



# Multifunctional shape memory polymers based on covalent adaptive networks

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## University of Liege, Belgium



ULiege:  
-23000 students  
-11 faculties

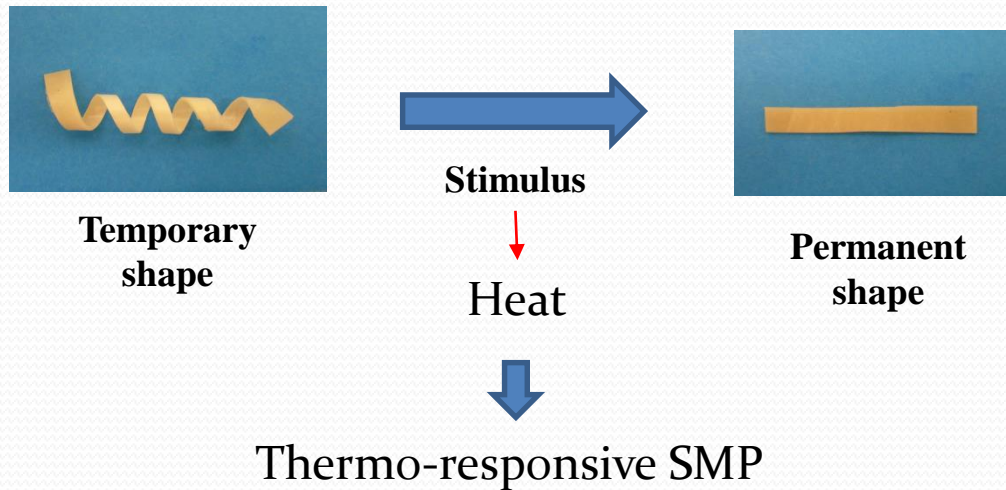


**Center for  
Education and  
Research on  
Macromolecules**

~25 researchers  
4 permanents



## Shape-memory polymers (SMP)



### Applications:

- Heat shrinkable tubes
- Medical devices: stents, resorbable self-tightening sutures



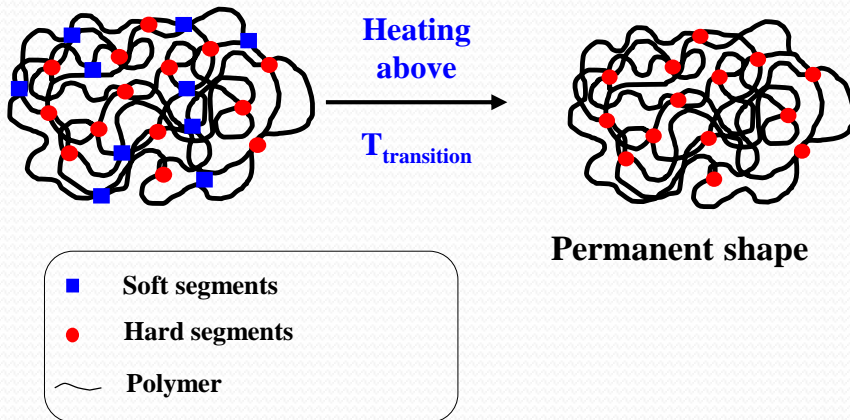
## Thermo-responsive shape-memory polymers

Hard segments: fix the **permanent shape**

Soft segments: fix the **temporary shape**

**Physical or covalent bonds**

**Crystallites or glassy regions**





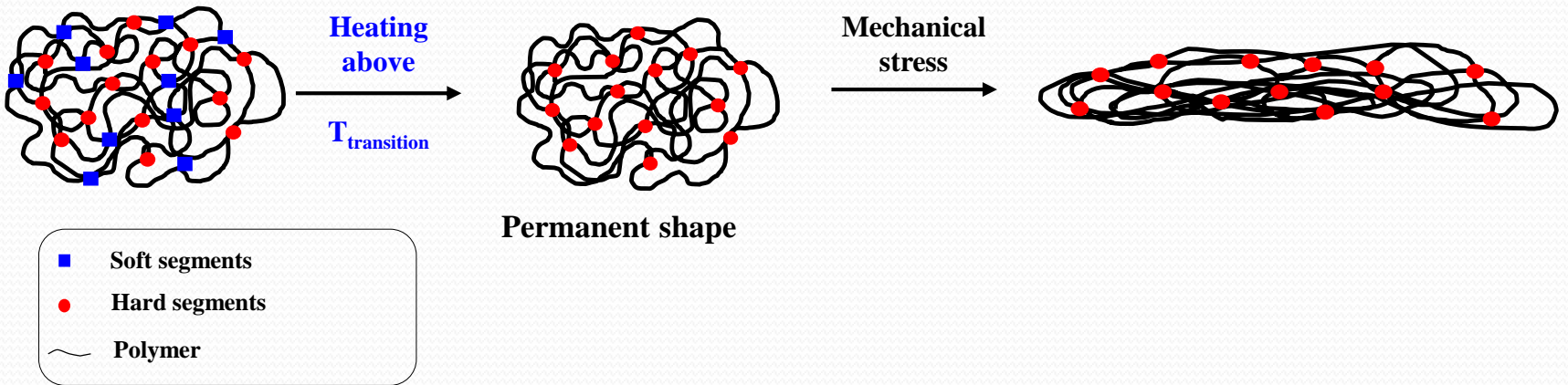
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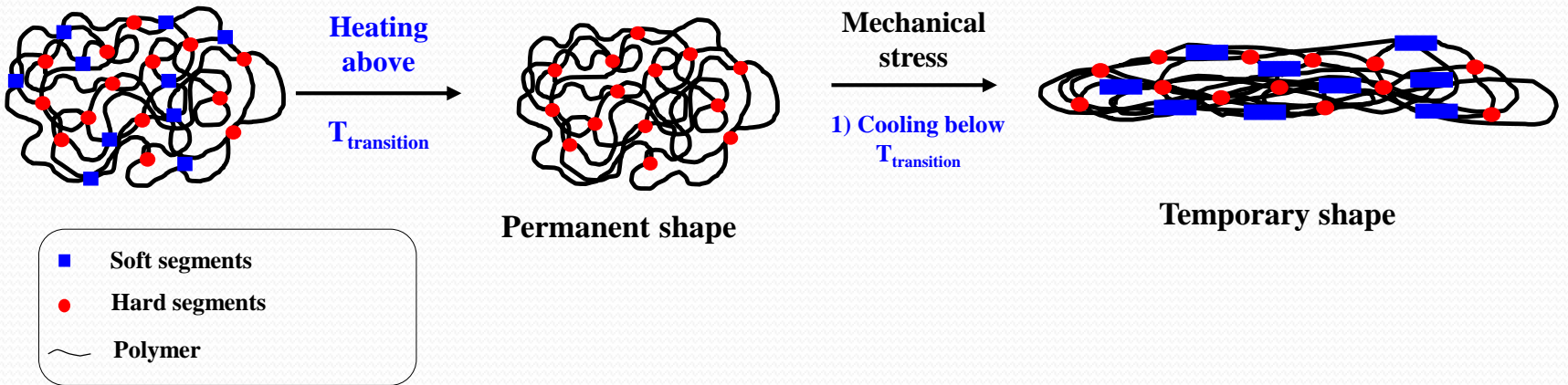


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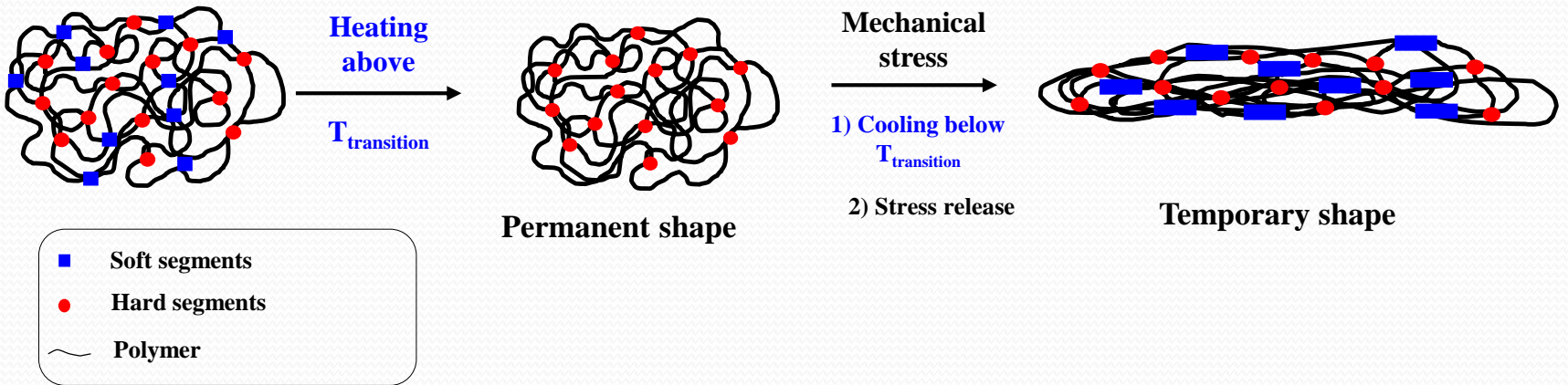


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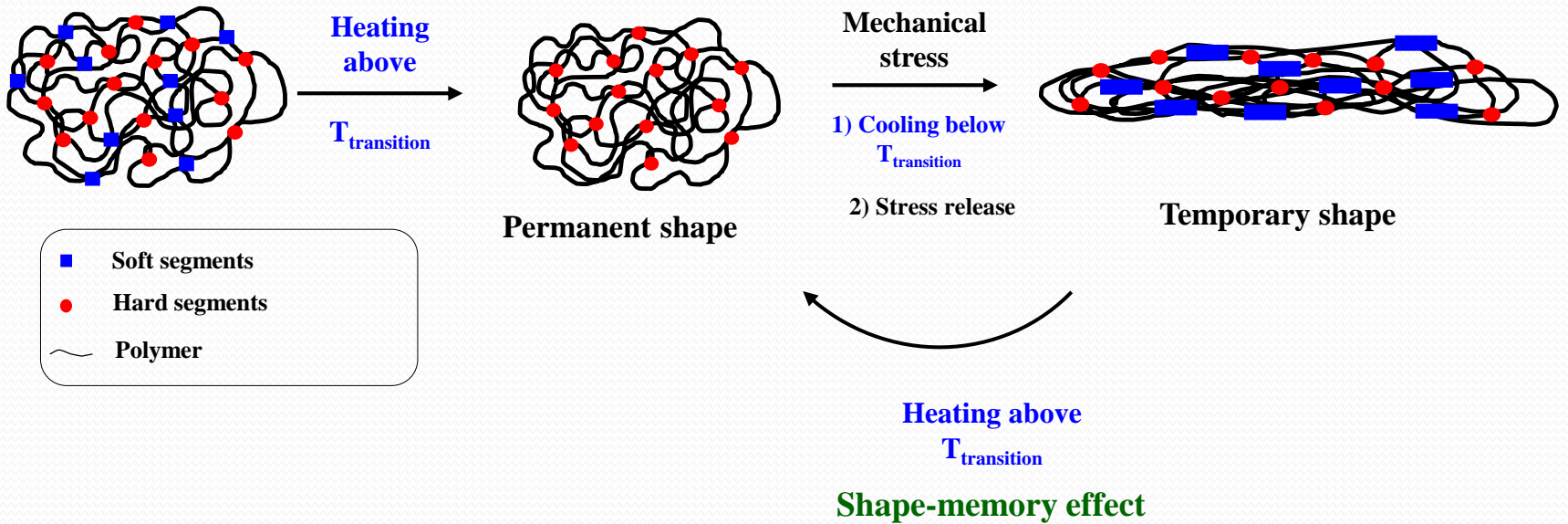


# Thermo-responsive shape-memory polymers

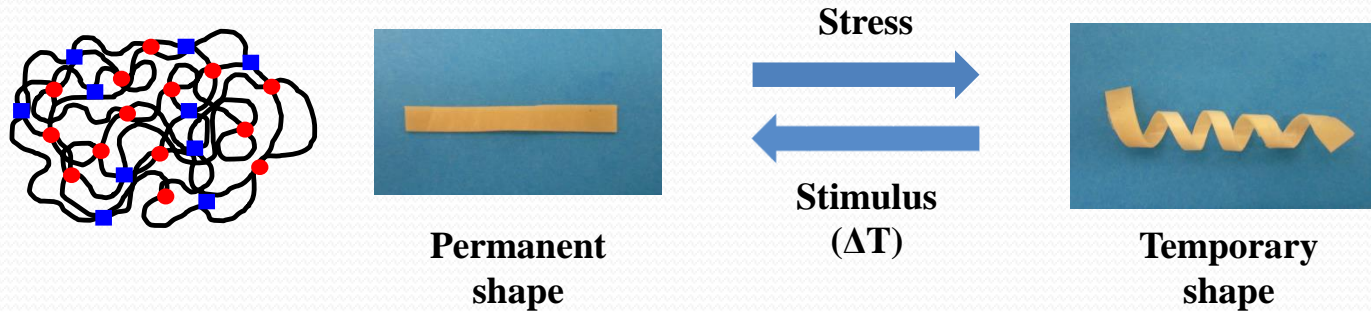
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**Physical or covalent bonds**  
**Crystallites or glassy regions**

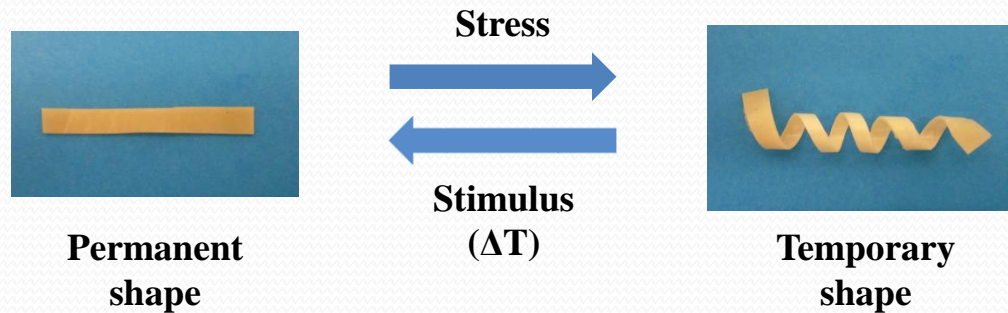


## Thermo-responsive shape-memory polymers



Classes	Hard segments	Soft segments
Covalently cross-linked glassy thermoset networks (class I)	Covalent bonds	Glassy domains
Covalently cross-linked semi-crystalline networks (class II)	Covalent bonds	Crystallites
Physically cross-linked glassy copolymers (class III)	Physical bonds	Glassy domains
Physically cross-linked semi-crystalline block copolymers (class IV)	Physical bonds	Crystallites

## Thermo-responsive shape-memory polymers



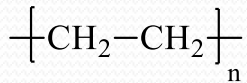
Classes	Hard segments	Soft segments
Covalently cross-linked glassy thermoset networks (class I)	Covalent bonds	Glassy domains
Covalently cross-linked semi-crystalline networks (class II)	Covalent bonds	Crystallites
Physically cross-linked glassy copolymers (class III)	Physical bonds	Glassy domains
Physically cross-linked semi-crystalline block copolymers (class IV)	Physical bonds	Crystallites



## Covalently cross-linked semi-crystalline networks (class II)

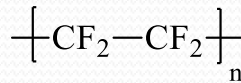
Heat shrinkable tubings or films

Crosslinking by electron beam irradiation ( $\beta$  irradiation)



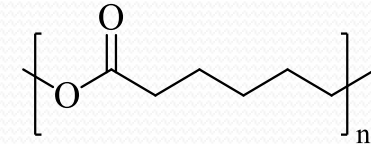
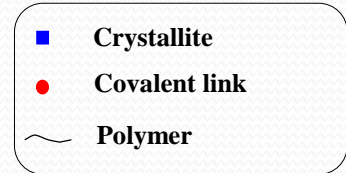
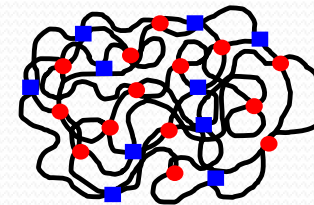
Cross-linked  
PE

$T_m \sim 120^\circ\text{C}$



Cross-linked  
PTFE (Teflon®)

$T_m \sim 320^\circ\text{C}$



Cross-linked poly( $\epsilon$ -caprolactone) (PCL)  
 $\gamma$  irradiation  
 $T_m = 50^\circ\text{C}$

Degradable and biocompatible

**Class II covalent networks**

**=> High shape memory performances**



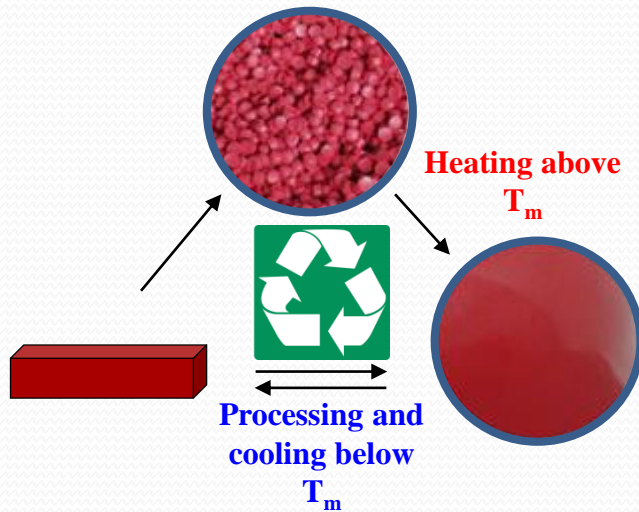
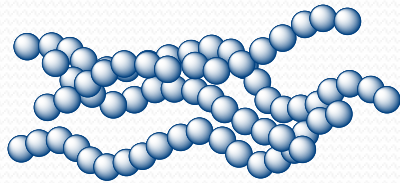
W. C. Rainer, E. M. Redding, J. J. Hitov, A. W. Sloan and W. D. Stewart, *US Pat.*, 3144398, **1964**.

R. Hosemann, J. Loboda-Cackovic and H. Cackovic, *Z. Naturforsch., A: Astrophys. Phys. Phys. Chem.*, **1972**, 27, 478.

G. Zhu, G. Liang, Q. Xu and Q. Yu, *J. Appl. Polym. Sci.*, **2003**, 90, 1589.

## Processing the permanent shape: melt-flow injection

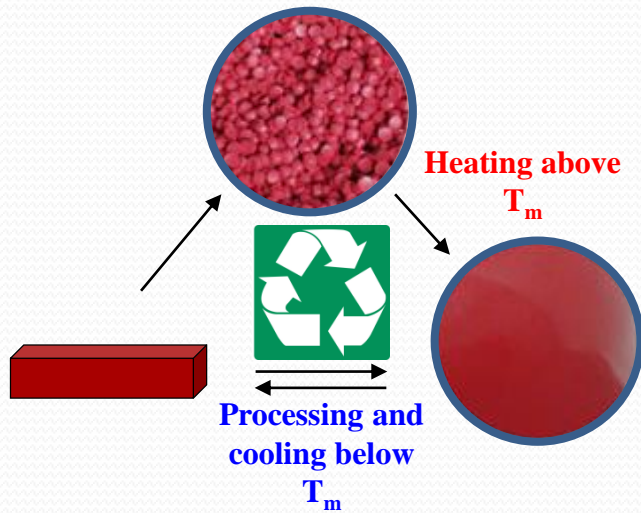
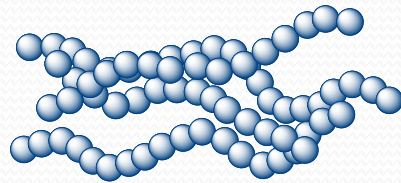
### Thermoplastics



Injection molding

# Polymer processing: melt-flow injection

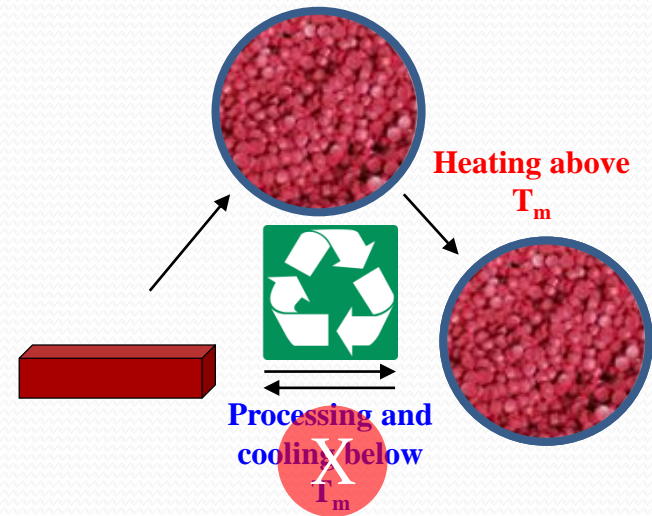
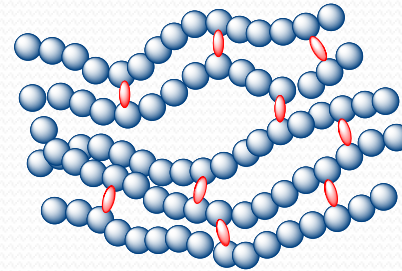
**Thermoplastics**



Injection molding

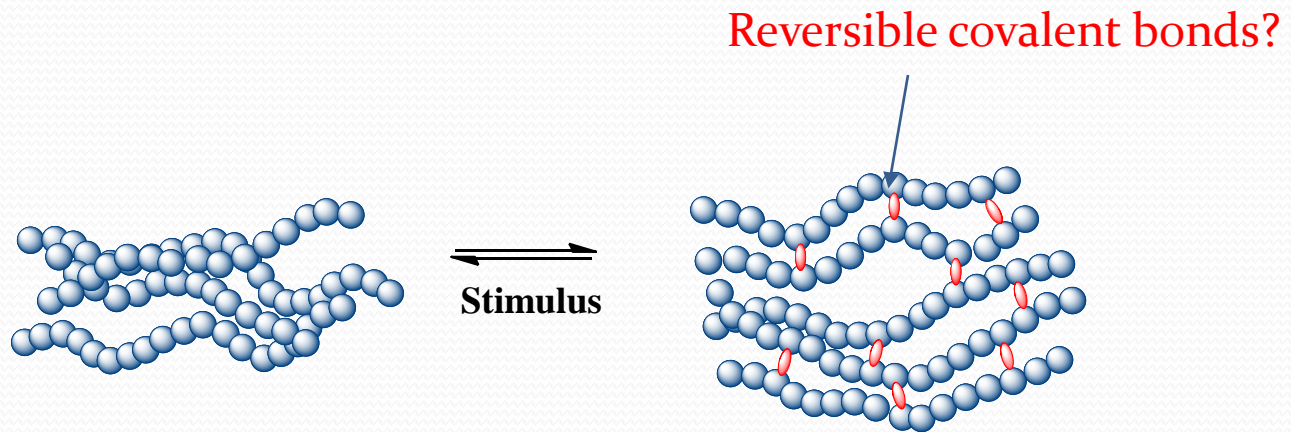
**Polymer networks do not flow!**

**Cross-linked polymers = network**





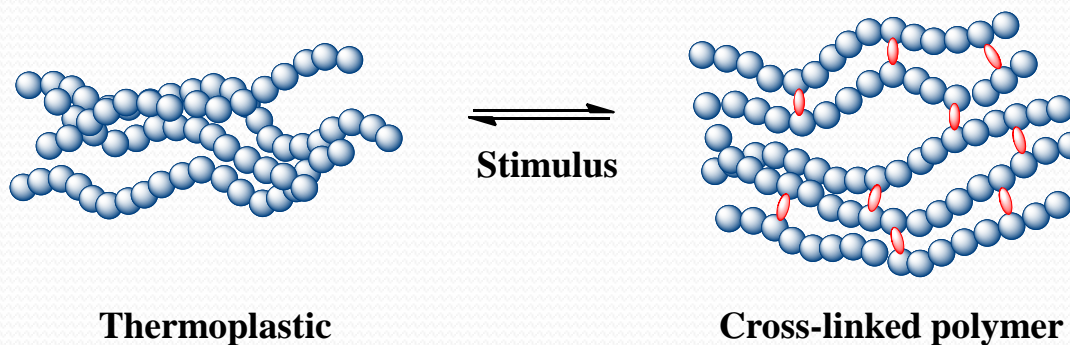
## Goal of the research: reversible covalent networks



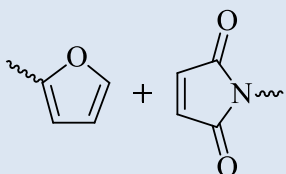
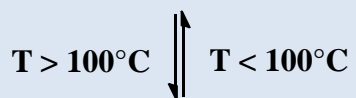
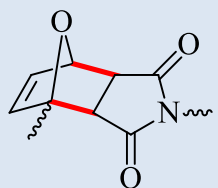
Melt-flow processing

Highly stable covalent network

## Covalent adaptable networks (CANs)



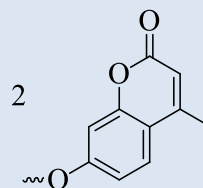
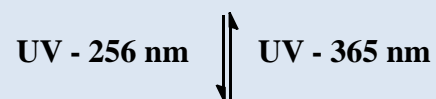
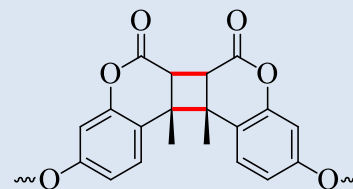
Heat



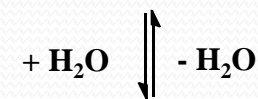
Redox



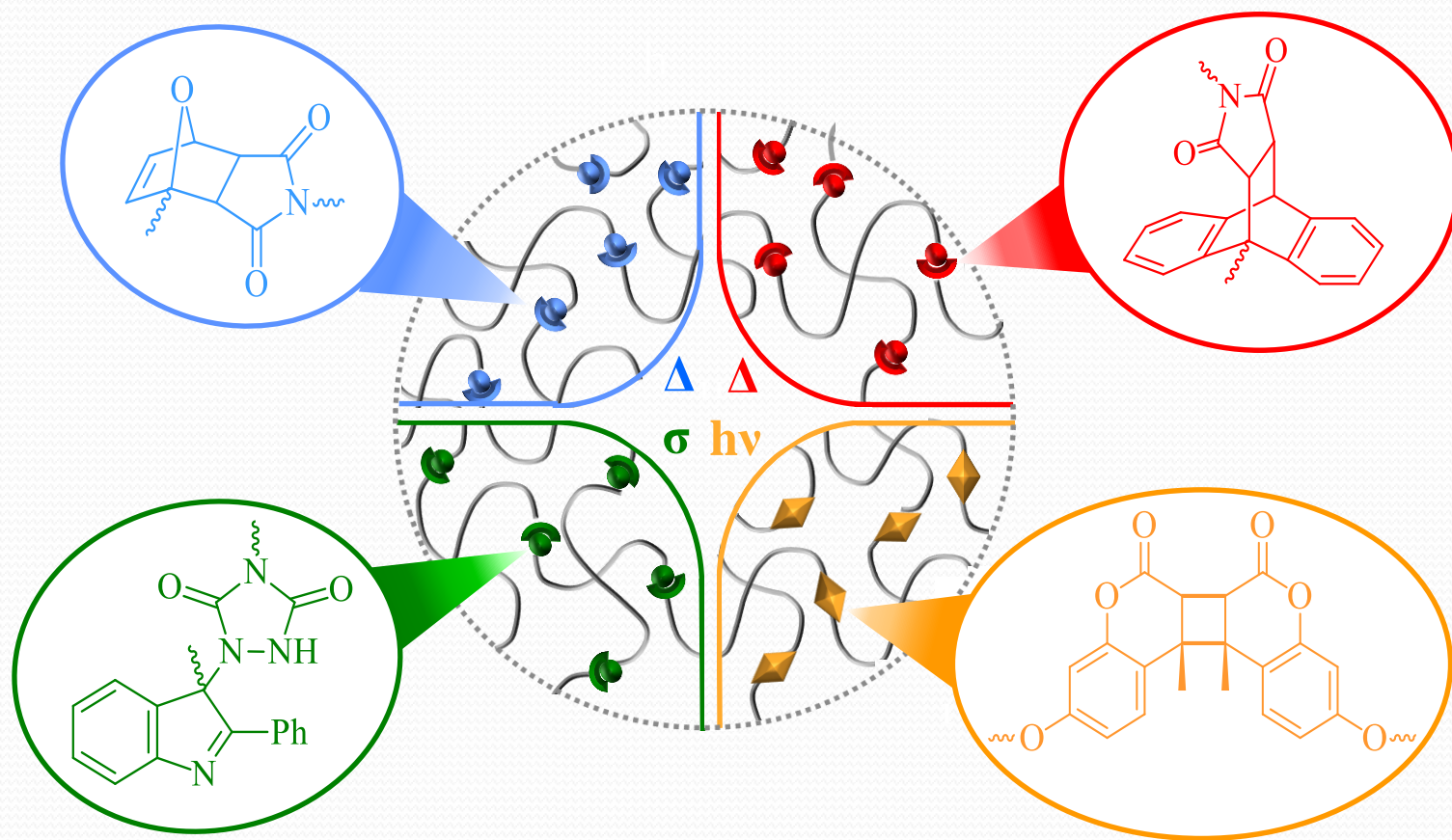
Light



Moisture



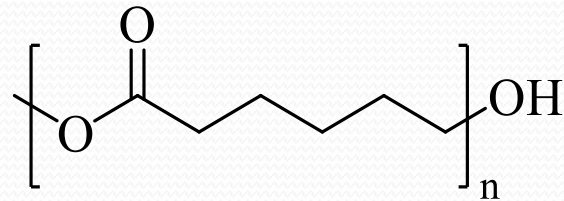
## Selected reversible bonds for this work





## Insertion of these bonds into PCL networks

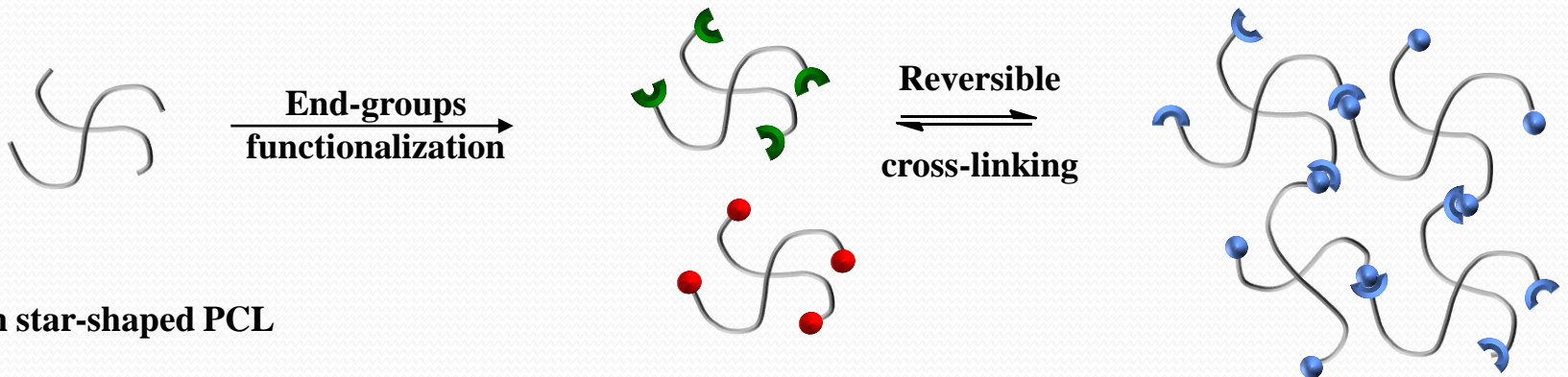
**Degradable  
Biocompatible  
Shape memory**



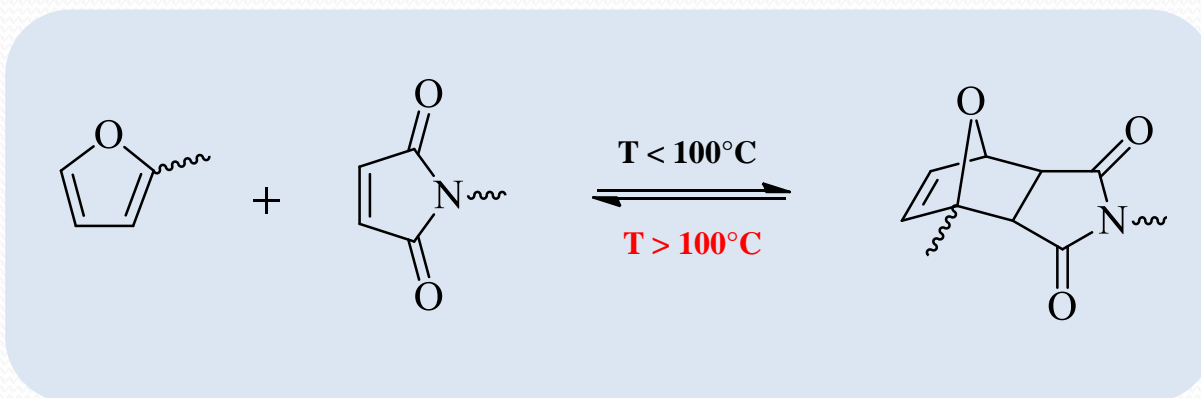
Polymer matrix : Poly(ε-caprolactone) or PCL :  
 $T_g = -60^\circ\text{C}$ ;  $T_m = 50^\circ\text{C}$

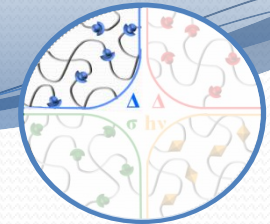
**Semi-crystalline** polymer

### General synthesis strategy

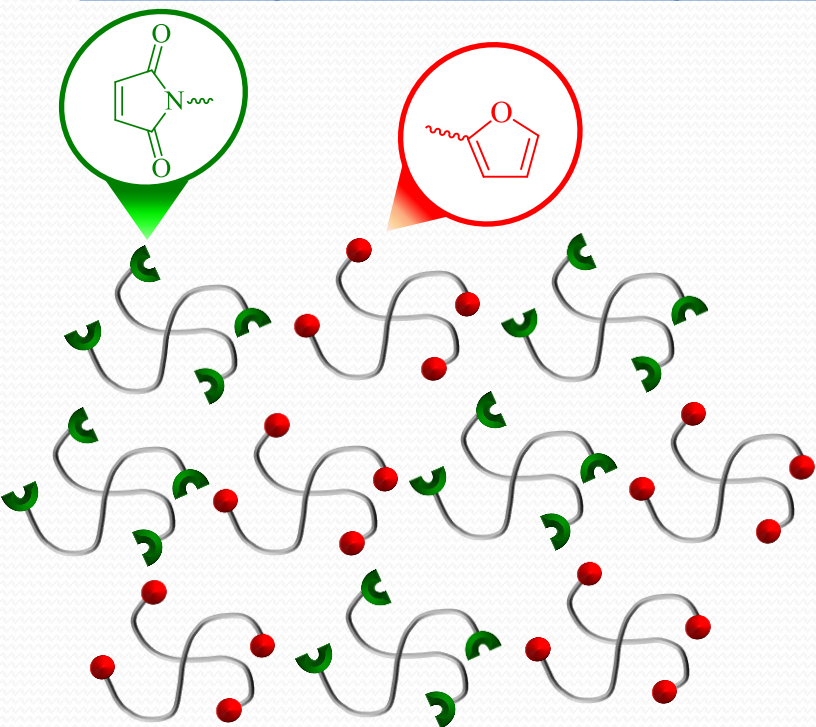


## Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)





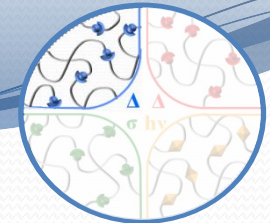
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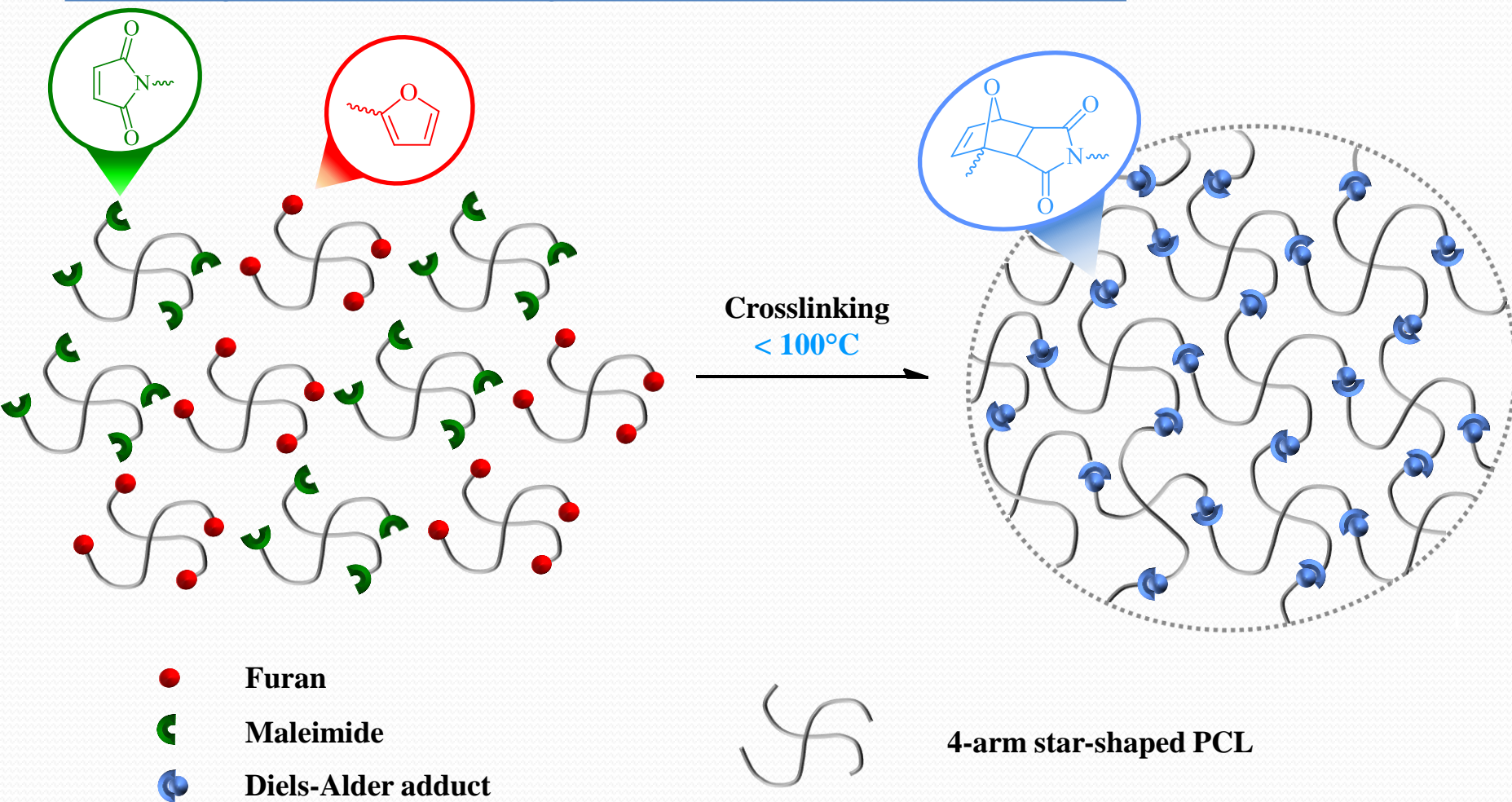
- Furan
- ◐ Maleimide

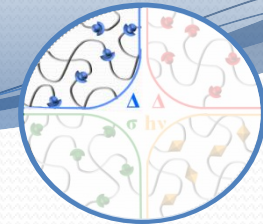


**4-arm star-shaped PCL**

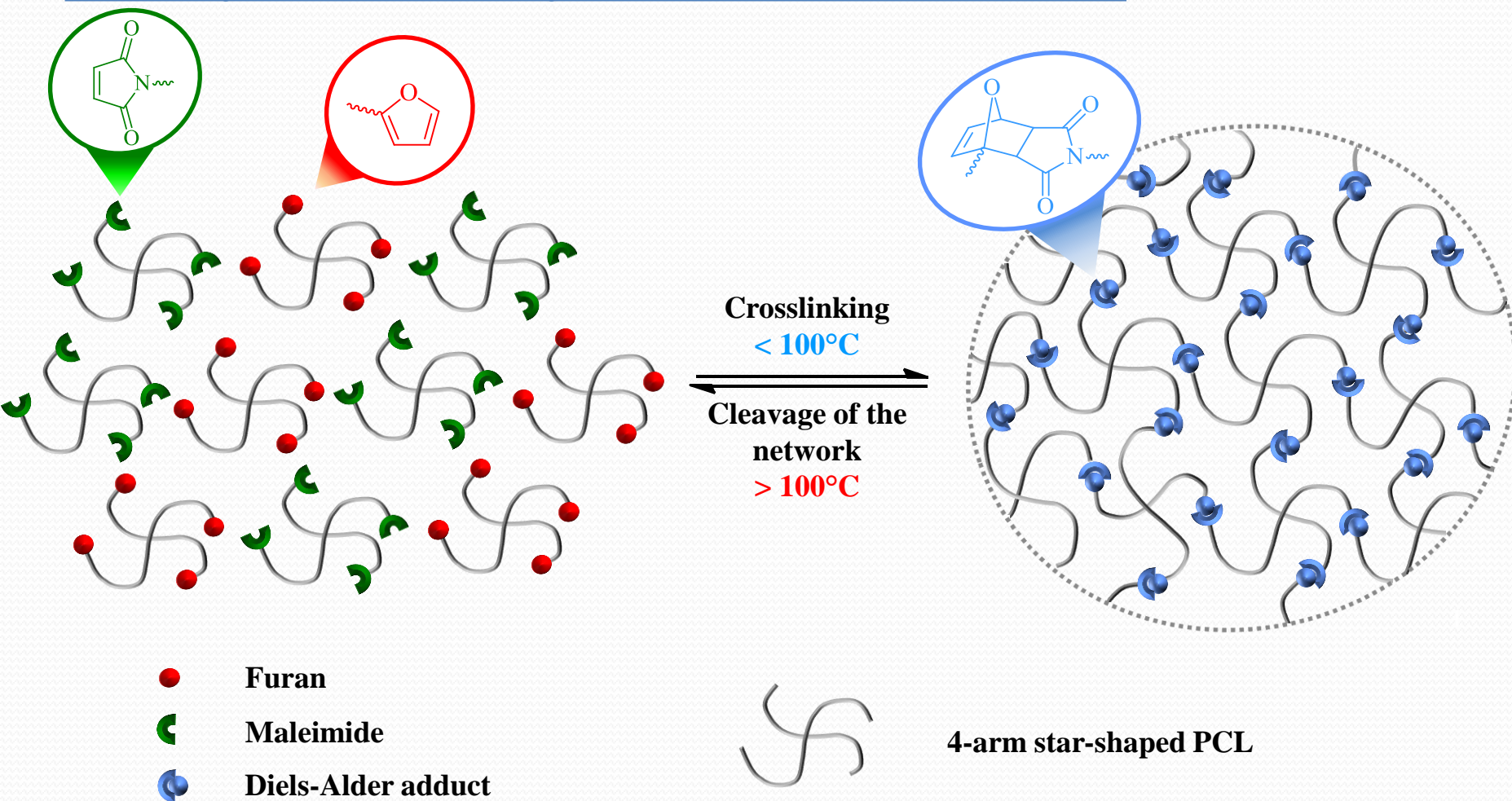


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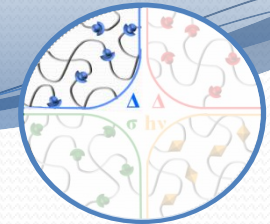




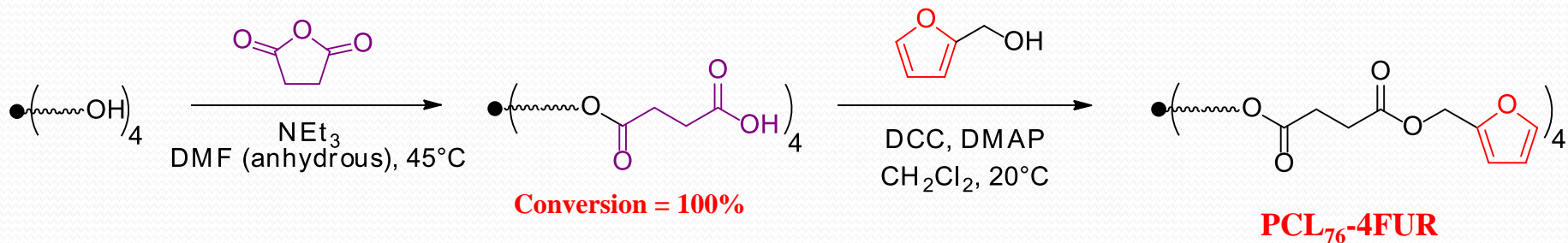
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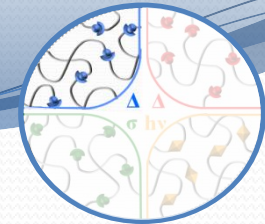




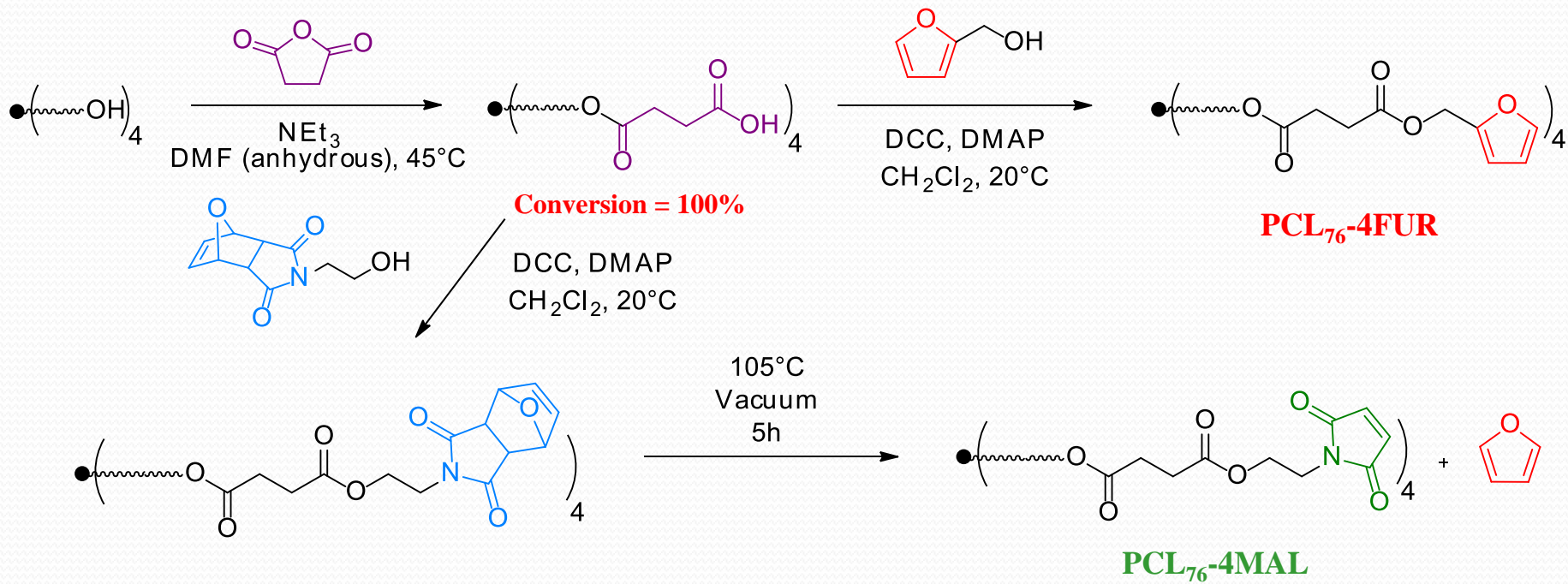


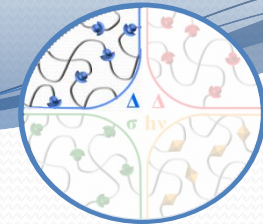
## Functionalization of 4-arm star-shaped PCL



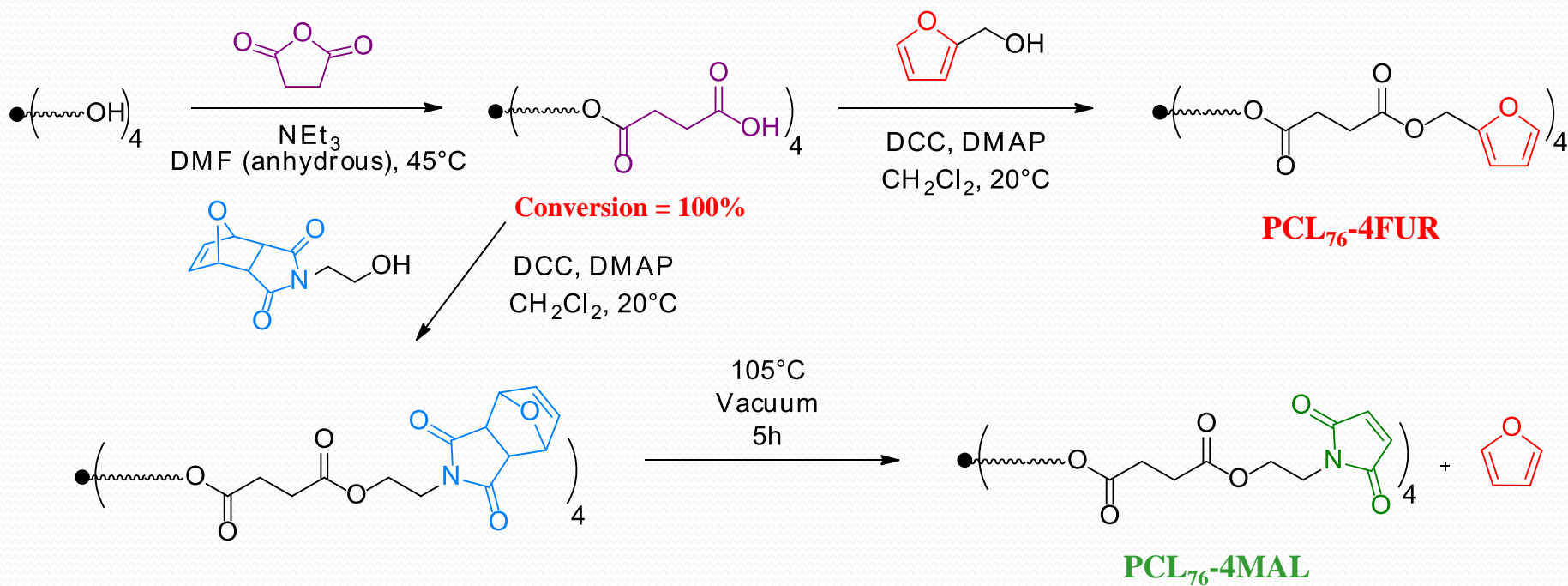


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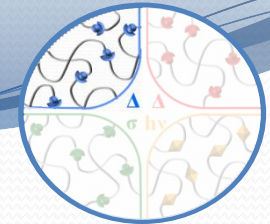


Precursors	Number of chain-ends	DP <sup>a</sup>	Chain-ends conversion <sup>a</sup>	M <sub>n</sub> ( <sup>1</sup> H NMR) <sup>b</sup>	D (SEC) <sup>c</sup>
<b>PCL<sub>76</sub>-4MAL</b>	4	76	95%	9600 g/mol	1.20
<b>PCL<sub>76</sub>-4FUR</b>	4	76	88%	9400 g/mol	1.20

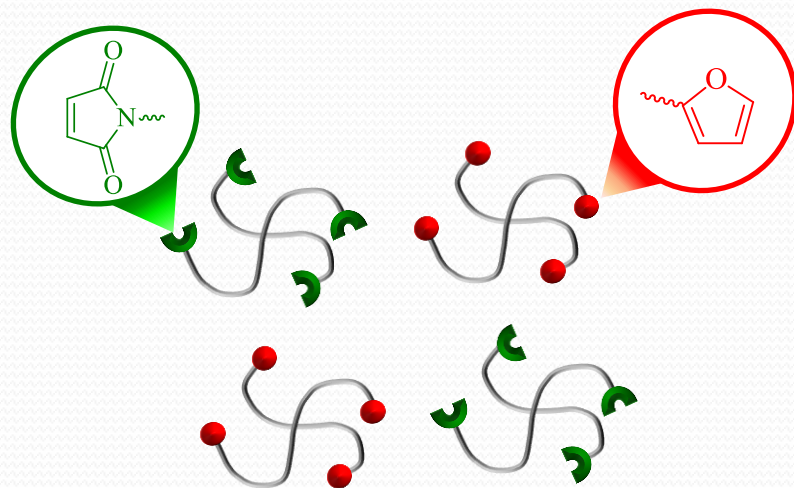
a) Conversion of the hydroxyl end groups into furan or maleimide determined by <sup>1</sup>H NMR

b) Average molar mass (DP x 114.14 g/mol + 400 g/mol (for PCL<sub>76</sub>-4FUR and PCL<sub>76</sub>-4MAL) or 200 g/mol (for PCL<sub>38</sub>-2MAL) + molar mass of maleimide or furan end groups x chain-end conversion)

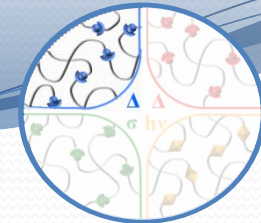
c) Molar mass distribution measured by SEC in THF at 45°C



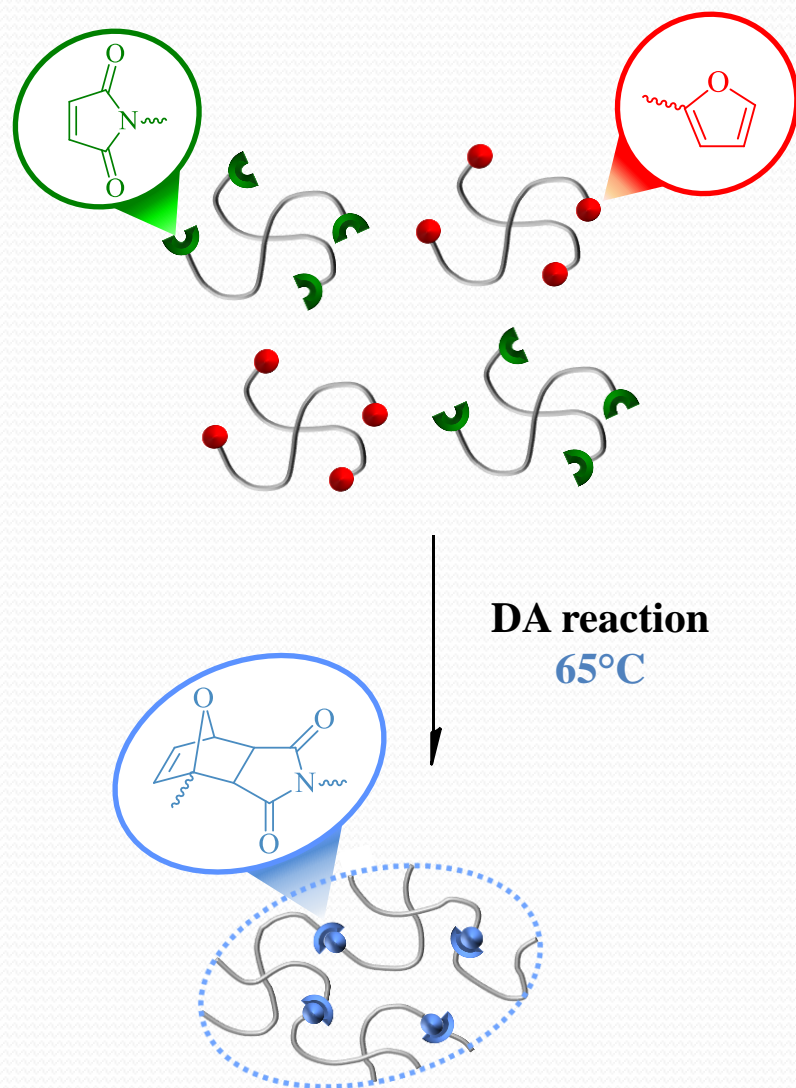
## Mixing of the precursors



**Mixing in a mini-extruder at 105°C**

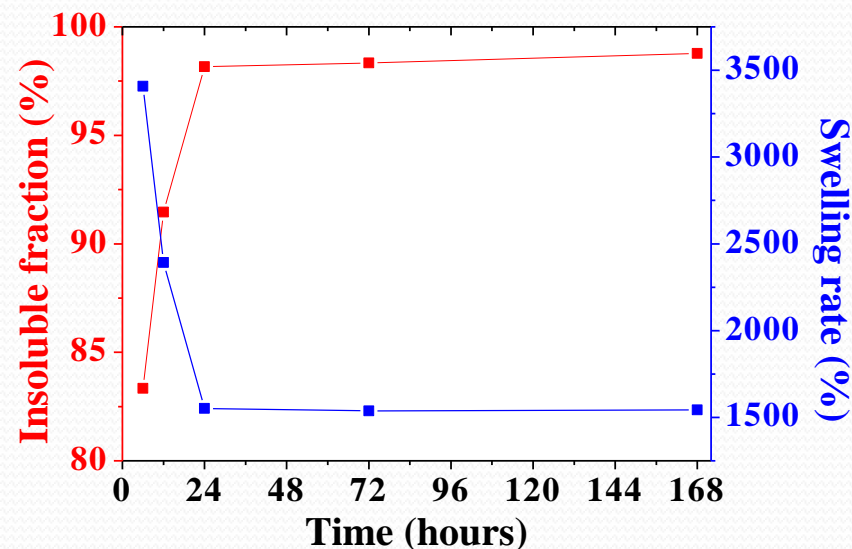


## Crosslinking study by swelling experiments



### Determination of the optimal time of curing at 65°C

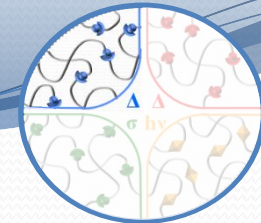
Crosslinking in a ventilated oven at 65°C:  
Diels-Alder adduct formation in the molten state



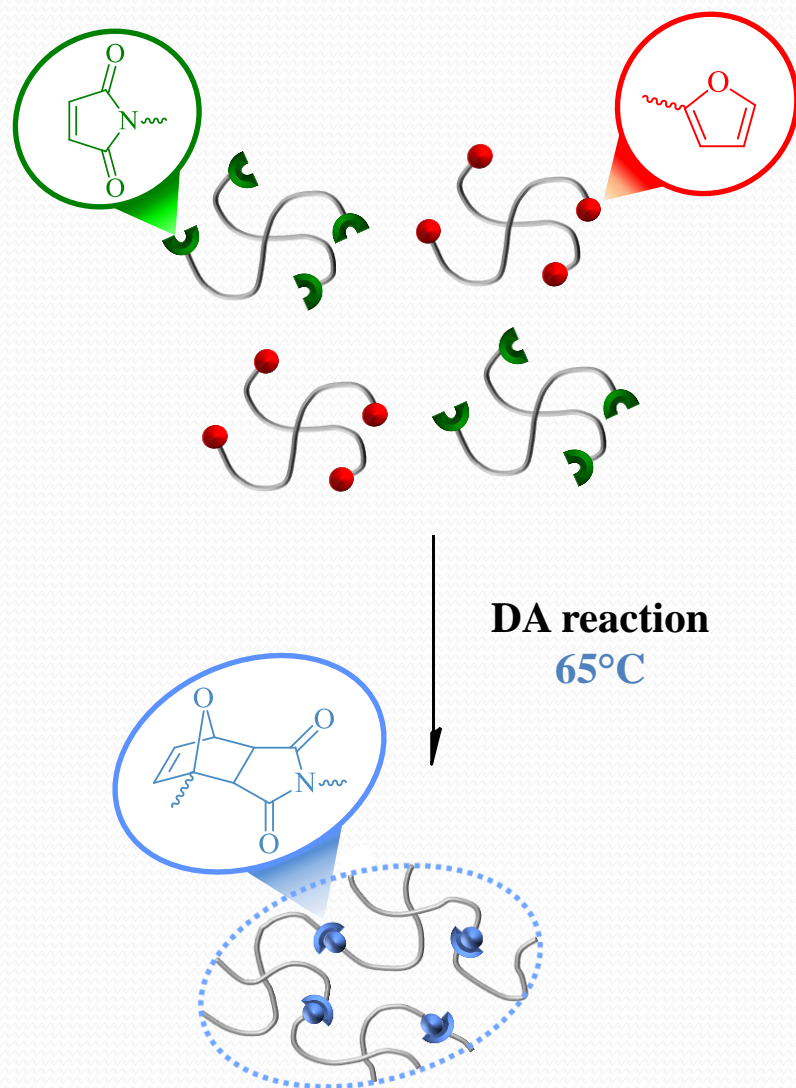
Evolution of the **insoluble fraction** and of the **swelling rate** (in chloroform) with curing time at 65°C for the mix composed of **PCL<sub>76</sub>-4MAL** and **PCL<sub>76</sub>-4FUR**

Efficient cross-linking of the material after 24h at  
65°C



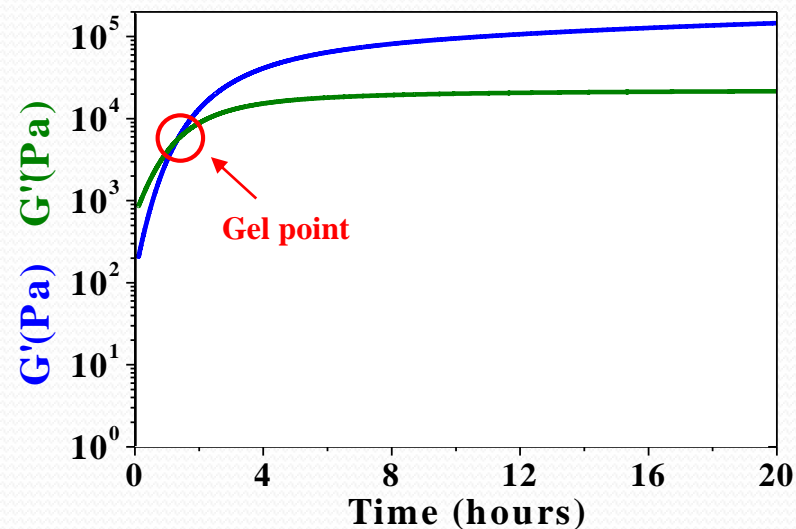


## Crosslinking study by rheology (TA Ares G2 : 1% deformation, 65°C)



### Crosslinking kinetics by rheology at 65°C

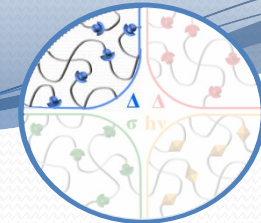
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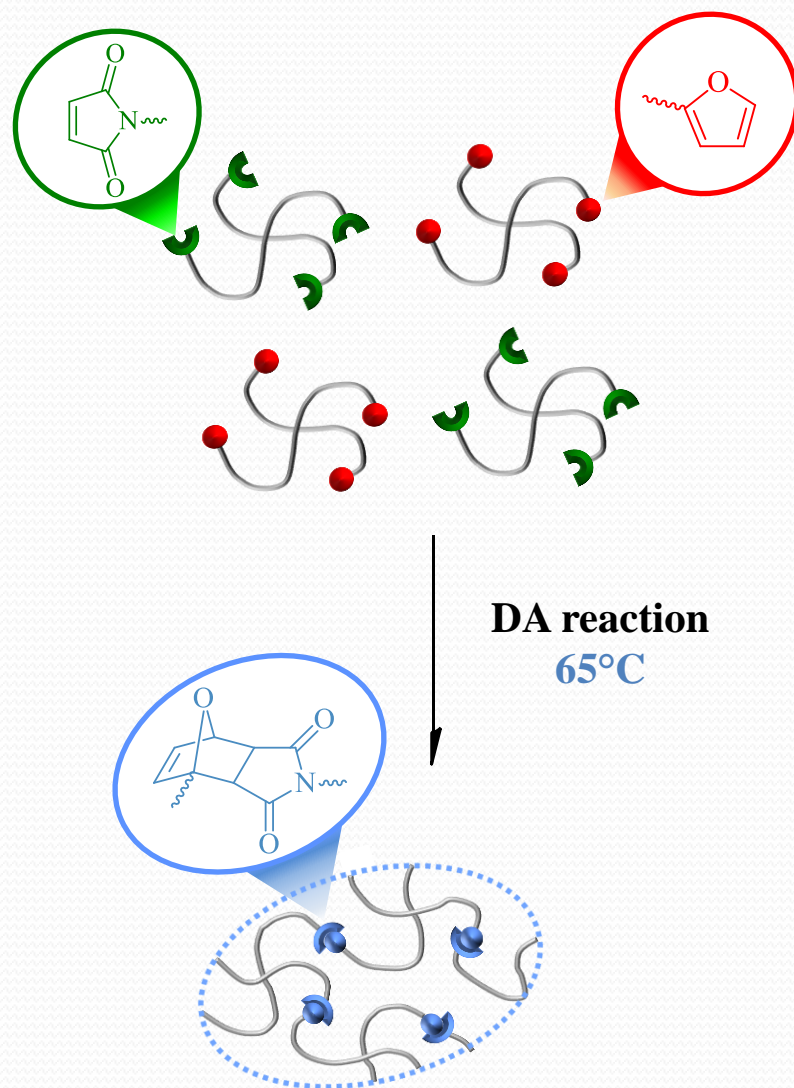
Evolution of the **gain modulus** and of the **loss modulus**  
with curing time at 65°C for the mix composed of  
**PCL<sub>76</sub>-4MAL** and **PCL<sub>76</sub>-4FUR**

At 65°C: - **G'** increases due to network formation

- **G''** increases due to viscosity increase

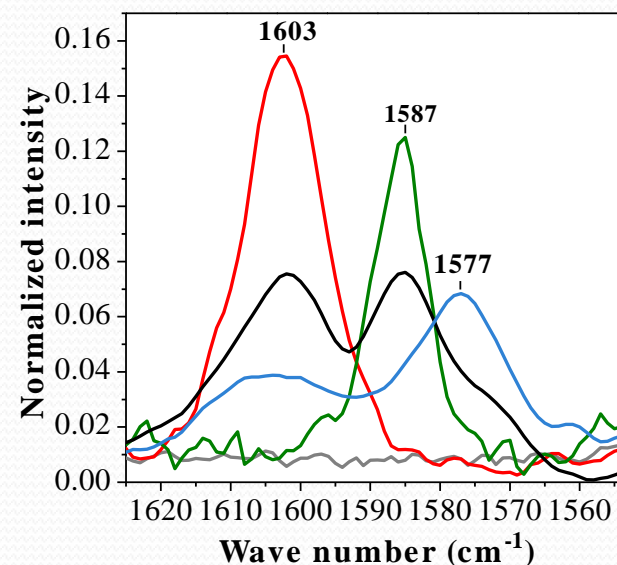


## Crosslinking study by Raman spectroscopy



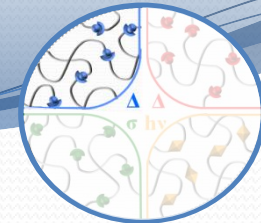
## Crosslinking kinetics by RAMAN spectroscopy

Crosslinking in a ventilated oven at 65°C:  
Diels-Alder adduct formation in the molten state

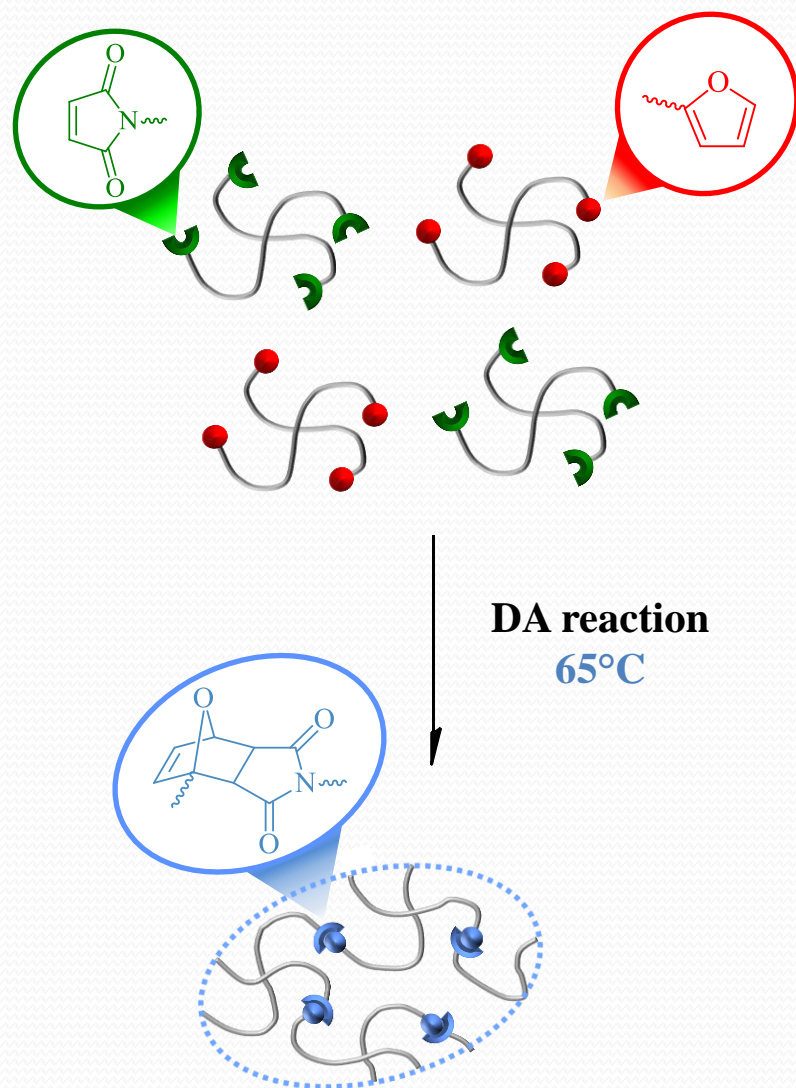


Zoom on the diffusion bands of interest of furan (1603  $\text{cm}^{-1}$ ), maleimide (1587  $\text{cm}^{-1}$ ) and DA adduct (1577  $\text{cm}^{-1}$ )

- **PCL<sub>76</sub>-4FUR**
- **PCL<sub>76</sub>-4MAL**
- **Mix before crosslinking**
- **Mix after crosslinking during 24h at 65°C**

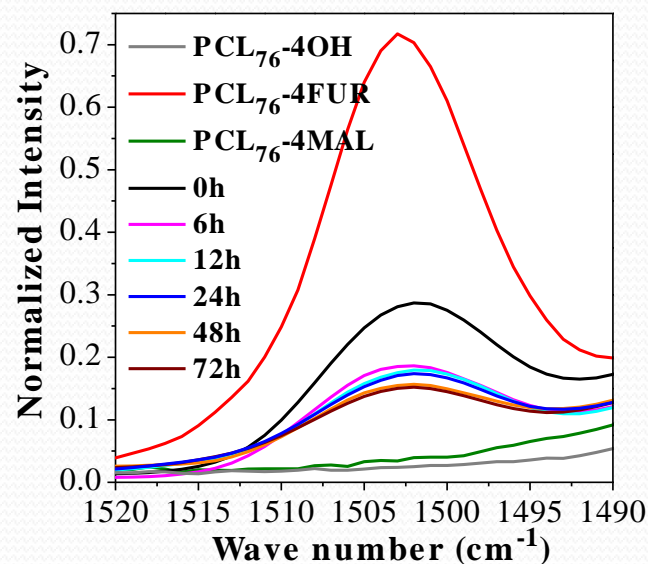


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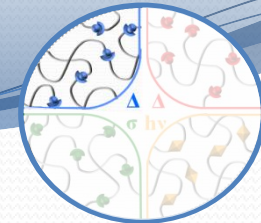
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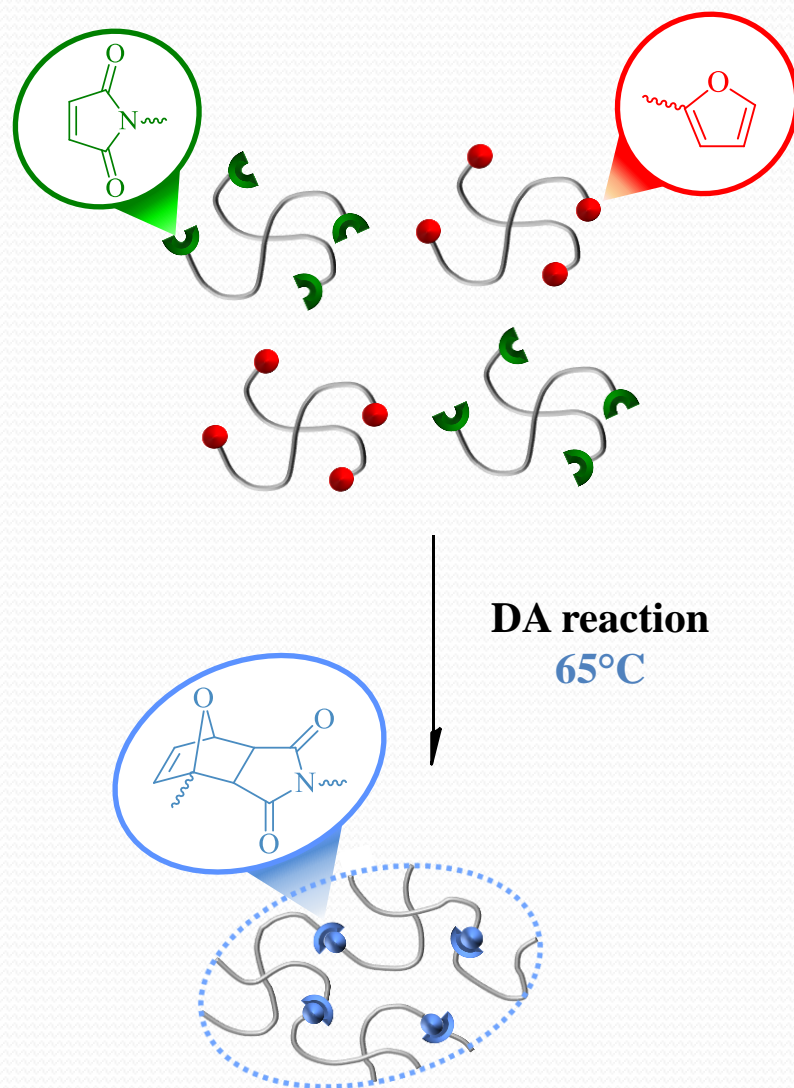


RAMAN spectroscopy = quantitative analysis

$$\text{Conversion of furan (\%)} = 100 - \frac{I(1503 \text{ cm}^{-1}) \text{ for the mix}}{I(1503 \text{ cm}^{-1}) \text{ for PCL-4FUR/2}} \cdot 100$$

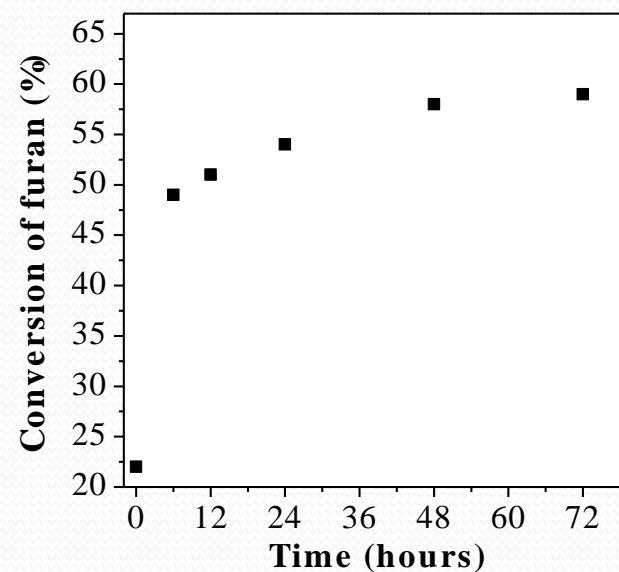


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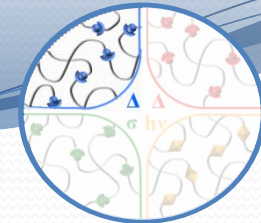
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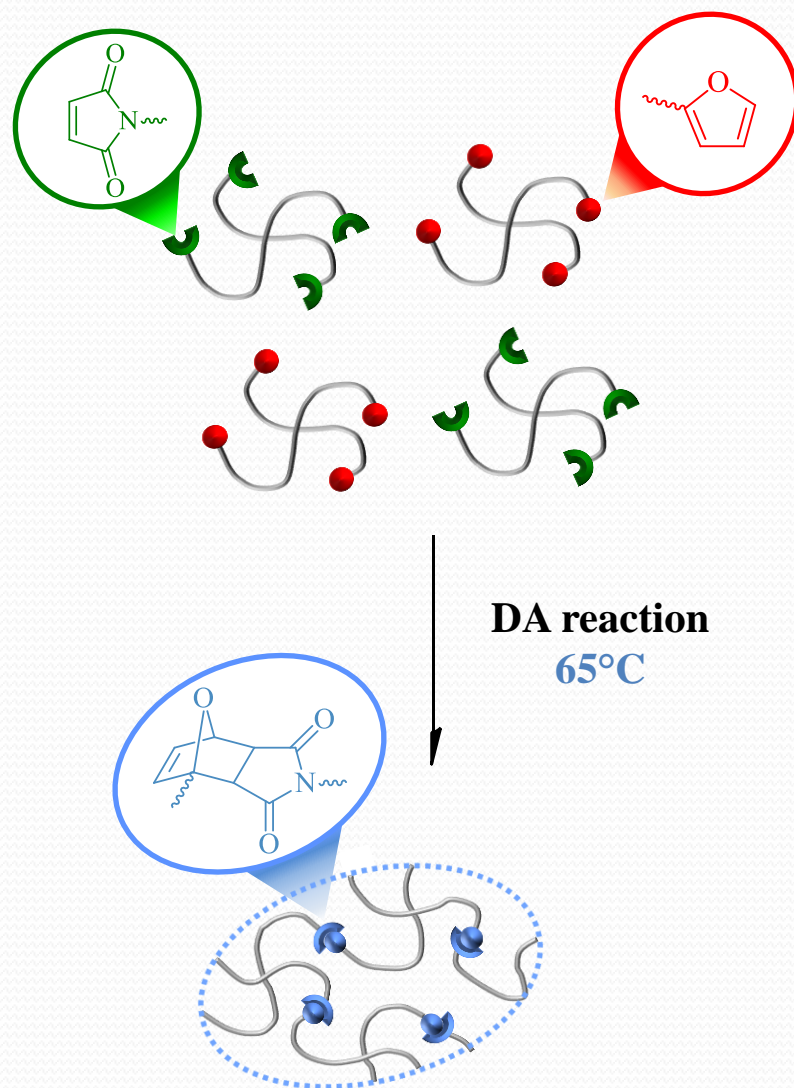


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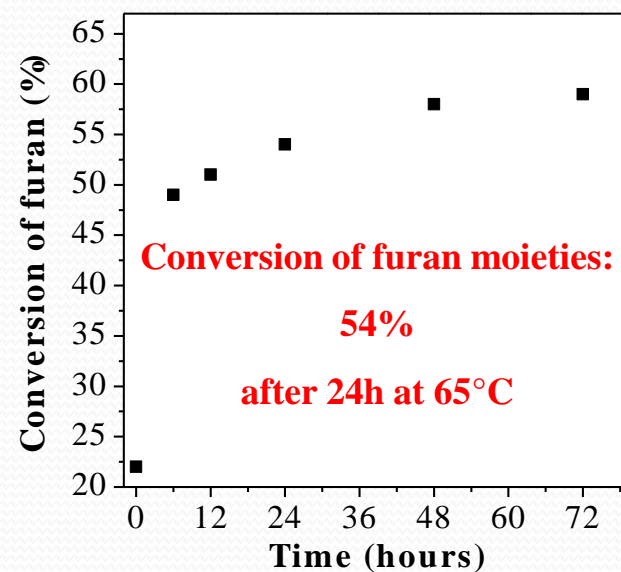


## Crosslinking study by Raman spectroscopy



## Crosslinking kinetics by RAMAN spectroscopy

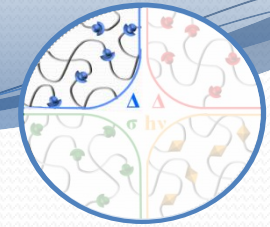
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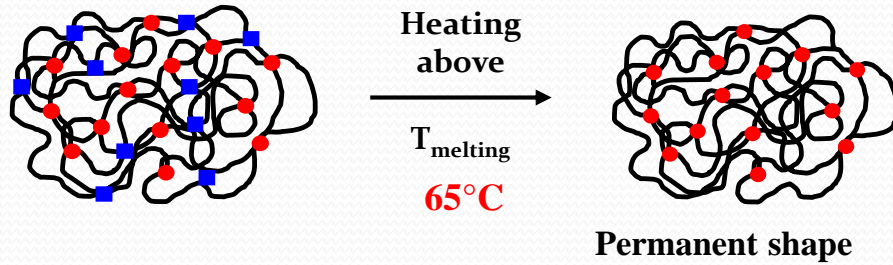
RAMAN spectroscopy = quantitative analysis

$$\text{Conversion of furan (\%)} = 100 - \frac{I(1503 \text{ cm}^{-1}) \text{ for the mix}}{I(1503 \text{ cm}^{-1}) \text{ for PCL-4FUR/2}} \cdot 100$$

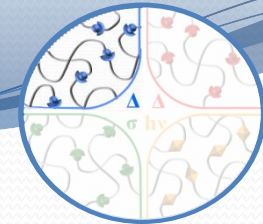




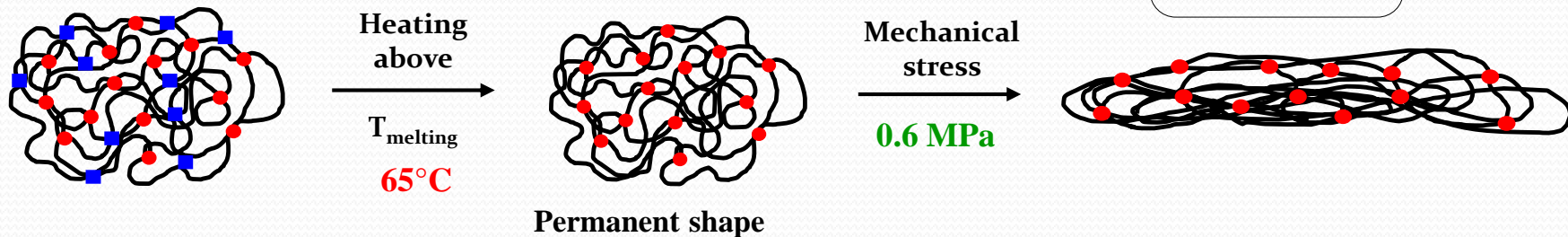
# Shape-memory properties



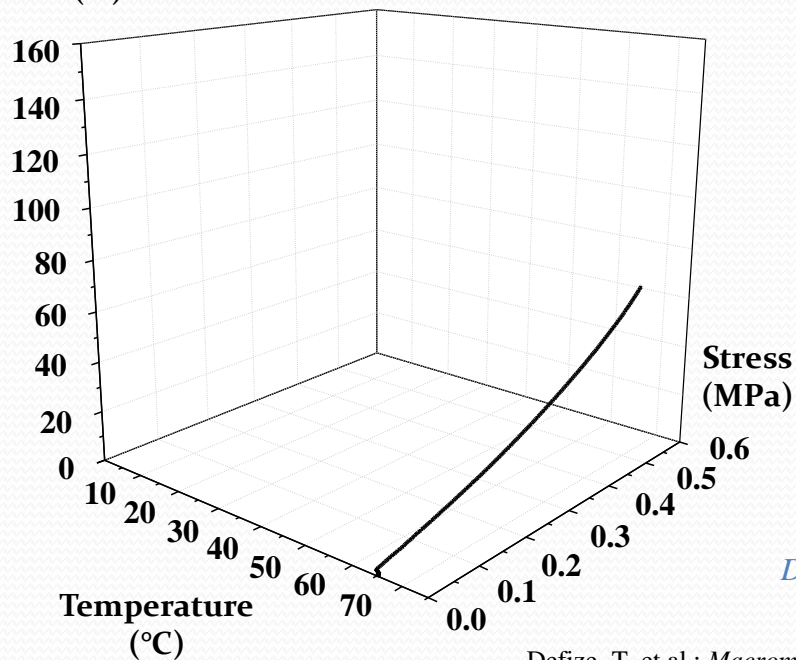
- crystallite
- covalent link
- PCL



# Shape-memory properties



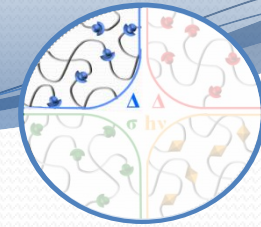
Strain (%)



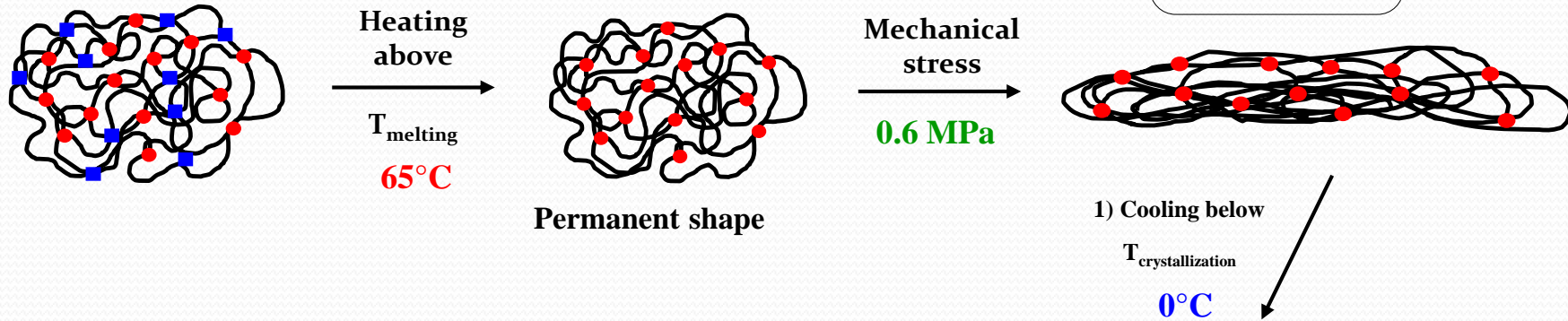
5 min isotherm at  $65^{\circ}\text{C}$

Stress-controlled deformation  
( $0.06 \text{ MPa/min}$  up to  $0.6 \text{ MPa}$ )

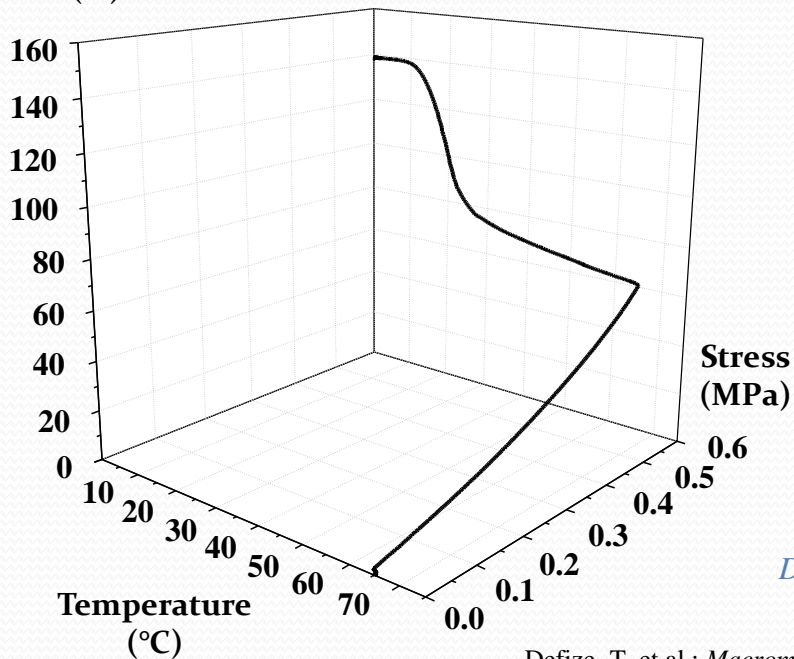
*DMTA Q800, tensile mode, controlled stress, sample :  $5 \times 5 \times 0.5 \text{ mm}$*



# Shape-memory properties



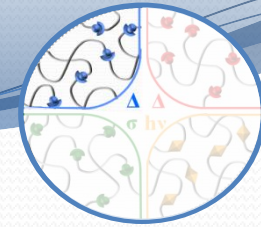
Strain (%)



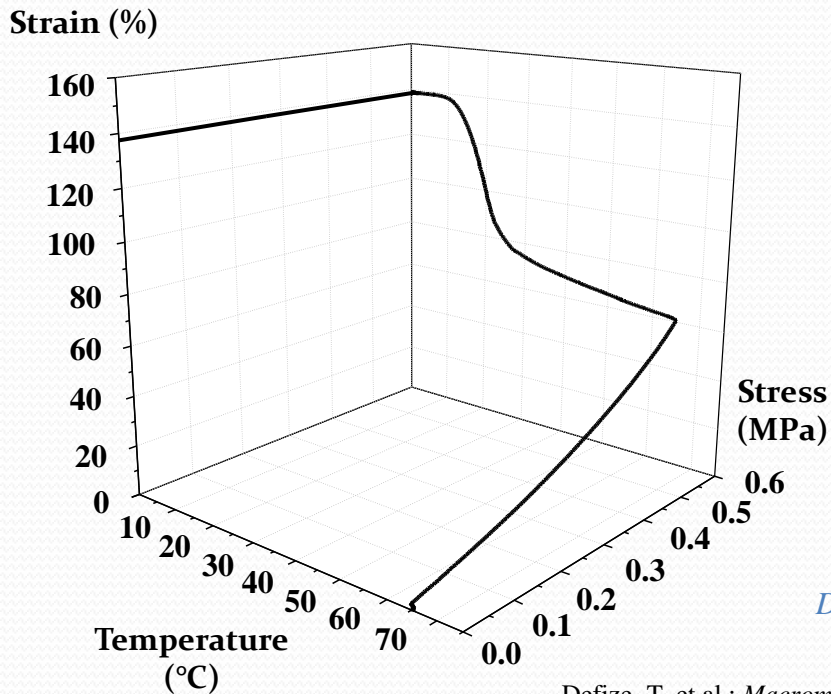
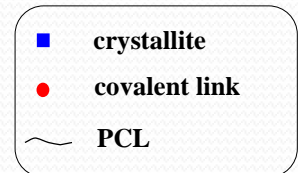
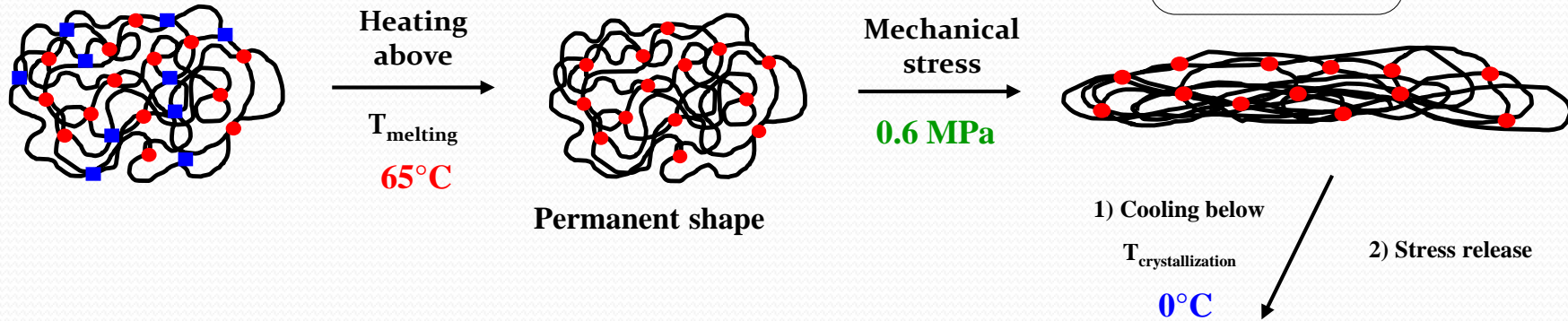
Stress maintained at 0.6MPa

Cooling ( $3^{\circ}\text{C}/\text{min}$  to  $0^{\circ}\text{C}$ )

*DMTA Q800, tensile mode, controlled stress, sample : 5x5x0.5 mm*



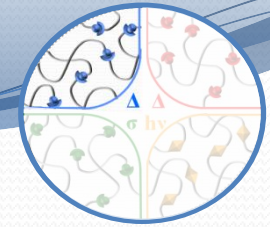
# Shape-memory properties



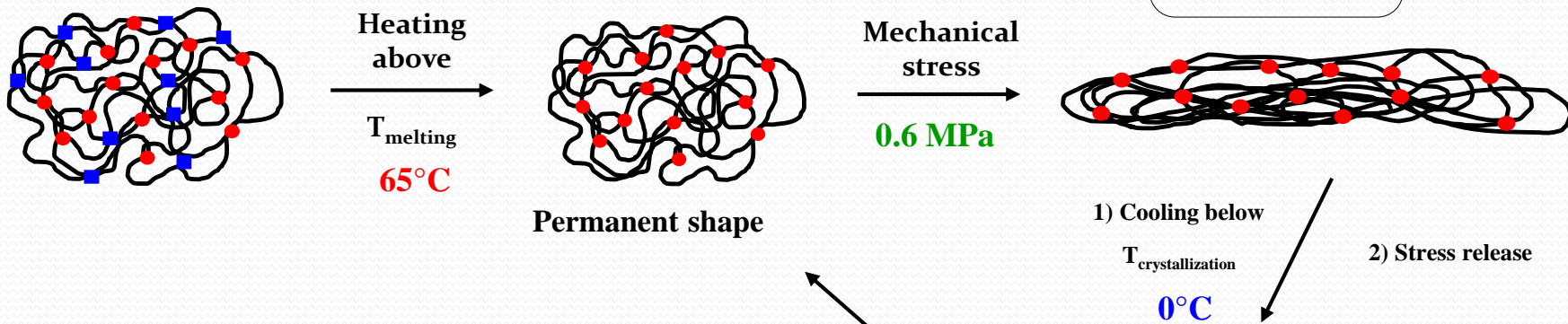
Release of the mechanical stress

**Fixity : >99%**

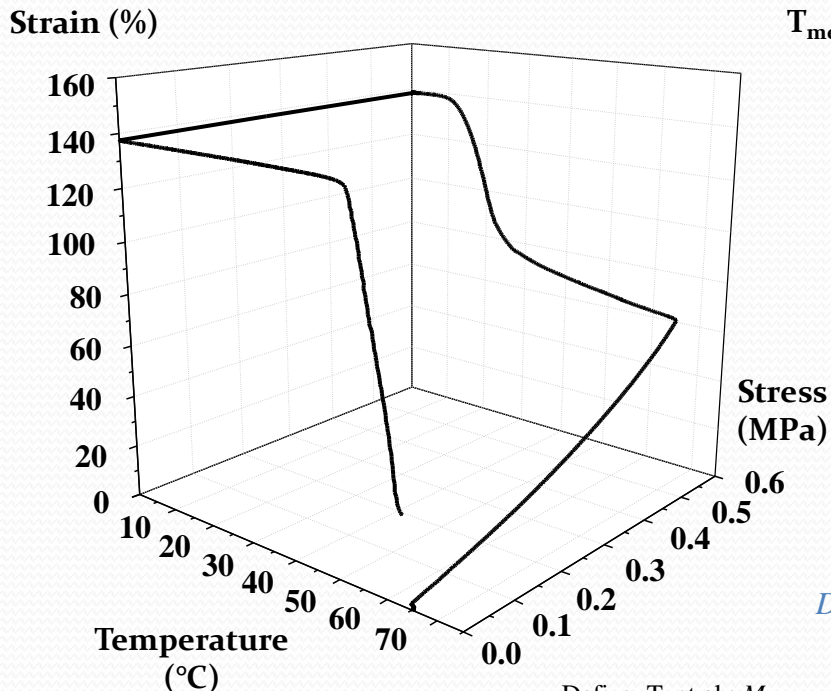
*DMTA Q800, tensile mode, controlled stress, sample : 5x5x0.5 mm*



# Shape-memory properties



■ crystallite  
● covalent link  
 ~ PCL



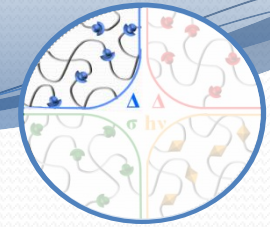
Heating (3°C/min to 65°C)

Isotherm 5 min at 65°C

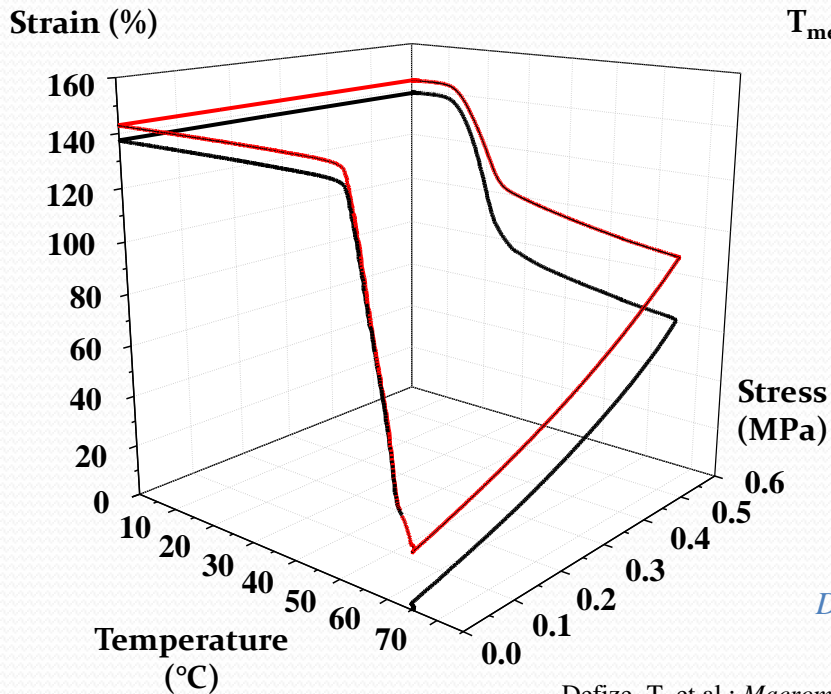
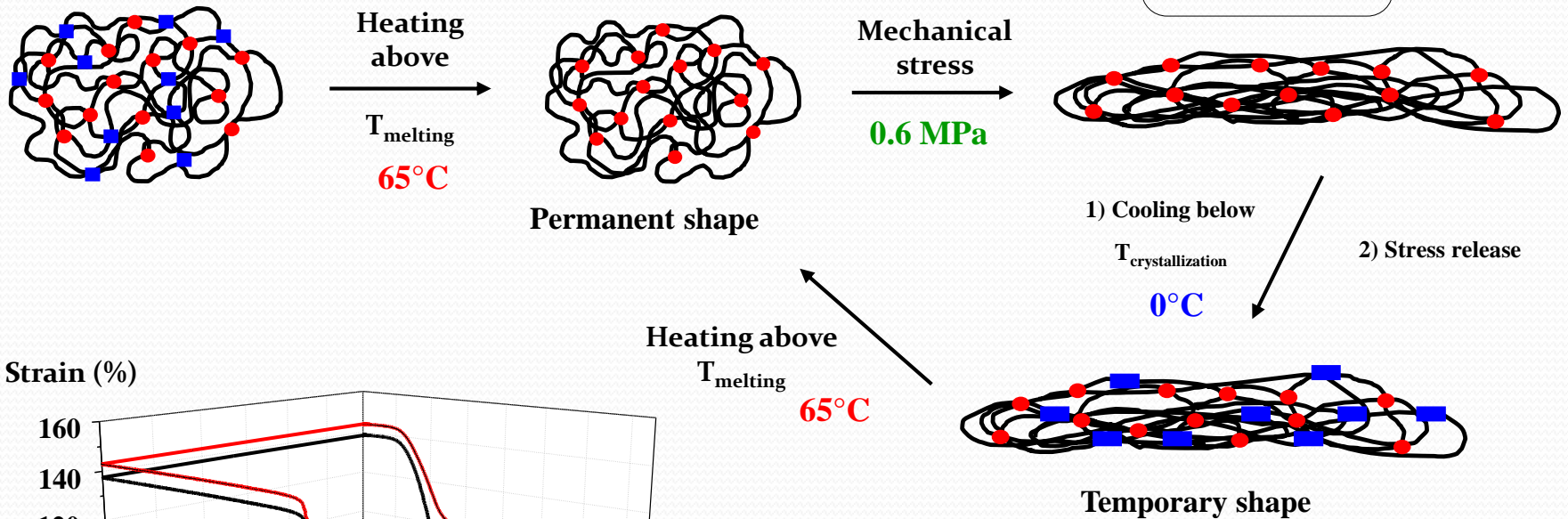
**Fixity** : >99%

**Recovery** : 88%

*DMTA Q800, tensile mode, controlled stress, sample : 5x5x0.5 mm*



# Shape-memory properties



Fixity : >99%

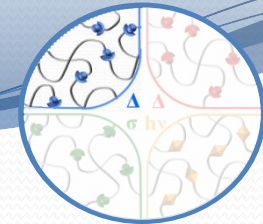
Recovery : 88%

Fixity : >99%

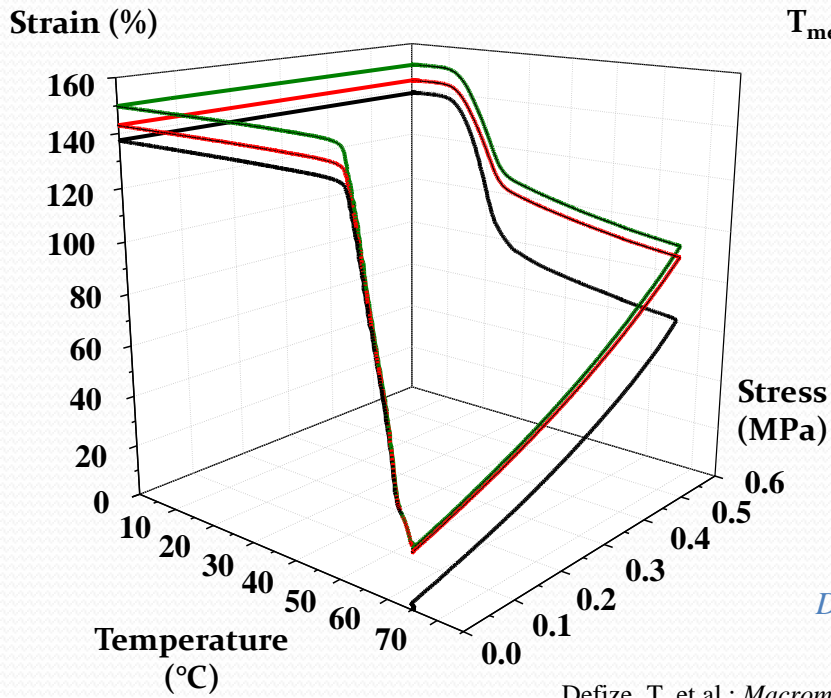
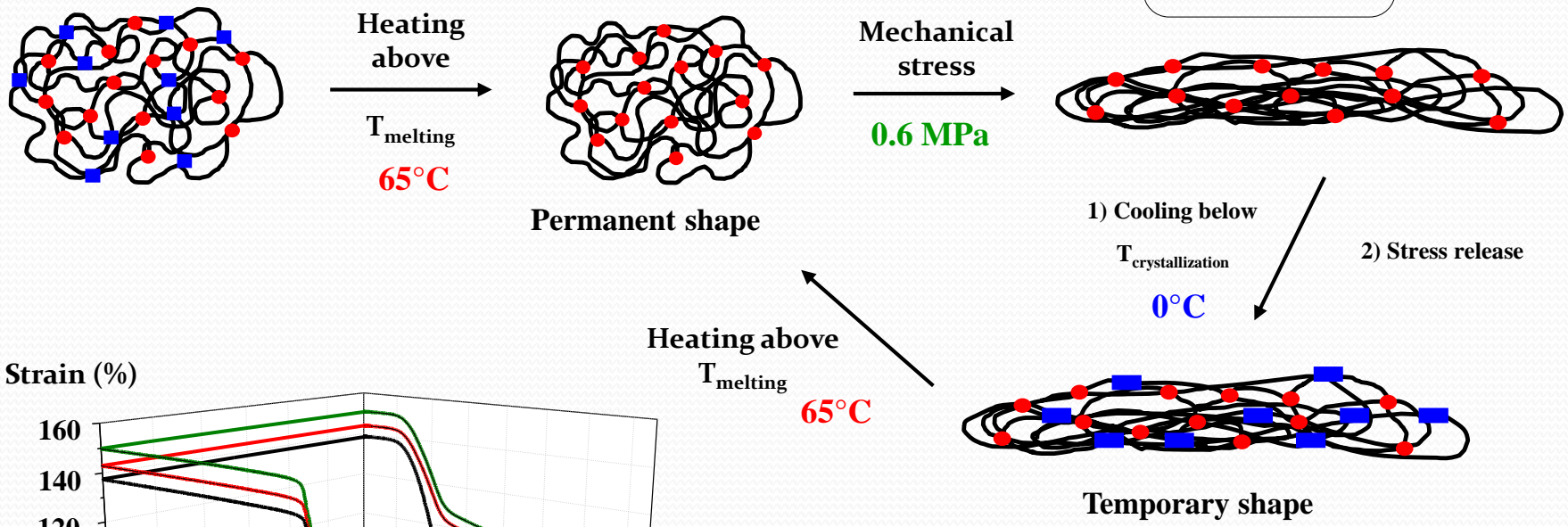
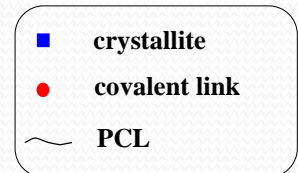
Recovery : >99%

*DMTA Q800, tensile mode, controlled stress, sample : 5x5x0.5 mm*





# Shape-memory properties

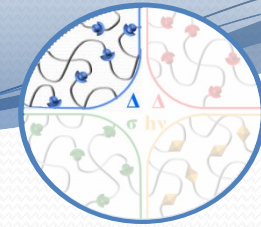


**Fixity : >99%**  
**Recovery : 88%**

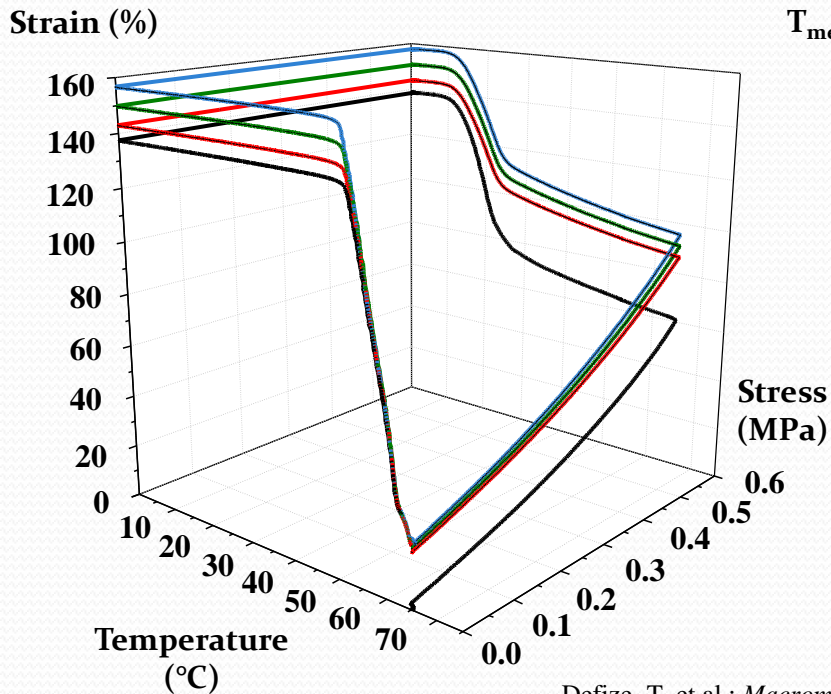
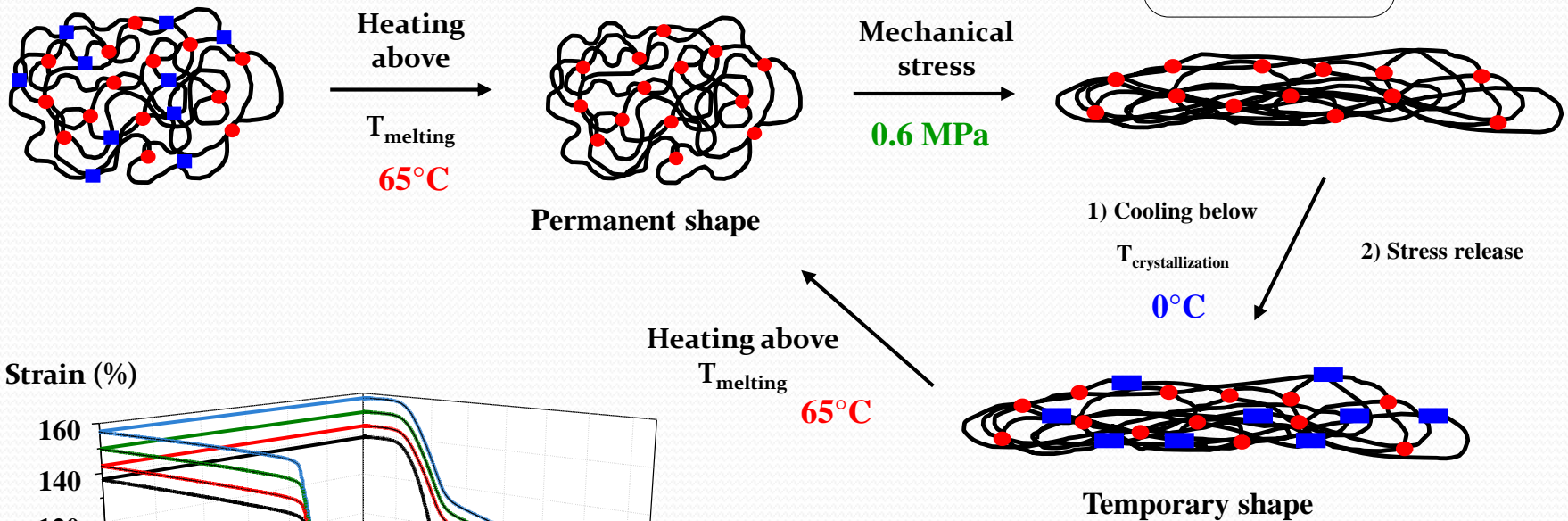
**Fixity : >99%**  
**Recovery : >99%**

**Fixity : >99%**  
**Recovery : >99%**

*DMTA Q800, tensile mode, controlled stress, sample : 5x5x0.5 mm*



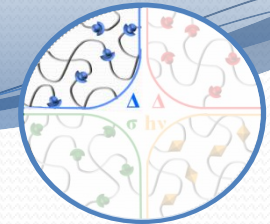
# Shape-memory properties



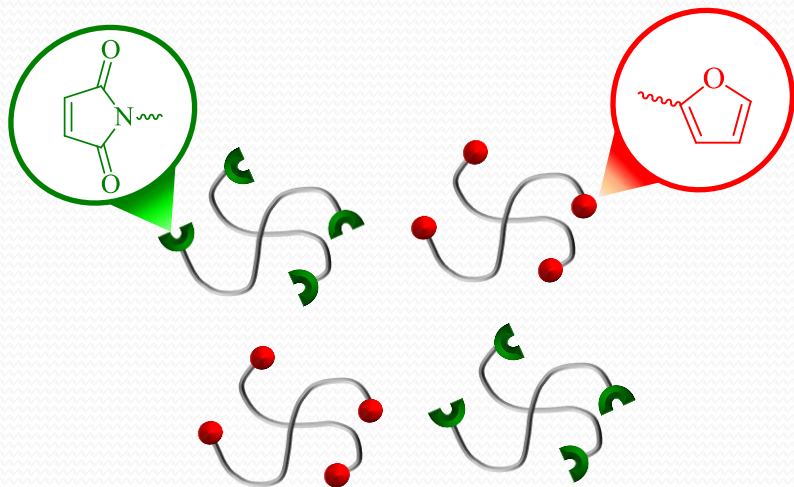
<b>Fixity</b> : >99%	<b>Fixity</b> : >99%
<b>Recovery</b> : 88%	<b>Recovery</b> : >99%
<b>Fixity</b> : >99%	<b>Fixity</b> : >99%
<b>Recovery</b> : >99%	<b>Recovery</b> : >99%



**Excellent fixity and recovery for each cycle**

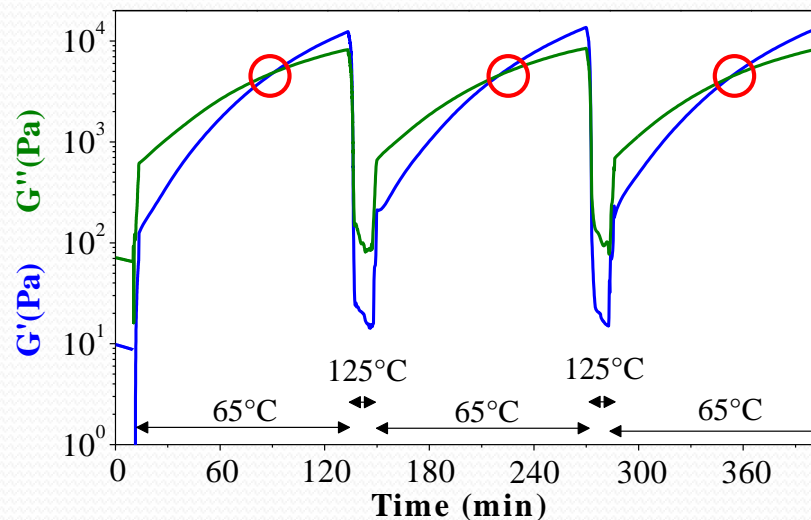
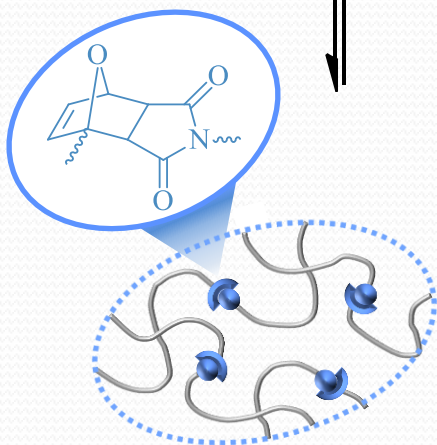


# Study of the network thermoreversibility by rheology



DA reaction  
65°C

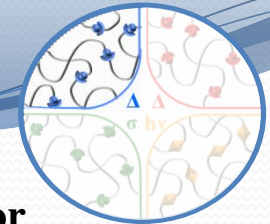
retro-DA reaction  
125°C



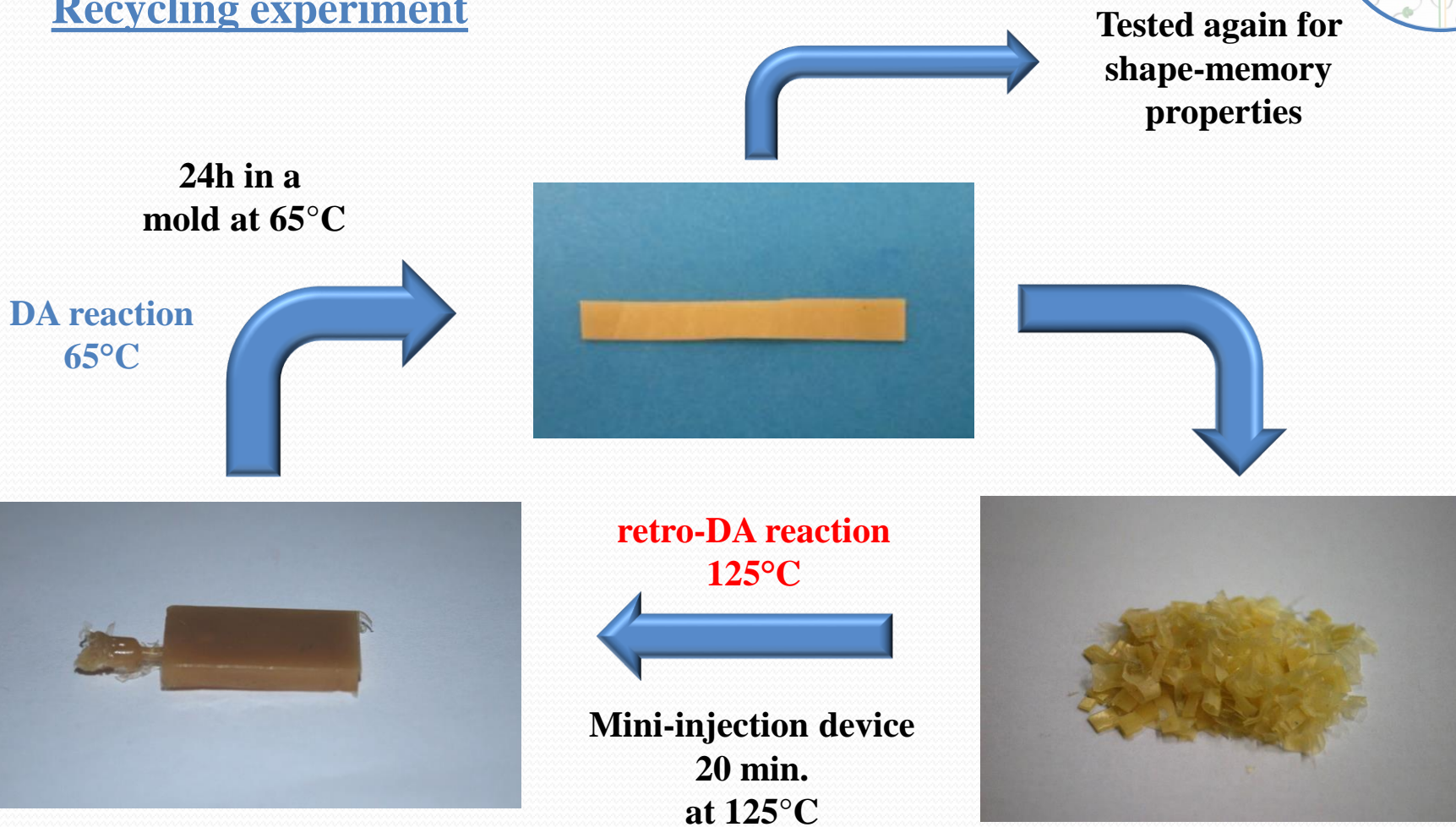
At 65°C: -  $G'$  increases due to network formation  
-  $G''$  increases due to viscosity increase

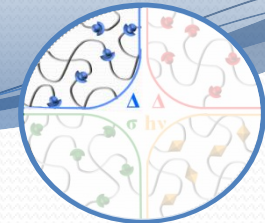
At 125°C: -  $G'$  decreases (network cleavage)  
-  $G''$  decreases (viscosity decrease)

- ✓ Gel points reached for the same  $G'$  and  $G''$  values
- ✓ Almost perfect reversibility
- ✓ High number of crosslinking/cleavage cycles can be achieved



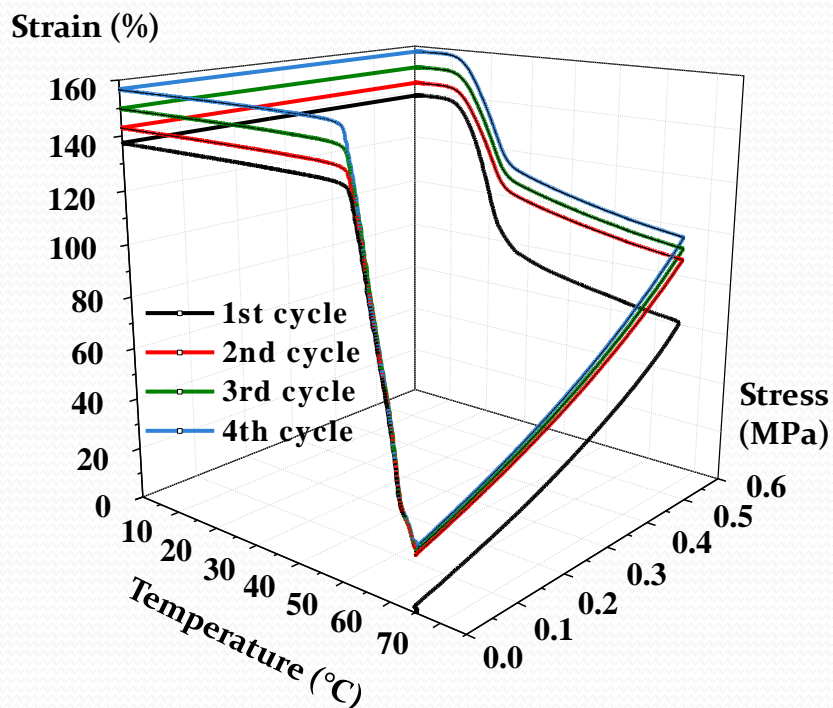
## Recycling experiment



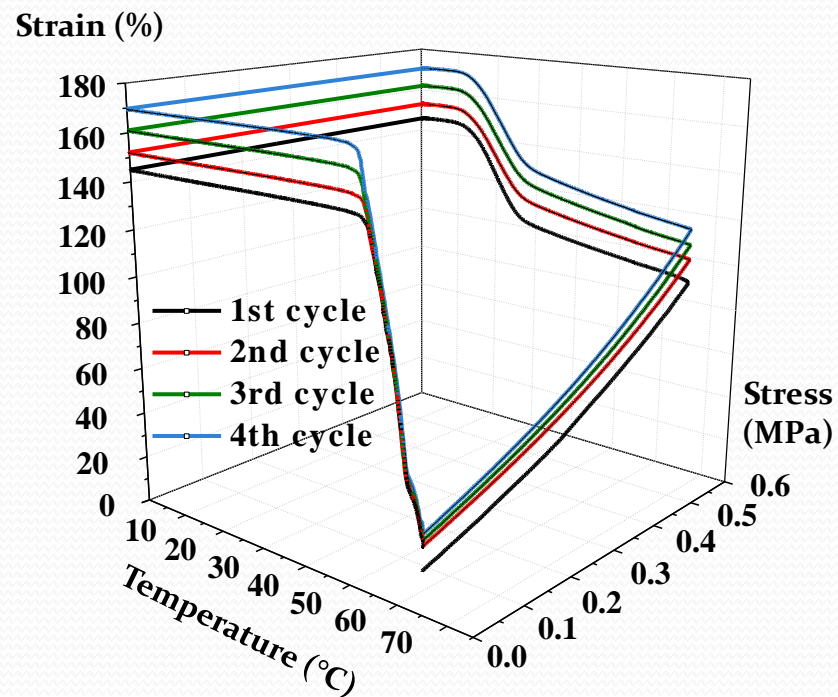


## Shape-memory properties before and after recycling

### Initial material



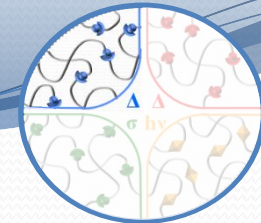
### Recycled material



- ✔ Excellent fixity and recovery for each cycle
- ✔ Similar mechanical properties before and after recycling

Diels-Alder/retro-Diels-Alder reactions allow recycling of cross-linked shape-memory materials

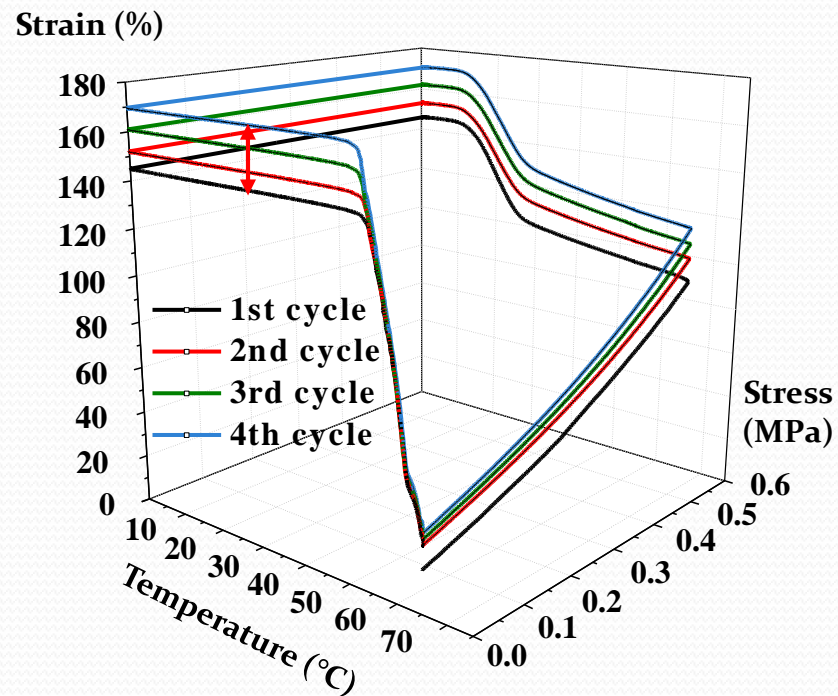
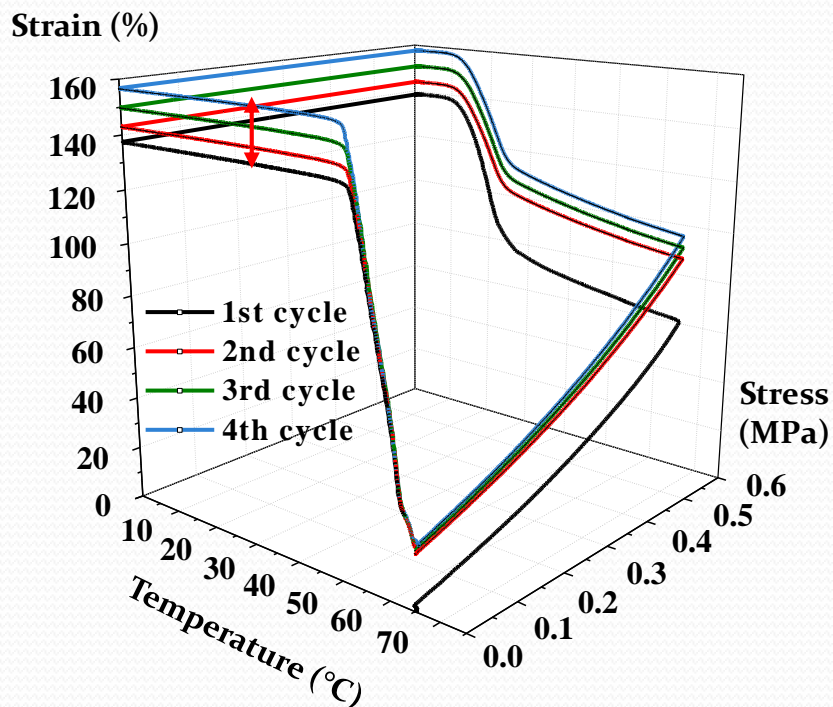




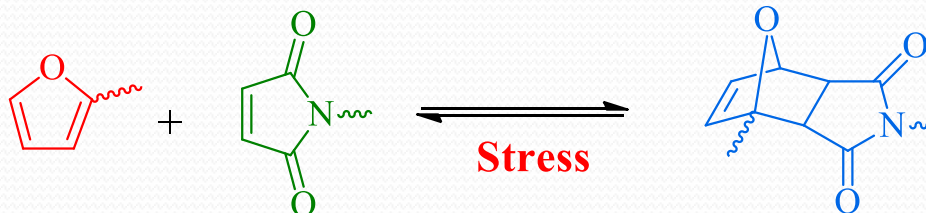
# Shape-memory properties before and after recycling

## Initial material

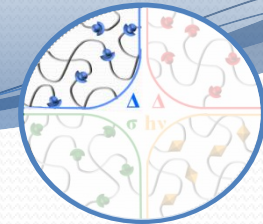
## Recycled material



Creep occurs under stretching



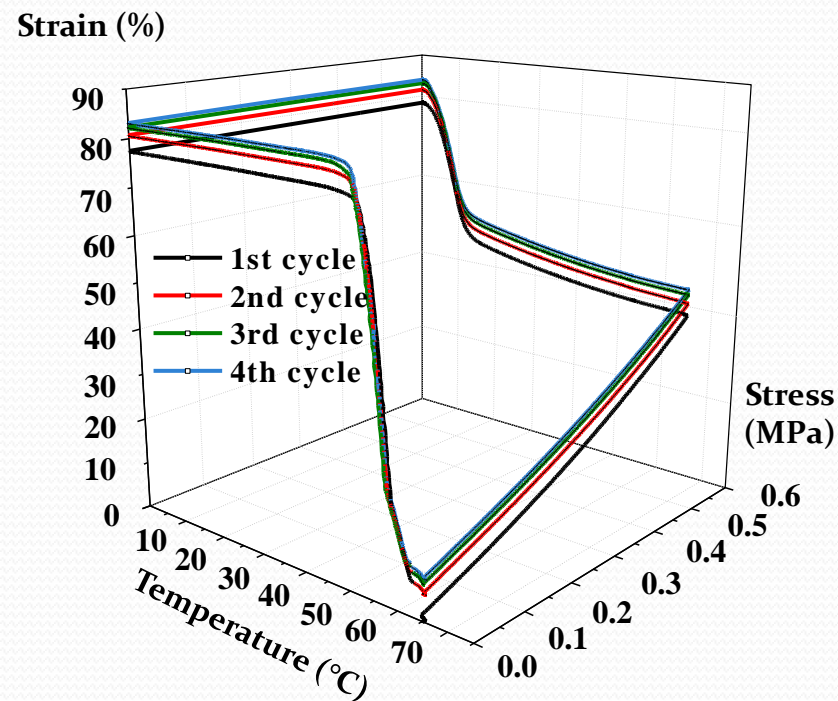
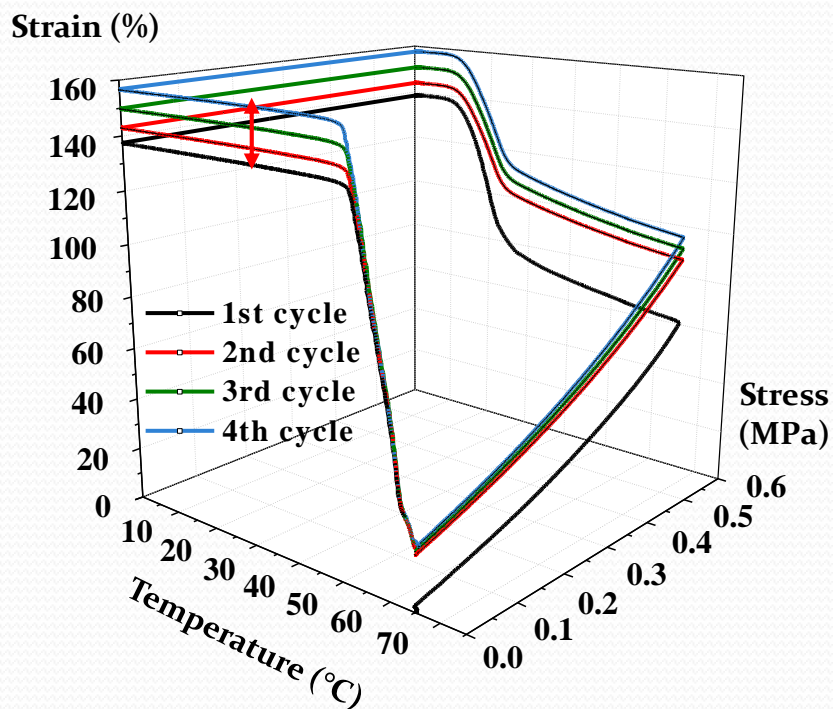
Some DA adducts break under elongation stress



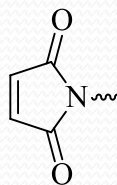
# What happens with a more stable Diels-Alder adduct ?

## Furan/maleimide material

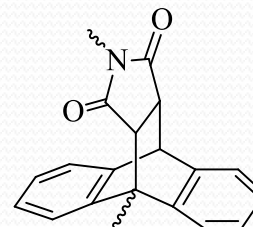
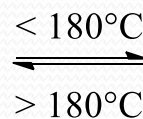
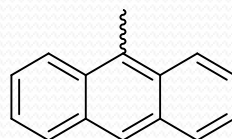
## Anthracene/maleimide material



Substitution of the furan  
by the anthracene group



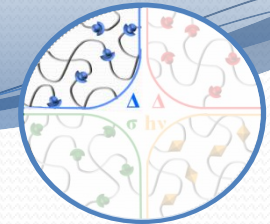
+



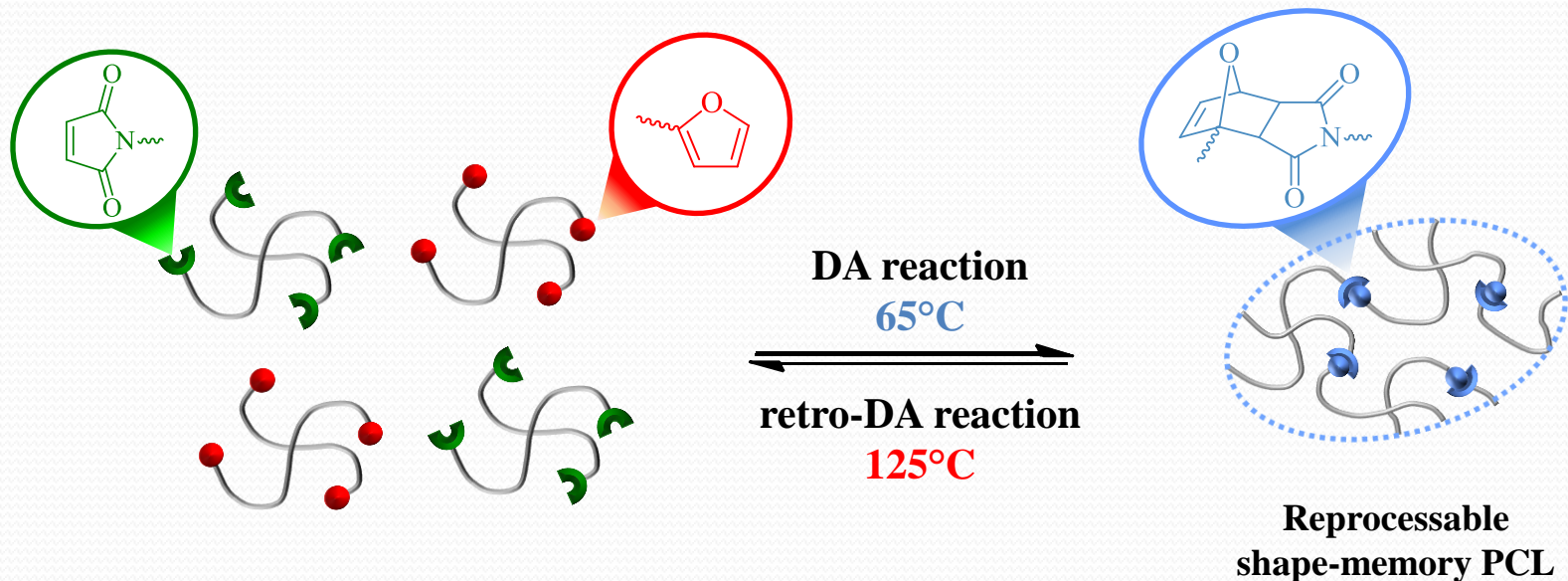
Thermally-stable adduct

**No creep**



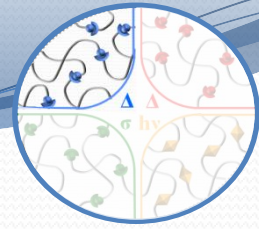


## Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)

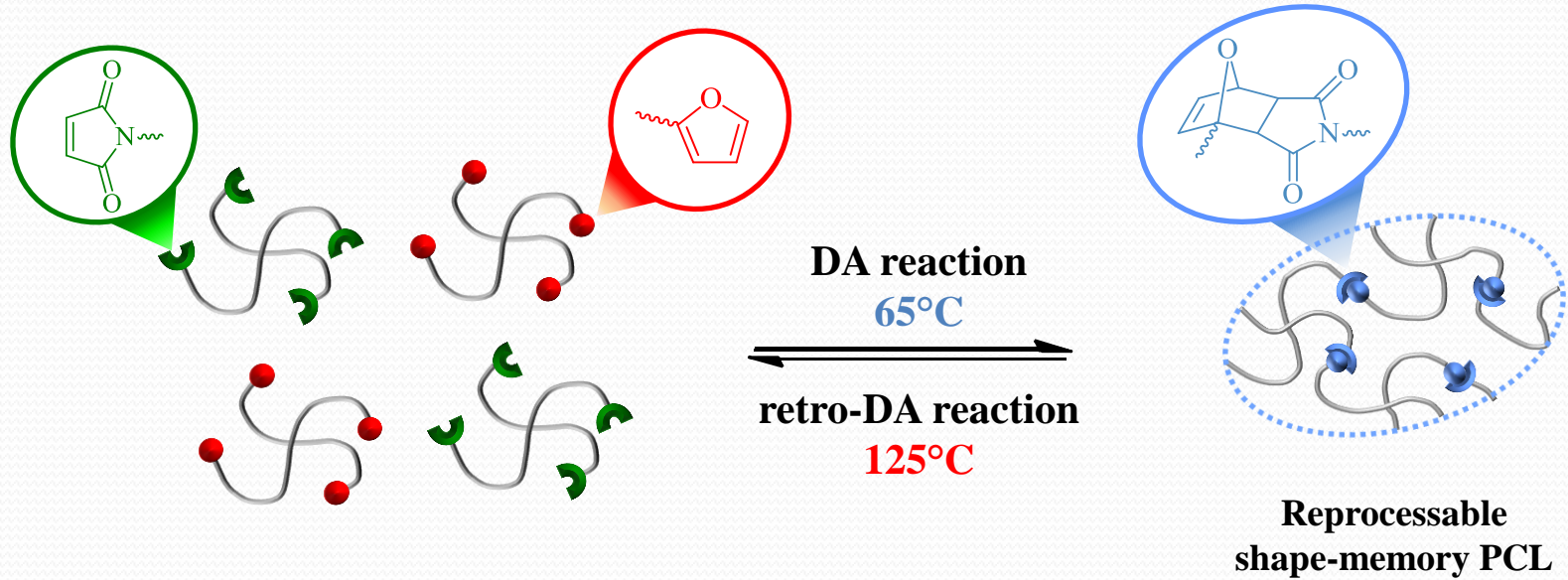


### Advantages

- ✓ Excellent shape-memory properties
- ✓ Good reversibility (proven by rheology)
- ✓ Easy melt reprocessability

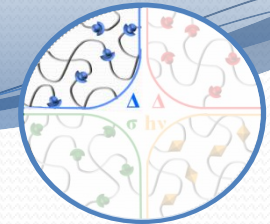


## Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)

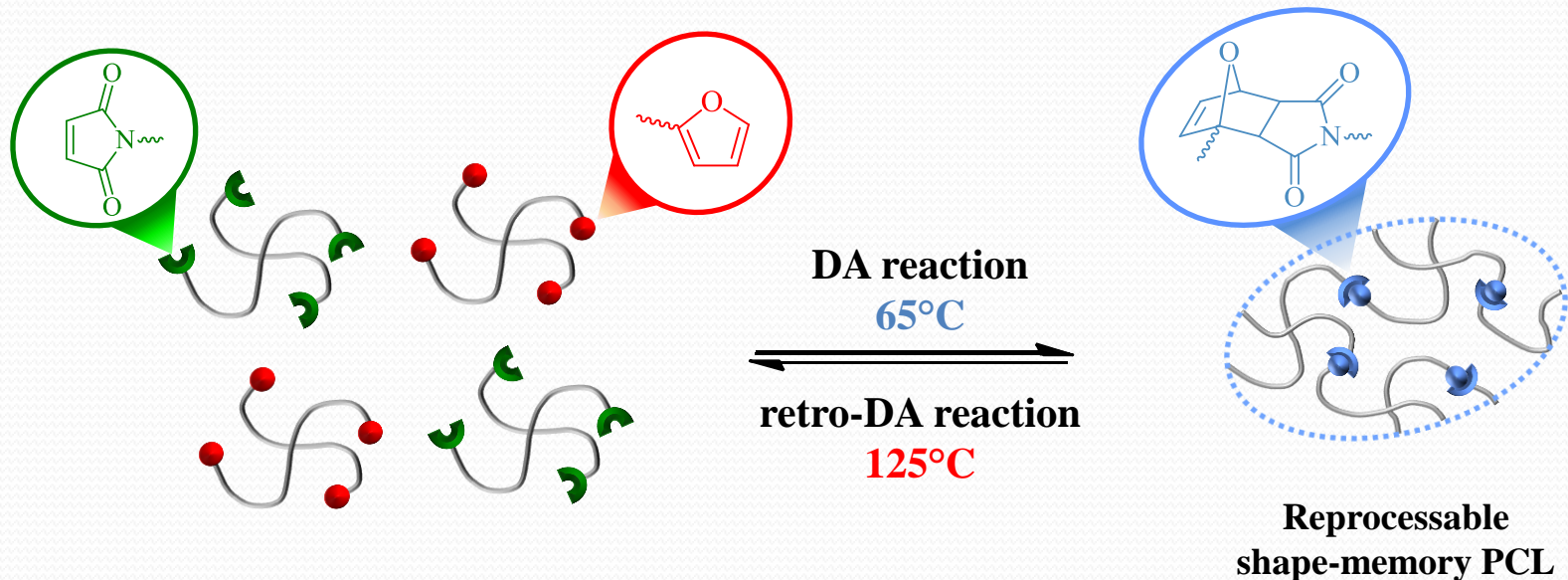


### Drawbacks

- ❌ Slow Diels-Alder reaction rate (24h to reach the equilibrium state at 65°C)
- ❌ Creep occurring under stress due to the disruption of some DA-adducts



## Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)



### Drawbacks

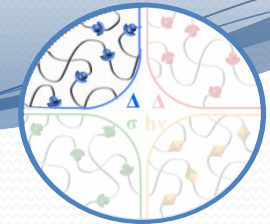
❌ **Slow Diels-Alder reaction rate (24h to reach the equilibrium state at  $65^{\circ}\text{C}$ )**

❌ **Creep occurring under stress due to the disruption of some DA-adducts**

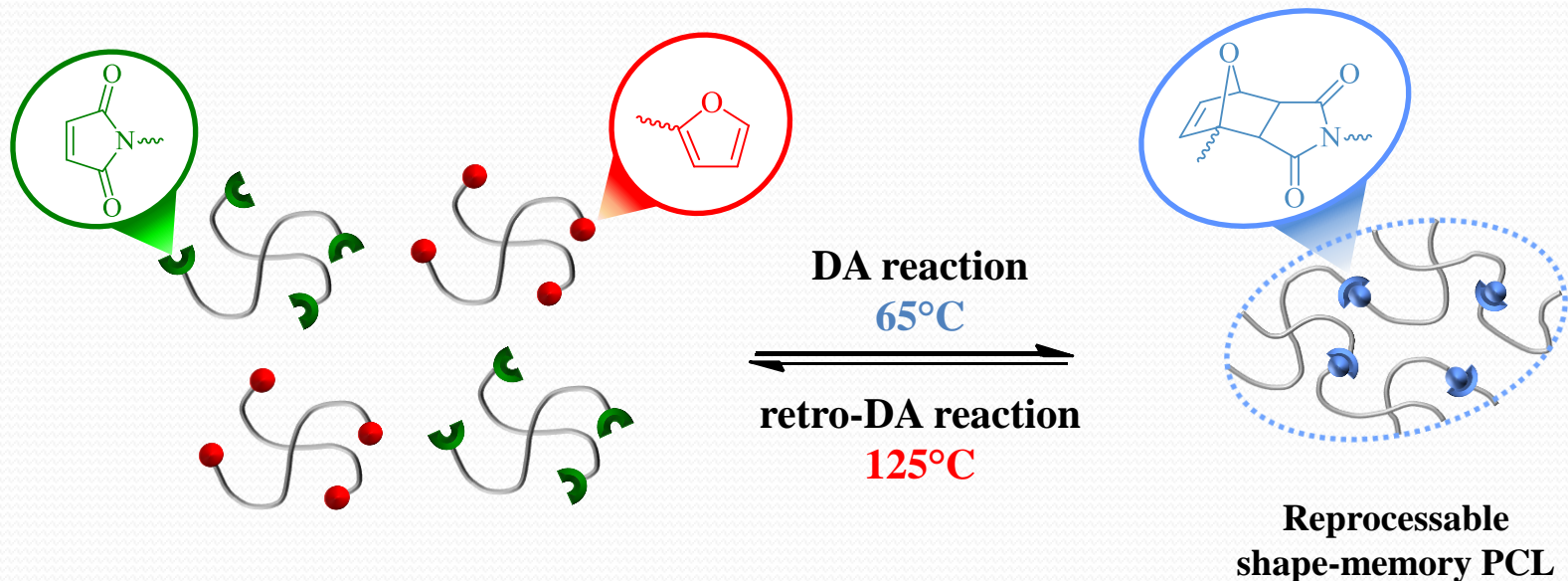


**Use of a faster thermally-reversible reaction**

**TAD-Indole reaction**



## Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)



### Drawbacks



Slow Diels-Alder reaction rate (24h to reach the equilibrium state at  $65^{\circ}\text{C}$ )



Use of a faster thermally-reversible reaction

TAD-Indole reaction

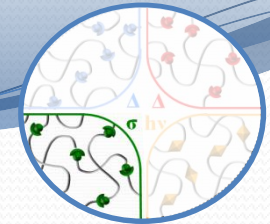


Creep occurring under stress due to the disruption of some DA-adducts

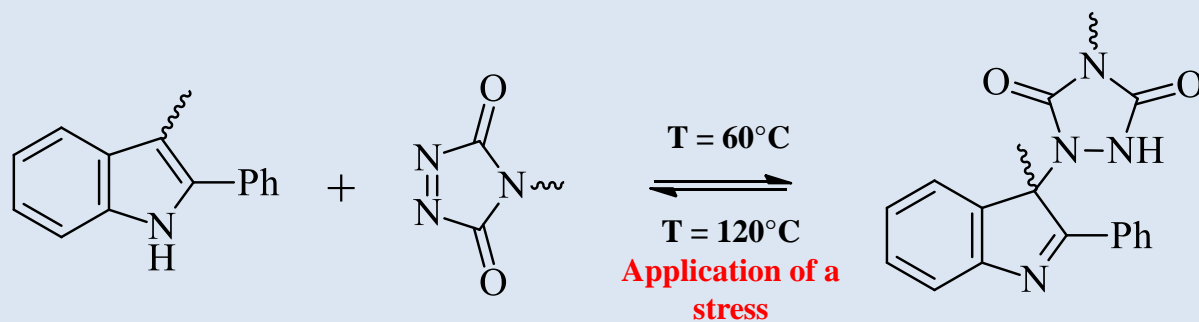


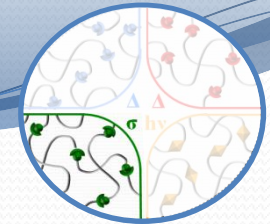
Use of photoreversible reaction (thermally stable)

Dimerization of coumarin

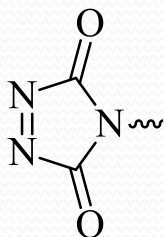


## Reversible TAD/Indole Alder-ene reaction

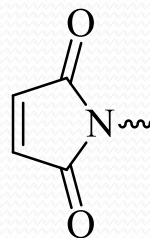




## 1,2,4-triazoline-3,5-dione (TAD)

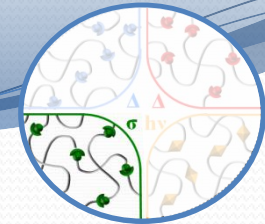


**TAD**  
**red**

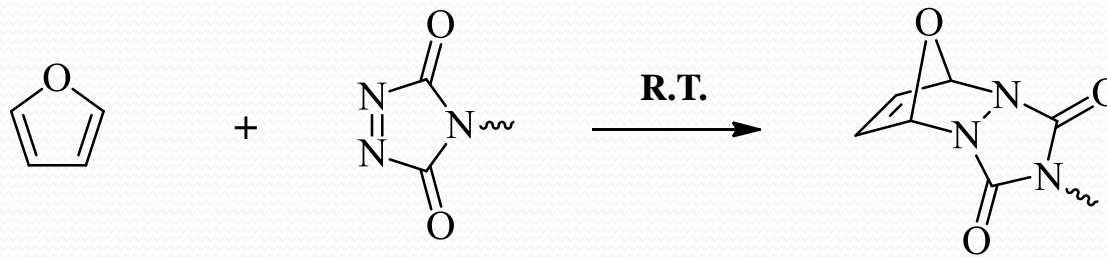


**maleimide**

+ **High reactivity of TAD**



## 1,2,4-triazoline-3,5-dione (TAD)



**Furan**

**TAD**  
**red**

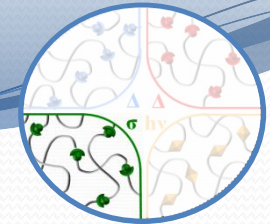
**TAD-Furan**  
**adduct**

**Irreversible**  
**adduct**

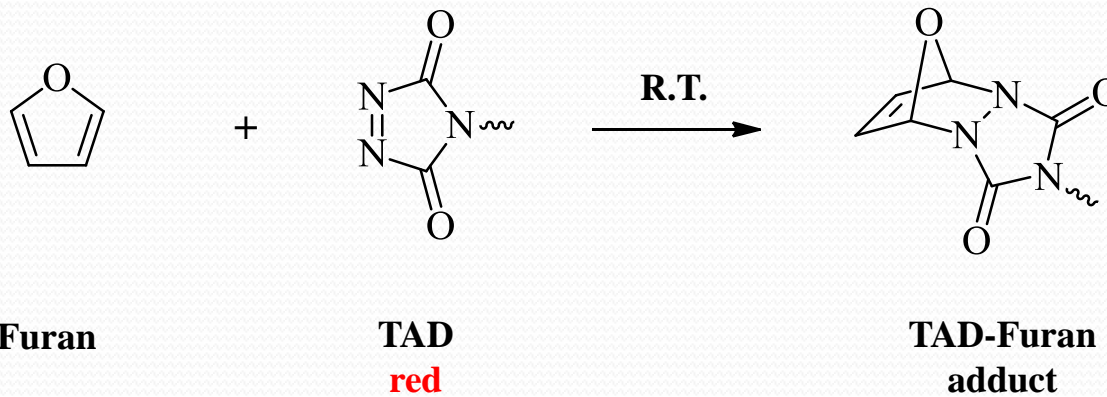
- + **High reactivity of TAD**
- + **Extremely fast reaction**
- + **Visual feedback**







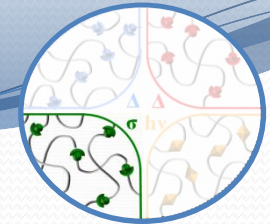
## 1,2,4-triazoline-3,5-dione (TAD)



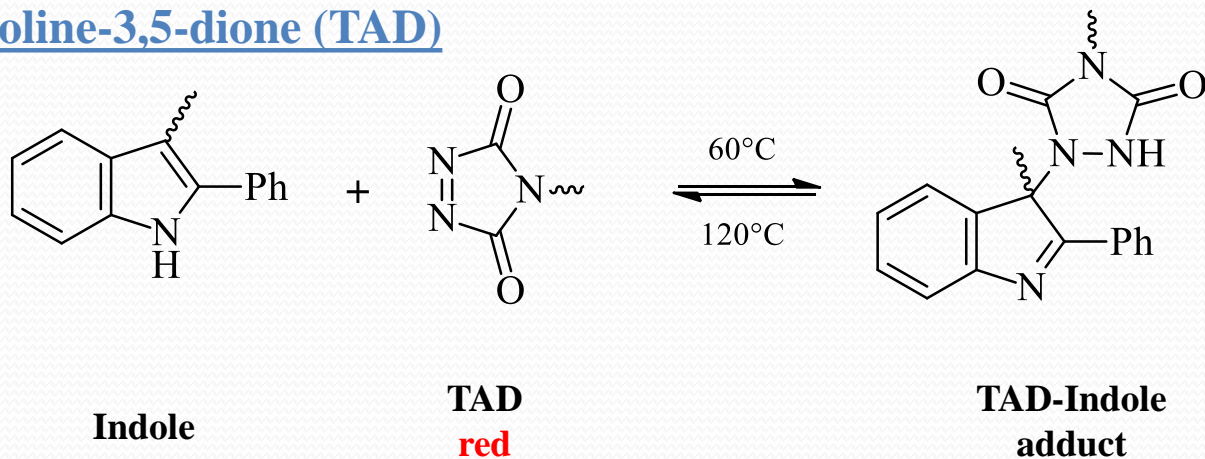
**Irreversible  
adduct**

- + **High reactivity of TAD**
- + **Extremely fast reaction**
- + **Visual feedback**





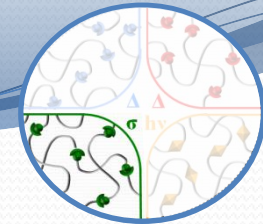
## 1,2,4-triazoline-3,5-dione (TAD)



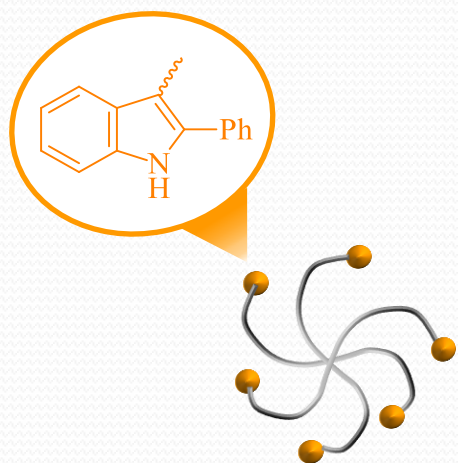
**Thermo-reversible  
Alder-ene adduct**

- + **High reactivity of TAD**
- + **Extremely fast reaction**
- + **Visual feedback**

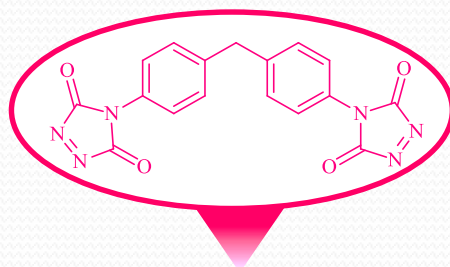
**Reversible reaction between TAD and indole**



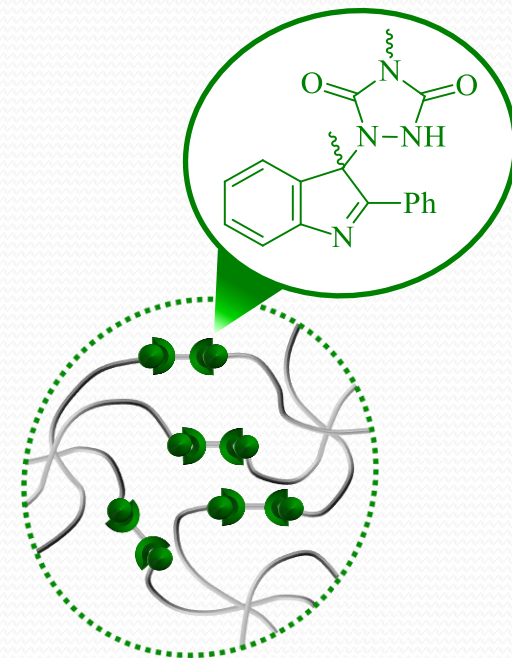
## General Strategy – TAD-Indole crosslinking



**PCL-6Indole**

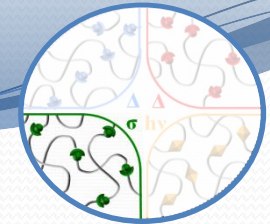


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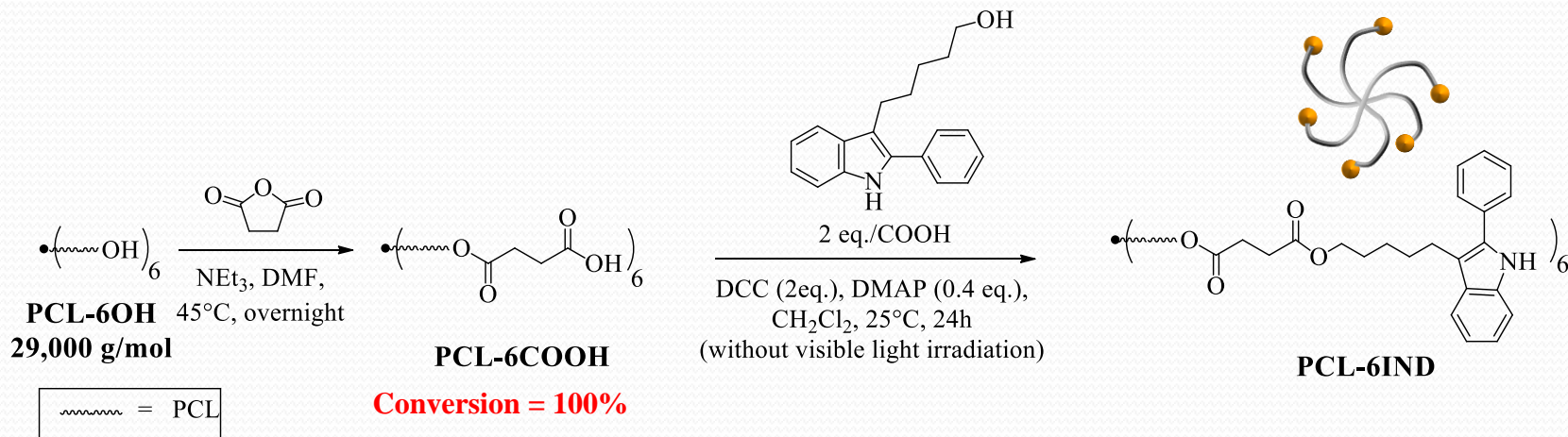


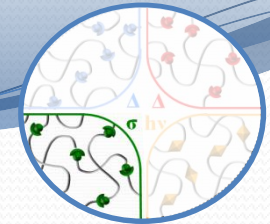
**Cross-linked PCL**

- Synthesis of 6-arm star-shaped PCL by ring opening polymerization of  $\epsilon$ -caprolactone
- Use of a bis-TAD (**functionalization of PCL with TAD moieties is not easy**)

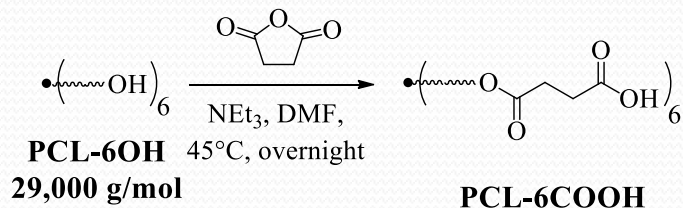


## Functionalization of PCL by indole moieties

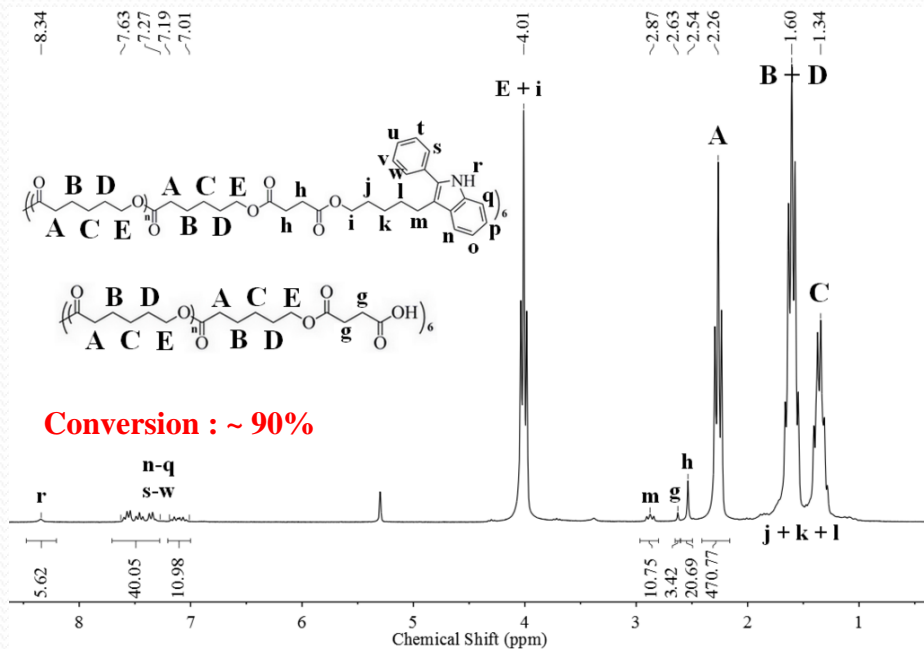
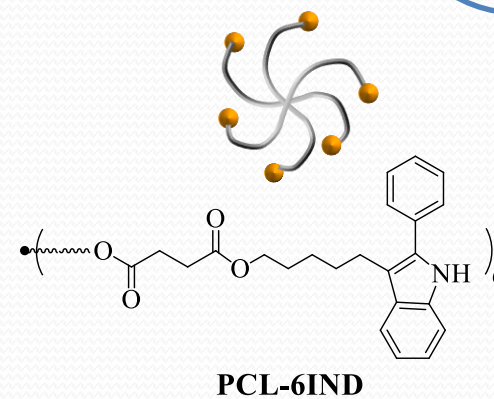
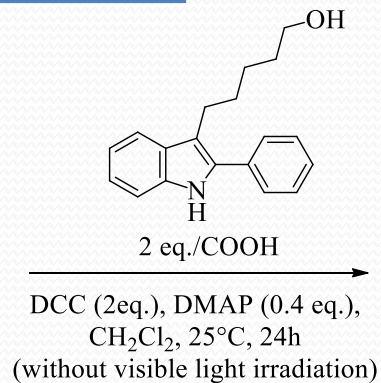
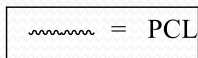


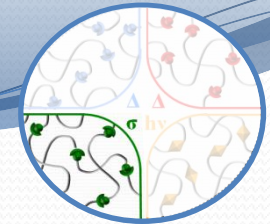


## Functionalization of PCL by indole moieties

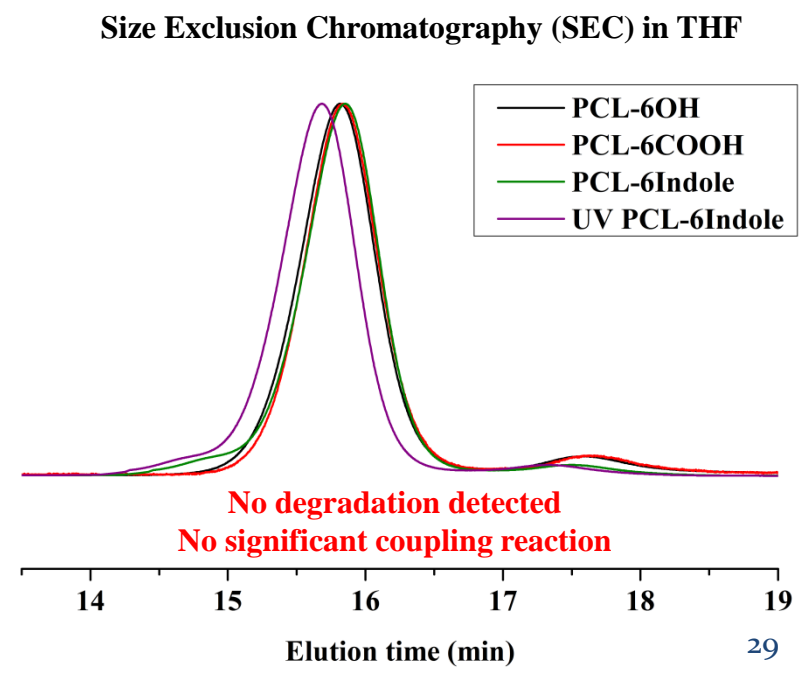
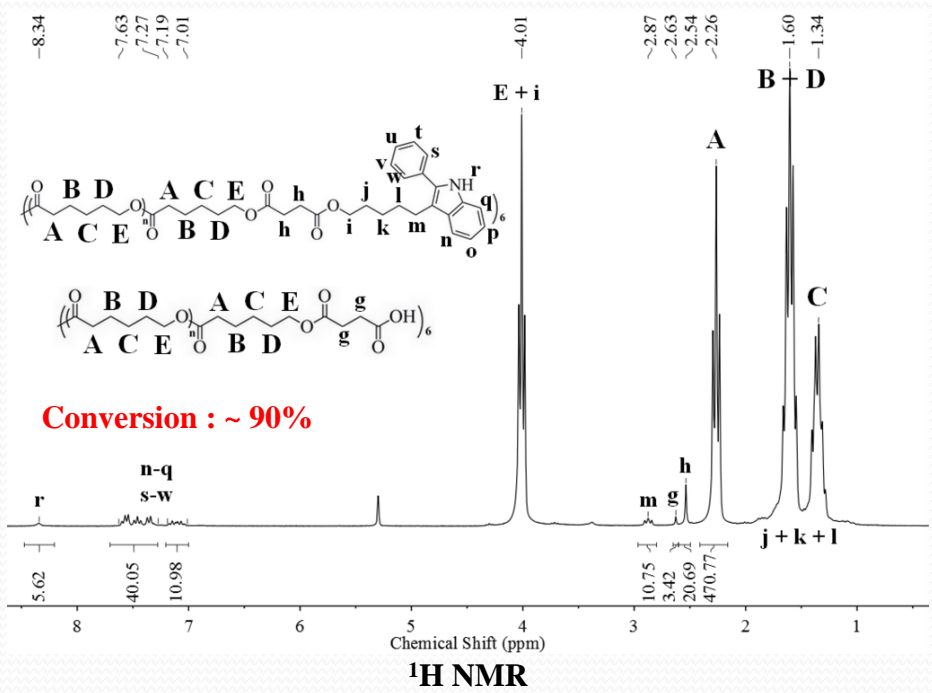
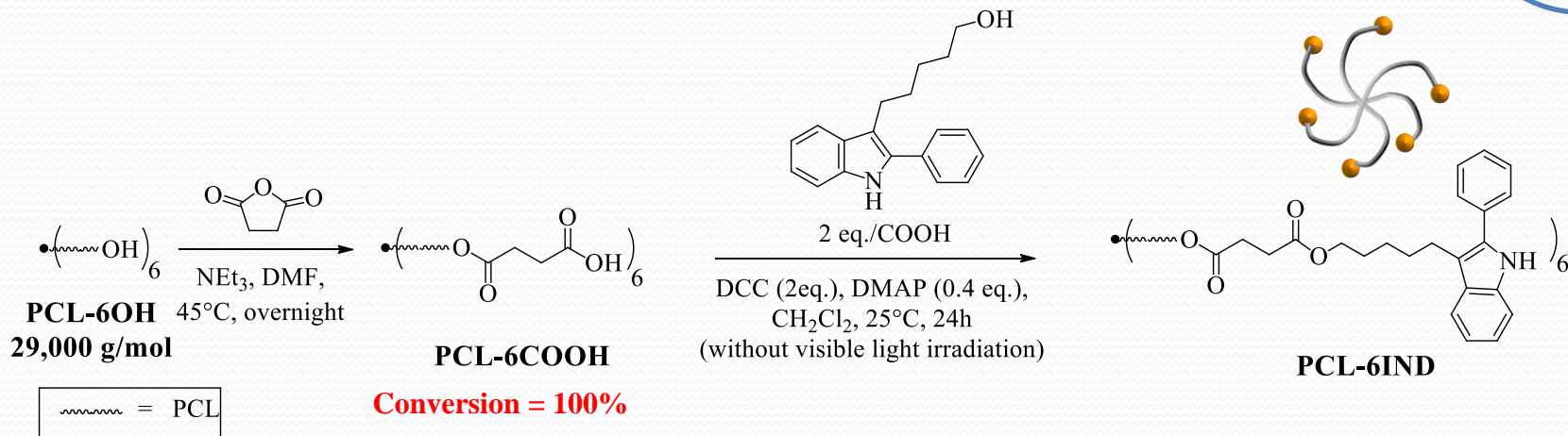


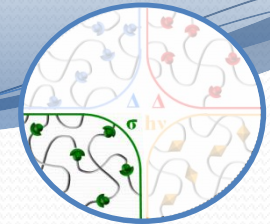
**Conversion = 100%**





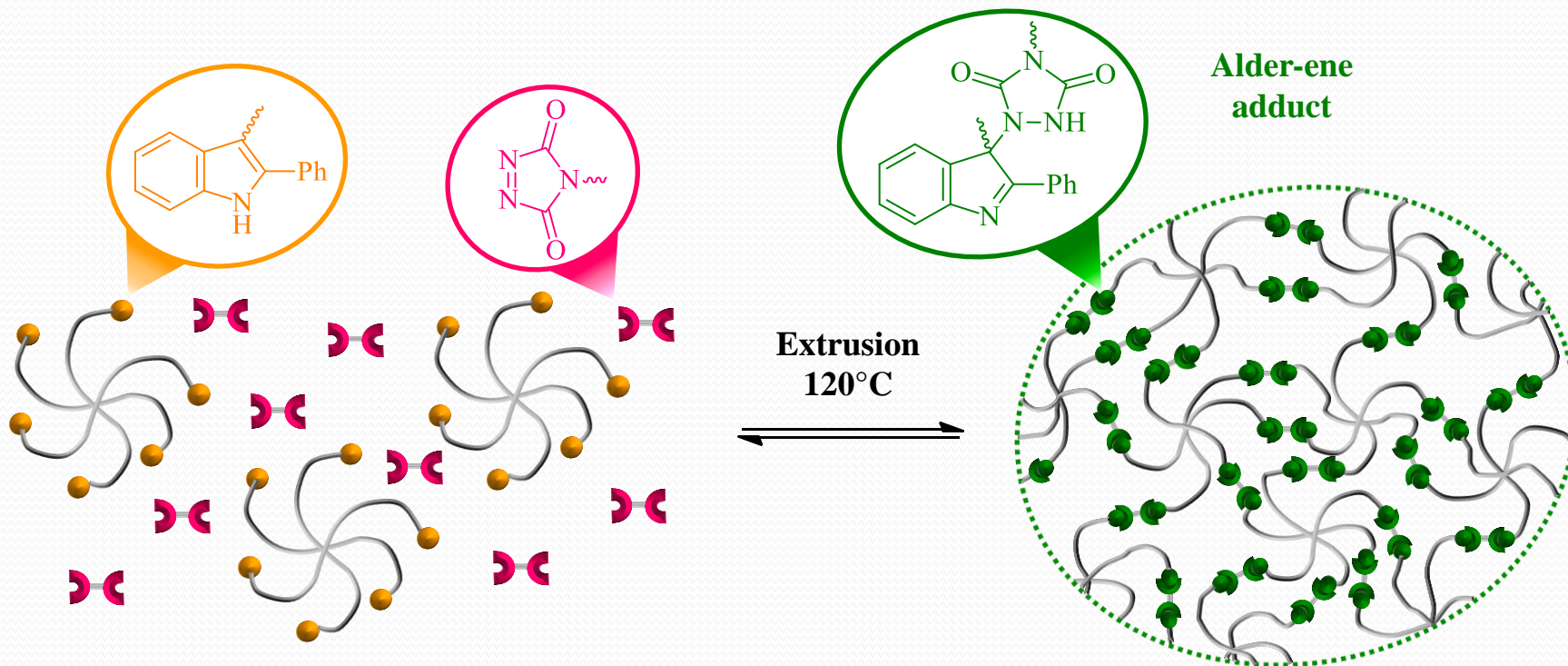
## Functionalization of PCL by indole moieties





## Processing of the precursors

Stoichiometric amounts in reactive groups of **PCL-6Indole** and **bis-TAD** were grinded, mixed together and injected in a mini-extruder at 120°C.



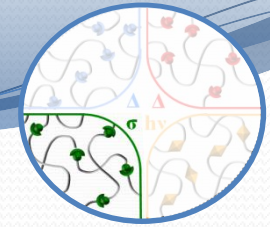
- Mixing during 15min (50 rpm) at 120°C
- A cross-linked material is recovered



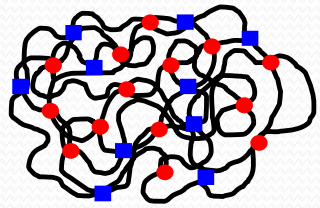
Crosslinking occurred at 120°C and/or during the cooling of the blend

- Preparation of films by compression molding (1h, 120°C, 100 bars)



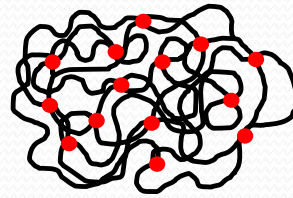


# Shape-memory properties



Heating above

$T_{\text{melting}}$   
65°C

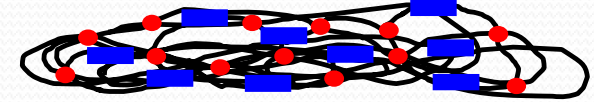


Permanent shape

Mechanical stress  
0.3 MPa

Cooling below  
 $T_{\text{crystallization}}$  (0°C)

Stress release



Temporary shape

- crystallites
- covalent links
- PCL

Heating above  
 $T_{\text{melting}}$   
65°C

Fixity : >99%

Recovery : 88%

Fixity : >99%  
Recovery : >99%

Fixity : >99%

Recovery : >99%

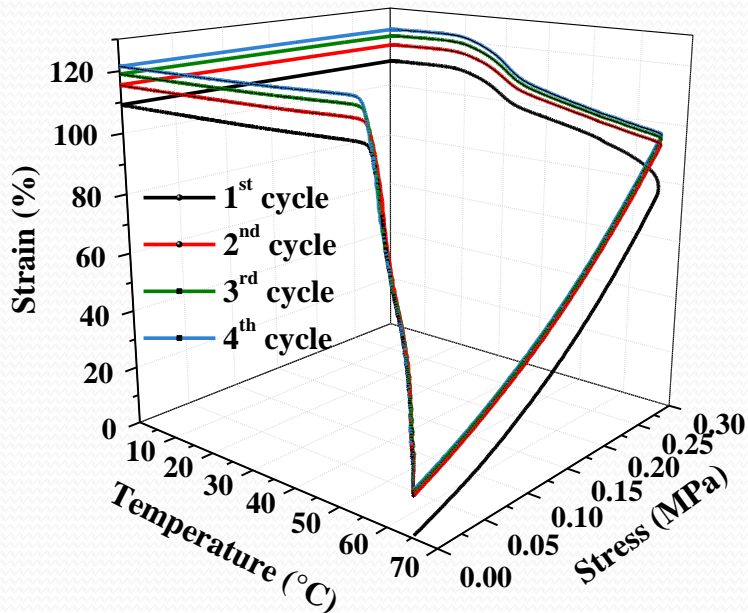
Fixity : >99%  
Recovery : >99%

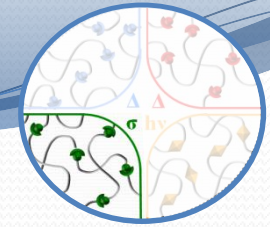


Excellent fixity and recovery for each cycle

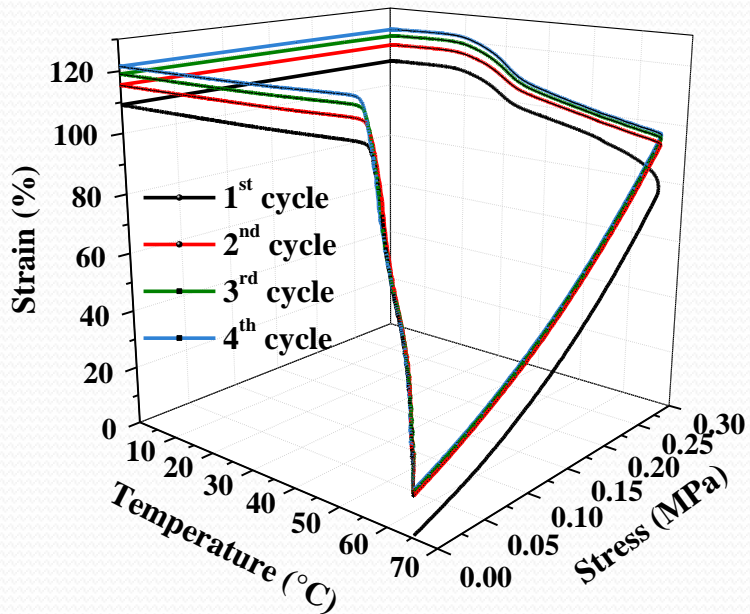
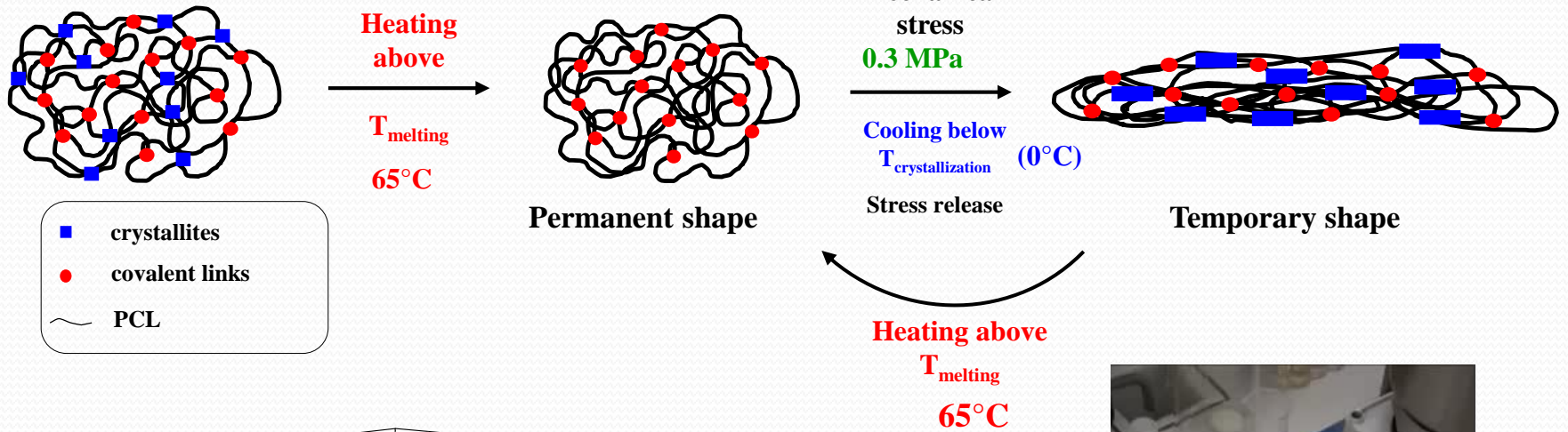


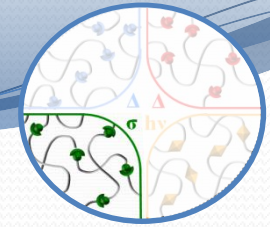
Low creep effect from cycle to cycle



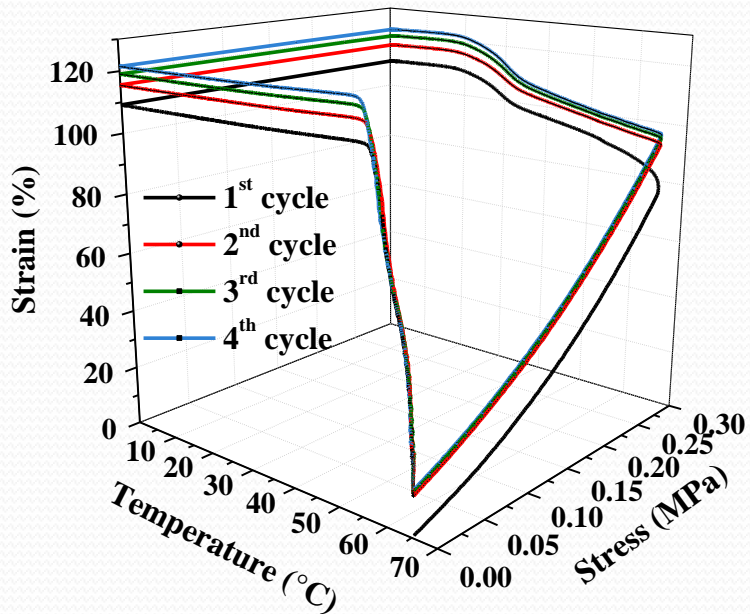
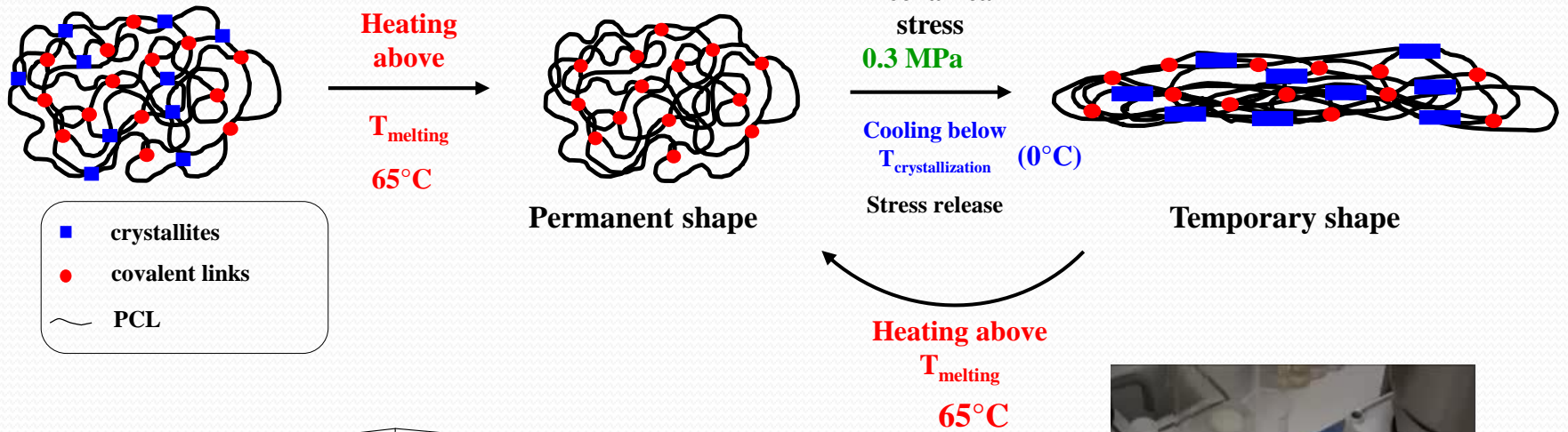


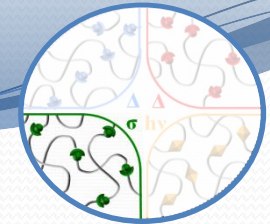
# Shape-memory properties





# Shape-memory properties



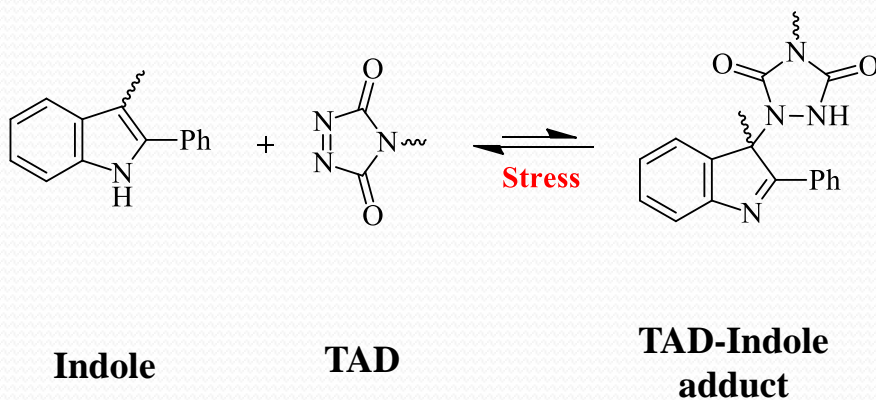
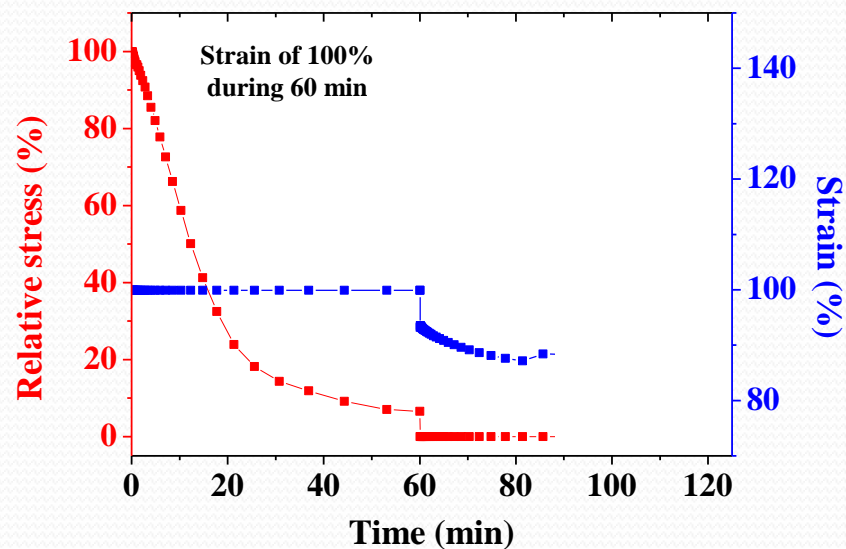


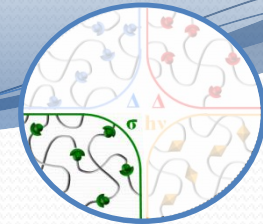
## Stress-relaxation experiment

- Application of a constant strain to the sample (100%)
- Measurement of the stress in the function of time at 120°C

### Upon long-time strain (1h)

- Relaxation of the material by the dynamic breaking-up/formation of the adducts at 120°C
- Formation of a novel network :
  - The disruption of TAD-indole adducts under stress
  - The formation of new TAD-indole adducts
- Permanent deformation of the material (90%)



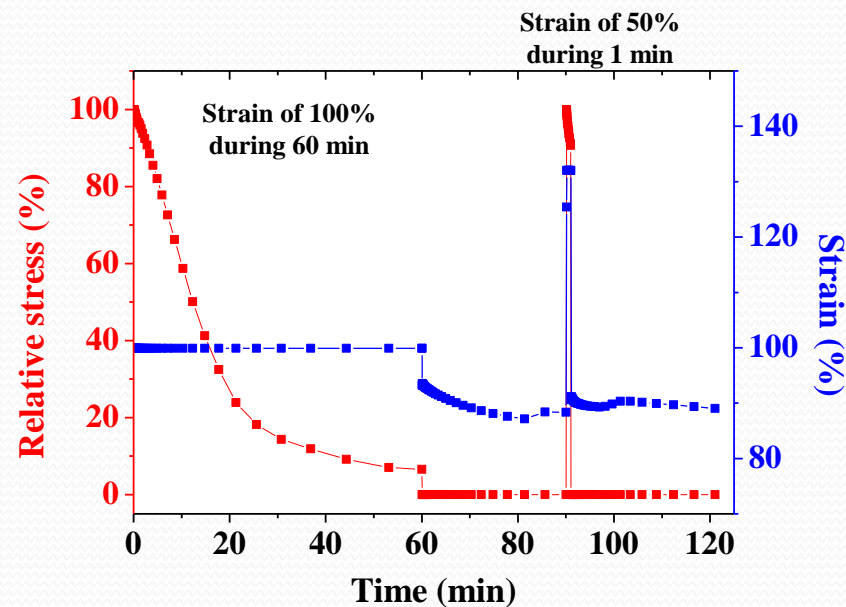


## Stress-relaxation experiment

- Application of a constant strain to the sample (100%)
- Measure of the stress in the function of time at 120°C

### Upon long-time strain (1h)

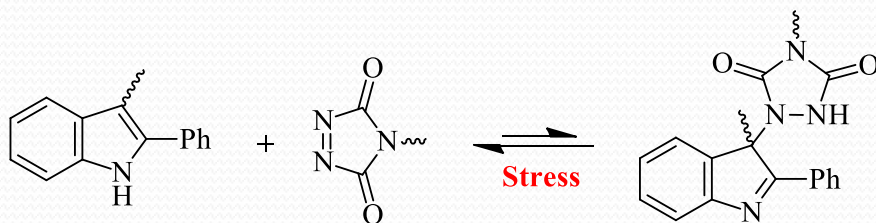
- Relaxation of the material by the dynamic breaking-up/formation of the adducts at 120°C.
- Formation of a novel network :
  - The disruption of TAD-indole adducts under stress
  - The formation of new TAD-indole adducts
- Permanent deformation of the material (90%)



### Upon short-time strain (1 min)

- Minimal stress relaxation (~90% of the initial stress)
- No permanent deformation of the material (3%)

**The material is not able to reorganize within this short time frame**

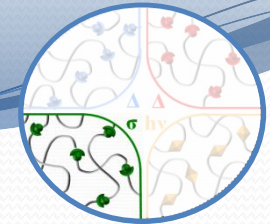


Indole

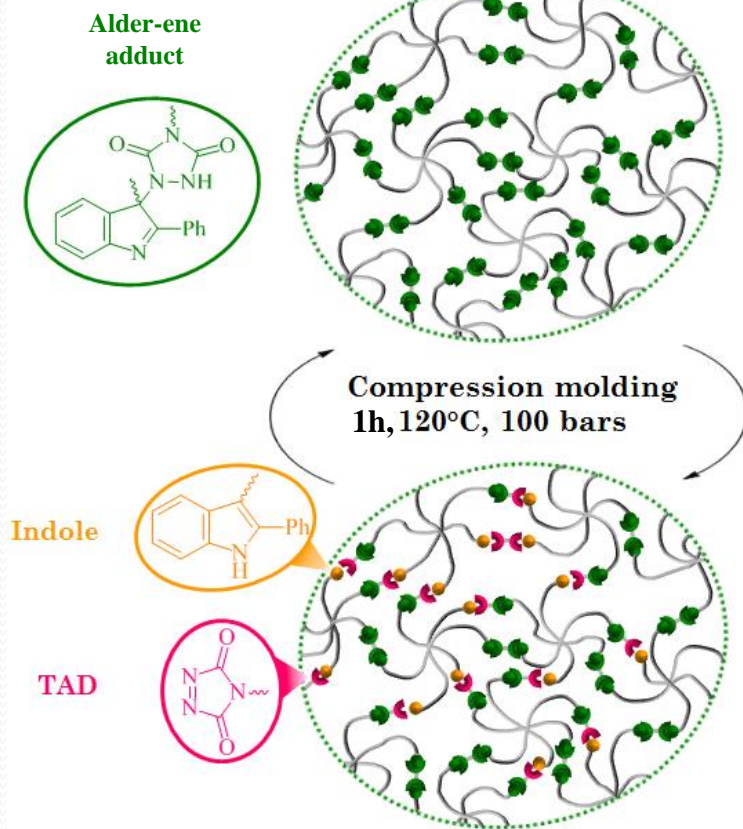
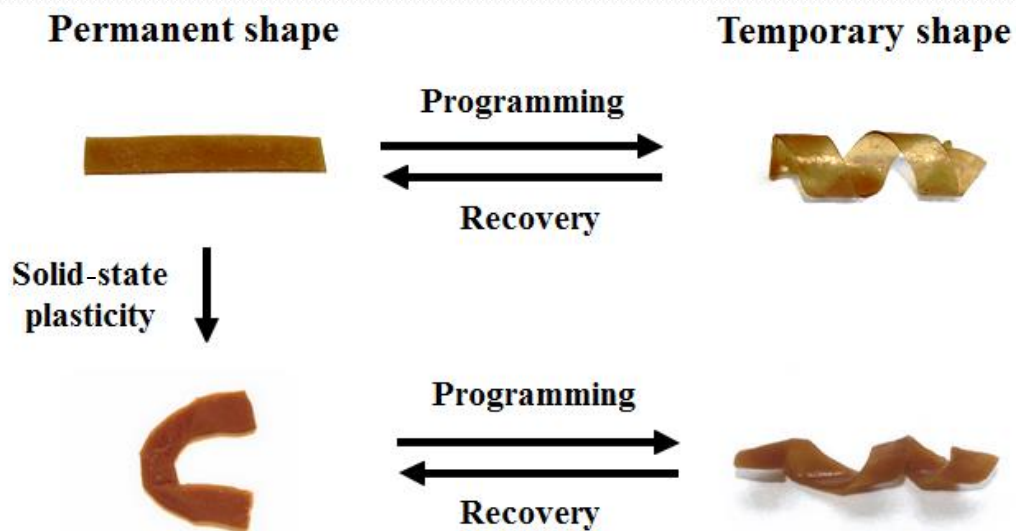
TAD

TAD-Indole  
adduct



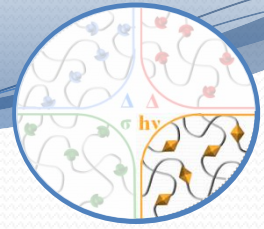


## Reprocessing experiment

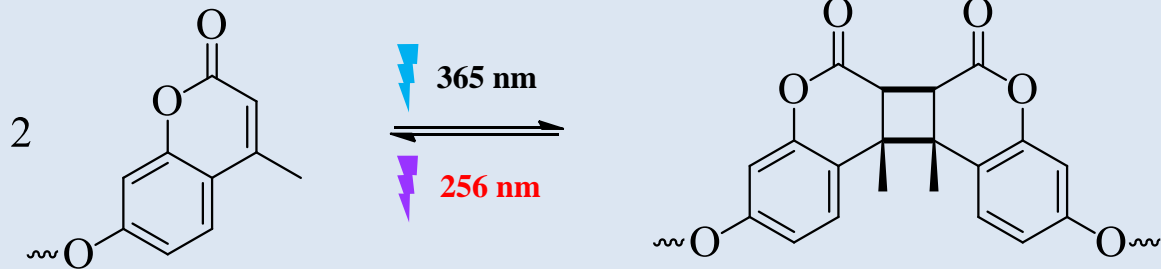


- Dissociation of TAD/indole adducts under stress
- Formation of new TAD/indole adducts

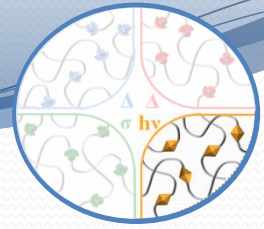
**Solid-state plasticity enables the material to be reprocessed**



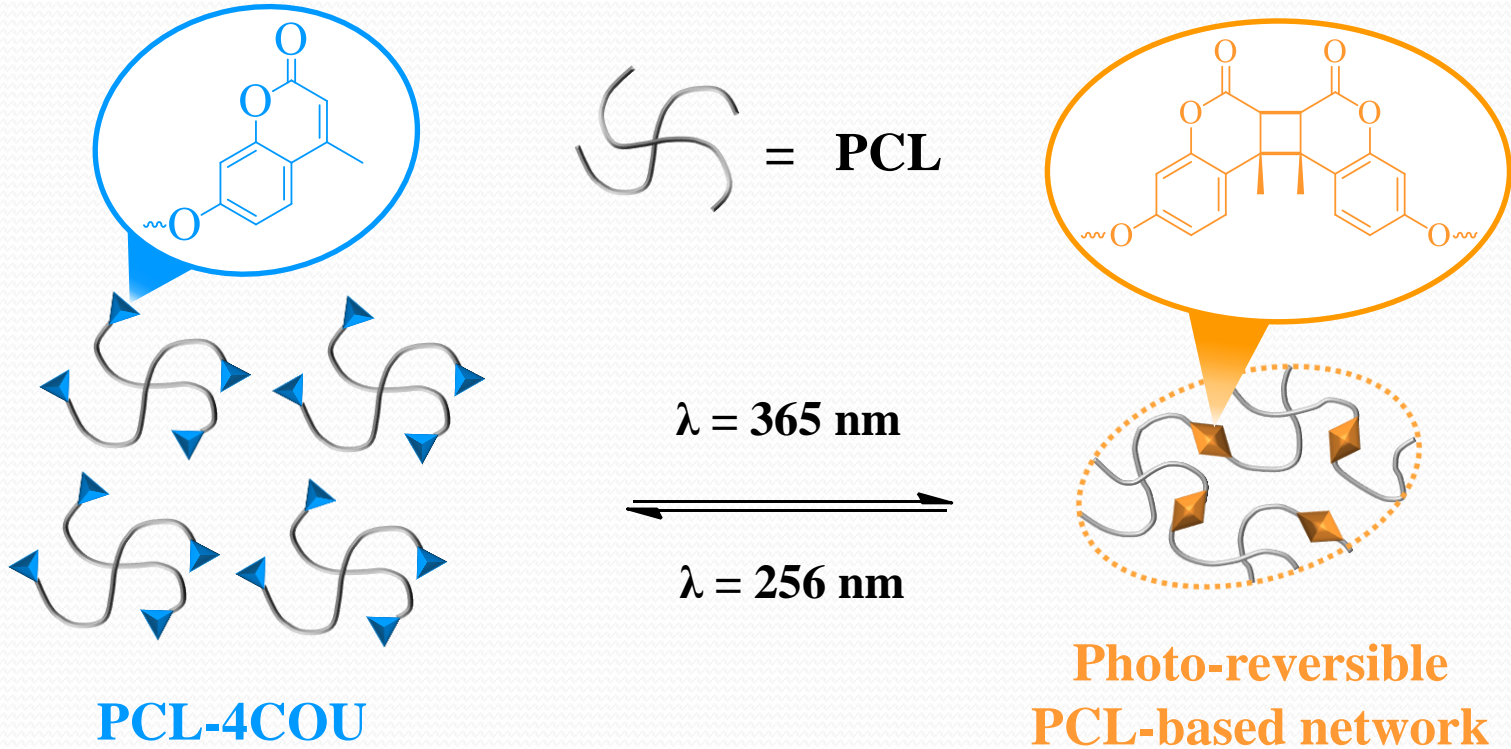
## Photo-reversible coumarin dimerization



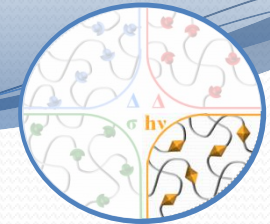




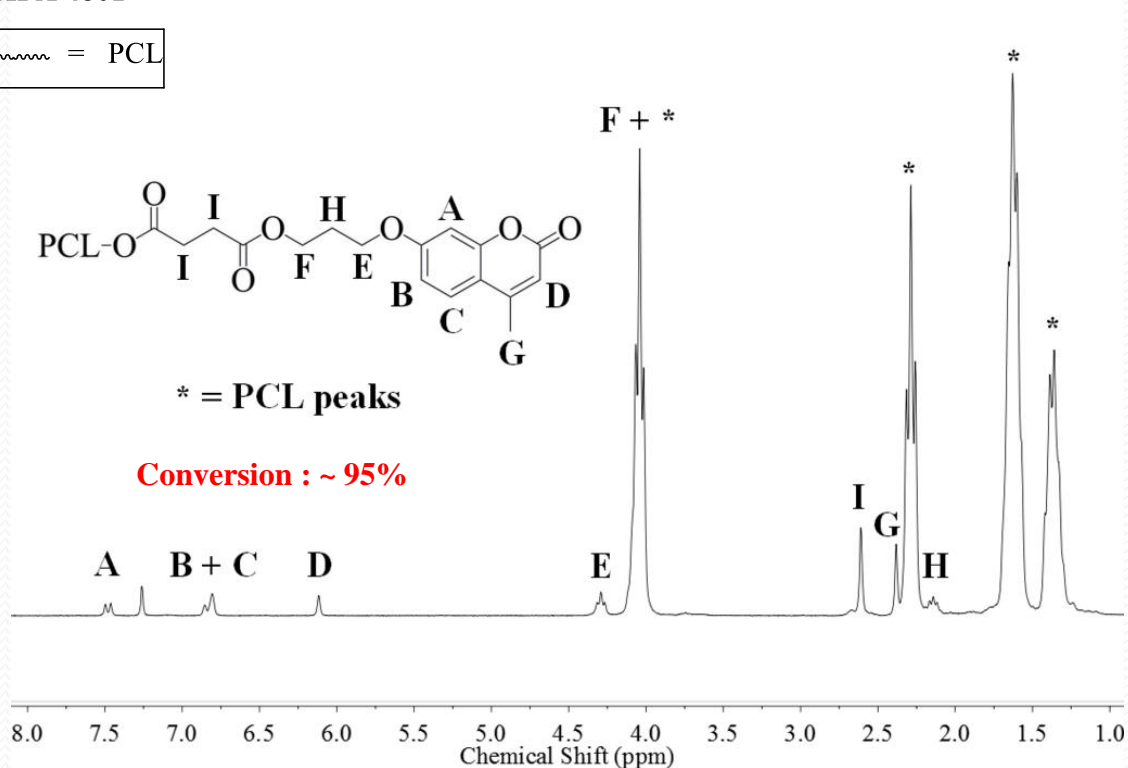
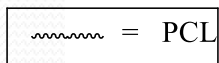
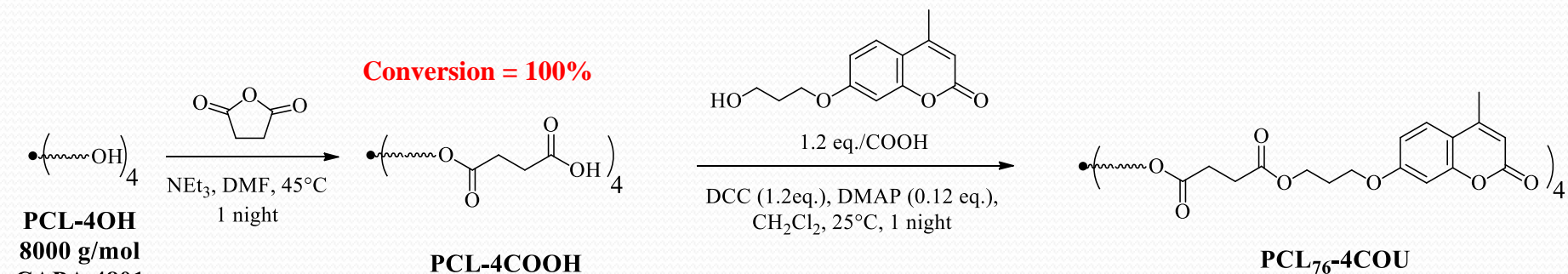
## General Strategy – coumarin dimerization

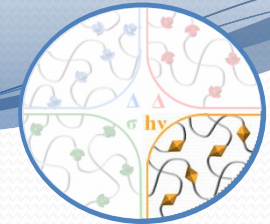


- Crosslinking of 4-arm star-shaped PCL by coumarin dimerization
- Photo-reversible dimer
- Thermo-stable PCL network



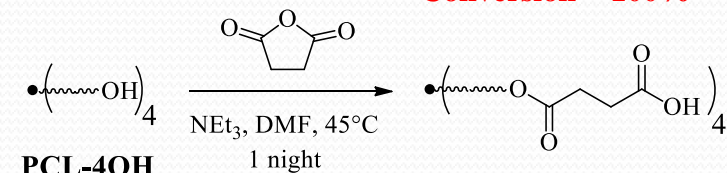
## Functionalization of PCL by coumarin moieties





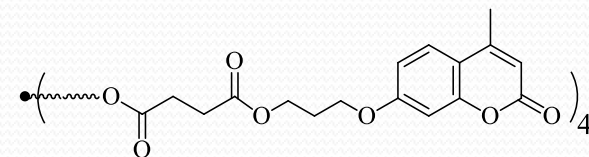
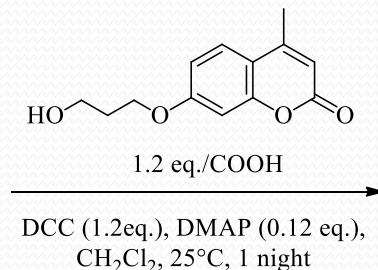
## Functionalization of PCL by coumarin moieties

**Conversion = 100%**



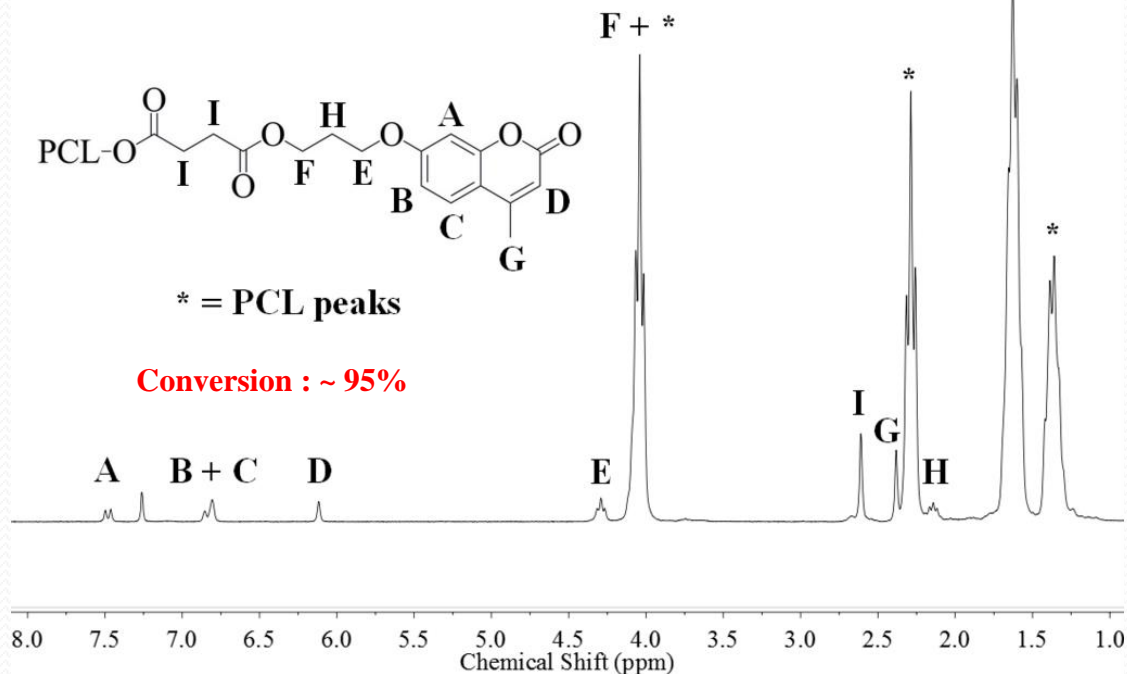
**PCL-4OH**  
8000 g/mol  
CAPA 4801

**PCL-4COOH**



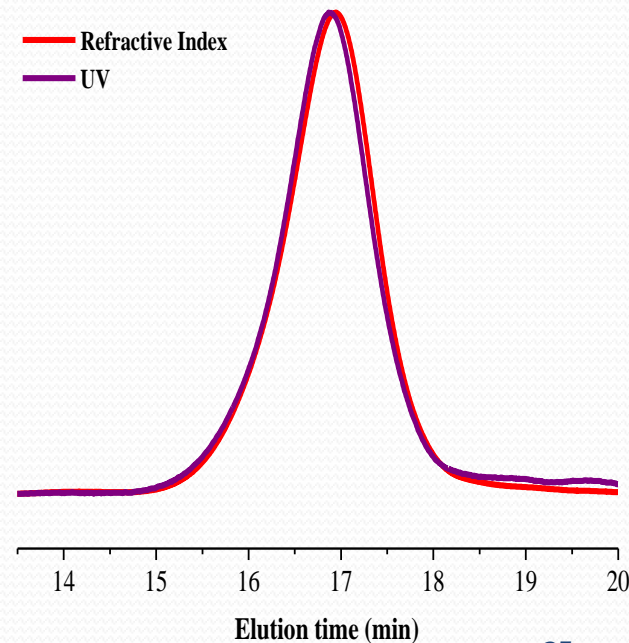
**PCL<sub>76</sub>-4COU**

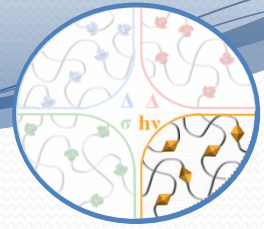
= PCL



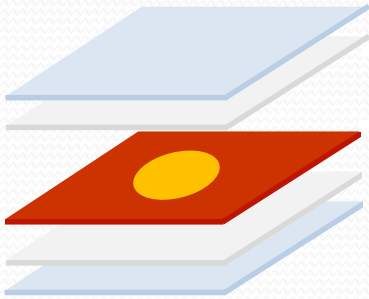
**No degradation detected**  
**No coupling reaction**




— Refractive Index  
— UV





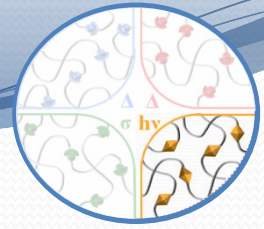
## Processing of the precursor



-  Quartz plate
-  Cross-linked PDMS film
-  Mold

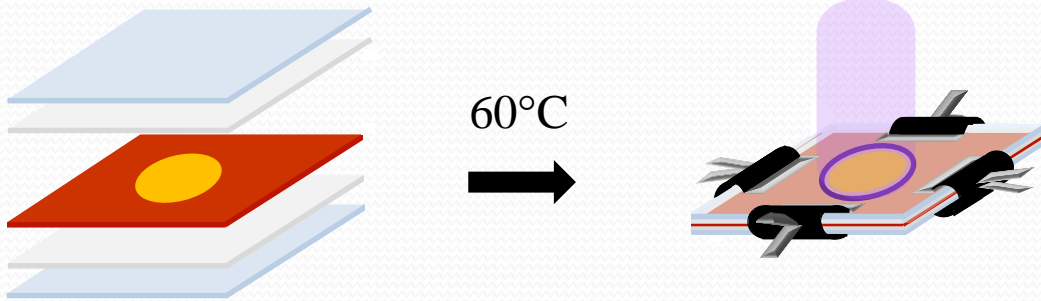
  $PCL_{76}$ -4COU











## Processing of the precursor

$\lambda = 365 \text{ nm}$

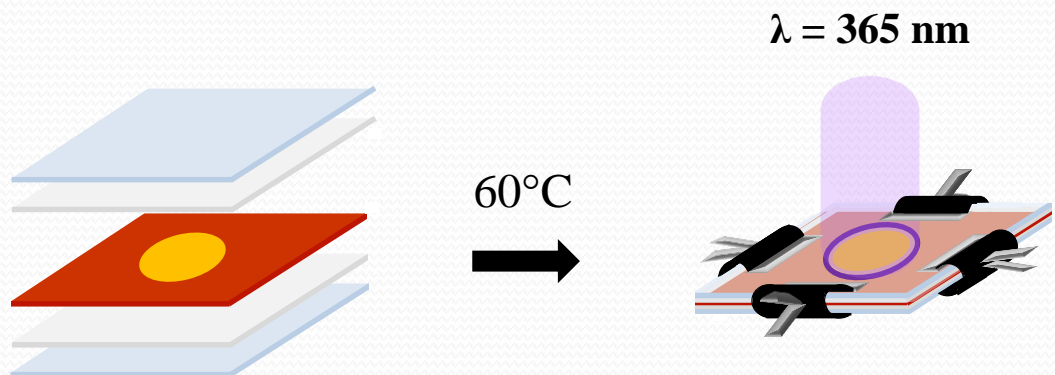


-  Quartz plate
-  Cross-linked PDMS film
-  Mold

-  PCL<sub>76</sub>-4COU
-  UV irradiation
-  Clamp



## Processing of the precursor



 Quartz plate

 Cross-linked PDMS film

 Mold

 PCL<sub>76</sub>-4COU

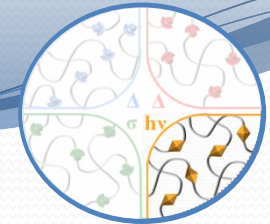
 UV irradiation

 Clamp

### Addition of a photosensitizer (benzophenone)

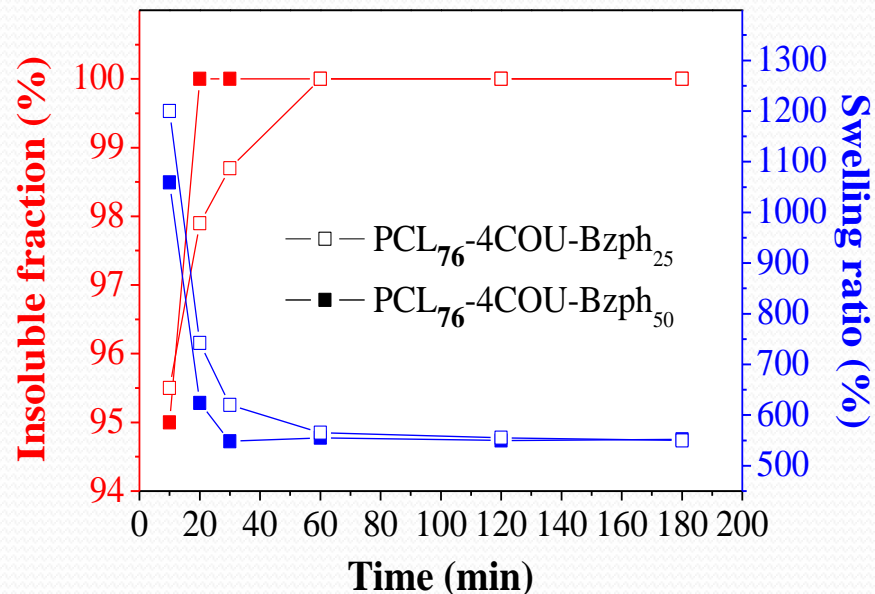
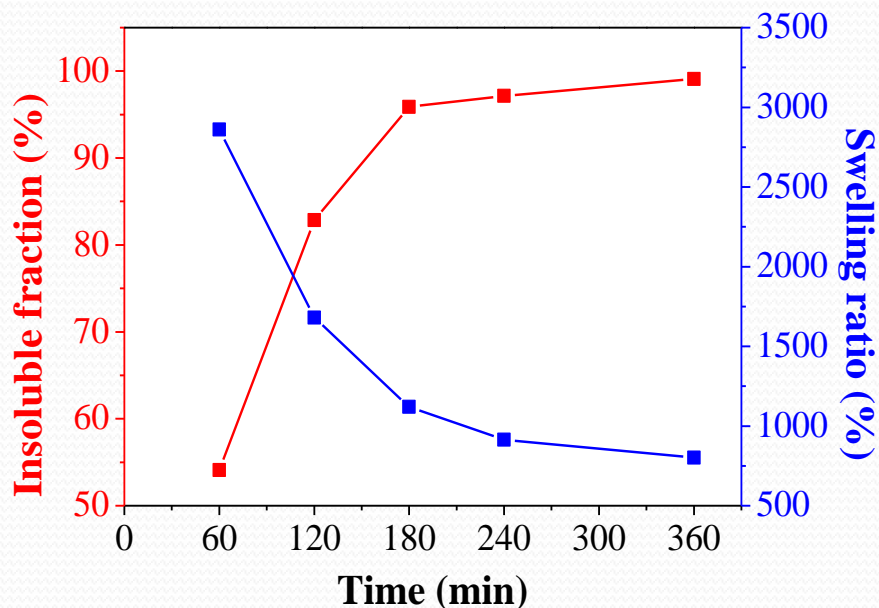
- PCL-4COU with 0%mol Bzph: PCL<sub>76</sub>-4COU-Bzph<sub>0</sub>
- PCL-4COU with 25%mol Bzph: PCL<sub>76</sub>-4COU-Bzph<sub>25</sub>
- PCL-4COU with 50%mol Bzph: PCL<sub>76</sub>-4COU-Bzph<sub>50</sub>





## Crosslinking study by swelling experiments

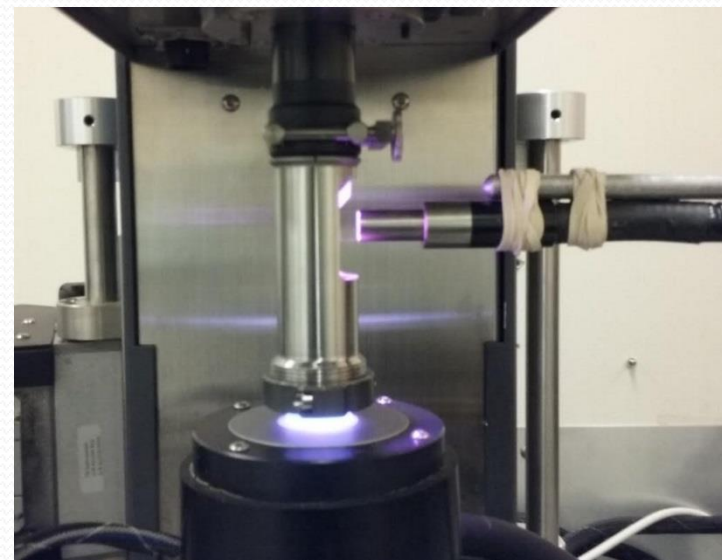
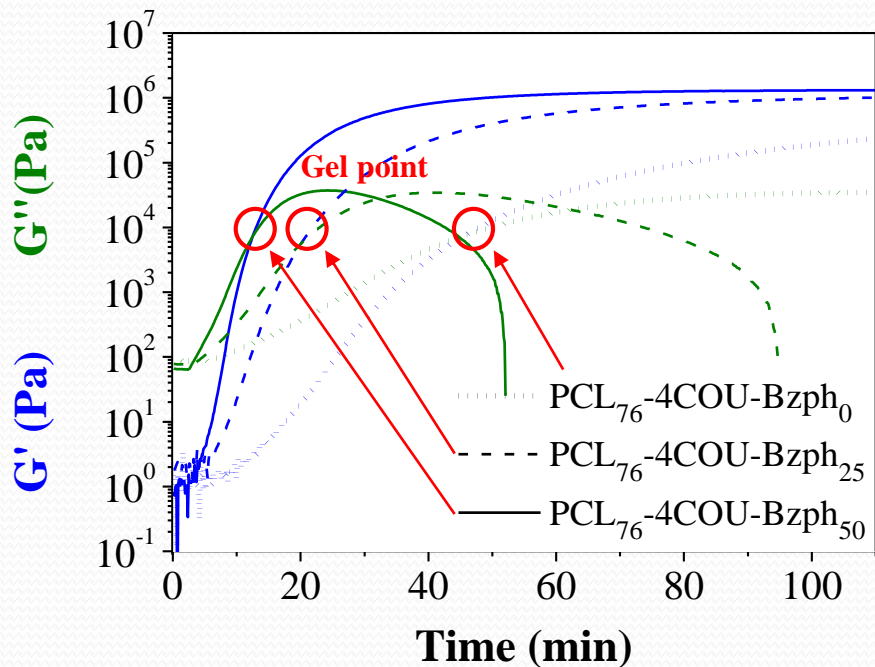
### PCL<sub>76</sub>-4COU-Bzph<sub>0</sub>



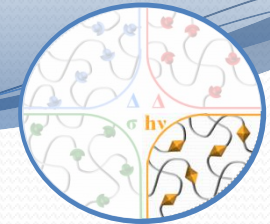
- Optimal swelling rate and insoluble fraction after:
  - 360 min without benzophenone
  - 30 min and 60 min with 25 or 50mol% of benzophenone, respectively
- Dramatic increase of the dimerization rate with benzophenone



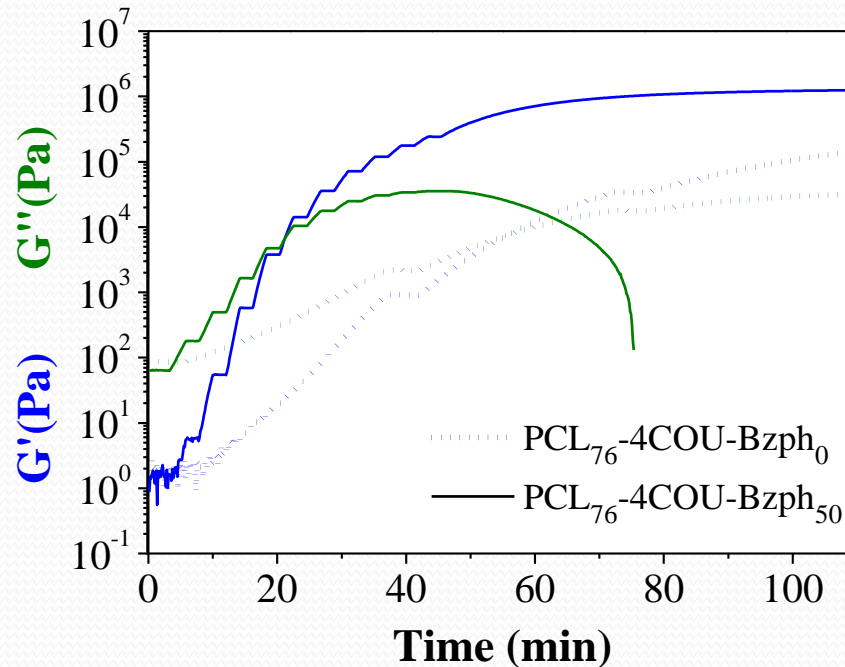
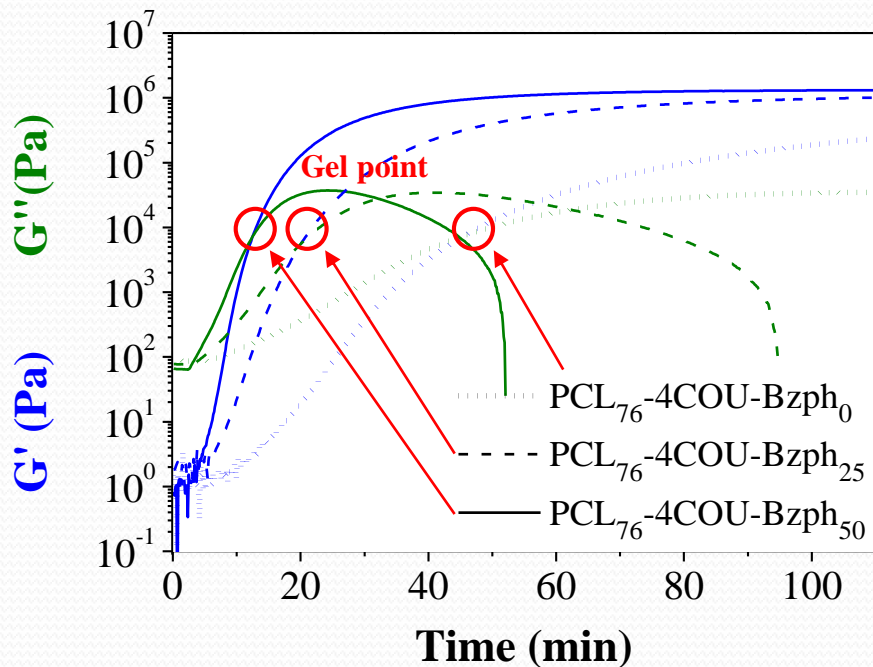
## Crosslinking study by rheology



- Irradiation of the sample at 365 nm ➔ Dimerization of coumarin
- Dramatic increase of the dimerization rate with benzophenone

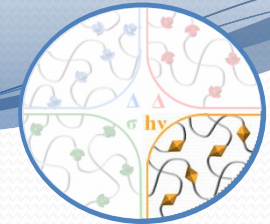


## Crosslinking study by rheology

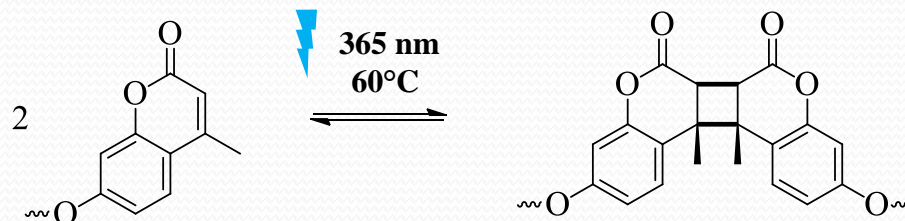


- Irradiation of the sample at 365 nm ➡ Dimerization of coumarin
- Dramatic increase of the dimerization rate with benzophenone
- Switching on/off cycles

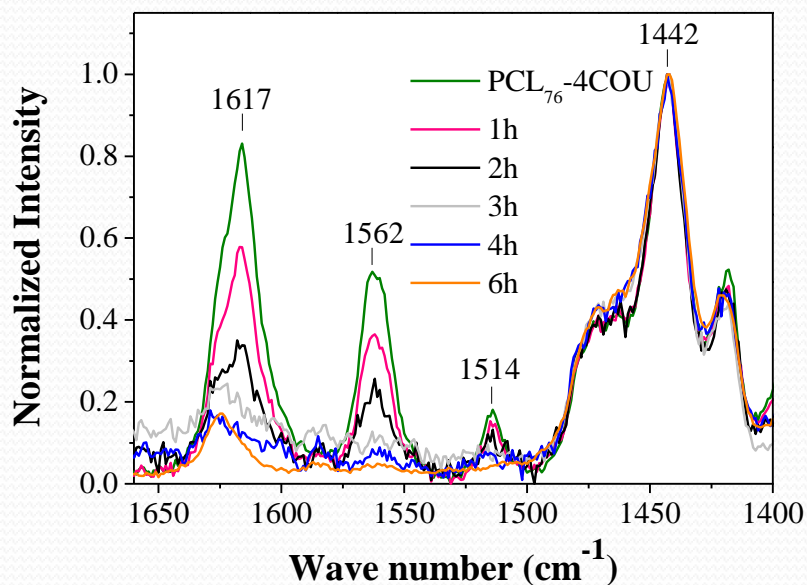
Remote control of the cross-linking process



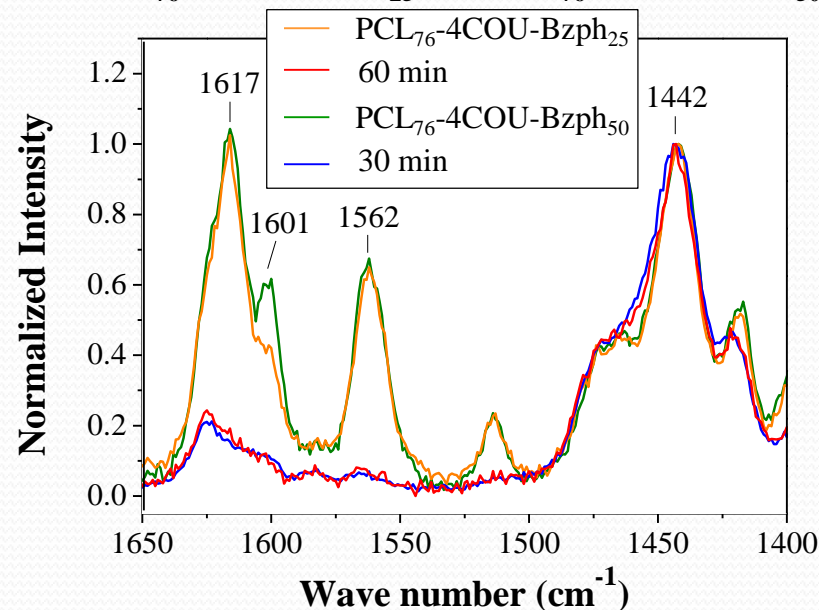
## Crosslinking study by Raman spectroscopy



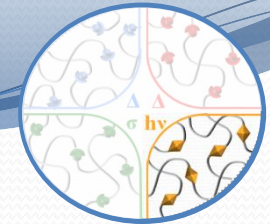
**PCL<sub>76</sub>-4COU-Bzph<sub>0</sub>**



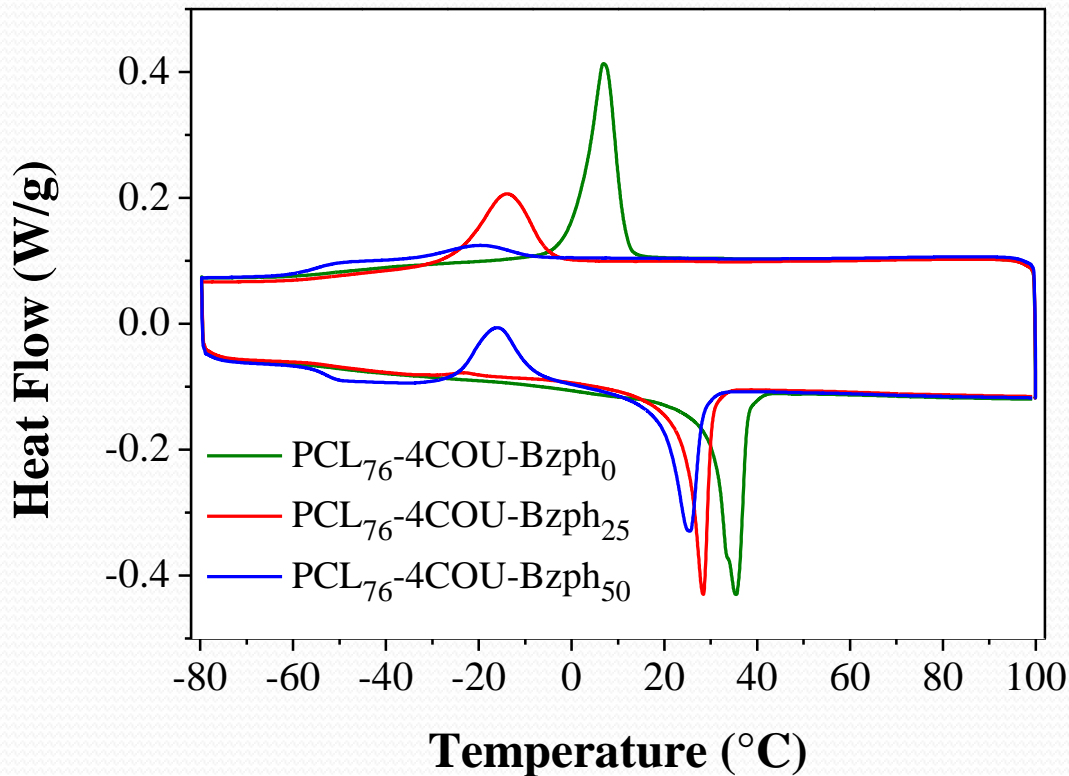
**PCL<sub>76</sub>-4COU-Bzph<sub>25</sub> and PCL<sub>76</sub>-4COU-Bzph<sub>50</sub>**



**Quantitative** conversion of the coumarin groups after the optimal time of irradiation



## Determination of the crystallization temperature

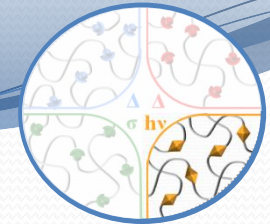


- $T_c$  of  $\text{PCL}_{76}\text{-4COU-Bzph}_0$  :  $7^\circ\text{C}$
- $T_c$  of  $\text{PCL}_{76}\text{-4COU-Bzph}_{25}$  :  $-14^\circ\text{C}$
- $T_c$  of  $\text{PCL}_{76}\text{-4COU-Bzph}_{50}$  :  $-19^\circ\text{C}$

Cooling below  $0^\circ\text{C}$  is mandatory

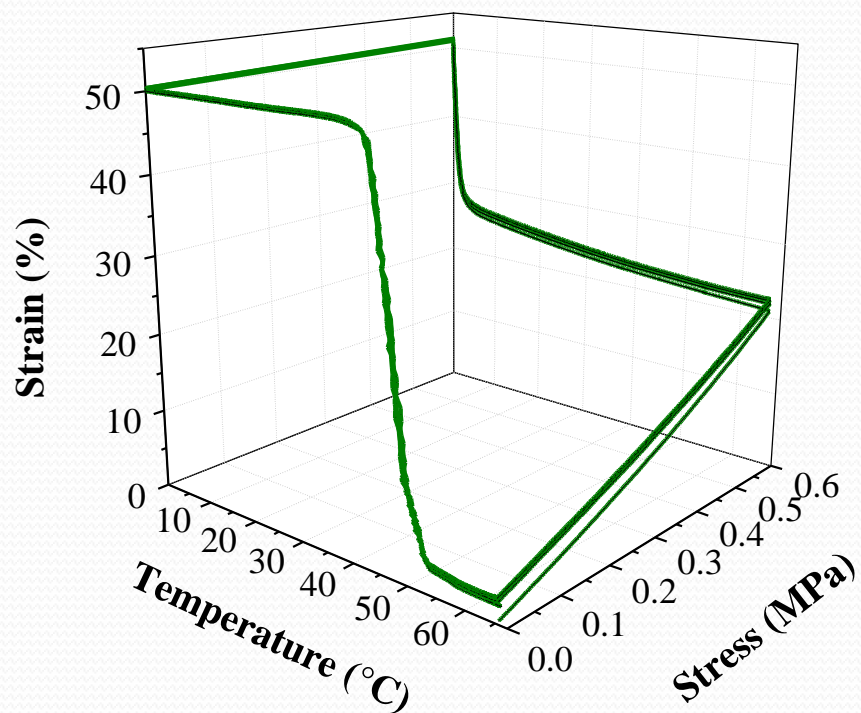


Stable temporary shape at R.T.



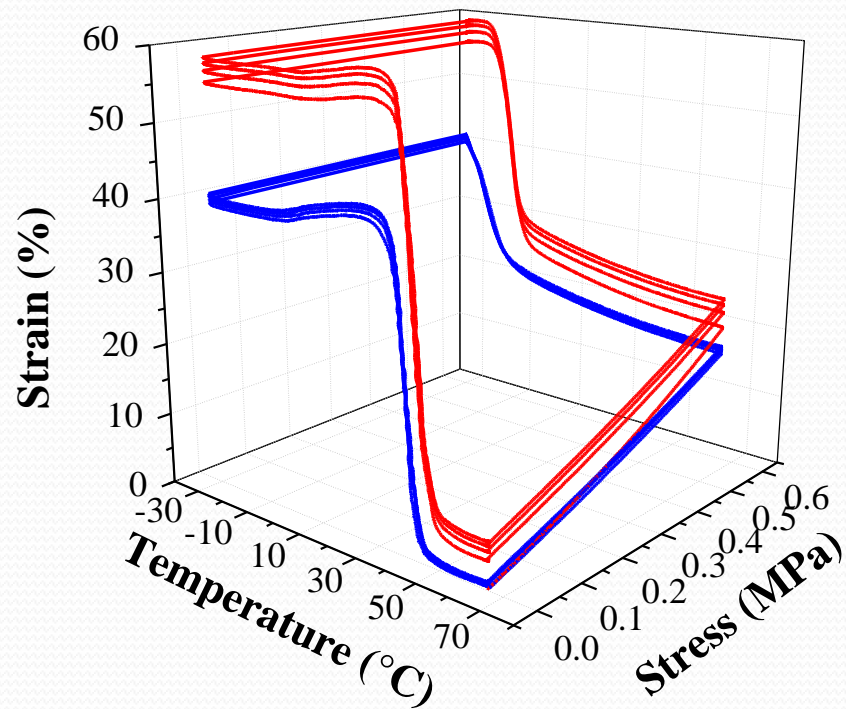
## Shape-memory properties

**PCL<sub>76</sub>-4COU-Bzph<sub>0</sub>**



**Fixity : >99%**    **Recovery : >99%**

**PCL<sub>76</sub>-4COU-Bzph<sub>25</sub> and PCL<sub>76</sub>-4COU-Bzph<sub>50</sub>**

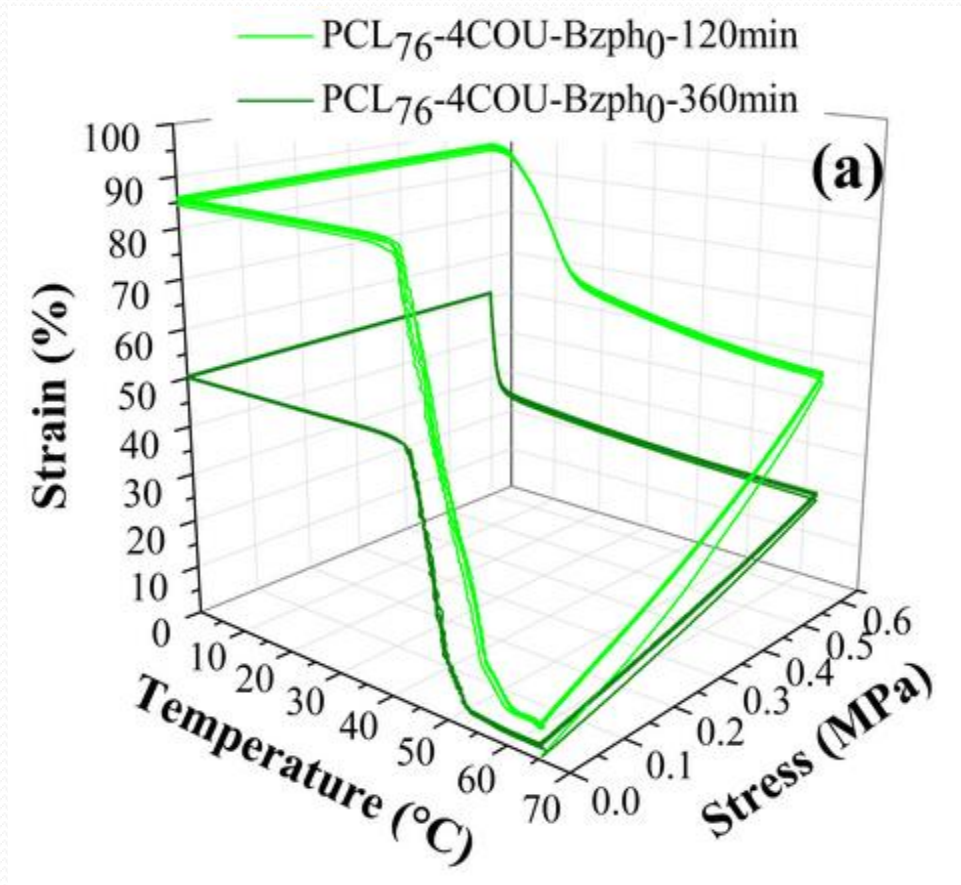


**Fixity : >99%**  
**Recovery : >99%**

**Fixity : >99%**  
**Recovery : >99%**

- ✔ Excellent fixity and recovery for each cycle
- ✔ NO creep from cycle to cycle

## Adjustment of the mechanical properties by controlling the irradiation time

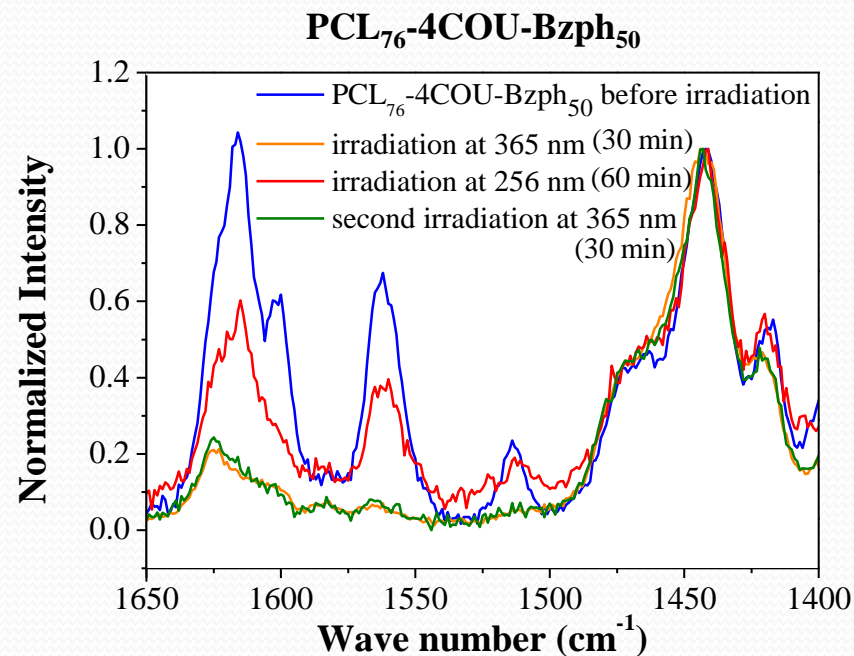
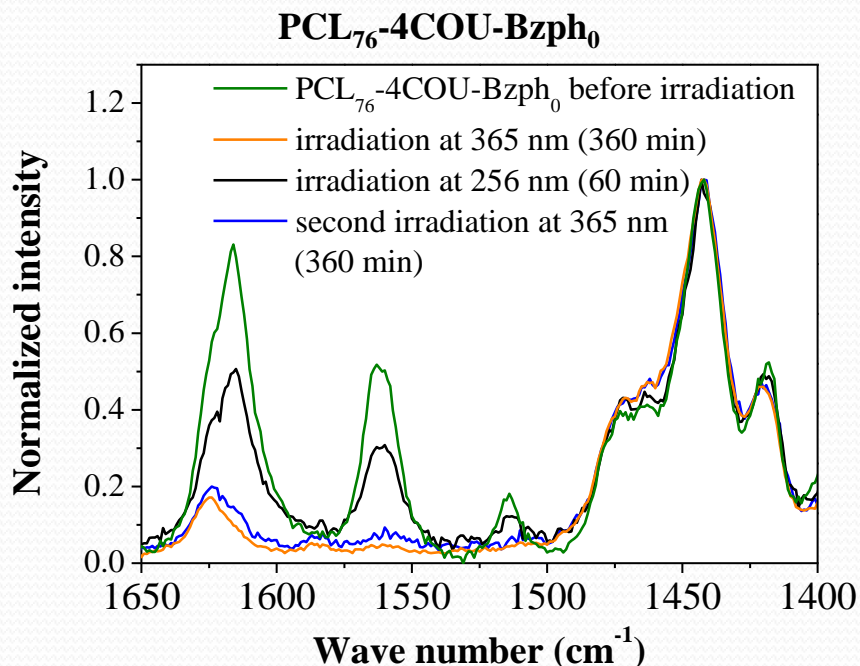
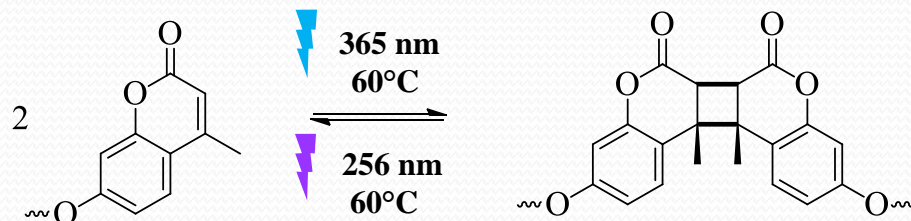


**Remote control of the cross-linking density => fine tuning of the mechanical properties of the network**

**In presence of benzophenone, 5min. of irradiation leads already to SMP**



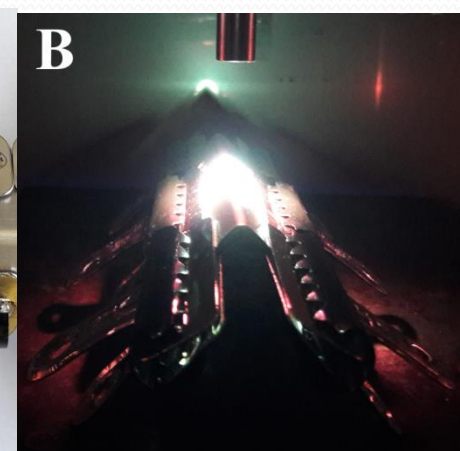
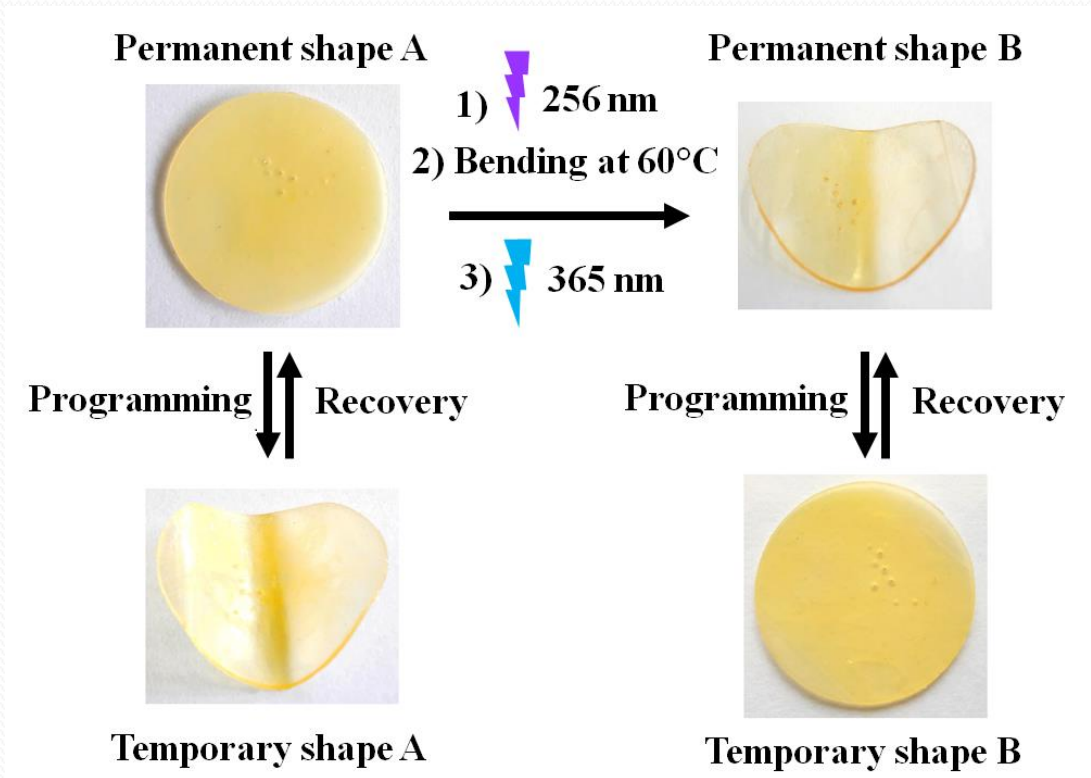
## Study of the dimerization/cleavage by Raman spectroscopy



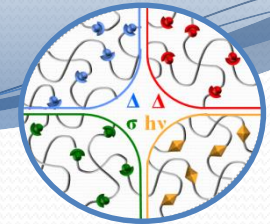
- Regeneration of 50% of the coumarin groups under irradiation at 256 nm (60 min)
- No influence of the benzophenone on the cleavage rate of the dimer
- Quantitative conversion of the coumarin groups under a second irradiation at 365 nm


















## Reprocessing experiment



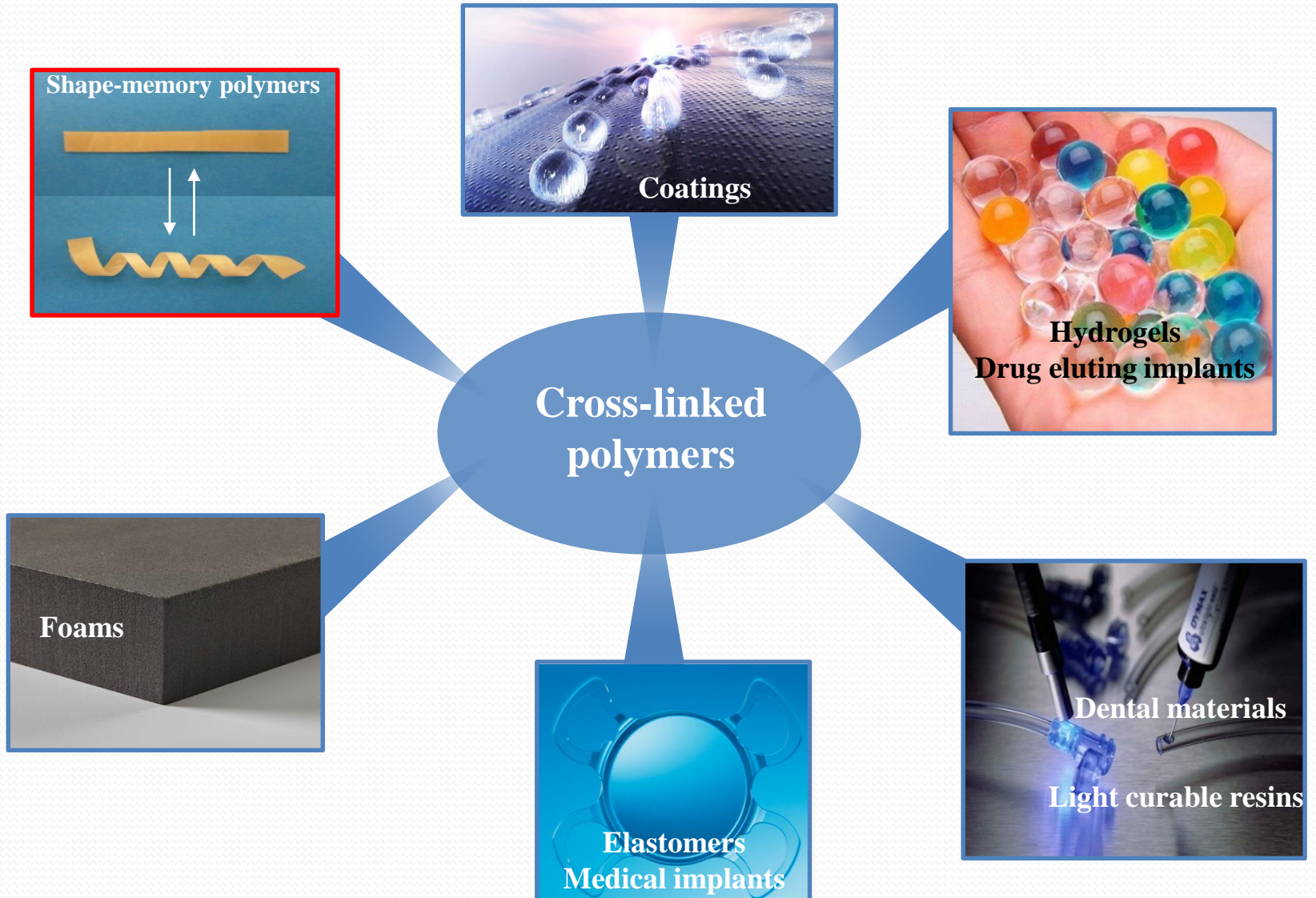
The dimerization of coumarin and the cleavage of coumarin dimers allow the shape-memory material to be reprocessed



# Conclusions

	Stability of the precursor(s)	Crosslinking rate	Control on the crosslinking process	Shape-memory properties	Reprocessing
<b>Furan/maleimide</b>					
<b>TAD/indole</b>					
<b>Coumarin</b>					

## Applications of cross-linked polymers



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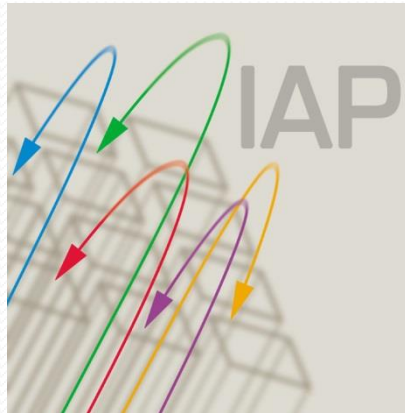
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