



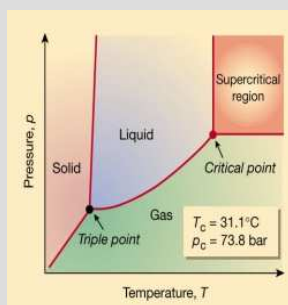
# Functionalization of aliphatic polyesters by "click chemistry" in supercritical carbon dioxide

Bruno Grignard, Stéphanie Schmeits, Raphaël Riva, Christophe Detrembleur, Philippe Lecomte, Christine Jérôme

raphael.riva@ulg.ac.be, University of Liège, Sart-Tilman, B6a, B-4000 Liège

**Abstract** : Functionalization by « click chemistry » is a very efficient strategy to improve or to impart new properties to aliphatic polyesters. Nevertheless, the presence of solvent traces and catalyst residues in the final product are severe limitations for the development of new biomedical applications. The aims of this work is to extend the "click" functionalization previously carried out in organic solvents to a non toxic and environmentally friendly solvent, such as supercritical carbon dioxide. Last but not least, scCO<sub>2</sub> turned out to be very efficient to extract copper residues.

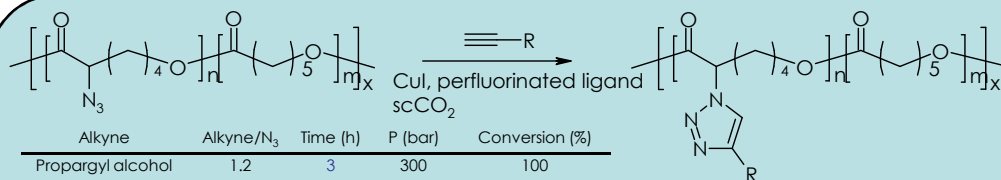
## Supercritical carbon dioxide scCO<sub>2</sub>



- Low viscosity and high diffusivity (gas-like)
- High density (liquid-like)
- Tunable strength of the solvent
- Inert, non-toxic, inflammable, cheap

### Drawbacks

- Poor solubility of organo-metallic compounds
- Polymers are insoluble except non crystalline fluoropolymers and silicones



Alkyne	Alkyne/N <sub>3</sub>	Time (h)	P (bar)	Conversion (%)
Propargyl alcohol	1.2	3	300	100
Propargyl amine	2	3	300	100
Ethynyl pyrene	1.2	3	300	100
ATRP initiator	1.2	3	300	100
Pentynoic acid	1.2	3	300	25
PDMS	1.2	24	300	<5

Successful synthesis of functional polyesters by Huisgen's cycloaddition without degradation of the aliphatic polyesters

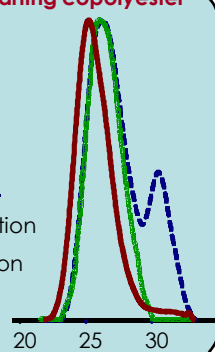
### PCL-g-PDMS potential surfactant in scCO<sub>2</sub>

### Grafting of propargyl alcohol

THF 35°C 2 hours => Partial degradation

scCO<sub>2</sub> 40°C 3 hours => No degradation

Benefit effect of scCO<sub>2</sub>



### Optimization of the propargyl alcohol grafting

#### Reaction time

Time (h)	Alkyne/N <sub>3</sub>	P (bar)	Conversion (%)
3	1.2	300	100
2	1.2	300	100
1	1.2	300	100
0.5	1.2	300	100
3	1.2	100	100
2	1.2	100	100
1	1.2	100	100
0.5	1.2	100	100

Quantitative conversion after 30 min with 10% of catalyst

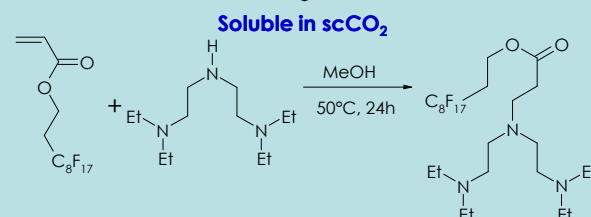
#### Amount of catalyst

Cu/alkyne (%)	Alkyne/N <sub>3</sub>	P (bar)	Conversion (%)
10	1.2	300	100
5	1.2	300	100
3	1.2	300	100
No Cu	1.2	300	/
10	1.2	100	100
5	1.2	100	100
3	1.2	100	100
No Cu	1.2	100	/

Quantitative reaction with only 3% of catalyst even after 30 min  
No reaction without Cu

### Extraction of catalyst

#### Use of a perfluorinated polyamine



Removal of the catalyst by supercritical fluid extraction (5ml/min, 300 bar, 300 ml of CO<sub>2</sub>, 40°C)

residual copper content = 1853 ppm, [Cu]<sub>0</sub> = 50000 ppm

96 % of Cu extracted

**Conclusions** : scCO<sub>2</sub> turned out to be a very efficient solvent for click chemistry. Even under heterogeneous conditions, the functionalization of insoluble PCL is quantitative in shorter reaction time (30 min) and in presence of a lower amount of catalyst (3mol%) than in organic solvent, such as THF. This increase of the reaction rate is due to the fast diffusion of the Cu catalyst and the alkyne in the plasticized PCL matrix. In the case of grafting of propargyl alcohol, no degradation of the polyester chain was observed, which was not the case for the same reaction in THF. Moreover, the use of a perfluorinated amine as organic base allowed the extraction of more than 96% of the copper catalyst by supercritical fluid extraction leading to a copolyester polluted by a low amount of metallic residues.

