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LIFETIME PREDICTION OF THERMOPLASTIC ELASTOMER IN MARINE ENVIRONMENT

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General Context

Elastomers needed for marine applications (seal, protection)

Currently, **thermoset elastomers** are broadly used

- High chemical resistance
- Well known behaviour

1842: Vulcanization of NR by C. Goodyear

Thermoset Elastomers

They meet specifications

But… processing is laborious

- Compounding (curing system, filler, plasticizer…)
- Mixing
- Processing (extrusion, injection, moulding…)
- Curing

And many chemicals are used

REACH regulation (June 2017)
→ Restrictions over EU chemicals industries

Some of the chemicals required for thermoset elastomer synthesis and processing are concerned

ECHA
EUROPEAN CHEMICALS AGENCY

REACH regulation
Registration, Evaluation, Authorisation and Restriction of Chemicals

Alternative solution : thermoplastic elastomer (TPE)

TPEs = block copolymers

- Soft block: amorphous and rubbery
- Hard block: ½ crystalline

Long molecular chains physically tied with crystallites

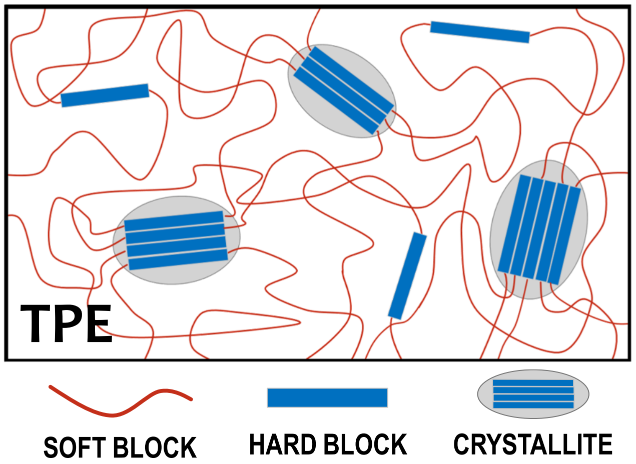
3D network, similar to thermoset

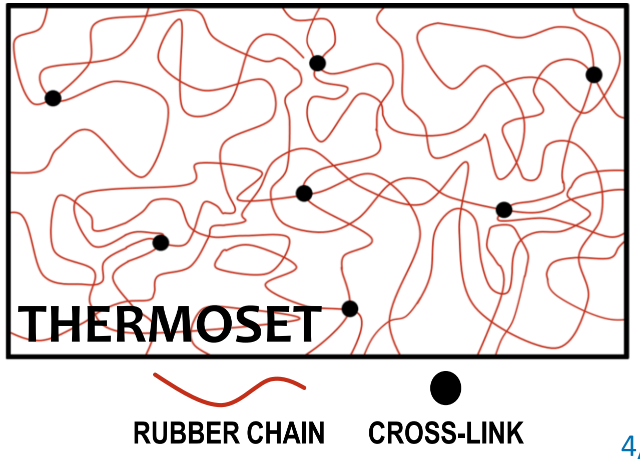
TPEs benefits :

- Less chemicals → REACH ✔
- Easily processed
- Reprocessable

But what about their behaviour in marine environment ?

How to predict their lifetime ?



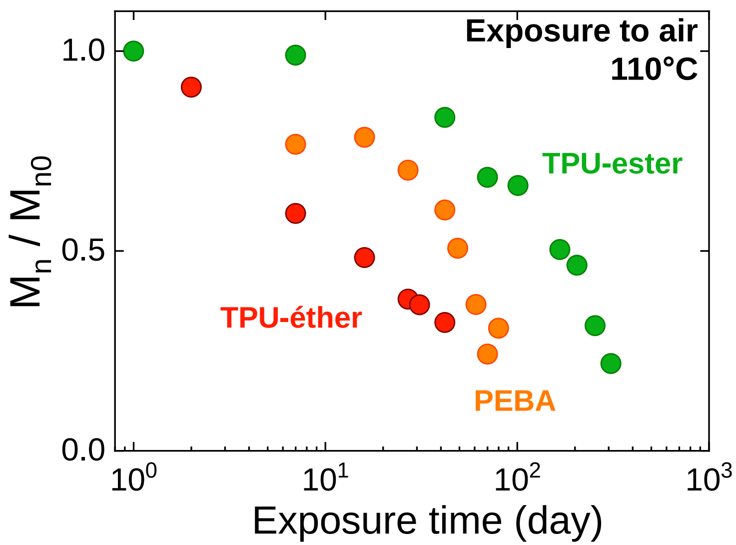


Materials

Marine environment : exposure to air and water

3 TPEs of different nature initially considered

	Soft block nature	Hard block nature	Resistance to water	Resistance to air
TPU-ester	Ester	Urethane	Bad	Good
TPU-ether	Ether	Urethane	Good	Bad
PEBA	Ether	Amide	Medium	Medium



TPU-ester highest resistance to air exposure

Water degradation will be the limiting phenomenon

Necessity to assess degradation kinetics induced by water to estimate lifetime

Lifetime prediction methodology: Arrhenius

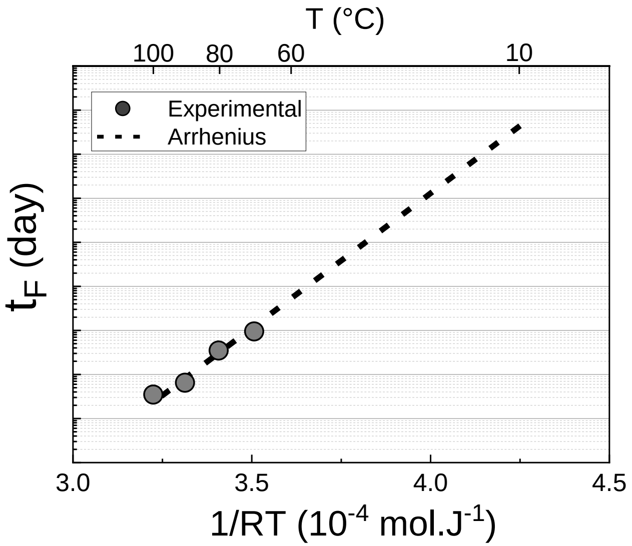
How lifetime prediction is made today ?

Usually, **Arrhenius law** is used to estimate the effect of temperature on ageing kinetics of polymers.

Assumption : “Polymer lifetime obeys Arrhenius law”

$$t_F = \tau_0 \exp\left(\frac{-E_a}{RT}\right)$$

t_F	Lifetime
τ_0	Pre-exponential constant
E_a	Activation energy (constant)
R	Ideal gas constant
T	Temperature



→ Accelerated ageing campaign

→ Extrapolation at real conditions temperature

Lifetime prediction methodology: Arrhenius

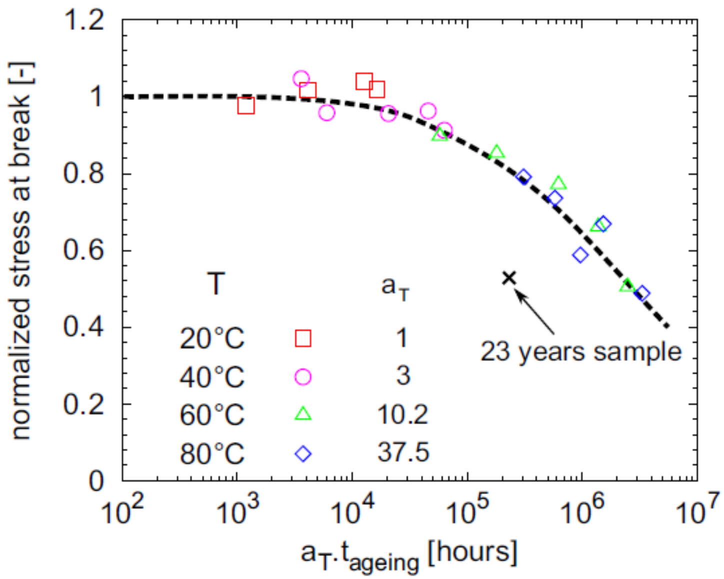
Attractive because extremely simple of use… But careful of over simplification.

Rigorously, Arrhenius law applies to the rate constant of an elementary chemical reaction

→ In most cases ageing process involves several mechanisms !

Example : CR rubber ageing in seawater

Comparison between Arrhenius extrapolation and naturally aged sample (23 years)

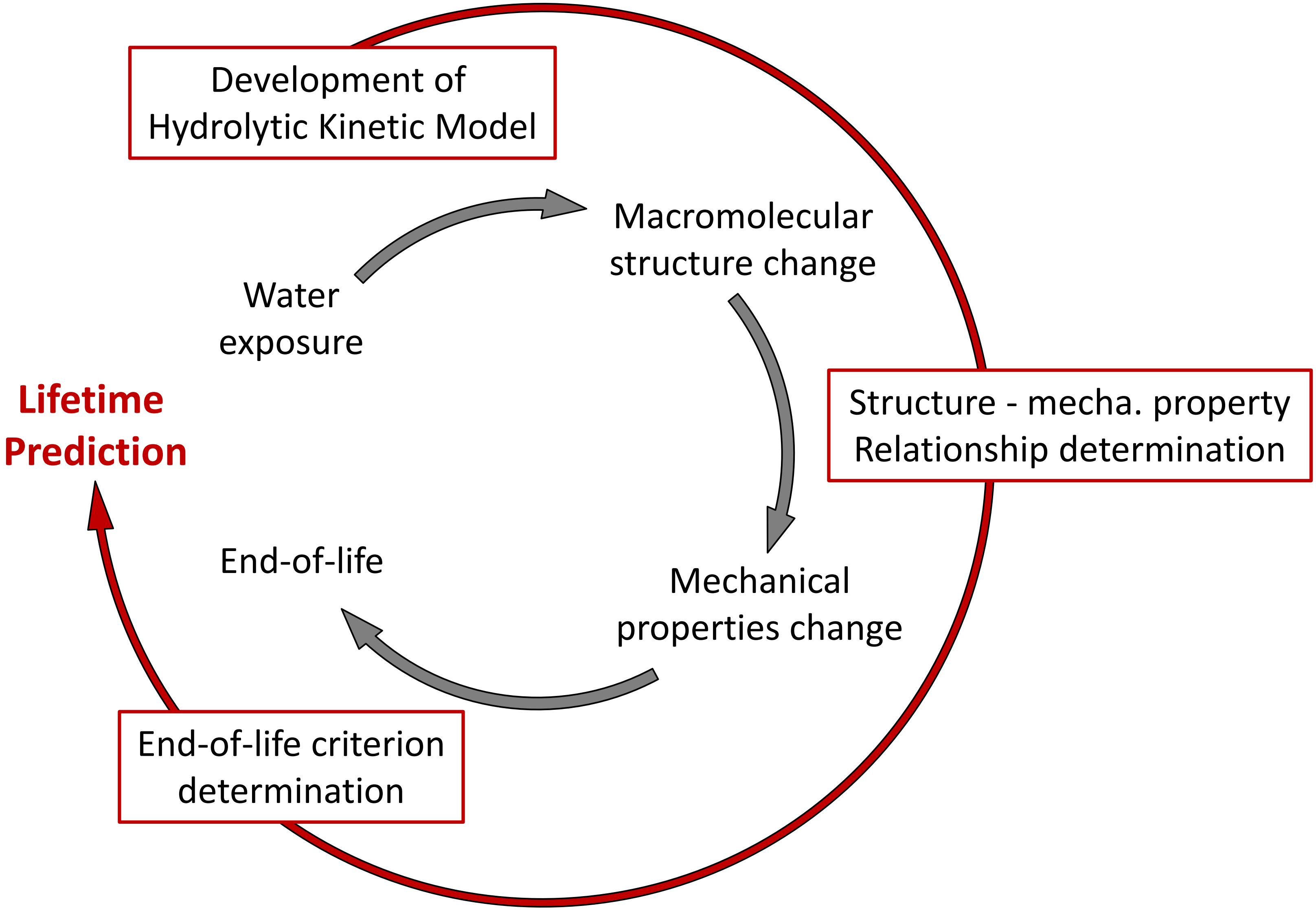


[Le Saux et al. 2013]

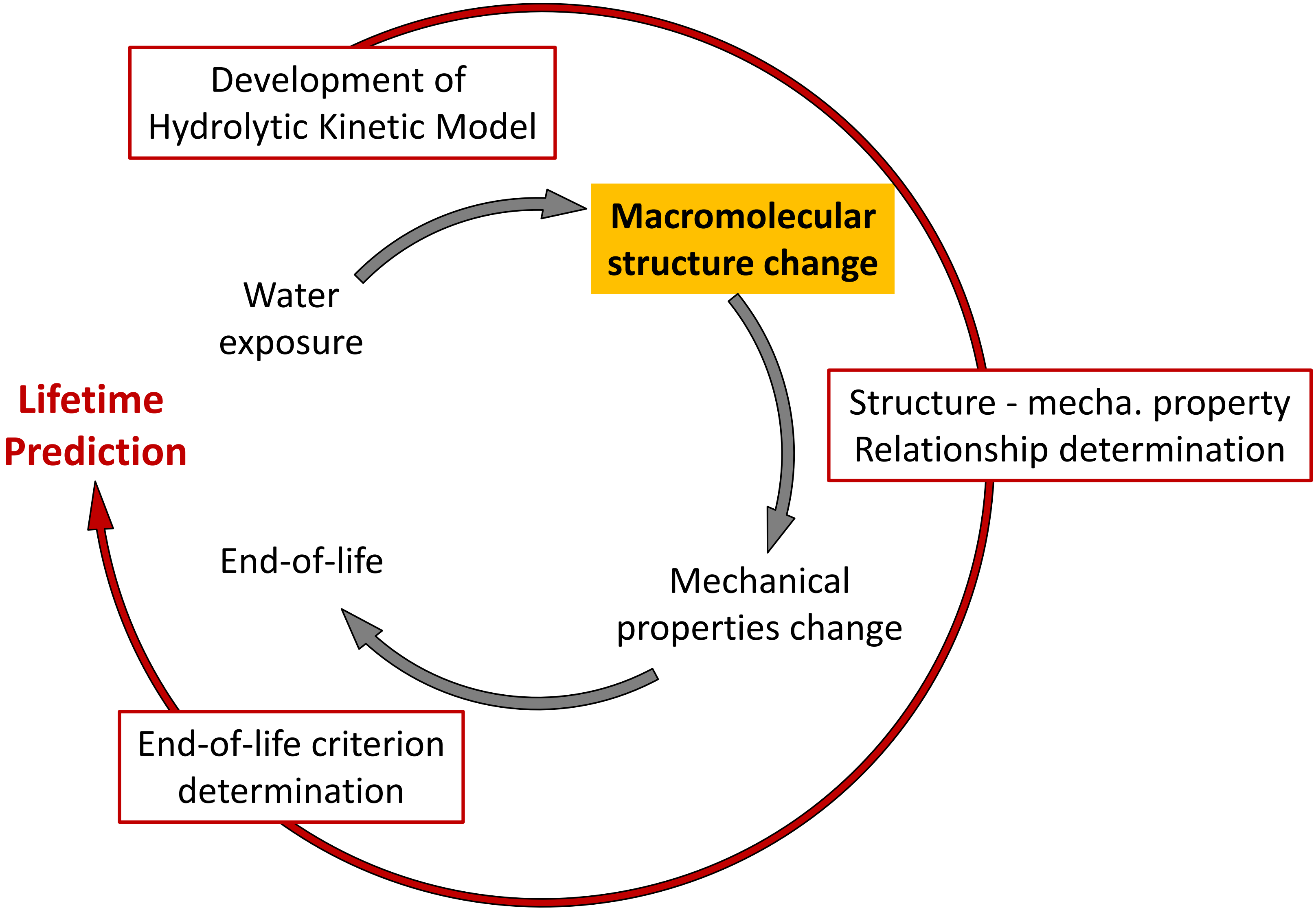
In most cases, Arrhenius law is actually not rigourously valid

→ **Necessity for a new lifetime prediction methodolgy**

Lifetime prediction methodology



Lifetime prediction methodology



Ageing conditions

Samples thickness chosen so diffusion phenomenon is not rate-limiting

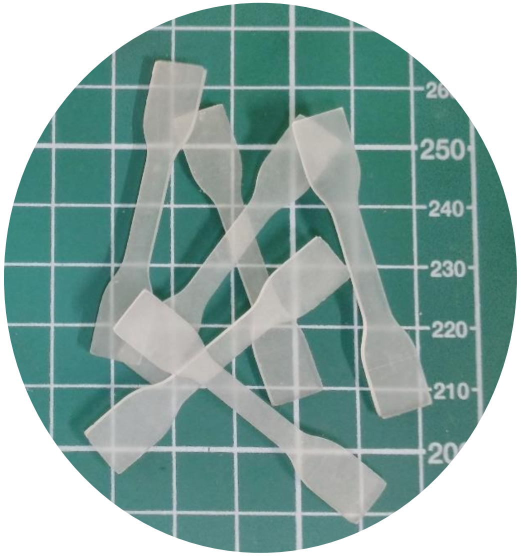
Annealing at 110°C for thermal stabilization

Immersion in natural seawater tanks

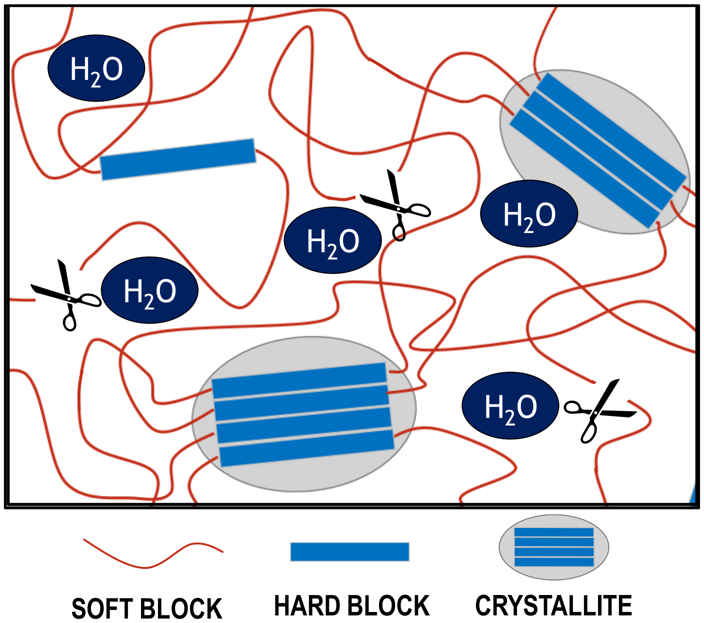
at 40, 60, 80 and 90°C

<u>Protocol</u>

- Immersion
- took out at determined time
- drying
- testing



Structure change: molecular chains scissions

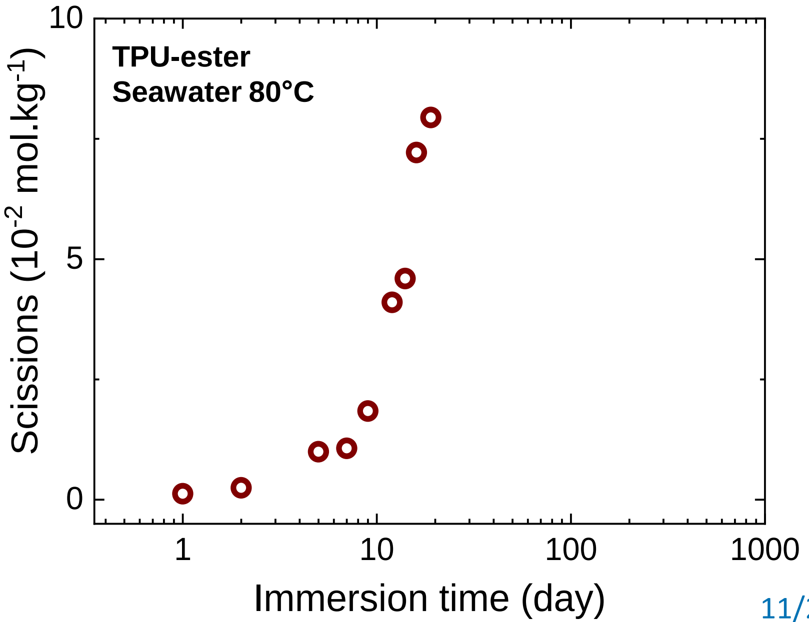


Water reacts with ester function (hydrolysis)

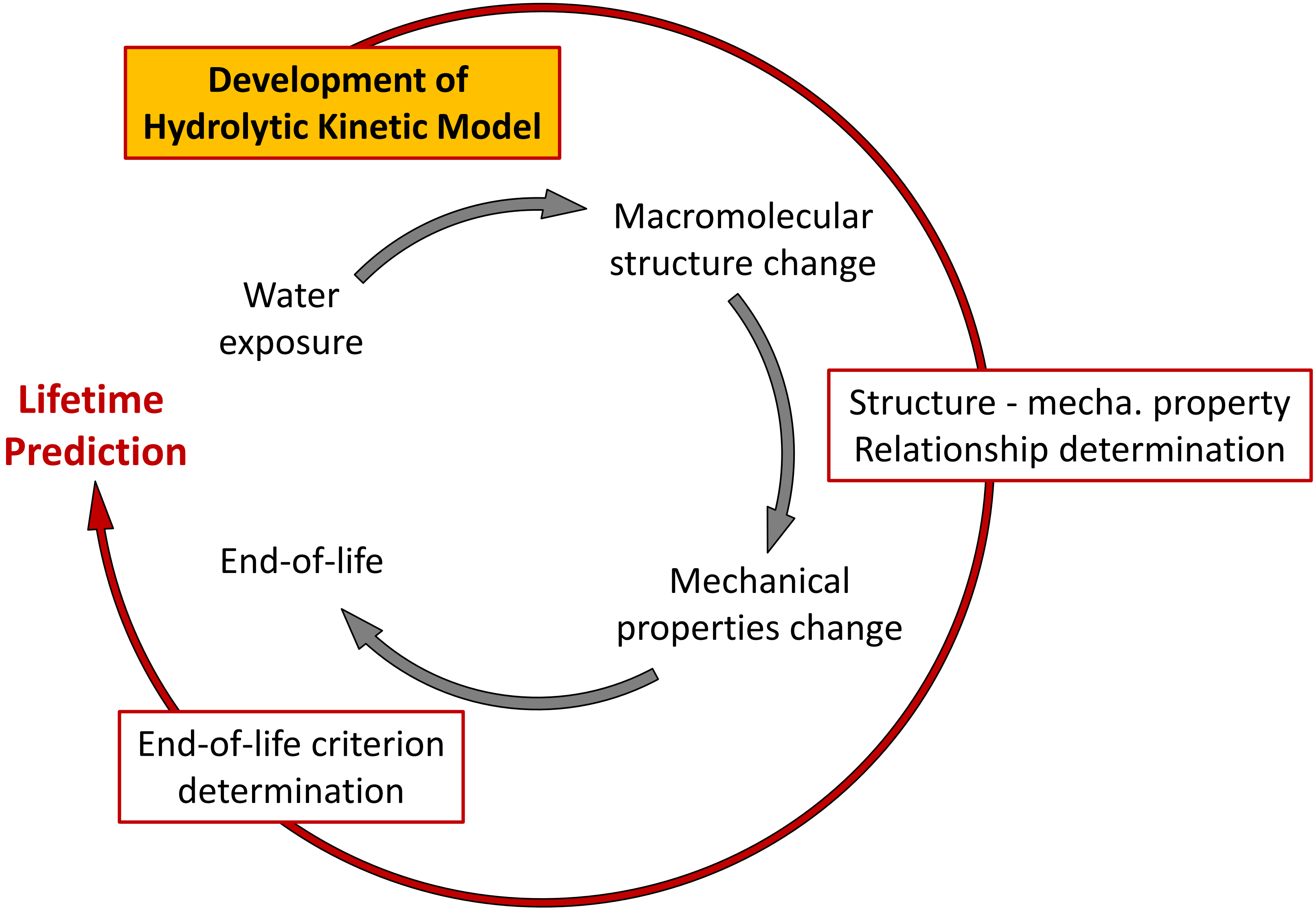
$$Ester + Water \rightarrow Carboxlyic\ acid + alcohol + \boldsymbol{scission}$$

The reaction causes a polymer chain scission

Macromolecular structural changes investigated through chains scissions (measured by GPC)



Lifetime prediction methodology



Scissions prediction: Hydrolytic kinetic model

Model based on chemical reactions intervening in ester hydrolysis

Input

[ester]$_0$

[water]$_0$

Reaction-rate constants

→

$$Ester + Water \xrightarrow{k_{Hu}} Carbox.Acid + scission$$

$$Ester + Water \xrightarrow{k_{Hc}\,(Acid)} Carbox.Acid + scission$$

$$Carbox.Acid \overset{K_a}{\leftrightarrow} proton$$

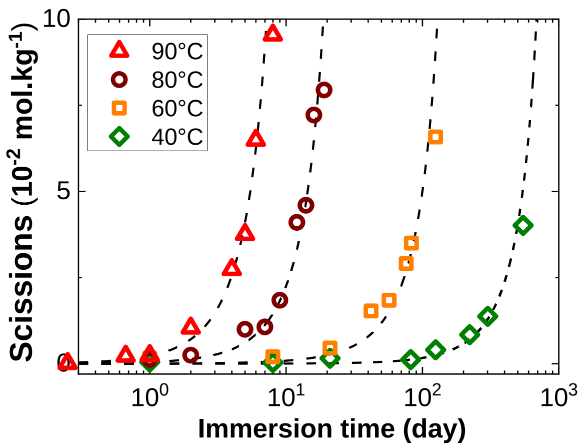
→

Output

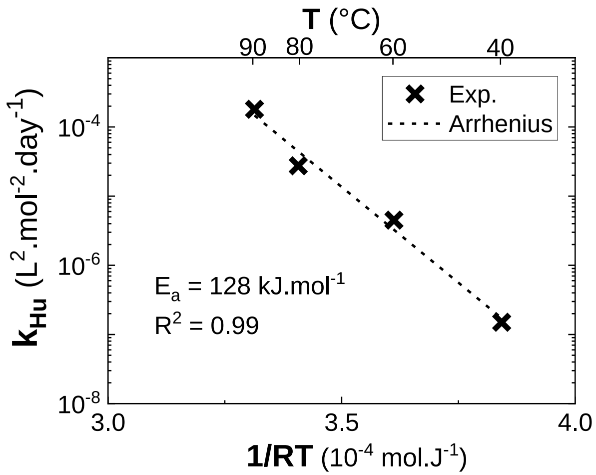
[scissions]

fct. immersion time

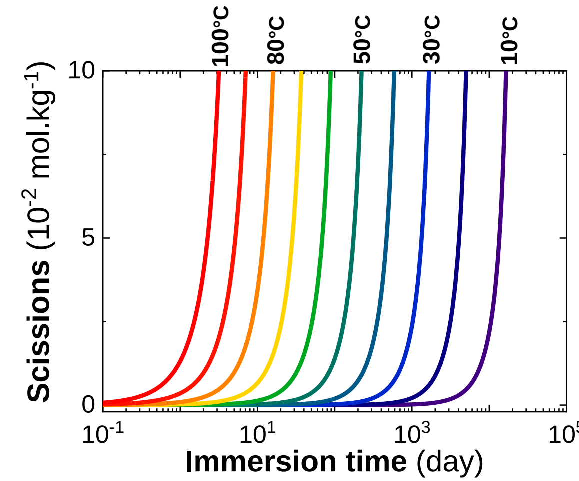
Constants adjusted so model fits experimental data



Constants temp. dependence is Arrhenian (valid !)

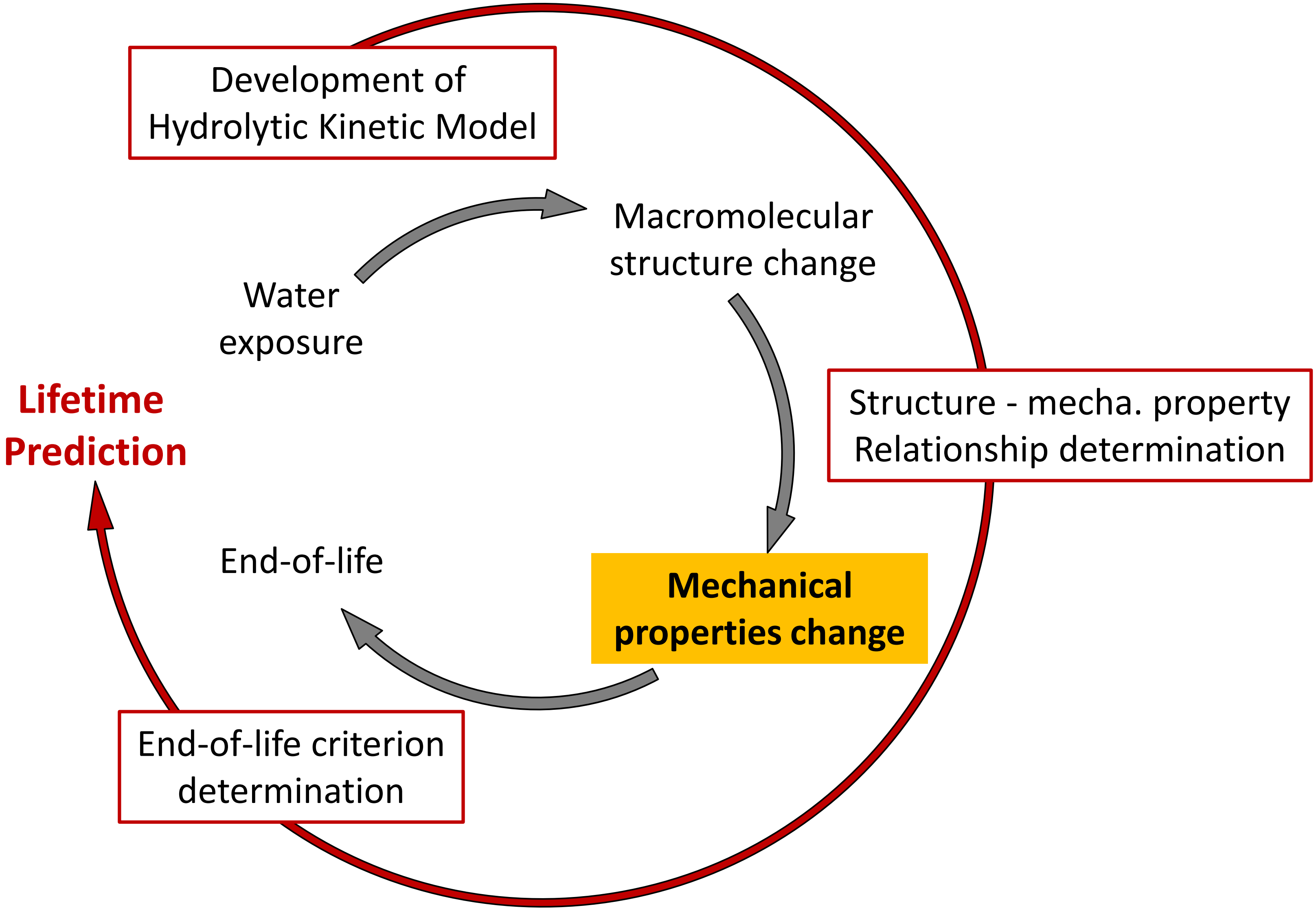


Scissions are predicted at any temp.



→ **Extrapolation of chain scissions at low ageing temperature**

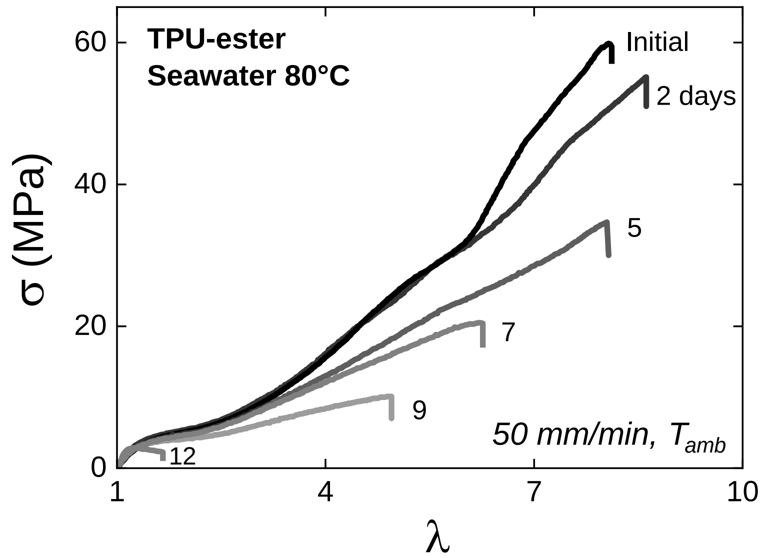
Lifetime prediction methodology



Mechanical properties change

<u>Characterized by uniaxial tensile test</u>

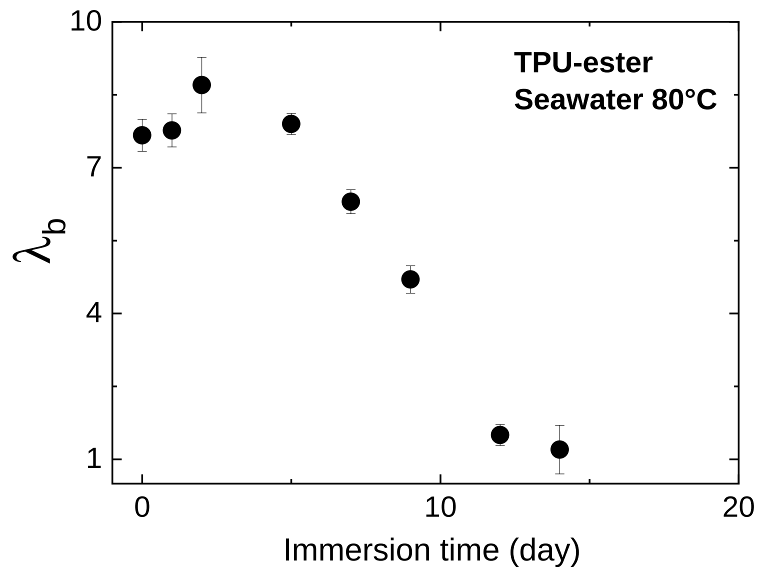
Mechanical behaviour is changed with immersion time

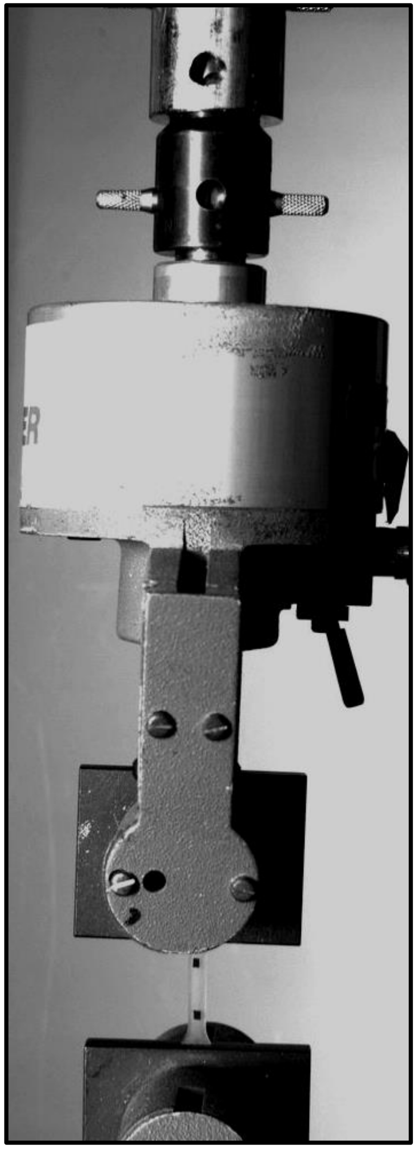


Property of interest :

Elongation at break λ_b

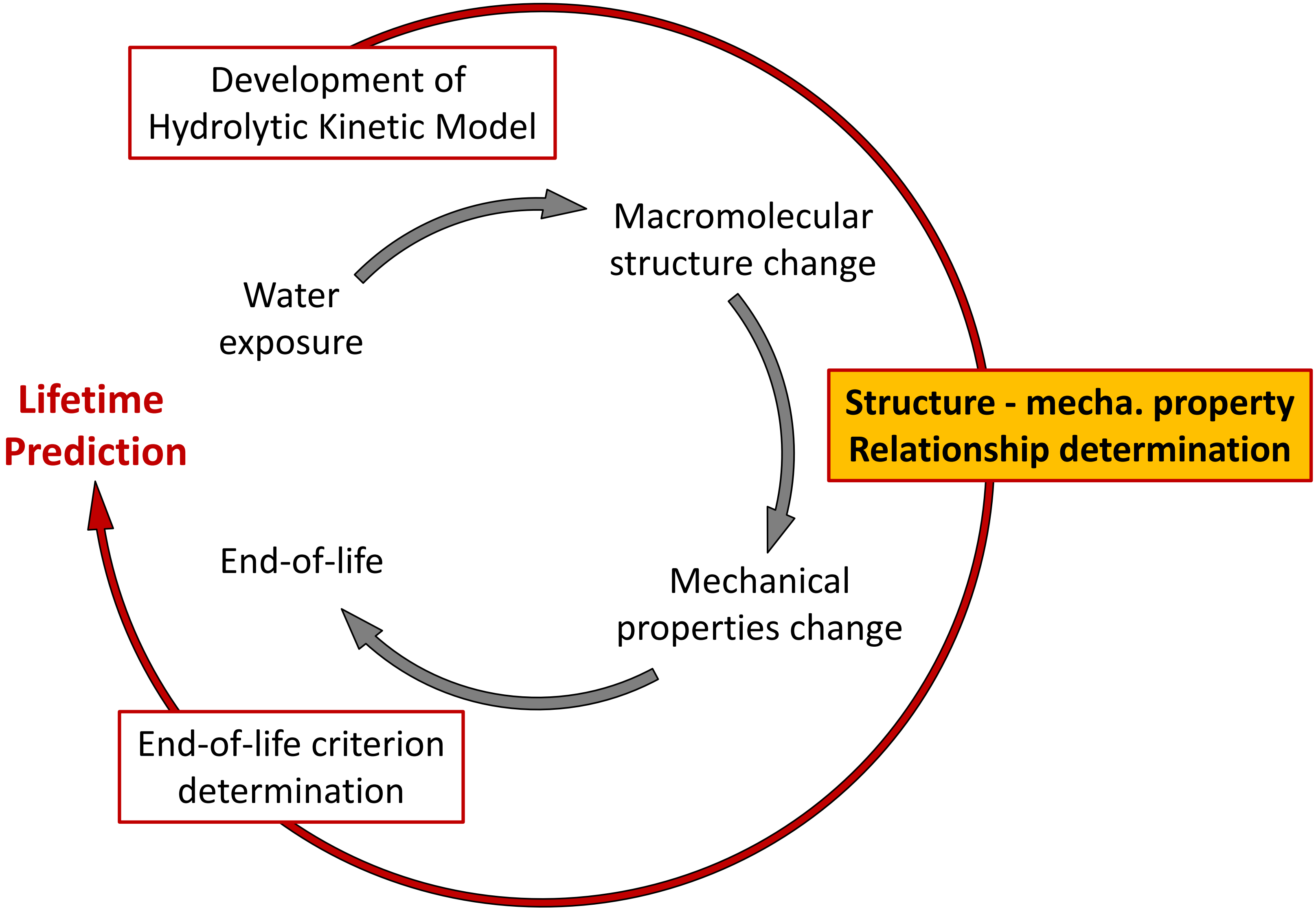
Shows a plateau and a drop





Accelerated x20

Lifetime prediction methodology



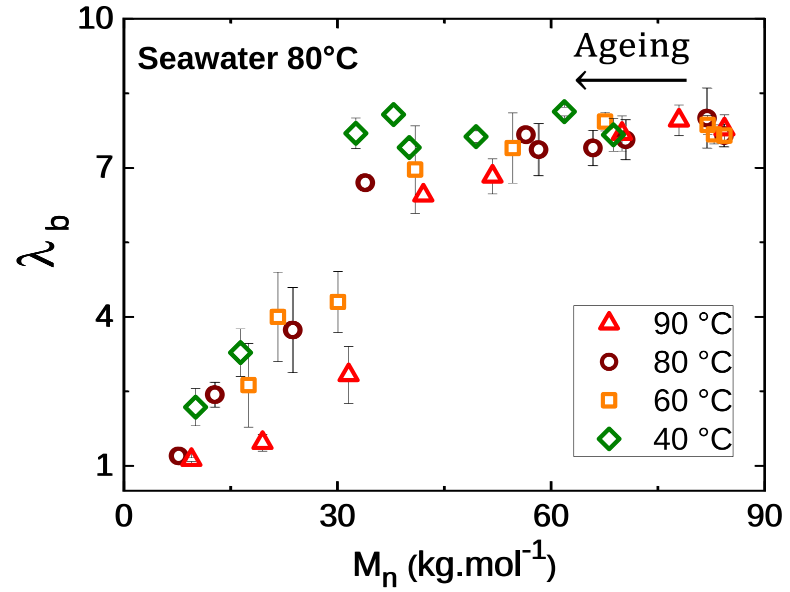
Structure – mechanical property relationship

Relationship between elongation at break and molar mass

Plateau + drop

Behaviour similar to thermoplastic polymers

Superposition of different ageing temp.
→ Master curve



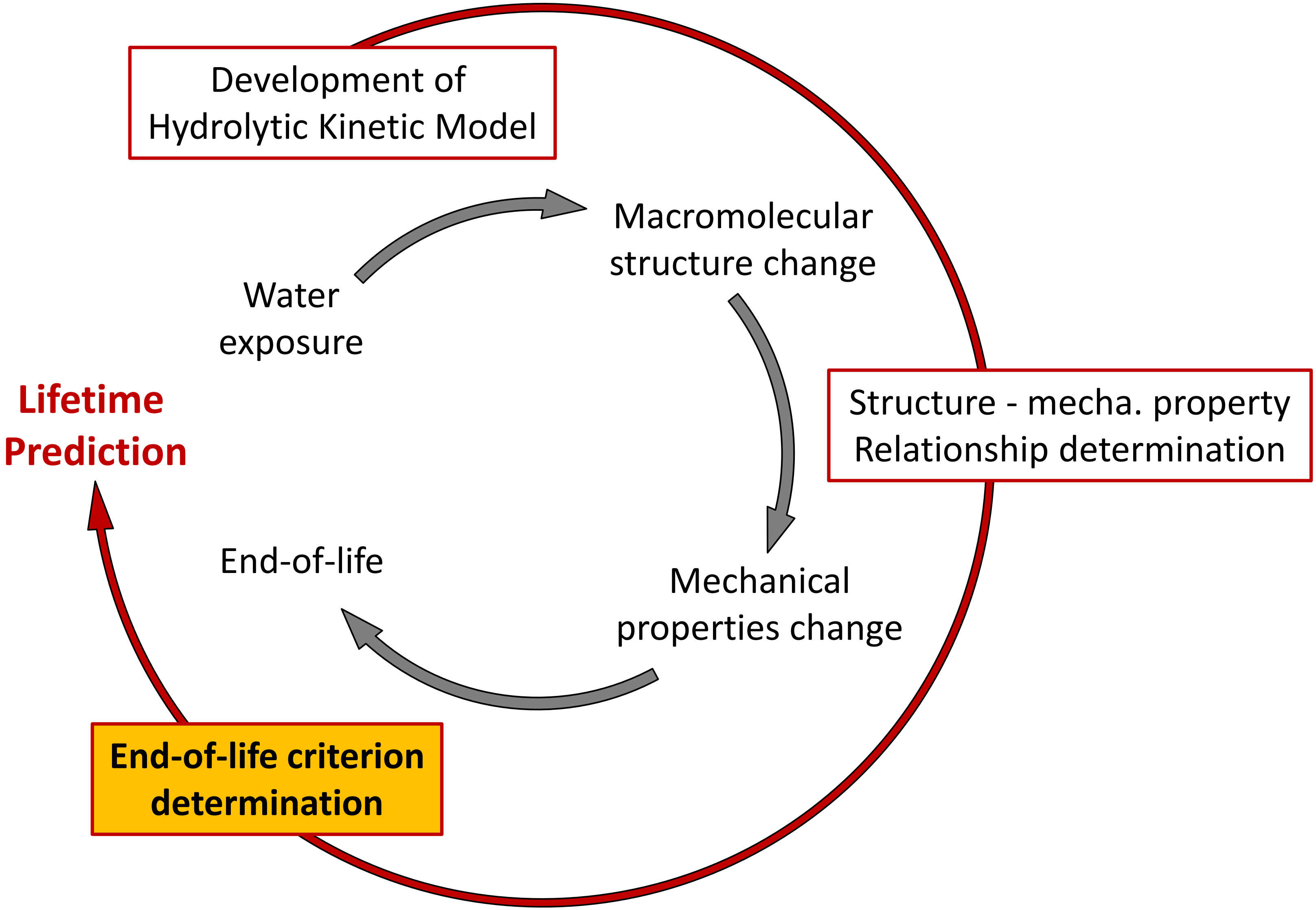
Relationship independent of degradation kinetics was highlighted

Note: molar mass M_n and scissions are equivalent

$$Scissions = \frac{1}{M_n} - \frac{1}{M_{n0}}$$

Both properties can be used to characterize material's structure

Lifetime prediction methodology

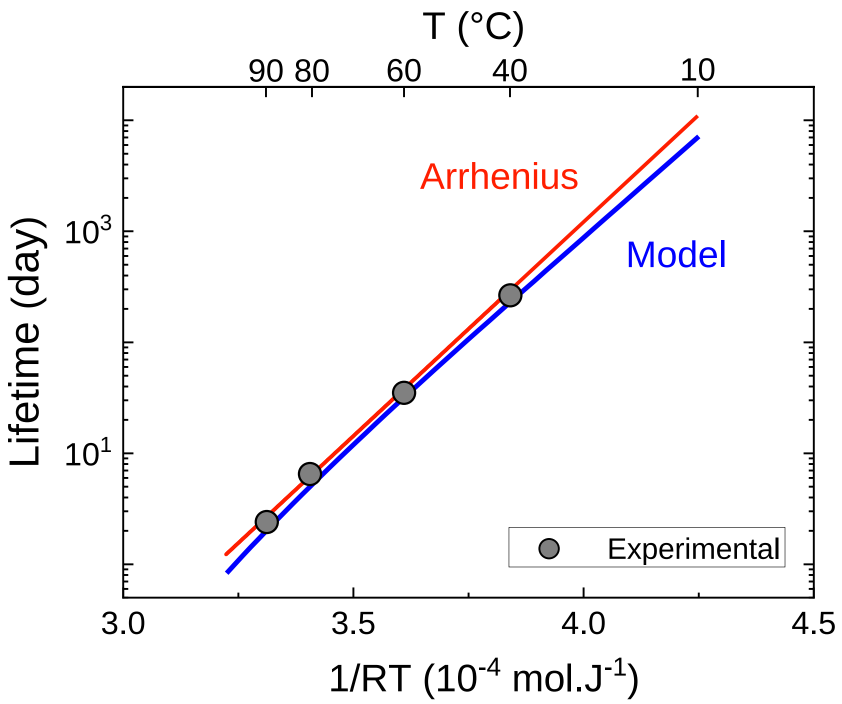


Lifetime prediction

Lifetime vs. ageing temperature

Lifetime prediction at any temperature

Prediction from model differs from Arrhenius law



Lifetime prediction at 10°C

Model : 19 years

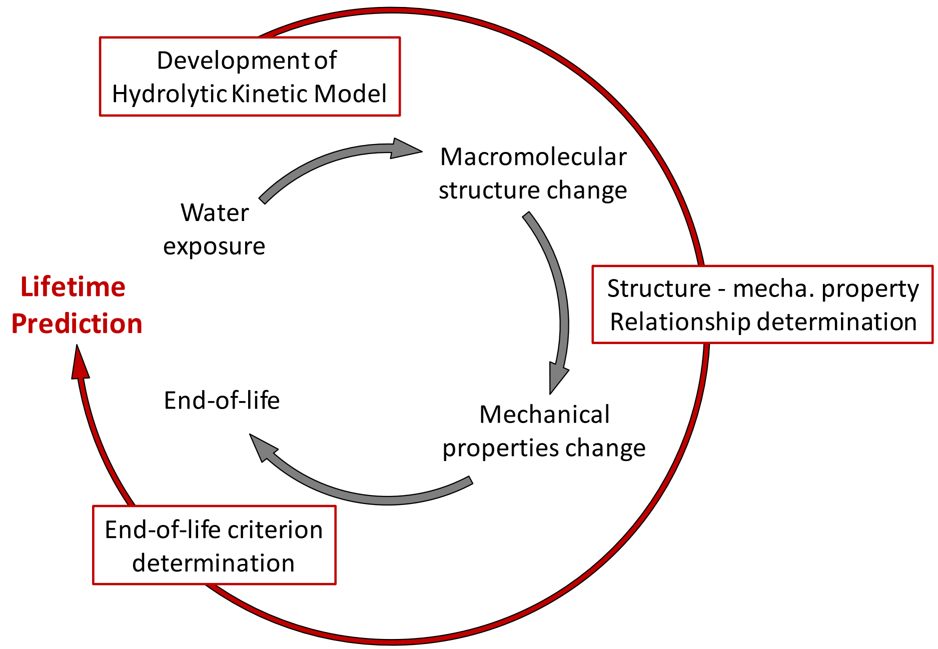
Arrhenius : 30 years

Significant difference !

Benefits of the proposed model

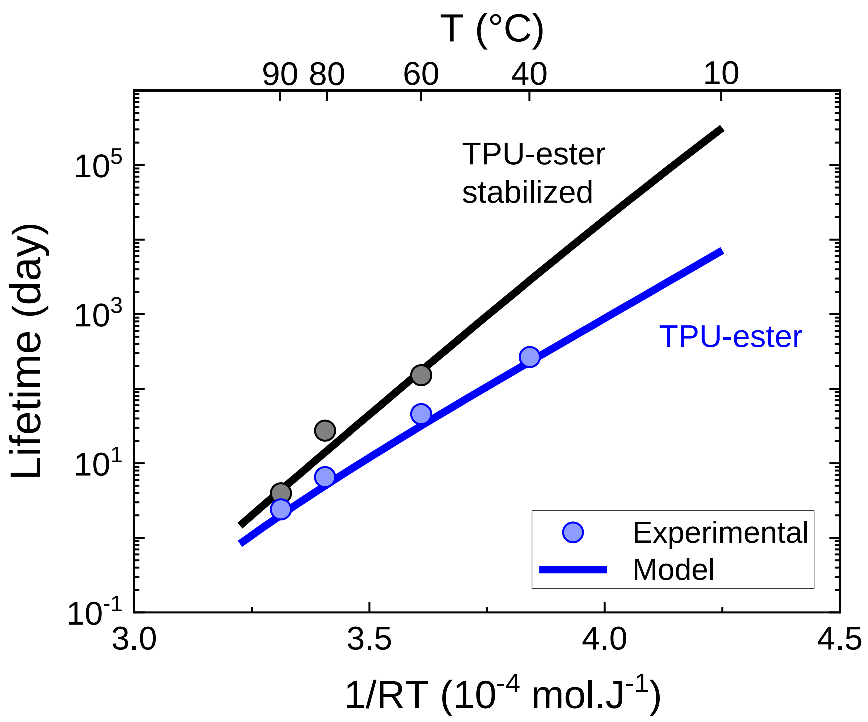
- Can predict non-Arrhenian behaviour
- Change of material formulation is easily taken into account

  With Arrhenius law, a new ageing campaign would be necessary…
- Can predict mechanical properties change



Perspectives

- Lifetime improvement with hydrolytic stabilizer



- Can the model be used on other TPEs ?

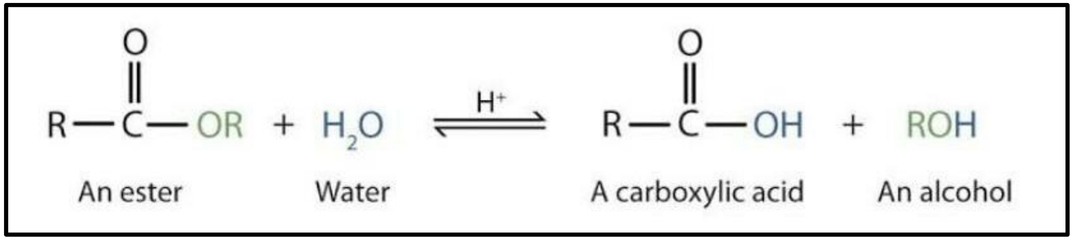
- Effect of coupling between oxidation and hydrolysis ?

Thank you for your attention

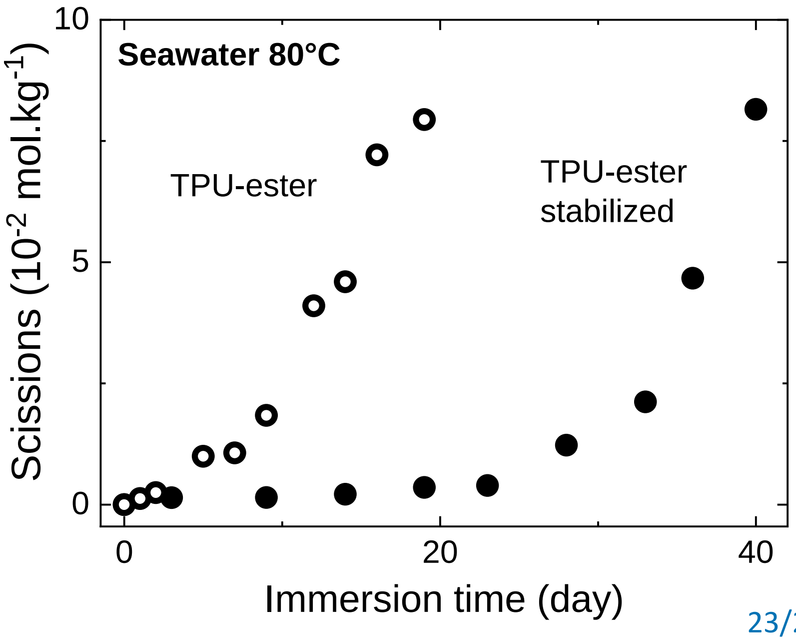
Hydrolytic stabilizer to increase lifetime

Hydrolytic stabilizer : a way to increase lifetime

Anti-catalysis agent, acts as an acid scavenger to inhibits catalysis



Slower degradation



Hydrolytic kinetic model

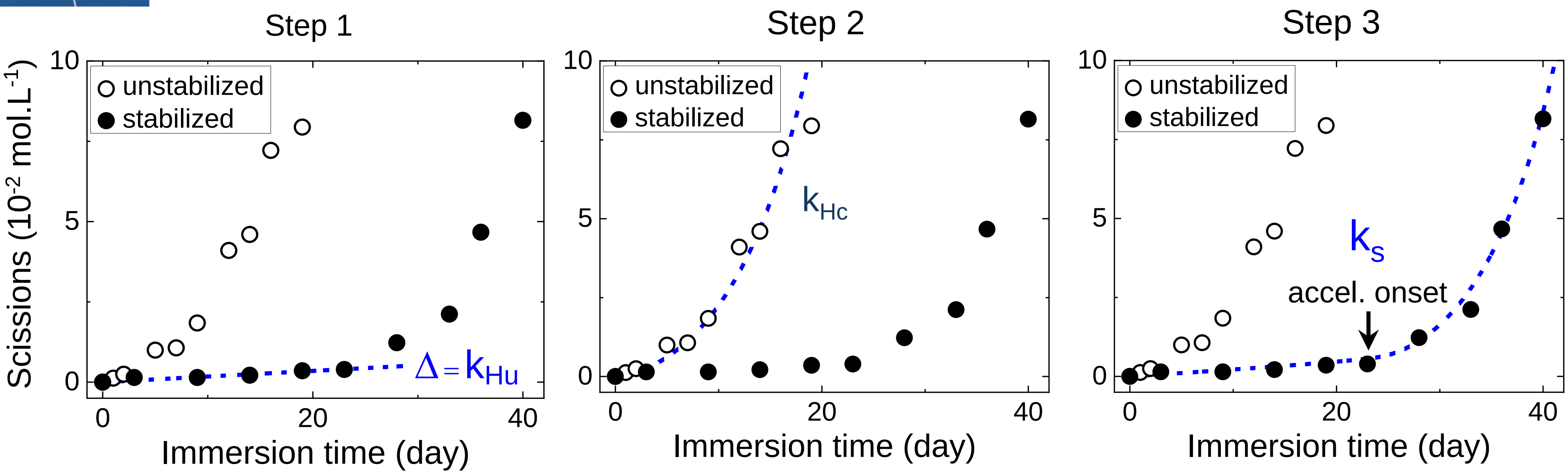
Constant determination

$$Ester + Water \xrightarrow{k_{Hu}} Carbox.Acid + scission$$

$$Ester + Water \xrightarrow{k_{Hc}\,(Acid)} Carbox.Acid + scission$$

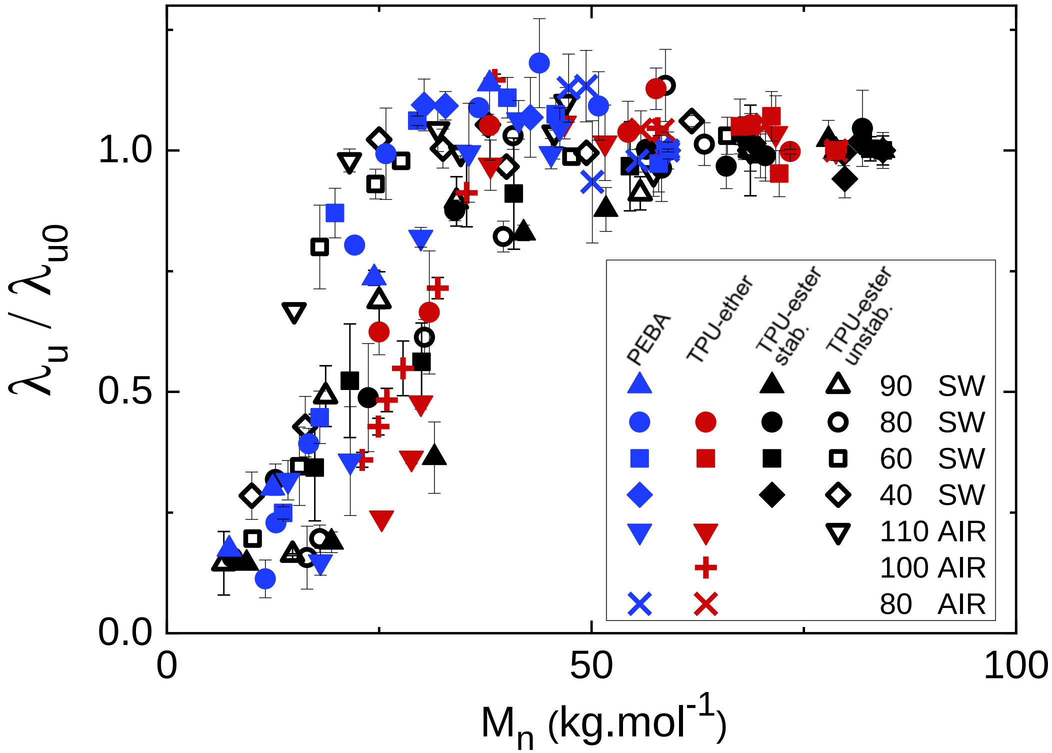
$$Carbox.Acid \overset{K_a}{\leftrightarrow} proton$$

$$Carbodiimide + Carbox.Acid \xrightarrow{k_s} Inactive\ Product$$



Structure – property relationship

Relation between elongation at break an molar mass



Master curve independent of

- degradation kinetic
- Material nature
- Exposure nature (air/water)