol Mater Eng, 290 (11), 1115, 2005
Neves et al., J Biomed Mater Res Part A, 72 (2), 393, 2005

VITRIFICATION

Photo-Calorimetry
Departure from autocatalytic behavior

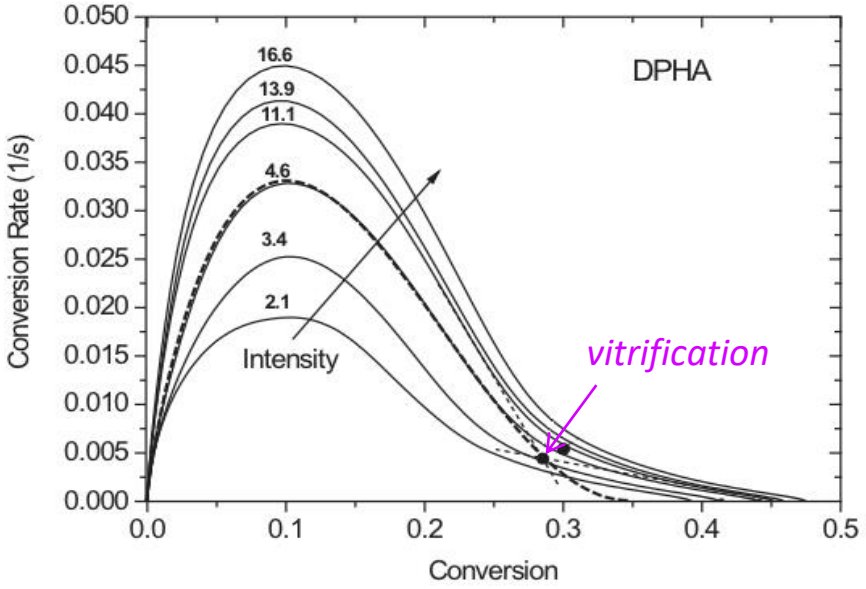
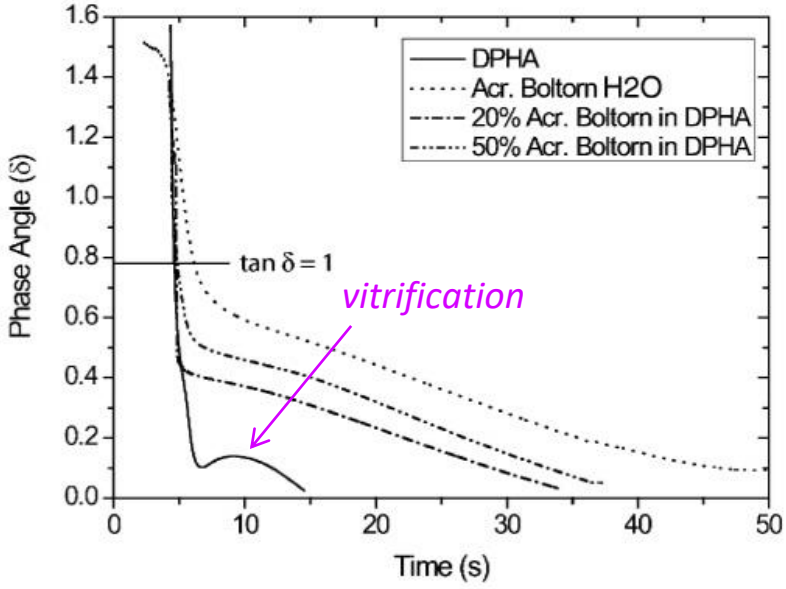


Photo-Rheology
Local maximum in tan (δ)

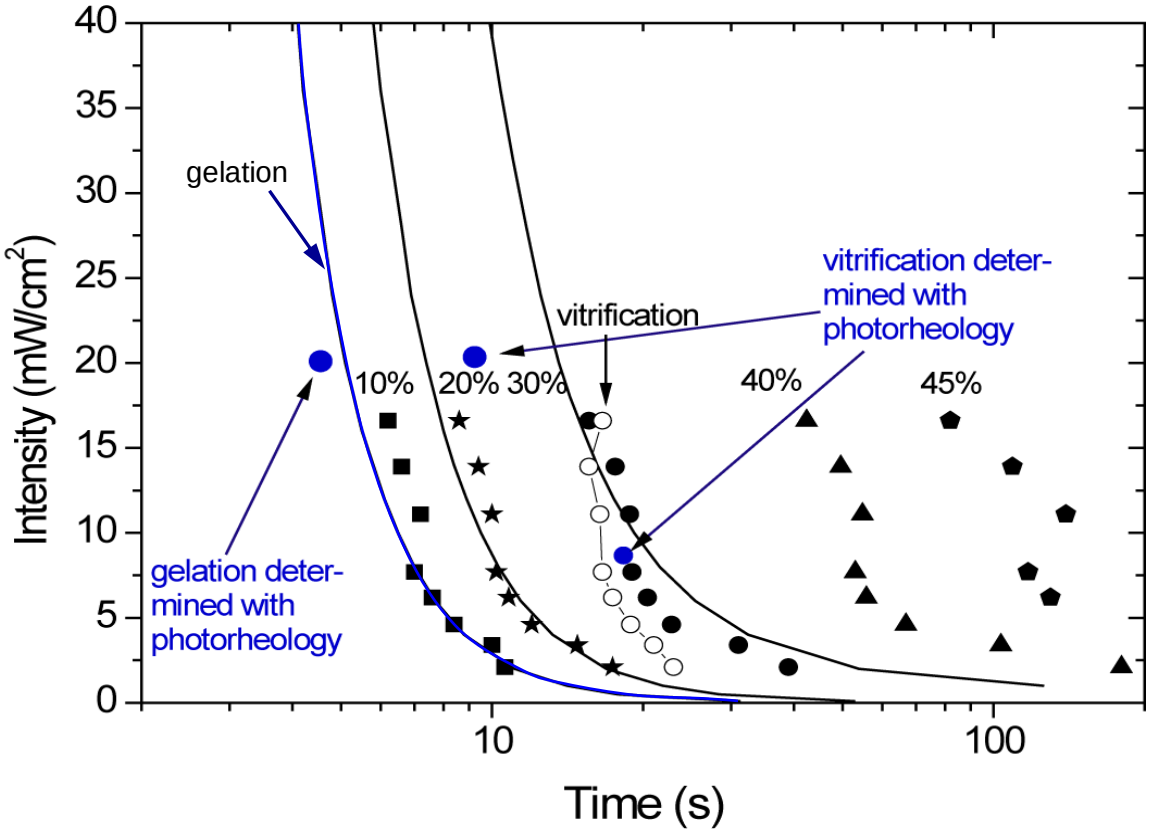


Geiser et al., J Appl Polym Sci, 114 (3), 1954, 2009
Schmidt et al., Macromol Mater Eng, 290 (11), 1115, 2005
Neves et al., J Biomed Mater Res Part A, 72 (2), 393, 2005

TIME-INTENSITY-TRANSFORMATION DIAGRAMS

Processing maps with combined information from photo DSC and photorheology

Infra-red spectroscopy in-situ in the rheometer can be useful!



Lee et al., Polymer J (2003)
Corcione et al., Polymer (2005)
Schmidt et al. JAPS (2007)

SHRINKAGE VS STIFFNESS BUILD-UP

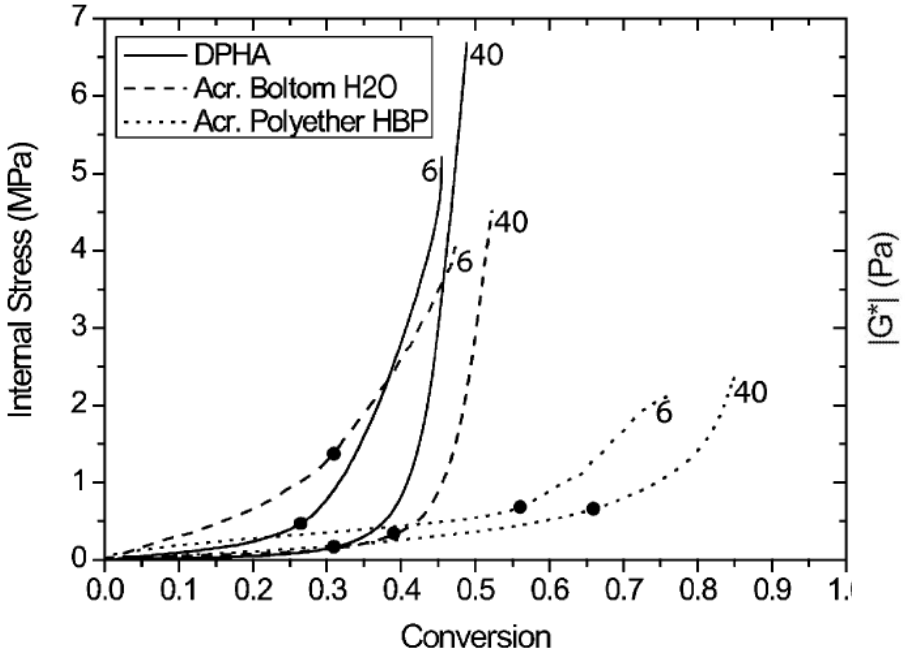
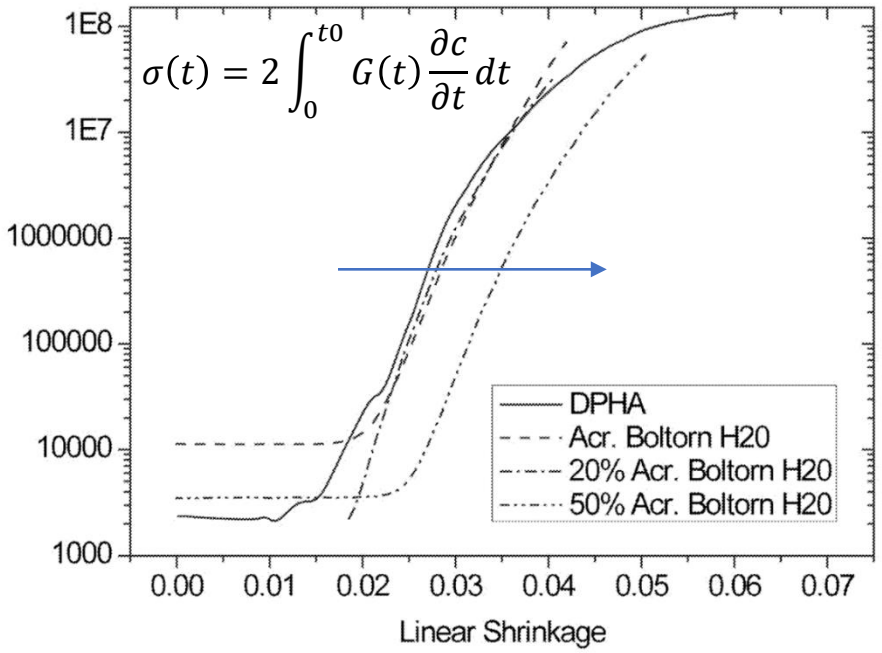


Fig. 10 Internal stress vs conversion. For each, the intensity is indicated in mW/cm^2. The *bold point* marks the onset of vitrification



'Stress nanosponge' effect (delayed macroscopic gelation and vitrification) in UV polymerization of acrylated HBP

Schmidt et al., J. Appl. Polym. Sci. (2007), Rheol Acta (2007)

SUMMARY

- **Real time FTIR** and **Photo-calorimetry**: conversion, gelation & vitrification
  - Identification of gelation and vitrification (free-radical systems)
  - Conversion behavior predictable for any intensity with autocatalytic model
  - FTIR can follows specific reactive groups while photo-DSC does not distinguish different reactions
- **Photo-rheology**: viscoelastic properties, gelation & vitrification
- **Photo-interferometry**, bending and tensile setups: cure shrinkage and stress dynamics
- Application to **process optimization** in fast-cure systems