Multifunctional shape memory polymers based on covalent adaptive networks

Prof. Christine JEROME

CERM, CESAM, University of Liege, Belgium
c.jerome@uliege.be

Pregl Colloquium Series, Ljubljana, November 22nd, 2018
University of Liege, Belgium

ULiege:
- 23000 students
- 11 faculties

Center for Education and Research on Macromolecules

~25 researchers
4 permanents
Shape-memory polymers (SMP)

Temporary shape

Stimulus

Heat

Permanent shape

Thermo-responsive 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

Heating above $T_{\text{transition}}$

Permanent shape
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

Heating above $T_{transition}$

[Diagram showing the transition from a complex structure to a simpler one with mechanical stress applied]
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**

Heating above $T_{transition}$  
Permanent shape

Mechanical stress  
1) Cooling below $T_{transition}$  
Temporary shape

| Soft segments | Hard segments | Polymer |
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

![Diagram showing the transition between permanent and temporary shapes](image)

- Heating above $T_{\text{transition}}$
  - Permanent shape
- Mechanical stress
  - 1) Cooling below $T_{\text{transition}}$
  - 2) Stress release
- Temporary shape

Legend:
- Soft segments
- Hard segments
- Polymer
**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

**Heating above** $T_{\text{transition}}$

Permanent shape

**Mechanical stress**

1) Cooling below $T_{\text{transition}}$
2) Stress release

Temporary shape

**Heating above** $T_{\text{transition}}$

Shape-memory effect
# Thermo-responsive shape-memory polymers

![Diagram showing permanent and temporary shape transformation](https://example.com/diagram.png)

<table>
<thead>
<tr>
<th>Classes</th>
<th>Hard segments</th>
<th>Soft segments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalently cross-linked glassy thermoset networks (class I)</td>
<td>Covalent bonds</td>
<td>Glassy domains</td>
</tr>
<tr>
<td>Covalently cross-linked semi-crystalline networks (class II)</td>
<td>Covalent bonds</td>
<td>Crystallites</td>
</tr>
<tr>
<td>Physically cross-linked glassy copolymers (class III)</td>
<td>Physical bonds</td>
<td>Glassy domains</td>
</tr>
<tr>
<td>Physically cross-linked semi-crystalline block copolymers (class IV)</td>
<td>Physical bonds</td>
<td>Crystallites</td>
</tr>
</tbody>
</table>

## Thermo-responsive shape-memory polymers

**Permanent shape**

**Temporary shape**

**Stress**

**Stimulus** ($\Delta T$)

### Classes

<table>
<thead>
<tr>
<th>Classes</th>
<th>Hard segments</th>
<th>Soft segments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalently cross-linked glassy thermoset networks (class I)</td>
<td>Covalent bonds</td>
<td>Glassy domains</td>
</tr>
<tr>
<td>Covalently cross-linked semi-crystalline networks (class II)</td>
<td>Covalent bonds</td>
<td>Crystallites</td>
</tr>
<tr>
<td>Physically cross-linked glassy copolymers (class III)</td>
<td>Physical bonds</td>
<td>Glassy domains</td>
</tr>
<tr>
<td>Physically cross-linked semi-crystalline block copolymers (class IV)</td>
<td>Physical bonds</td>
<td>Crystallites</td>
</tr>
</tbody>
</table>

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

Heat shrinkable tubings or films

Crosslinking by electron beam irradiation (β irradiation)

\[ \text{Cross-linked PE} \]
\[ T_m \sim 120^\circ C \]

\[ \text{Cross-linked PTFE (Teflon®)} \]
\[ T_m \sim 320^\circ C \]

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

Degradable and biocompatible

Class II covalent networks

=> High shape memory performances

Processing the permanent shape: melt-flow injection

Thermoplastics

Heating above $T_m$

Processing and cooling below $T_m$

Injection molding
Polymer processing: melt-flow injection

Thermoplastics

Processing and cooling below $T_m$

Heating above $T_m$

Injection molding

Polymer networks do not flow!

Cross-linked polymers = network

Processing and cooling below $T_m$

Heating above $T_m$
Goal of the research: reversible covalent networks

Melt-flow processing

Highly stable covalent network

Reversible covalent bonds?
Covalent adaptable networks (CANs)

Thermoplastic

Cross-linked polymer

Heat

Redox

Light

Moisture

Selected reversible bonds for this work
Insertion of these bonds into PCL networks

Polymer matrix: Poly(ε-caprolactone) or PCL:
\[ T_g = -60^\circ C; \ T_m = 50^\circ C \]
Semi-crystalline polymer

Degradable
Biocompatible
Shape memory

General synthesis strategy

End-groups functionalization

Reversible cross-linking

4-arm star-shaped PCL
Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)
Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)

![Diagram of thermally-controlled [4+2] cycloaddition](image)

- Furan
- Maleimide

4-arm star-shaped PCL
**Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)**

Crosslinking $\leq 100^\circ C$

- Furan
- Maleimide
- Diels-Alder adduct

4-arm star-shaped PCL
Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)

Crosslinking $< 100^\circ C$

Cleavage of the network $> 100^\circ C$

- Furan
- Maleimide
- Diels-Alder adduct
- 4-arm star-shaped PCL
Functionalization of 4-arm star-shaped PCL

\( (\text{OH})_4 \xrightarrow{\text{NET}_3, \text{DMF (anhydrous), 45°C}} (\text{O})_4 \xrightarrow{\text{DCC, DMAP, CH}_2\text{Cl}_2, 20°C} \)  

Conversion = 100%

\( \text{PCL}_{76}-4\text{FUR} \)
Functionalization of 4-arm star-shaped PCL

Conversion = 100%

PCL_{76}-4FUR

PCL_{76}-4MAL
Functionalization of 4-arm star-shaped PCL

\[
\text{Conversion} = 100\%
\]

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Number of chain-ends</th>
<th>DP (^a)</th>
<th>Chain-ends conversion (^a)</th>
<th>(M_n) ((^1\text{H NMR})) (^b)</th>
<th>D (SEC) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL(_{76})-4MAL</td>
<td>4</td>
<td>76</td>
<td>95%</td>
<td>9600 g/mol</td>
<td>1.20</td>
</tr>
<tr>
<td>PCL(_{76})-4FUR</td>
<td>4</td>
<td>76</td>
<td>88%</td>
<td>9400 g/mol</td>
<td>1.20</td>
</tr>
</tbody>
</table>

\(\text{a) Conversion of the hydroxyl end groups into furan or maleimide determined by } ^1\text{H NMR}\)

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

\(\text{c) Molar mass distribution measured by SEC in THF at 45°C}\)

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$_{76}$-4MAL and PCL$_{76}$-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

Crosslinking in the rheometer at 65°C: Diels-Alder adduct formation in the molten state

Evolution of the gain modulus and of the loss modulus with curing time at 65°C for the mix composed of PCL$_{76}$-4MAL and PCL$_{76}$-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 cm\(^{-1}\)), maleimide (1587 cm\(^{-1}\)) and DA adduct (1577 cm\(^{-1}\))

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

 normalized intensity
wave number (cm⁻¹)

conversion of furan (%)

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

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

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

Conversion of furan (%): 54% after 24h at 65°C

Conversion of furan moieties:

\[ \text{Conversion of furan} = \left( \frac{I(1503 \text{ cm}^{-1}) \text{ for the mix}}{I(1503 \text{ cm}^{-1}) \text{ for PCL} - 4 \text{FUR} / 2} \right) \times 100 \]

Shape-memory properties

Heating above $T_{\text{melting}}$

$65^\circ\text{C}$

Permanent shape

Shape-memory properties

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

Mechanical stress 0.6 MPa

5 min isotherm at 65°C

Stress-controlled deformation (0.06 MPa/min up to 0.6 MPa)

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

Shape-memory properties

- Heating above $T_{\text{melting}}$, 65°C
- Permanent shape
- Mechanical stress, 0.6 MPa

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

Stress maintained at 0.6 MPa

Cooling (3°C/min to 0°C)

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

**Shape-memory properties**

1) Cooling below $T_{\text{crystallization}}$

2) Stress release

**Release of the mechanical stress**

Fixity: $>99\%$

---

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

Shape-memory properties

1) Cooling below \( T_{\text{crystallization}} \)

2) Stress release

Heating above \( T_{\text{melting}} \)

Permanent shape

Mechanical stress 0.6 MPa

Temporary shape

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

1) Cooling below $T_{\text{crystallization}}$

2) Stress release

Heating above $T_{\text{melting}}$

Permanent shape

Temporary shape

Fixity: >99%
Recovery: 88%

Fixity: >99%
Recovery: >99%

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

Shape-memory properties

1) Cooling below $T_{\text{crystallization}}$
2) Stress release

Permanent shape

Temporarry shape

- Fixity: >99%
- Recovery: 88%

Shape-memory properties

1) Cooling below $T_{\text{crystallization}}$

2) Stress release

Fixity: >99%
Recovery: >99%

Fixity: >99%
Recovery: >99%

Fixity: >99%
Recovery: >99%

Excellent fixity and recovery for each cycle

Study of the network thermoreversibility by rheology

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)

Almost perfect reversibility
High number of crosslinking/cleavage cycles can be achieved
Recycling experiment

24h in a mold at 65°C

DA reaction 65°C

retro-DA reaction 125°C

Mini-injection device 20 min. at 125°C

Tested again for shape-memory properties

Shape-memory properties before and after recycling

Initial material

Recycled material

\[ \text{Strain (\%)} \]

\[ \text{Stress (MPa)} \]

\[ \text{Temperature (°C)} \]

- 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

\[ \text{Furan/maleimide material} \quad \text{Anthracene/maleimide material} \]

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

Advantages

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

DA reaction
65°C

retro-DA reaction
125°C

Reprocessable shape-memory PCL
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)**

![Diagram of Diels-Alder reaction](image)

**DA reaction 65°C**

**retro-DA reaction 125°C**

**Reprocessable shape-memory PCL**

**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

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

**TAD-Indole reaction**
**Thermally-controlled [4+2] cycloaddition (Diels-Alder reaction)**

![Diagram showing DA reaction and retro-DA reaction]

**DA reaction**
65°C

**retro-DA reaction**
125°C

**Reprocessable shape-memory PCL**

**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

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

**TAD-Indole reaction**

**Use of photoreversible reaction**
(thermally stable)

**Dimerization of coumarin**
Reversible TAD/Indole Alder-ene reaction

\[
\text{Ph} \quad + \quad \begin{array}{c}
\text{N} \\
\text{O} \\
\text{N}
\end{array} \xrightleftharpoons{T = 60^\circ C} \quad \begin{array}{c}
\text{O} \\
\text{N} \\
\text{N} \\
\text{NH}
\end{array} \xrightleftharpoons{T = 120^\circ C} \quad \text{Ph}
\]

Application of a stress
1,2,4-triazoline-3,5-dione (TAD)

+ High reactivity of TAD

Du Prez et al., *Nature Chemistry*, 2015, 6, 815–821
1,2,4-triazoline-3,5-dione (TAD)

\[
\begin{align*}
\text{Furan} & \quad + \quad \text{TAD} \quad \rightarrow \quad \text{TAD-Furan adduct} \\
\text{TAD red} & \quad \text{R.T.} \\
\end{align*}
\]

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

Du Prez et al., *Nature Chemistry*, 2015, 6, 815–821
1,2,4-triazoline-3,5-dione (TAD)

\[
\text{Furan} + \text{TAD} \xrightarrow{\text{R.T.}} \text{TAD-Furan adduct}
\]

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

Du Prez et al., *Nature Chemistry*, 2015, 6, 815–821
**1,2,4-triazoline-3,5-dione (TAD)**

\[
\text{Indole} \quad + \quad \text{TAD} \quad \xleftrightarrow{60^\circ C \text{ or } 120^\circ C} \quad \text{TAD-Indole adduct}
\]

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

**Reversible reaction between TAD and indole**

*Du Prez et al., Nature Chemistry, 2015, 6, 815–821*
General Strategy – TAD-Indole crosslinking

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

Functionalization of PCL by indole moieties

\[
\text{PCL-6OH} \xrightarrow{\text{NE}_3, \text{DMF}, 45^\circ C, \text{overnight}} \text{PCL-6COOH} \xrightarrow{2 \text{ eq./COOH}} \text{PCL-6IND}
\]

Conversion = 100%
Functionalization of PCL by indole moieties

\[ \text{PCL-6OH} \xrightarrow{\text{NEt}_3, \text{DMF, 45°C, overnight}} \text{PCL-6COOH} \]

Conversion: ~ 90%

PCL-6COOH

\[ \xrightarrow{2 \text{eq.} / \text{COOH~DCC (2eq.), DMAP (0.4 eq.), CH}_2\text{Cl}_2, 25°C, 24h \text{ (without visible light irradiation)}} \text{PCL-6IND} \]

Conversion: 100%

**1H NMR**

Functionalization of PCL by indole moieties

\[
\text{PCL-6OH} \rightarrow \text{PCL-6COOH} \rightarrow \text{PCL-6IND}
\]

Conversion: ~90%

PCL-6OH
29,000 g/mol

\[\text{PCL-6COOH} \quad \text{Conversion} = 100\%\]

\[\text{PCL-6IND} \quad \text{Conversion} = 100\%\]

Size Exclusion Chromatography (SEC) in THF

No degradation detected
No significant coupling reaction

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

- Excellent fixity and recovery for each cycle
- Low creep effect from cycle to cycle

Fixity : >99%
Recovery : 88%

Fixity : >99%
Recovery : >99%

Fixity : >99%
Recovery : >99%

Fixity : >99%
Recovery : >99%

Fixity : >99%
Recovery : >99%

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

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

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

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

Strain (%)

Temperature (°C)

Stress (MPa)

1st cycle
2nd cycle
3rd cycle
4th cycle

120
100
80
60
40
20
0

0 10 20 30 40 50 60
0.00
0.05
0.10
0.15
0.20
0.25
0.30
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%)

![Graph showing stress relaxation over time](image)

Strain of 100% during 60 min

0 20 40 60 80 100 120
0
20
40
60
80
100
Time (min)
Relative stress (%) 80
100
120
140

Strain (%)

Indole + TAD $\Rightarrow$ TAD-Indole adduct

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%)

![Diagram showing stress-relaxation experiment](image)

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

---

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

2

$\sim O$

$\sim O$

365 nm

256 nm
General Strategy – coumarin dimerization

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

PCL-4COU

\[ \lambda = 365 \text{ nm} \]

\[ \lambda = 256 \text{ nm} \]

Photo-reversible PCL-based network
Functionalization of PCL by coumarin moieties

Conversion: ~ 95%

Conversion = 100%

Functionalization of PCL by coumarin moieties

Conversion = 100%

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

**PCL-4COOH**

Conversion: ~ 95%

No degradation detected
No coupling reaction

Processing of the precursor

- Quartz plate
- Cross-linked PDMS film
- Mold

PCL_{76}-4COU
Processing of the precursor

Quartz plate
Cross-linked PDMS film
Mold

60°C

λ = 365 nm

PCL_{76}-4COU
UV irradiation
Clamp
Processing of the precursor

\[ \lambda = 365 \text{ nm} \]

- Quartz plate
- Cross-linked PDMS film
- Mold
- PCL\textsubscript{76}-4COU
- UV irradiation
- Clamp

Addition of a photosensitizer (benzophenone)

- PCL-4COU with 0\% mol Bzph: \textbf{PCL\textsubscript{76}-4COU-Bzph\textsubscript{0}}
- PCL-4COU with 25\% mol Bzph: \textbf{PCL\textsubscript{76}-4COU-Bzph\textsubscript{25}}
- PCL-4COU with 50\% mol Bzph: \textbf{PCL\textsubscript{76}-4COU-Bzph\textsubscript{50}}
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
- Dramatic increase of the dimerization rate with benzophenone
- Switching on/off cycles

Remote control of the cross-linking process

Crosslinking study by Raman spectroscopy

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

Determination of the crystallization temperature

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

Cooling below 0°C is mandatory

Stable temporary shape at R.T.

Shape-memory properties

PCL_{76}-4COU-Bzph_{0}

PCL_{76}-4COU-Bzph_{25} and PCL_{76}-4COU-Bzph_{50}

Fixity : >99%  Recovery : >99%

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

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

## Conclusions

<table>
<thead>
<tr>
<th></th>
<th>Stability of the precursor(s)</th>
<th>Crosslinking rate</th>
<th>Control on the crosslinking process</th>
<th>Shape-memory properties</th>
<th>Reprocessing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furan/maleimide</td>
<td>🌻</td>
<td>😞</td>
<td>😞</td>
<td>😞</td>
<td>🌻</td>
</tr>
<tr>
<td>TAD/indole</td>
<td>😞</td>
<td>🌻</td>
<td>😞</td>
<td>🌻</td>
<td>😞</td>
</tr>
<tr>
<td>Coumarin</td>
<td>🌻</td>
<td>🌻</td>
<td>🌻</td>
<td>🌻</td>
<td>😞</td>
</tr>
</tbody>
</table>
Applications of cross-linked polymers

- Shape-memory polymers
- Coatings
- Hydrogels
- Drug eluting implants
- Foams
- Elastomers
- Dental materials
- Medical implants
- Light curable resins
Acknowledgments

Dr. Thomas DEFIZE
Dr. Jean-Michel Thomassin
Dr. Raphaël Riva

Pr. B. Gilbert, Dr. C. Malherbe

Pr. F. Du Prez, N. Van Herck

Pr. P. Dubois, Dr. J.-M. Raquez

Pr. H. Ottevaere
Acknowledgments
Thank you for your attention