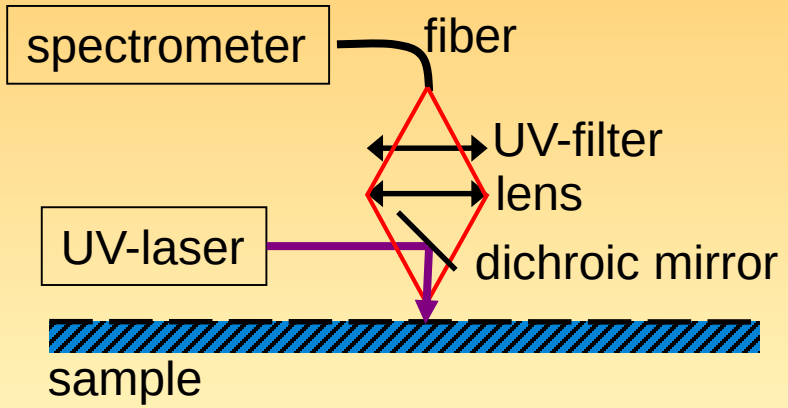
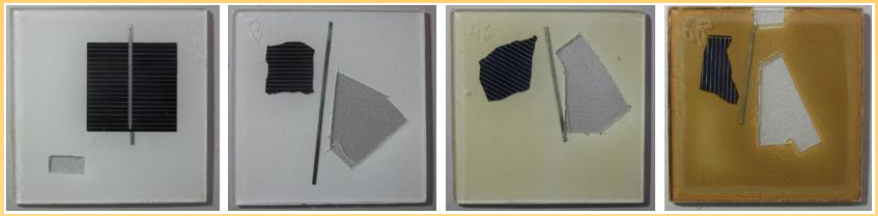
Prospects of 2D-luminescence spectroscopy for aging investigations of the embedding EVA polymer in PV modules

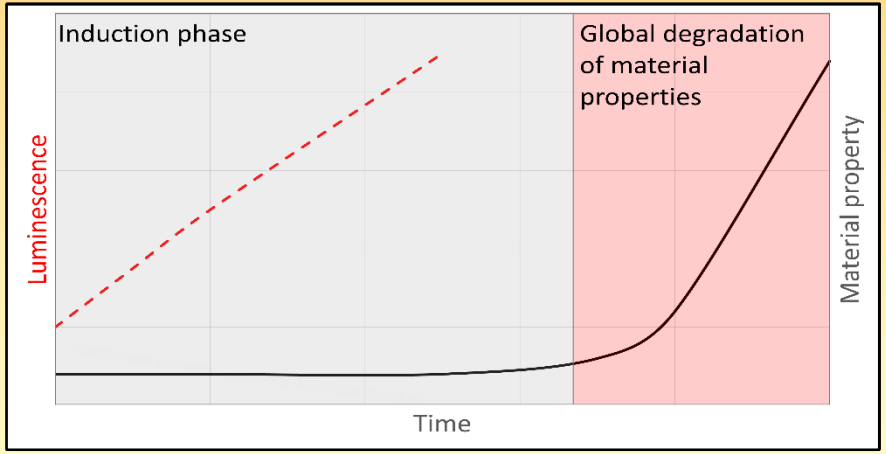
Beate Röder
Jan Schlothauer, Ronald Steffen

Luminescence upon accelerated aging

Sketch of the optical setup:



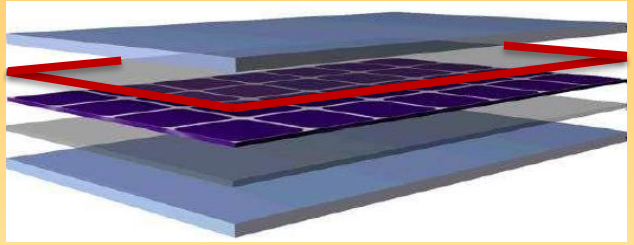


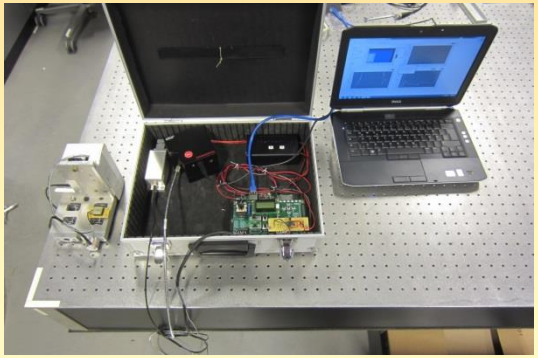


Luminescence shows a correlation to the aging duration from the beginning of accelerated aging.

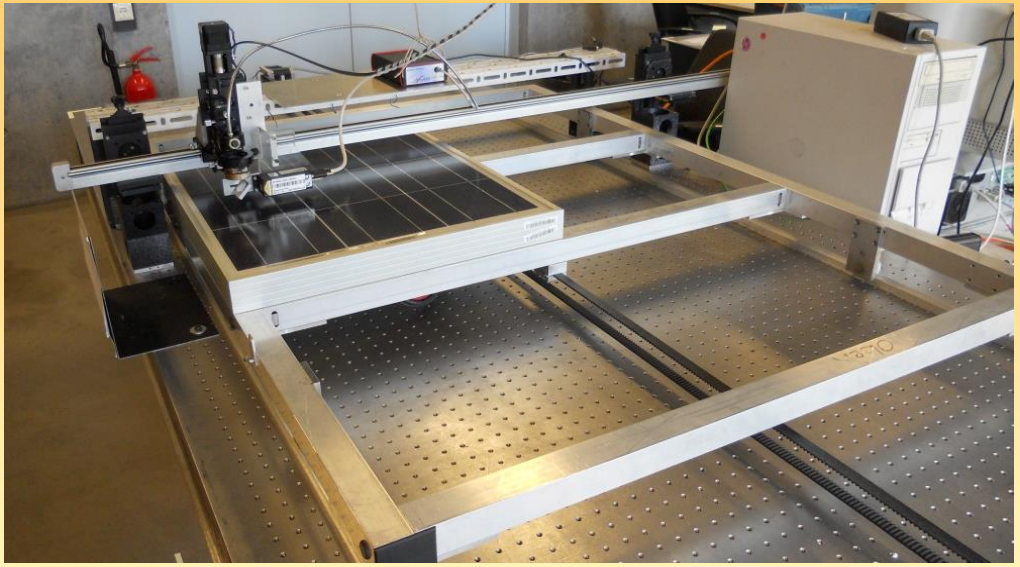
2D Luminescence scanning of commercial PV modules

Frontglass
EVA
Cells
EVA
Backsheet





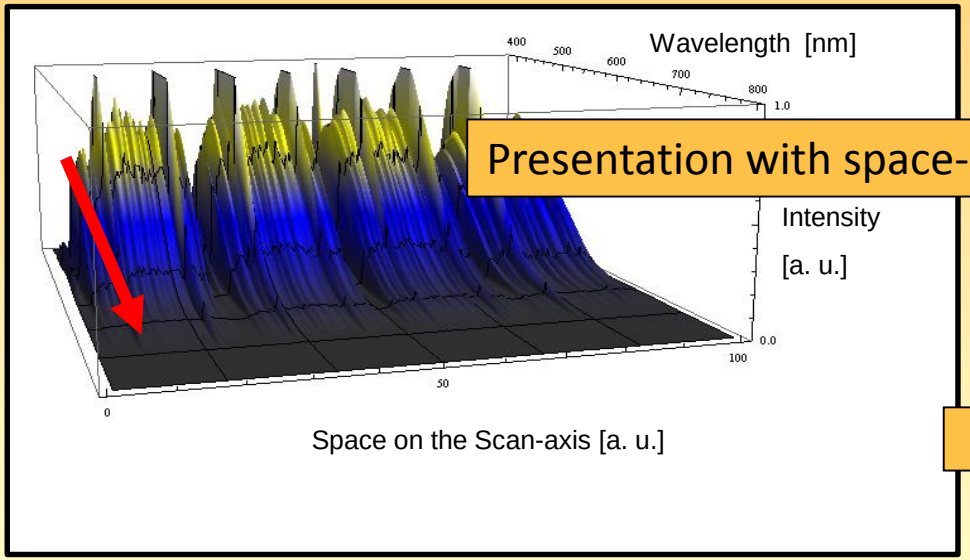
Field inspection set up



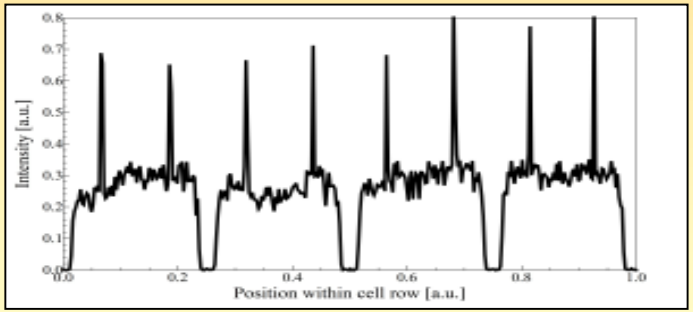
Setup for 2D-photoluminescence detection (scanning) of embedding polymers in PV-Modules

Spatially-resolved measurements on PV-Modules

First step of analysis: integration of luminescence spectra
and graphical presentation of the location dependent total intensity



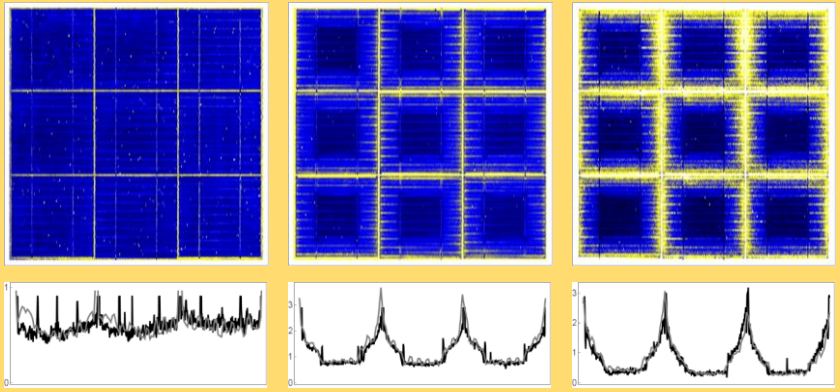
Presentation with space-resolution via integration of the spectra



Line-Scan – with spectral information

Line-Scan – Total intensity

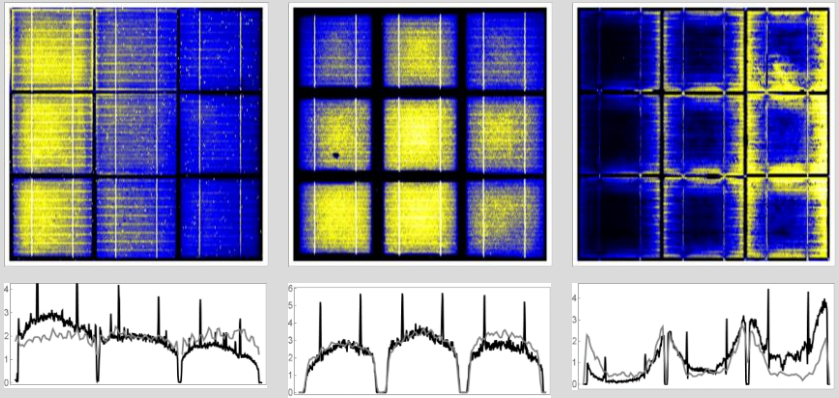
Luminescence patterns upon accelerated aging



2000h H | 2400h DH | 4000h DH

Dry heat (H), damp-heat (DH)

Accelerated aging without UV

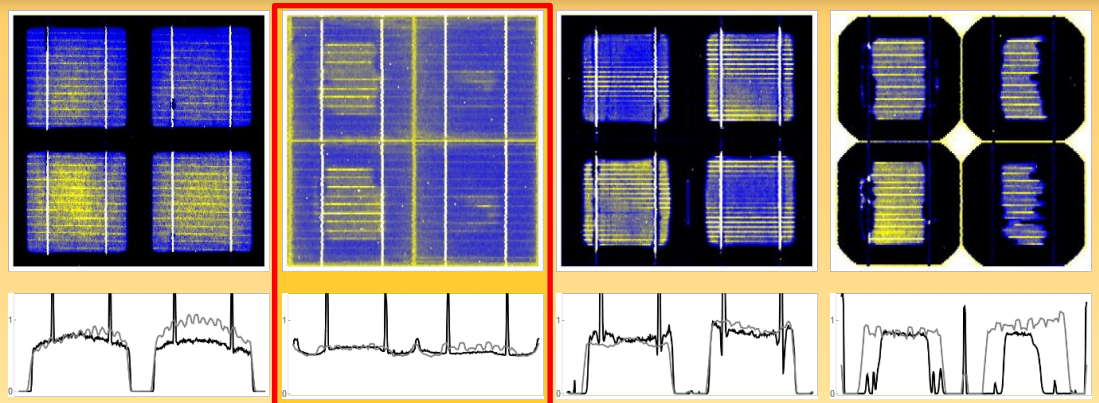


1000h UV | 1500h UV | 2750h DH + 700h UV

Accelerated aging with UV

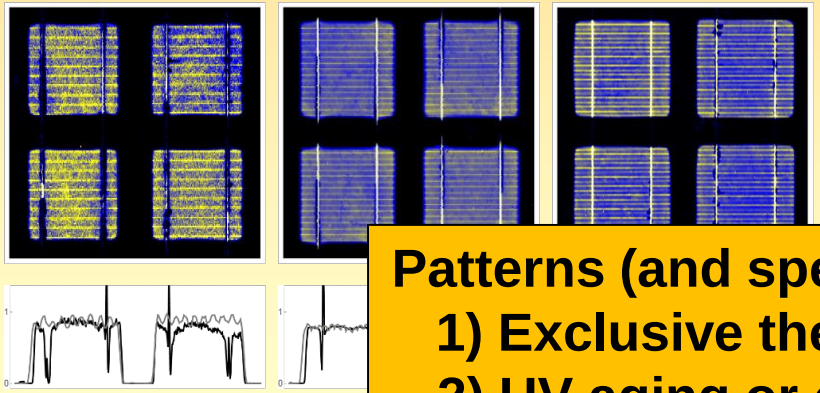
and DH aging followed by UV (DH+UV)

Luminescence patterns upon outdoor weathering



a) C1 b) C2 c) C3 d) C4

Similar patterns are observed in all modules



e) C5 f) C6

Patterns are most similar to those of accelerated aging with UV

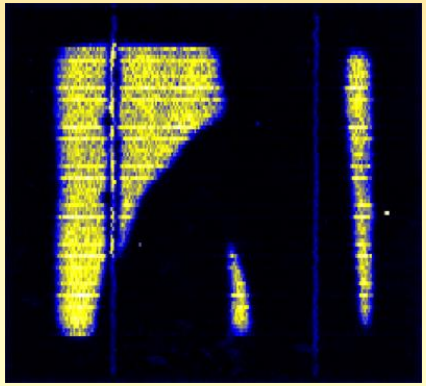
Modules of manufacturer C2 deviate

rved for UV aging).

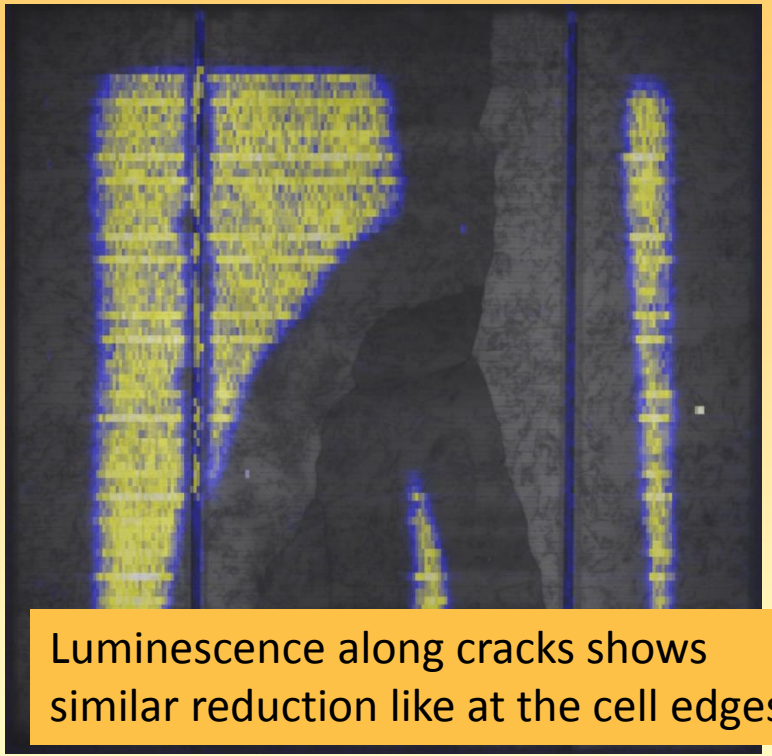
Patterns (and spectra) are distinct for:
1) Exclusive thermal aging
2) UV aging or outdoor weathering

Evaluation of damages

Electroluminescence image (EL)



Photoluminescence intensity

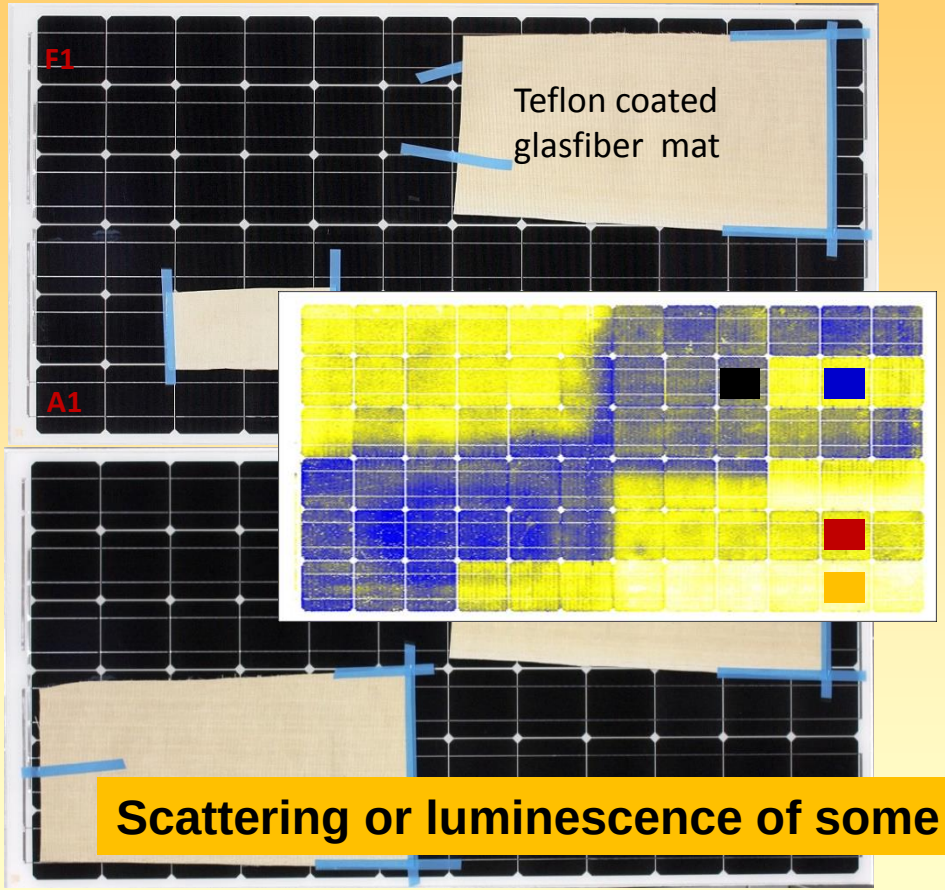


Luminescence along cracks shows similar reduction like at the cell edges

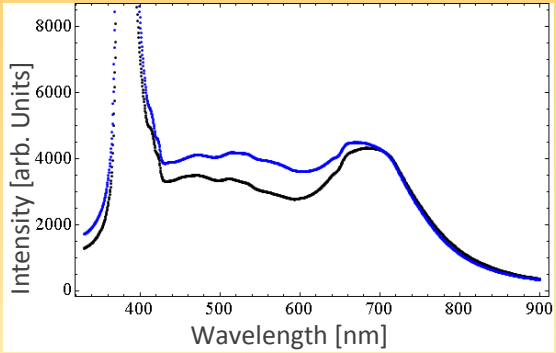
Overlay of EL and FL

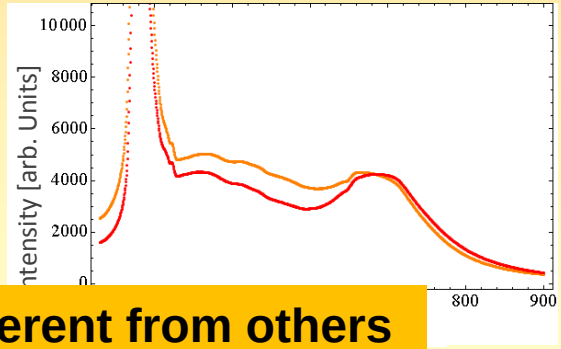
Schlothauer J., Jungwirth S., Röder B., Köhl M.: Photovoltaics International, 10 (2010) 149-154

Evaluation of EVA crosslinking efficiency



Preparation of the laminate

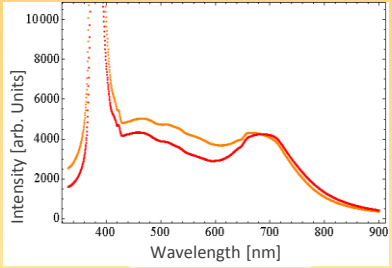


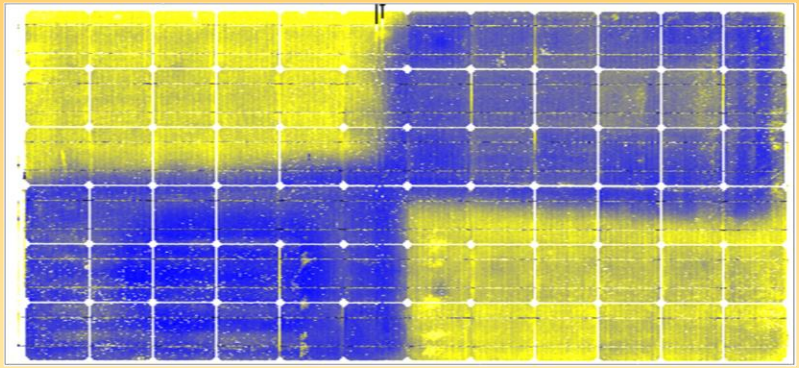


Scattering or luminescence of some cells is different from others

Evaluation of EVA crosslinking efficiency

Heuristically corrected luminescence image





Intensity at 460 nm, corrected by the intensity at 335 nm

Areas with one and two isolation layers can be distinguished

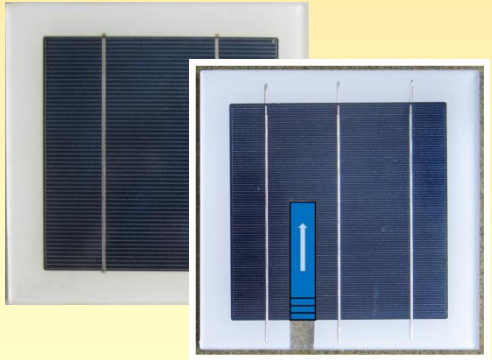
<u>Determination of crosslinking in PV Mini-modules:</u>

J.C. Schlothauer, C.Peter, Ch. Hirschl, G.Oreski, B. Röder: Non-destructive monitoring of EVA crosslinking in PV-modules by luminescence spectroscopy, J.Polymer Res., Nov. 2017, 24:233

Correlation to other material parameters

Investigation of PV mini modules (EVA-TPT)

Specimen	Type	Aging	Nominal duration
A-ref	Solon 2010	None	Reference
A-H	Solon 2010	H85	2600 h
A-DH	Solon 2010	DH (85/85)	2600 h
B-ref	Solon 2013	None	Reference
B-UV	Solon 2013	UV	180 kWh
B-H	Solon 2013	H85	2600 h
B-DH	Solon 2013	DH (85/85)	2600 h



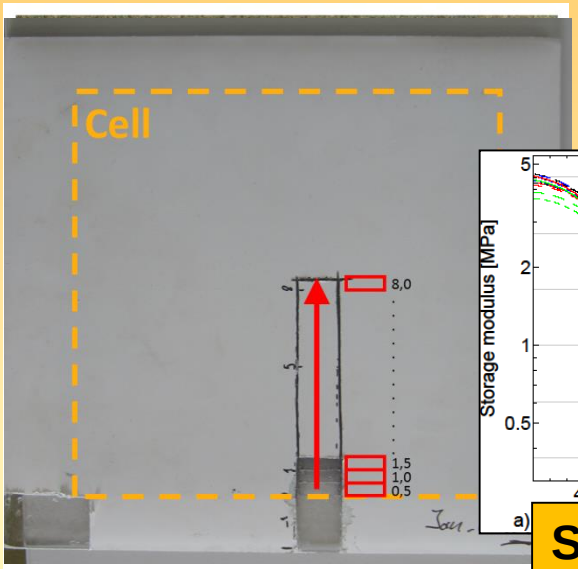
Methods

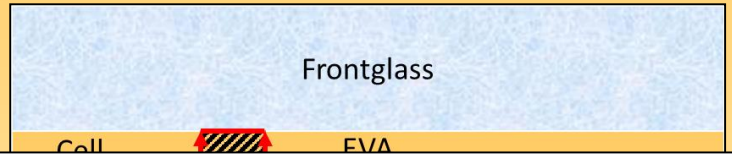
- *Luminescence*
- Dynamic mechanical analysis (DMA)
- Differential scanning calorimetry (DSC)
- Attenuated total reflection (ATR)
- Analysis of stabilizers

J.Schlothauer, B. Röder in: Servivce Life Prediction of Polymers and Plastics Exposed to Outdoor Weathering, Eds. C.C White, K.M. White, J.E.Pickett, pp161-183, Elsevier, William Andrew, 2017

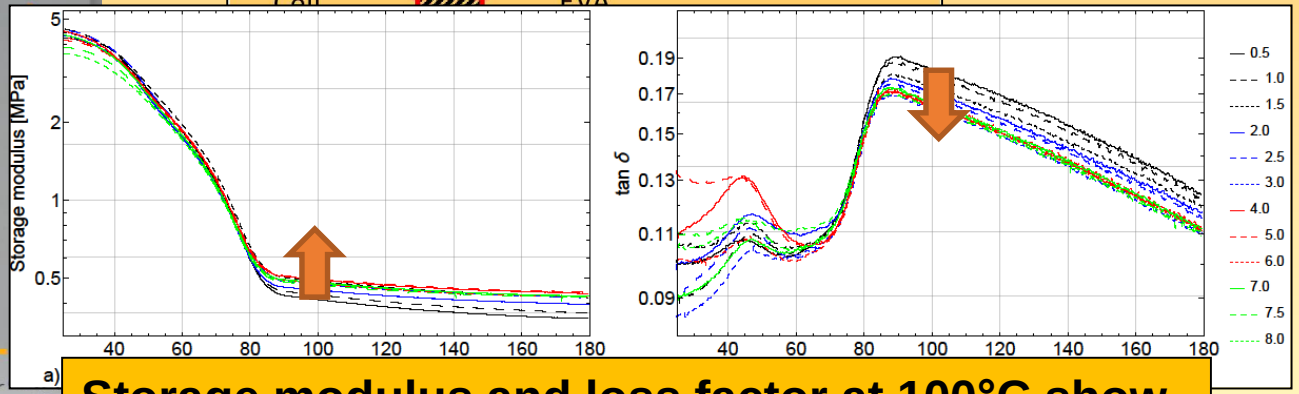
Investigation of EVA Samples by DMA

Extraction of EVA Samples





DMA thermal scans



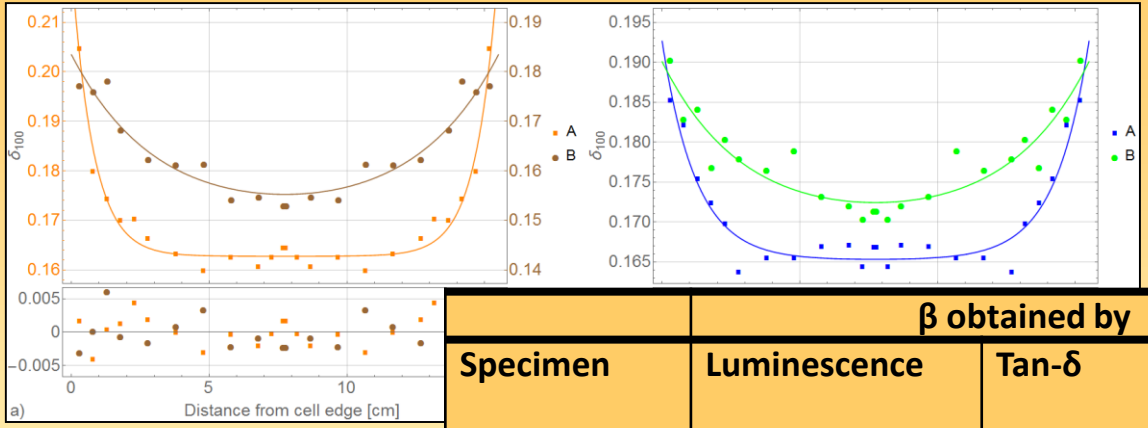
Storage modulus and loss factor at 100°C show a systematic change with sample location

Changes of crosslinking are the most likely reason

Correlation of DMA parameters and luminescence

H

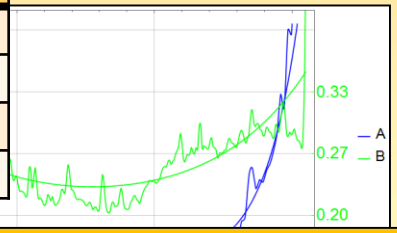
DH



Loss factor from DMA

	β obtained by		
Specimen	**Luminescence**	**Tan-δ**	**Storage modulus**
A - H	0.57	1.28	0.89
B - H	0.39	0.39	0.35
A - DH	0.81	0.82	1.24
B - DH	0.33	0.34	0.27

Luminescence



fitted with a function base

on first-order DLO:

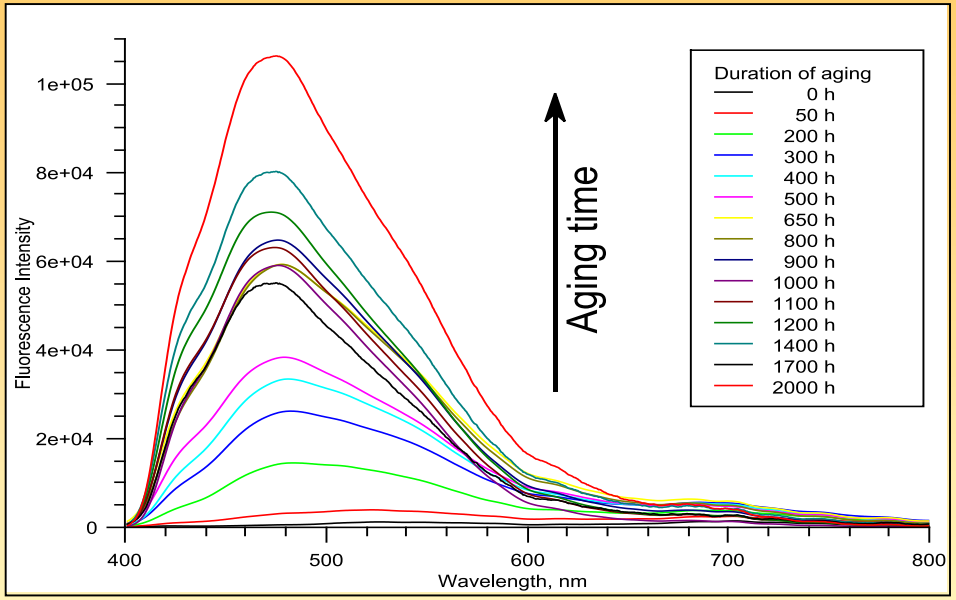
1) Luminescence intensity, storage modulus and loss factor at 100°C can be described by first-order DLO kinetics

2) The spatial pattern of luminescence and DMA are correlated

Conclusions

- **Luminescence intensity is an indicator for ageing time indoor and outdoor**
- Diffusion processes (mostly O_2) enable destruction of chromphores in the polymer resulting in decreased luminescence intensity
- The shape of the spectrum is different for DH and UV ageing (for higher UV intensities)
- **UV aging and outdoor weathering cause similar luminescence patterns**
- Spectral effects of UV and DH ageing can be separated also in case of outdoor weathered modules
- Using minimized Multi Stress Cabinet developed at HU Berlin different ageing parameters can be applied and differences in degradation behaviour can be analysed
- **Luminescence can be used for crack inspection (e.g. age of cracks)**
- It can be used for PV module inspection: in- and out-door
- **Luminescence can be used for evaluation of EVA coss linking efficency in PV-modules**
- **Luminescence correlates with other material parameters**

What about spectral distribution of luminescence ?



General Aspects of Degradation-Induced Polymer Luminescence
New Insights and Perspectives

S. Jungwirth, B. Röder, J. Schlothauer, M. Köhl: 5th European weathering symposium: Natural and Artificial Ageing of Polymers (2011) 337-346

Polymer Luminescence: A very short historic overview

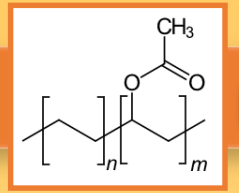
- Increase of emission intensity
- Bathochromic shift of excitation and emission spectra
- Emission maxima shift with excitation wavelength
- Luminescence universal between polymers
- Kinetics dependent on stabilizers
- Spectra comparable under photo- and thermal degradation

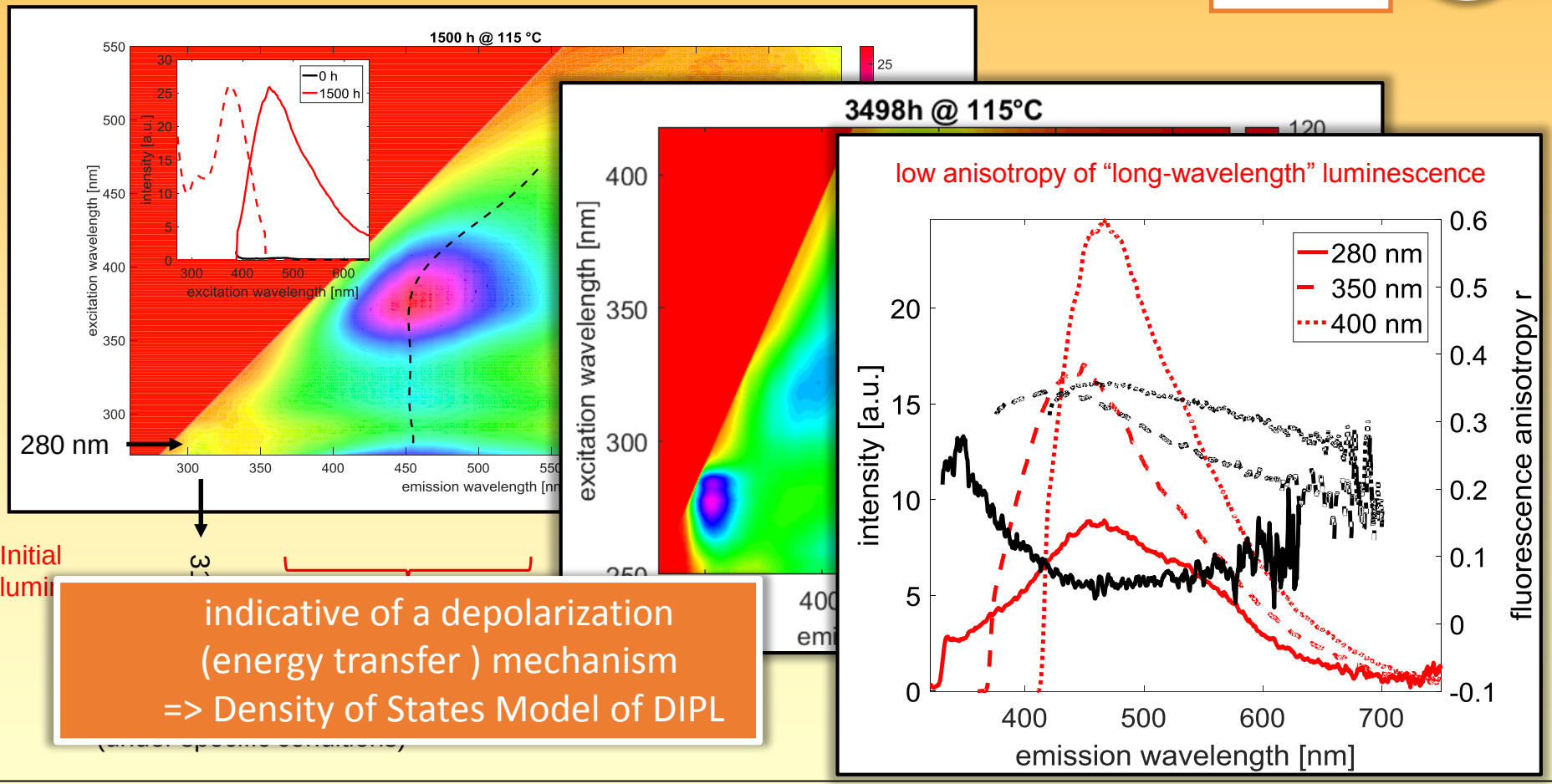
Identified degradation products:

- (α,β-unsaturated) carbonyl states
- (various length) polyenes
- oligoenimines

- ► Very complex spectro-temporal changes
- ► No kinetic evaluation of the luminescence signal was possible.

Thermo-Oxidative Degradation of EVA



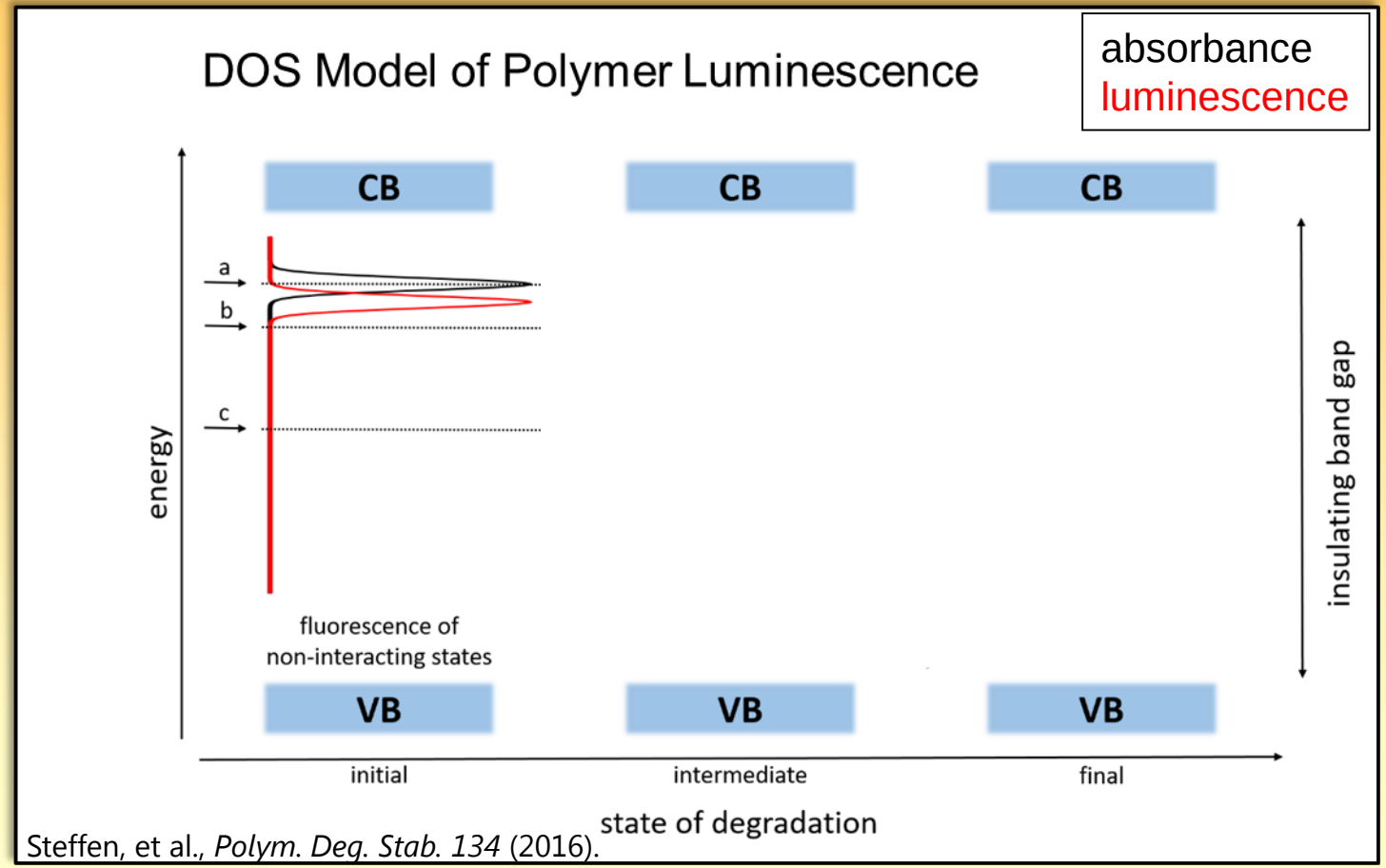


Initial lumi

indicative of a depolarization (energy transfer) mechanism
=> Density of States Model of DIPL

Steffen, et al., *Polym. Deg. Stab. 134* (2016).

The Density of States Model of Degradation-Induced Polymer Luminescence



Steffen, et al., *Polym. Deg. Stab. 134* (2016).

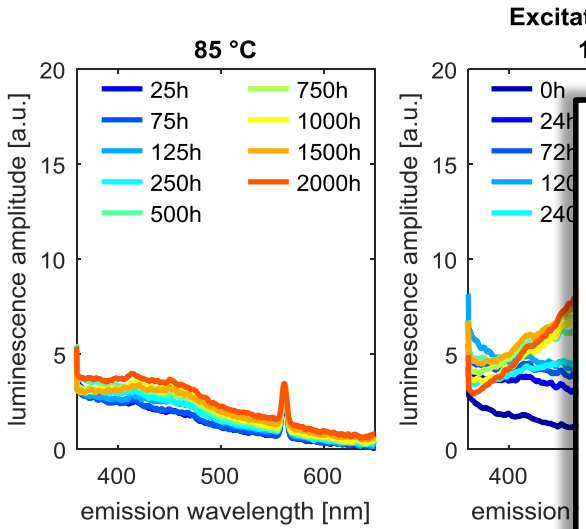
increase

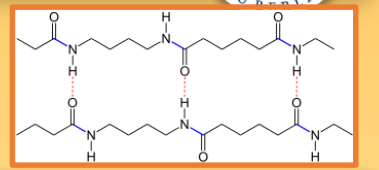
bathochromic shift of excitation and emission spectra

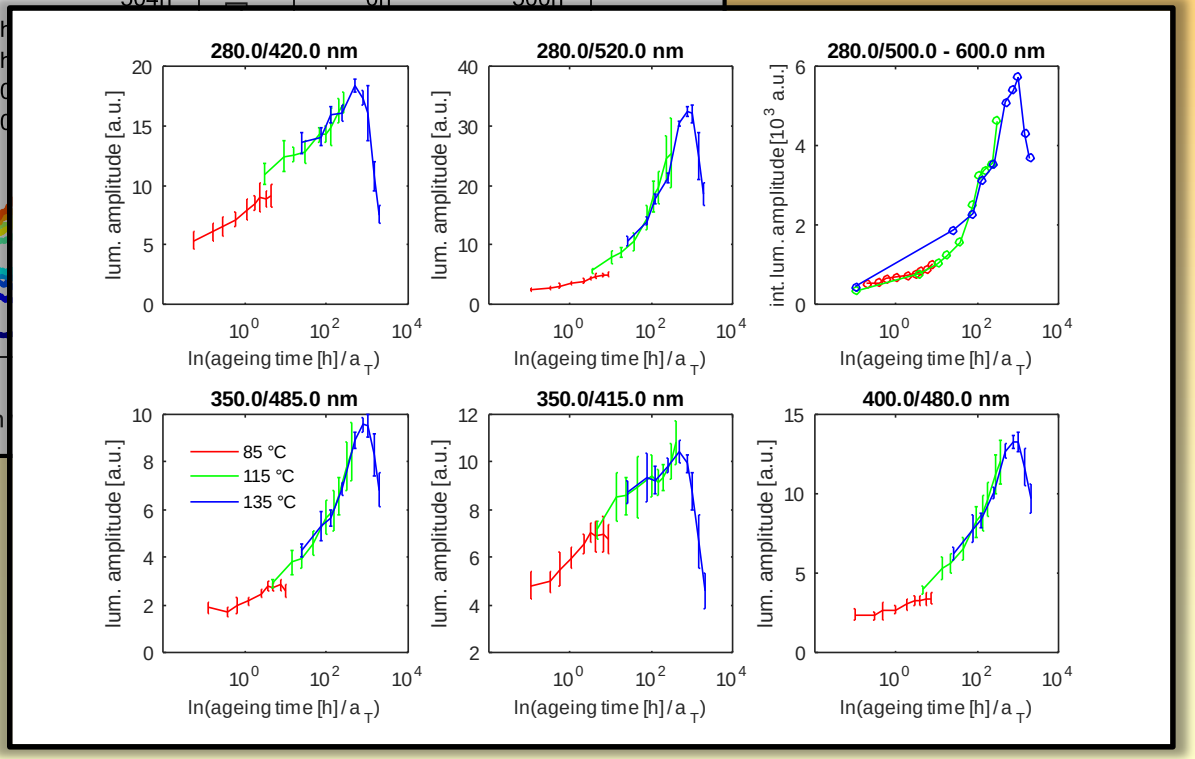
excitation wavelength dependent shift

Quantification of kinetic parameters : Thermal Degradation of Polyamide

Steffen, et al., *Polym. Deg. Stab.* 140 (2017).





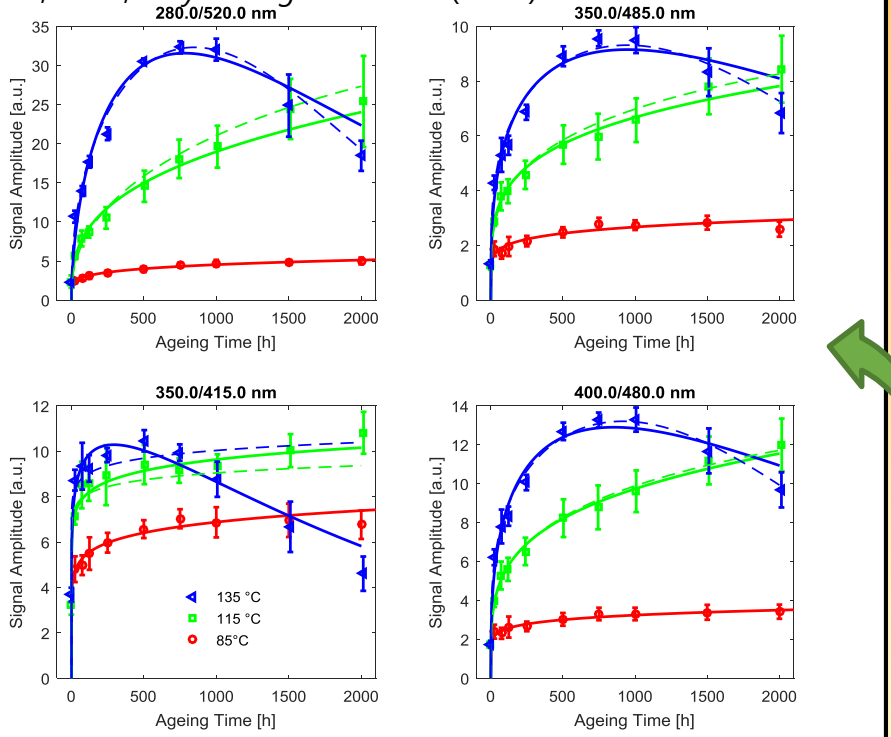


Kinetic analysis by Time-Temperature-Superposition confirms Arrhenius behavior with $E_A \approx 110 - 120$ kJ/mol.

Consistent with literature

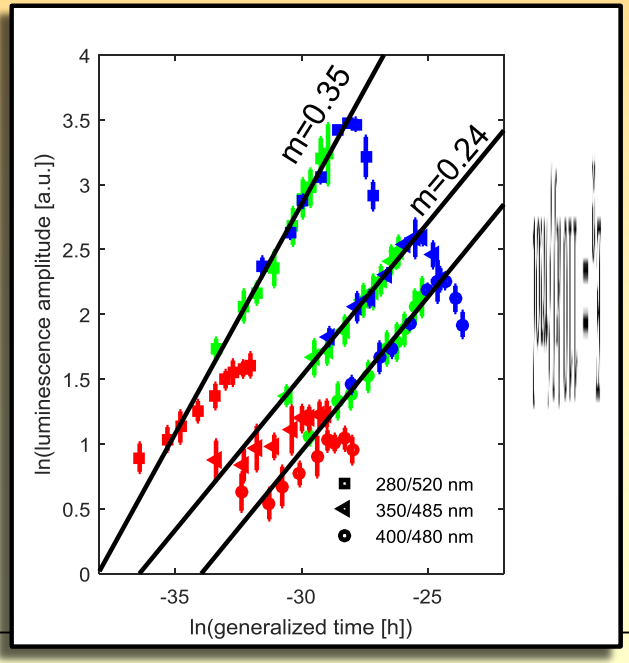
Modelling of Degradation Kinetics: Polyamide – Generalized Time Master Plot

Steffen, et al., *Polym. Deg. Stab.* 140 (2017).



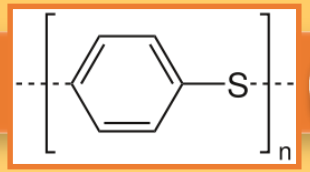
global fits

1) Plot against generalized time (Ozawa 1965): $\theta = t * exp(-E_a/RT)$
2) Double-logarithmic variable transformation for linearization (power law kinetics)
3) Decrease described by DOS-Model

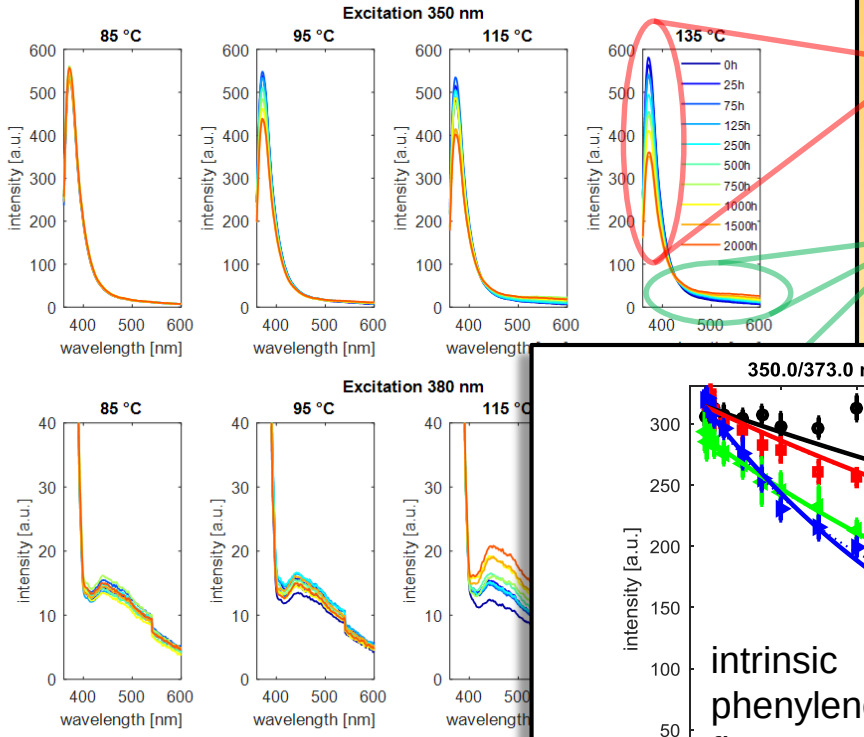


$$I_{\lambda_{em}}(T,t) = a * [k(T) * t]^m * \frac{1}{\sqrt{2(\Delta\lambda)^2\pi}} e^{-\frac{(\lambda_{em}-\mu_0-k(T)t)^2}{2(\Delta\lambda)^2}}$$

Quantification of kinetics: Thermal Degradation of PPS



Steffen, et al., *Polymer* (submitted).



backbone intrinsic phenylene fluorescence

degradation-induced luminescence (DIPL)

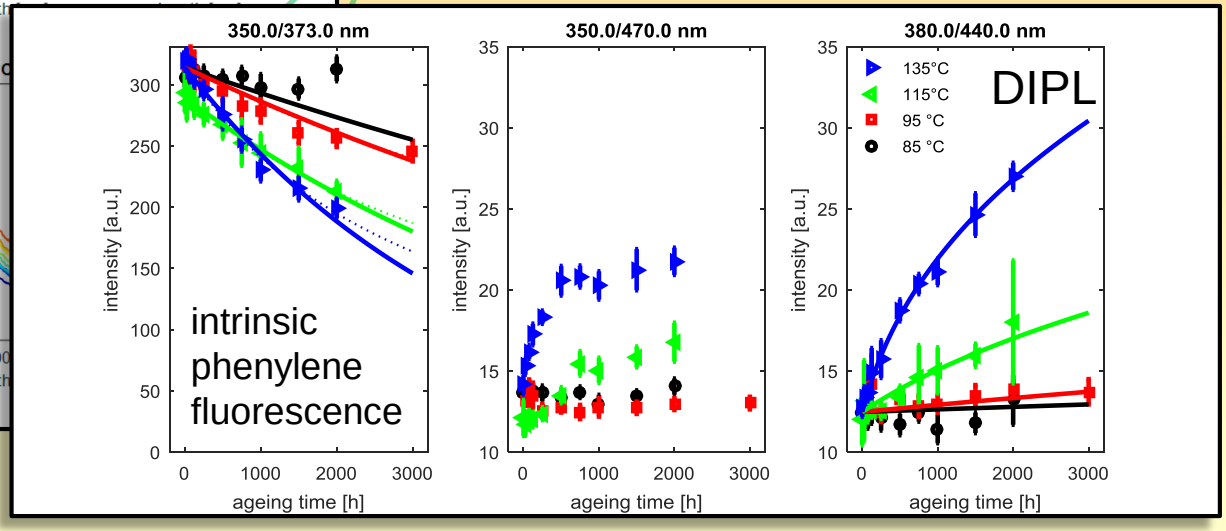
1sr or 2nd order kinetics

$E_a = 33\ kJ/mol$

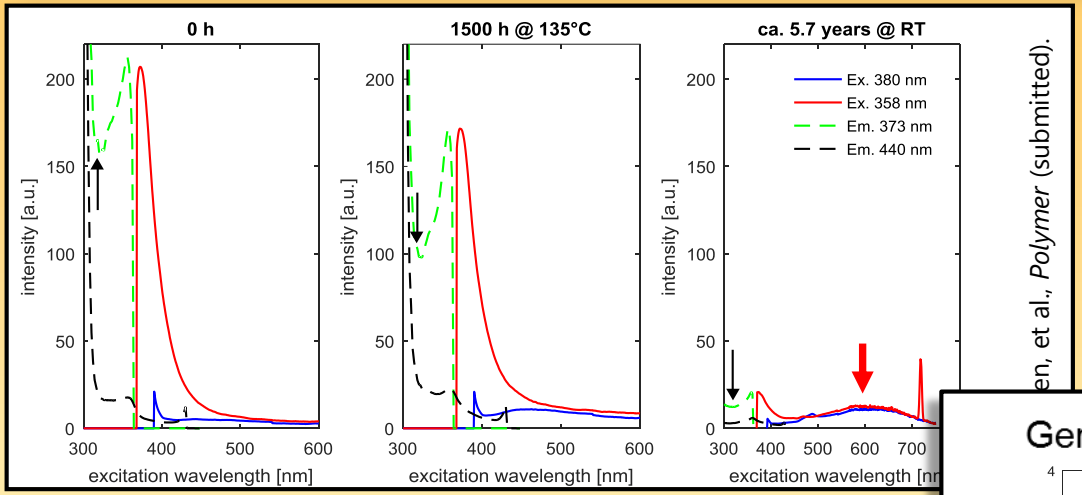
(secondary relaxation, viscous flow)

power law kinetics

$E_a = 113\ kJ/mol$



Predicting Degradation-Induced Polymer Luminescence at RT



Steffen, et al., *Polymer* (submitted).

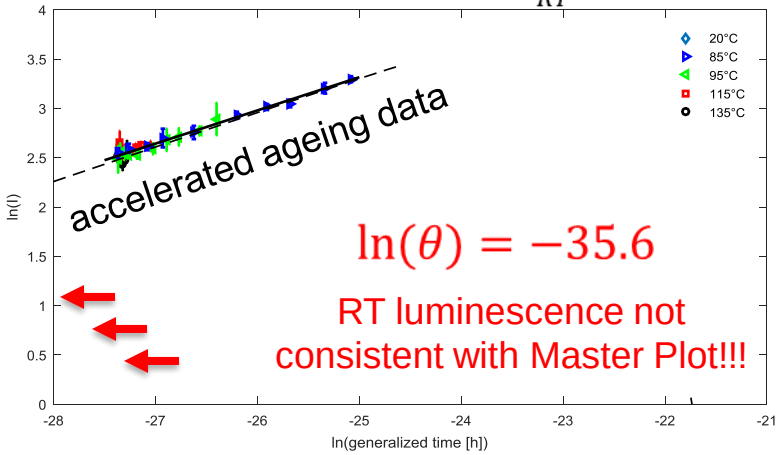
For 5.7 years at RT we obtain with $E_a = 113$ kJ/mol:

$$\ln(I_{440}) = 1.24$$
$$\ln(\theta) = -35.6$$

$$I_{\lambda_{em}}(T,t) = a * [A\theta]^m * \frac{1}{\sqrt{2(\Delta\lambda)^2\pi}} e^{-\frac{(\lambda_{em}-\mu_0-A\theta)^2}{2(\Delta\lambda)^2}}$$

$$\lambda_{em} = 440\ nm; \mathrm{m} = 0.35; \mathrm{E_a} = 113\ \mathrm{kJ/mol};$$
$$\mu_0 = 440\ nm; A = \cdots; \Delta\lambda = 200\ nm$$

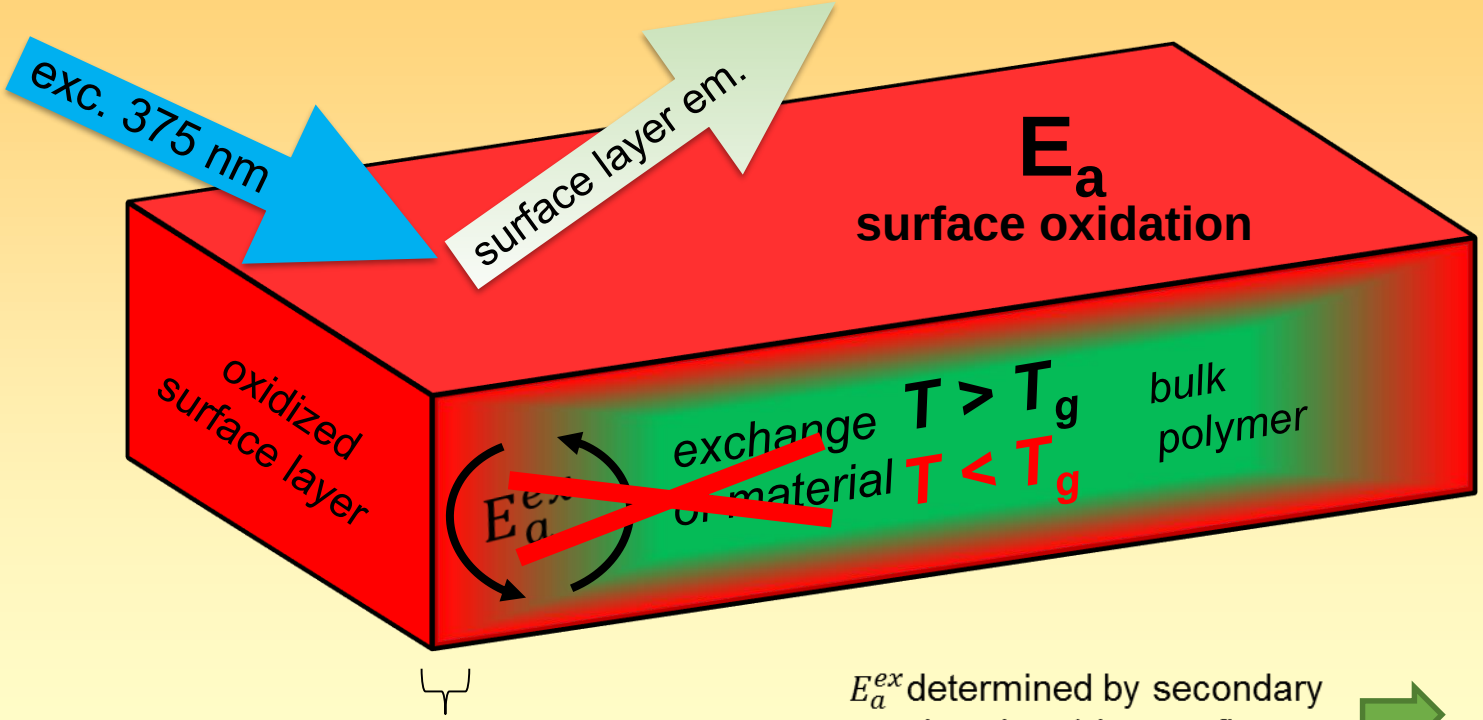
Generalized time $\theta = t * \exp(-\frac{E_a}{RT})$ Master Plot



Steffen, et al., *Polymer* (submitted).

Relationship between $E_a(T > T_g)$ and $E_a(T < T_g)$

$$E_a(T > T_g) = \mathrm{E_a(T < T_g)} + E_a^{ex}$$



Diffusion limited oxidation

$$E_a(T < T_g) =$$

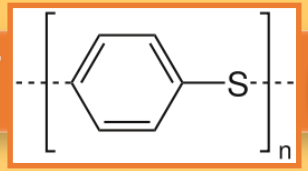
$$113\ kJ/mol$$

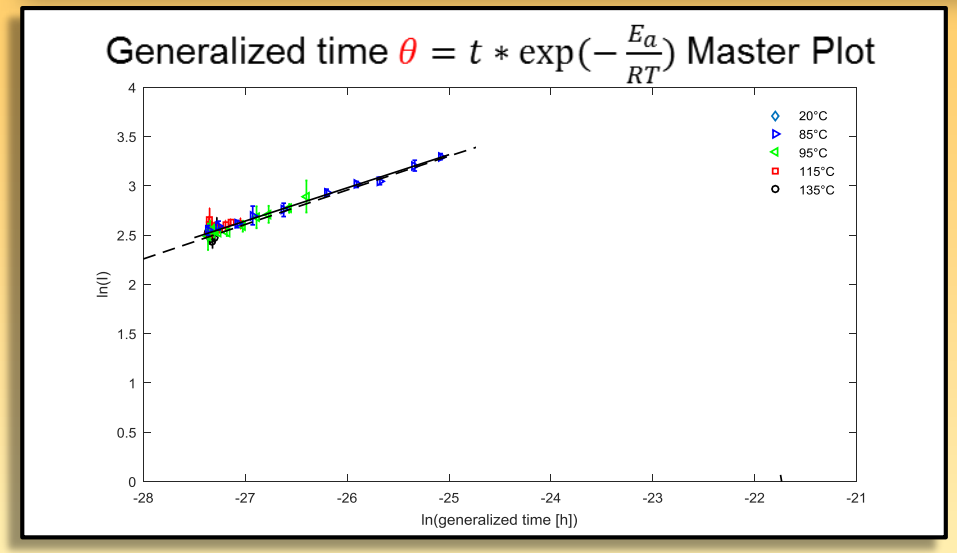
$$-33\ kJ/mol$$

$$80\ kJ/mol$$

E_a^{ex} determined by secondary relaxations/viscous flow ➡ given by phenylene fluorescence signal

Predicting Degradation-Induced Polymer Luminescence at RT



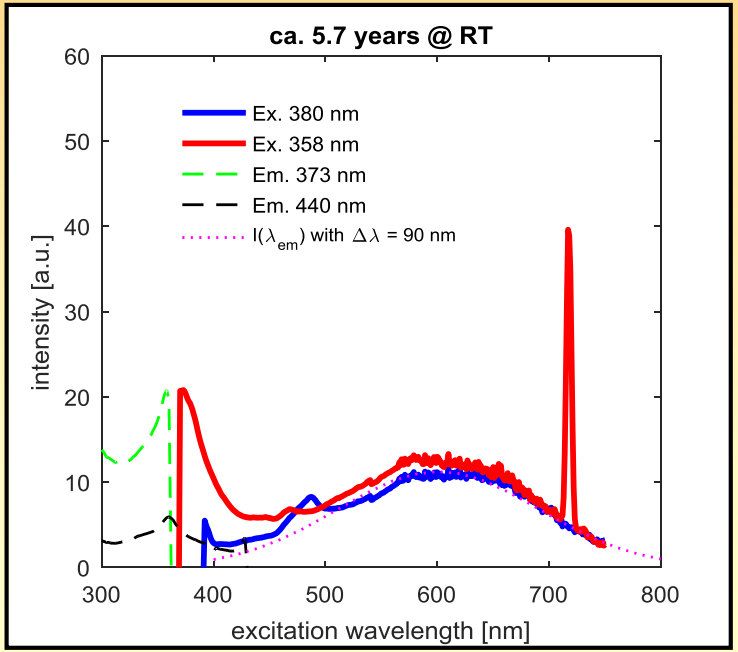


$$I_{\lambda_{em}}(T,t) = a * [A\theta]^m * \frac{1}{\sqrt{2(\Delta\lambda)^2\pi}} e^{-\frac{(\lambda_{em}-\mu_0-A\theta)^2}{2(\Delta\lambda)^2}}$$

$$\lambda_{em} = 440\ nm; \mathrm{m} = 0.35; \mathrm{E_a} = 113\ \mathrm{kJ/mol};$$
$$\mu_0 = 440\ nm; A = \cdots; \Delta\lambda = 200\ nm$$

For 5.7 years at RT we obtain with $\mathrm{E_a} = 80\ \mathrm{kJ/mol}$:

$$\ln(\theta) = -22$$
$$\ln(I) = 1.24$$



Summary

- We developed a Density of States (DOS) model of Degradation-Induced Polymer Luminescence that is able to consistently explain all observed spectral and kinetic properties of the luminescence signal
- We were able to extract quantitative information on kinetic parameters like, e.g. the apparent activation energy the can be used for polymer lifetime prediction
- We suggested a model to relate measured E_a above and below T_g that enables the prediction of the spectral development of the luminescence over many years of exposure at RT

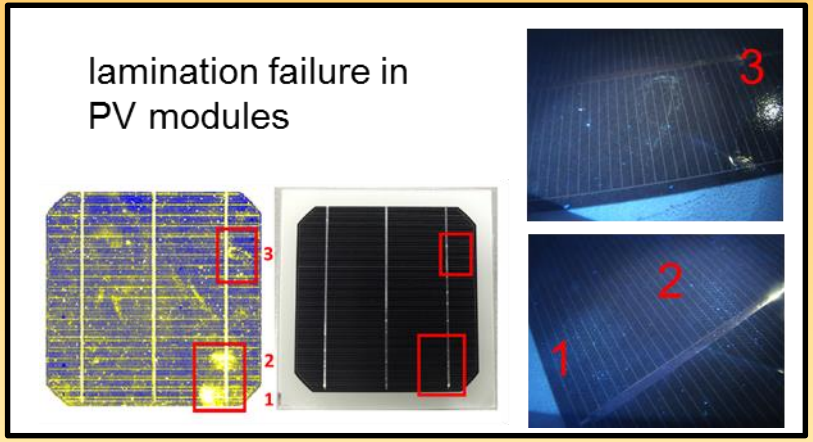
Applications of Degradation-Induced Polymer Luminescence

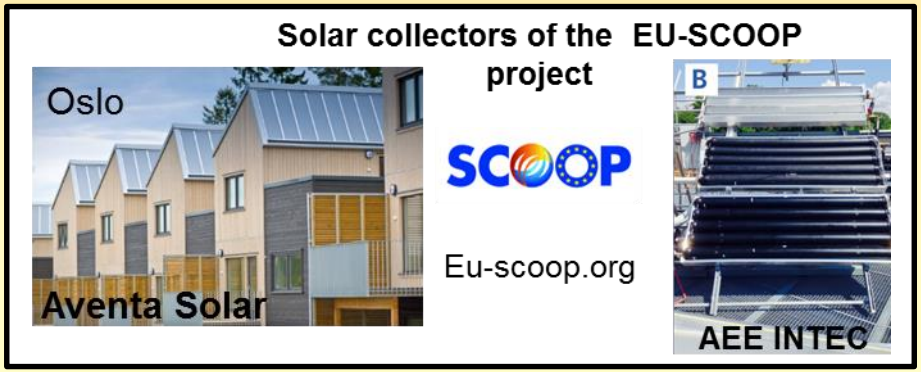
- non-invasive and very sensitive technique
- easy to implement (e.g. mobile system)

We applied the method in different fields:
- PE, PP as cable insulation material
- EVA for photovoltaic applications
- PA, PPS, PP for solar thermal collectors

- Quality control and characterization of failure modes in PV modules under outdoor weathering / accelerated ageing

More recently we were able to use DIPL for:
- Polymer lifetime characterization /prediction, i.e. quantification of kinetic parameters like apparent activation energy of the degradation process





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