Supercritical CO_2 as an effective medium for a novel conversion of glycerol in the heterogeneous telomerisation of butadiene

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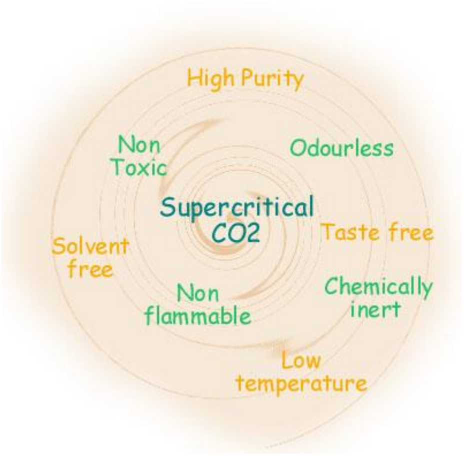
Green Chemistry
Solvents – non-conventional media

- **Solvent-free**
- **Water**
- **Ionic liquids**
- **Supercritical fluids**

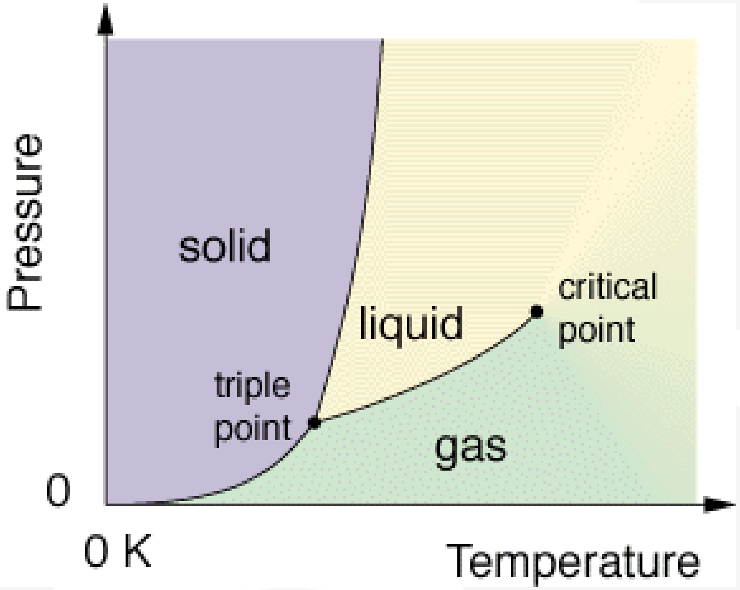
Properties of supercritical fluids

Typical supercritical solvents: CO_2, H_2O, propane, butane

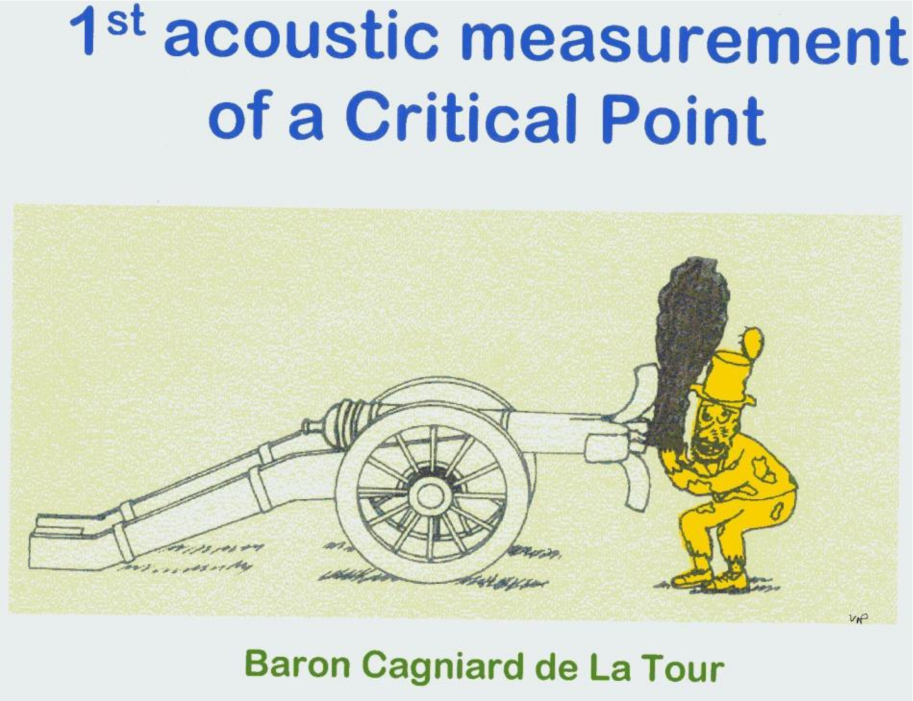


- GRAS - generally regardes as safe ($scCO_2$ and water)
- cheap, non-toxic (scH_2O, $scCO_2$)
- chemically inert, odourless, testeless
- non-flammable, non-explosive
- reaction gases (H_2, O_2) totally miscible
- reaction and separation step integrated

	Density (g/mL)	viscosity (P)
gas	$\sim 10^{-3}$	$0.5\text{-}3.5 \cdot 10^{-4}$
scF	0.2-0.9	$0.2\text{-}1.0 \cdot 10^{-3}$
liquid	0.8-1.2	$0.3\text{-}2.4 \cdot 10^{-2}$

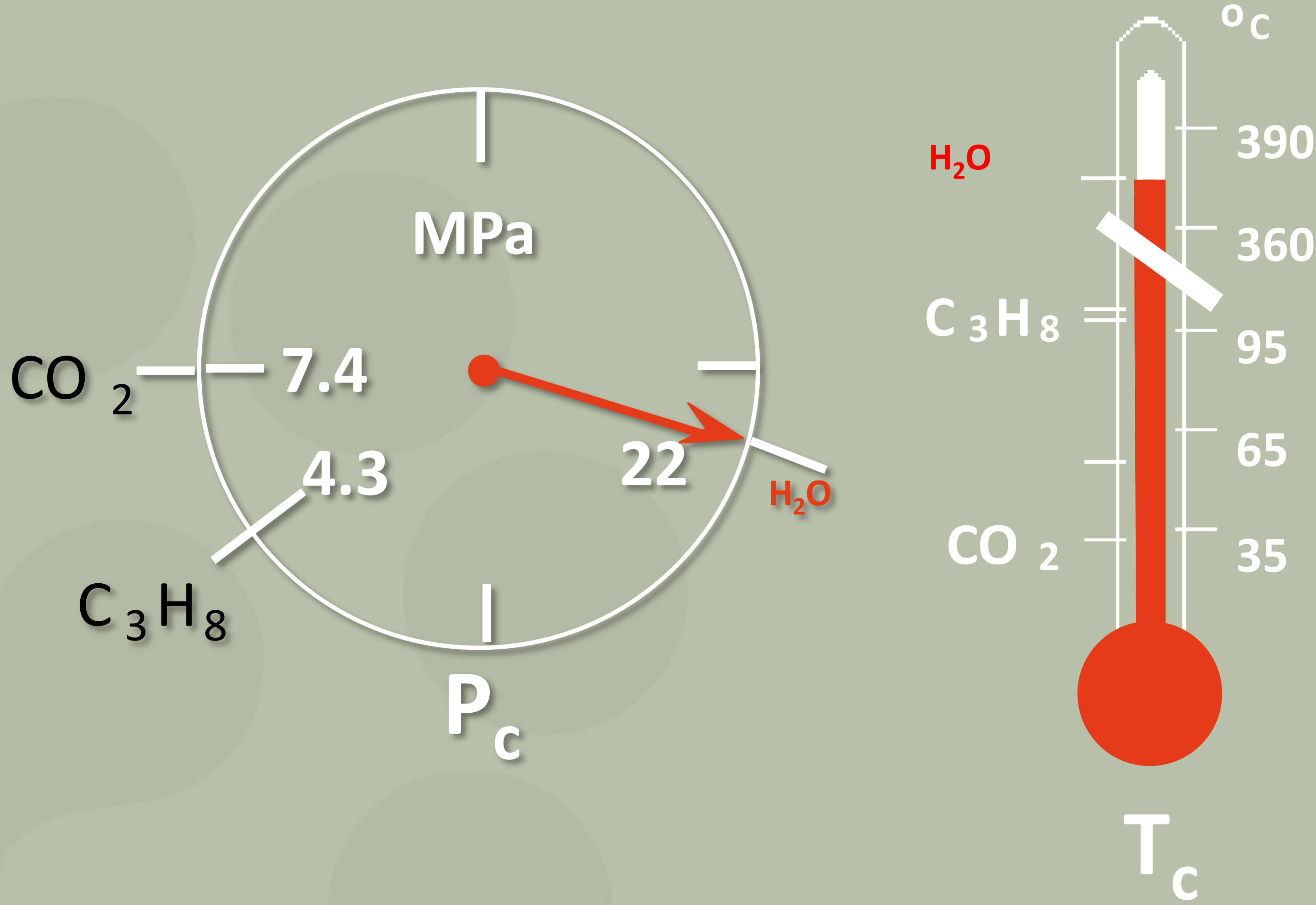


Supercritical fluids



In 1822, Charles Cagniard de La Tour discovered the critical point of a substance in his famous cannon barrel experiments. Listening to discontinuities in the sound of a rolling flint ball in a sealed cannon filled with fluids at various temperatures, he observed the critical temperature.

Properties of supercritical fluids



Supercritical fluids

Venus is the second planet from the Sun, and is Earth's closest neighbour in the solar system.

Pressure = 90 atm
T= 460°C
97% of its atmosphere is CO_2

→ **CO_2 is @ supercritical conditions**

Telomerisation

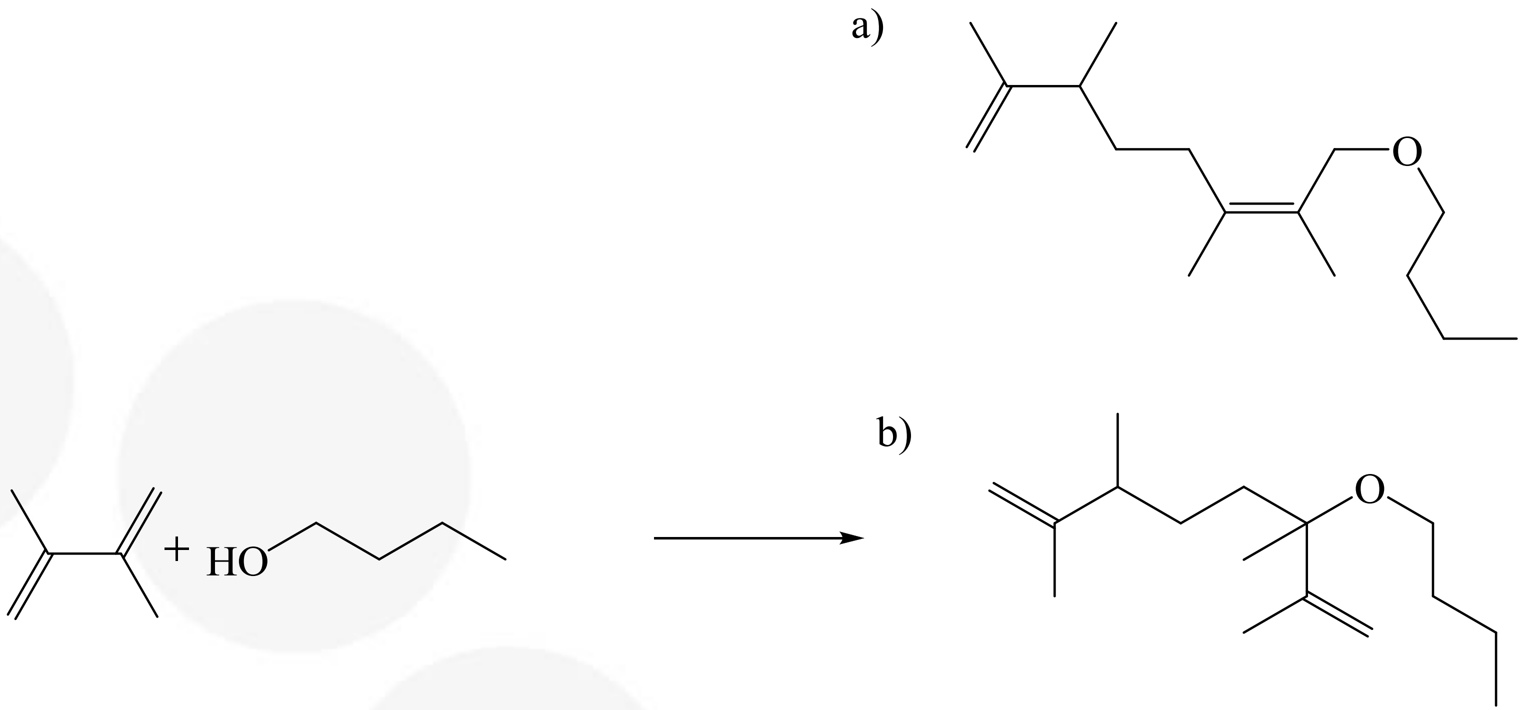
Reaction conditions:

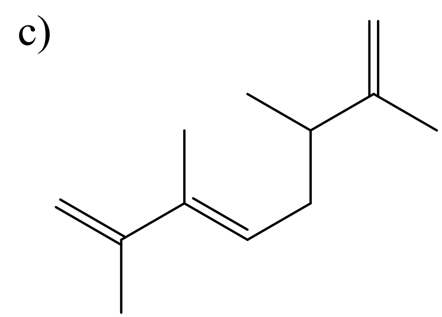
- organic solvent or CO_2 @ 90 or 120 bar
- T = 333.15K
- Time: 48h
- Catalyst: 5% Pd/Al_2O_3 powder

J. M. Lopes, Z. Petrovski, R. Bogel-Łukasik, E. Bogel-Łukasik, Heterogeneous palladium-catalyzed telomerization of myrcene with glycerol derivatives in supercritical carbon dioxide: a facile route to new building blocks, Green Chem., 2011, 13, 2013-2016.

L. Conceiçao, R. Bogel-Łukasik, E Bogel-Łukasik, Supercritical CO_2 as an effective medium for a novel conversion of glycerol and alcohols in the heterogeneous telomerisation of butadiene, Green Chem., 2012, 14, 673-681.

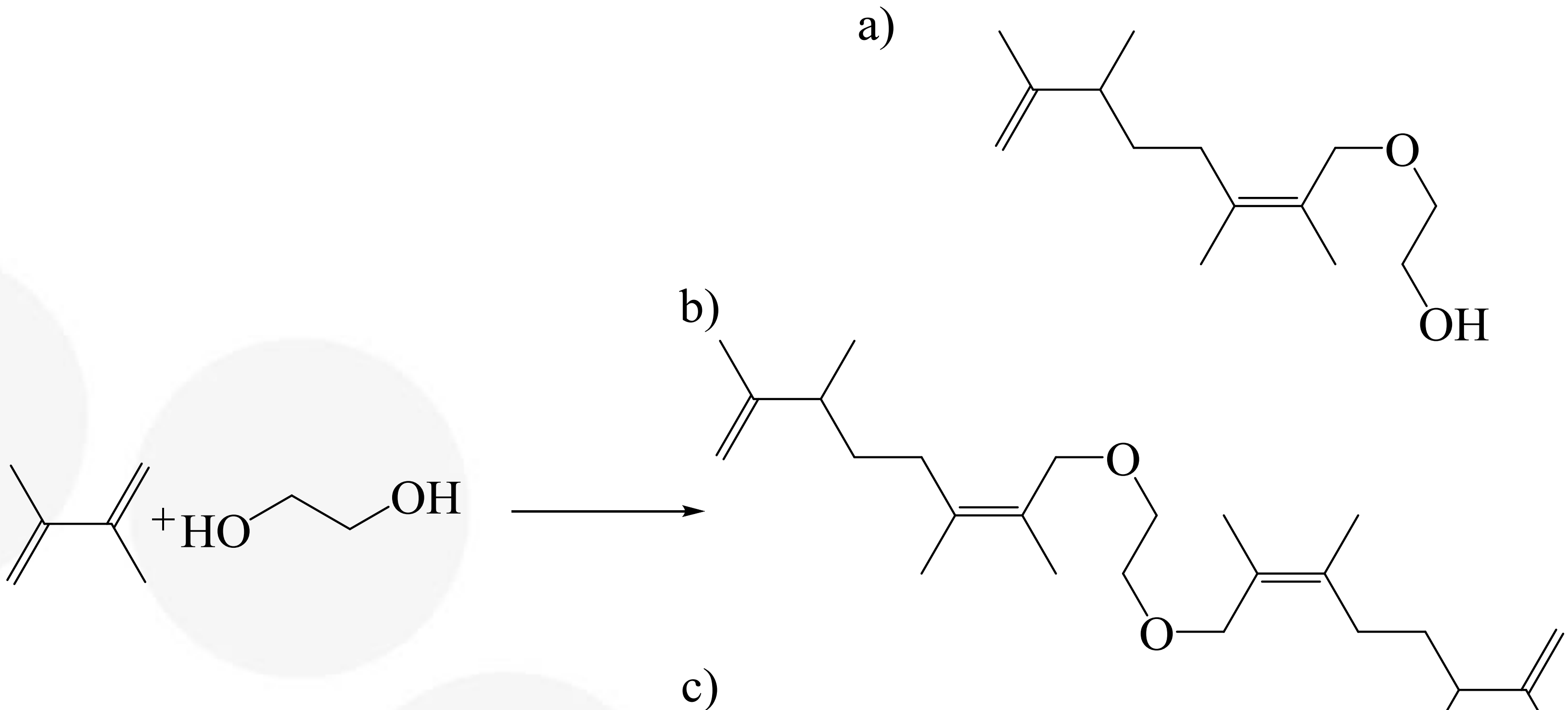
Reaction

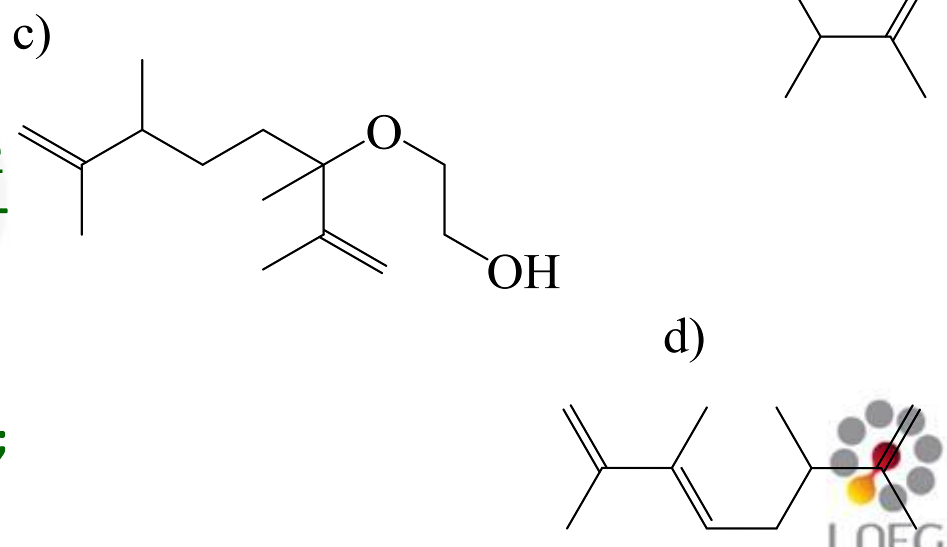




The general scheme of telomerisation of 2,3-dimethylbuta-1,3-diene with <u>1-butanol</u>: (a) (E/Z)-8-butoxy-2,3,6,7-tetramethylocta-1,6-diene; b) 3-butoxy-2,3,6,7-tetramethylocta-1,7-diene; c) (E/Z)-2,3,6,7-tetramethylocta-1,3,7-triene.

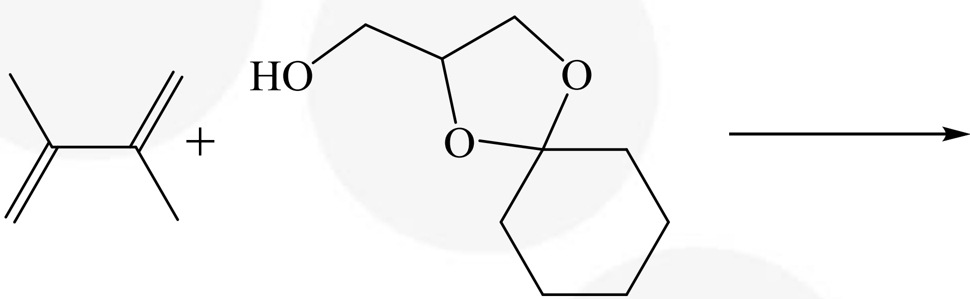
Reaction

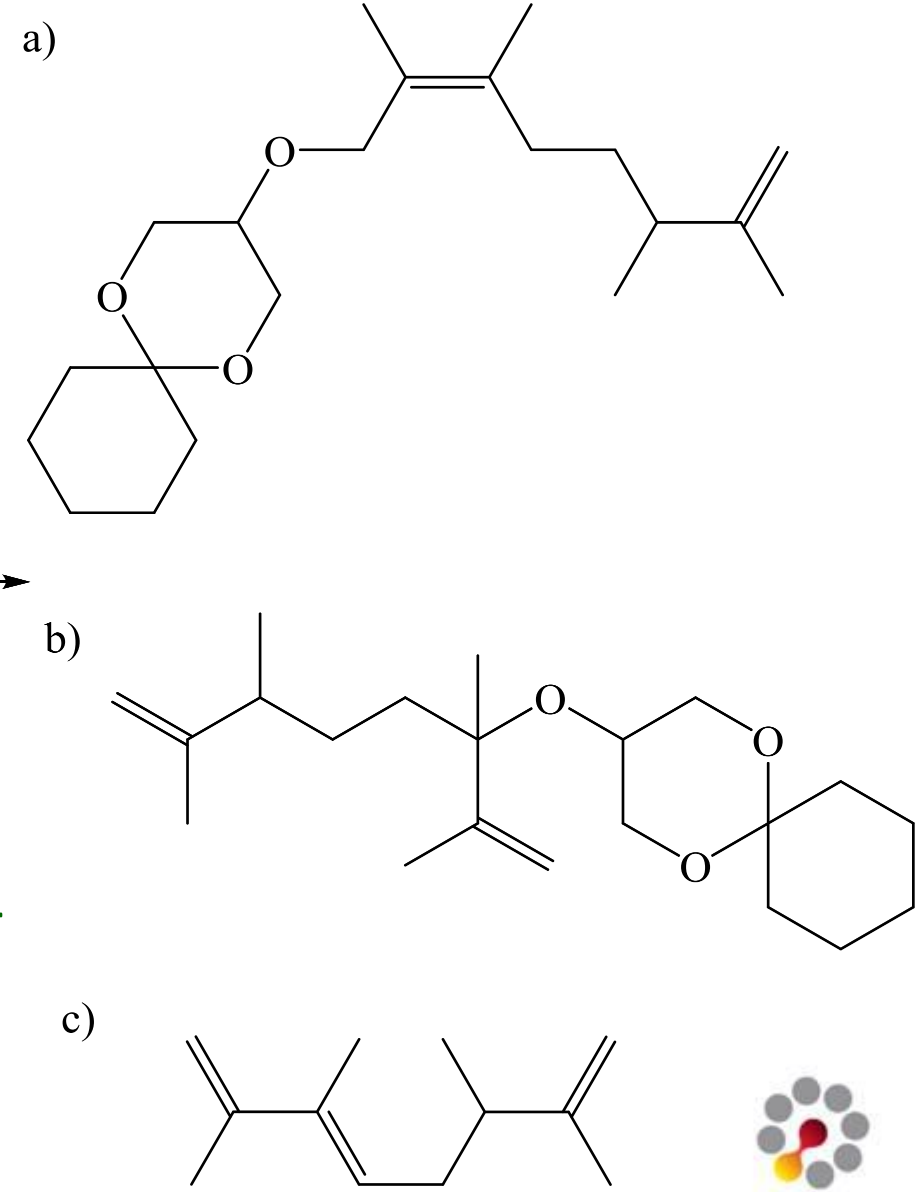




The general scheme of telomerisation of 2,3-dimethylbuta-1,3-diene with <u>ethylene glycol</u>: a) (E/Z)-2-(2,3,6,7-tetramethylocta-2,7-dienyloxy)ethanol; b) 1,2-bis((E/Z)-2,3,6,7-tetramethylocta-2,7-dienyloxy)ethane; c) 2-(2,3,6,7-tetramethylocta-1,7-dien-3-yloxy)ethanol; d) (E/Z)-2,3,6,7-tetramethylocta-1,3,7-triene.

Reaction





The general scheme of telomerisation of 2,3-dimethylbuta-1,3-diene with 1,4-dioxaspiro[4.5]decane-2-methanol: a) (E/Z)-3-(2,3,6,7-tetramethylocta-2,7-dienyloxy)-1,5-dioxaspiro[5.5]undecane; b) 3-(2,3,6,7-tetramethylocta-1,7-dien-3-yloxy)-1,5-dioxaspiro[5.5]undecane; c) (E/Z)-2,3,6,7-tetramethylocta-1,3,7-triene

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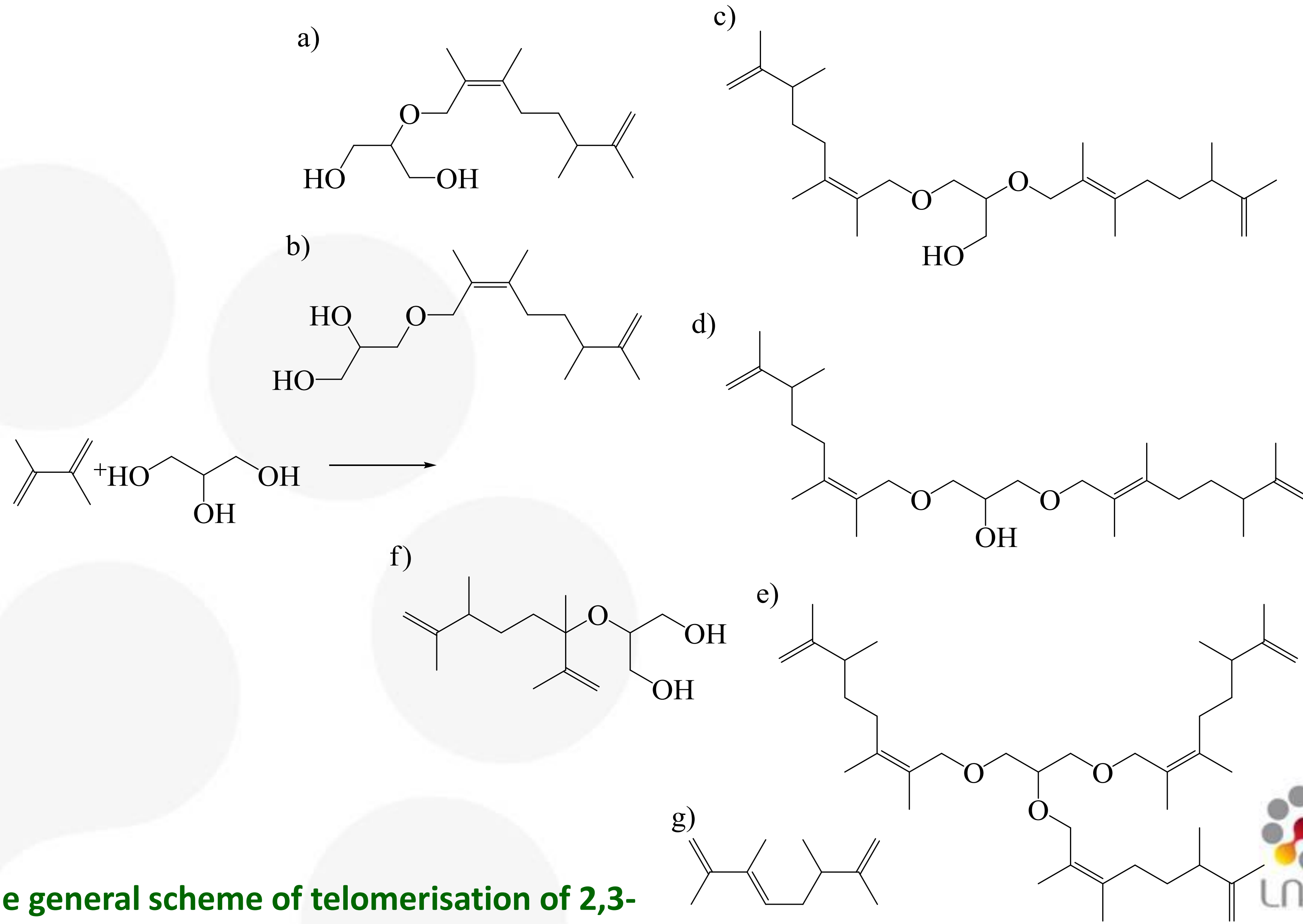
Reaction



The general scheme of telomerisation of 2,3-dimethylbuta-1,3-diene with <u>glycerol</u>

Results

Alcohol	[Products]/ mol%							∑[products]			
	a	b	c	d	e	f	g	mono- substituted	di- substituted	tri- substituted	dimmer
CO_2 at 90 bar											
1-butanol	90.17		9.83					90.17			9.83
ethylene glycol	61.65	28.57		9.77				61.65	28.57		9.77
1,4-dioxaspiro[4.5]decane -2-methanol	89.93		10.07					89.93			10.07
glycerol	54.64	27.32	5.46	2.73			9.84	81.97	8.20		9.84
CO_2 at 120 bar											
1-butanol	68.49	6.85	24.66					75.34			24.66
ethylene glycol	47.40	19.65	9.25	23.70				56.65	19.65		23.70
1,4-dioxaspiro[4.5]decane -2-methanol	61.15	15.29	23.57					76.43			23.57
glycerol	40.17	18.41	8.37	4.18	3.35	1.67	23.85	60.25	12.55	3.35	23.85

Results

alcohol	organic solvents		CO_2 90 bar		CO_2 120 bar	
	C/%	S/%	C/%	S/%	C/%	S/%
1-butanol	24.5	65.5	15.8	90.2	22.8	75.3
ethylene glycol	22.3	46.4	13.5	61.7	17.9	56.6
1,4-dioxaspiro[4.5]decane-2-methanol	19.8	66.3	12.1	89.9	18.1	76.4
glycerol	18.1	46.3	9.7	82.0	14.8	60.3

C/% - conversion of butadiene, S/% - selectivity towards monotelomer

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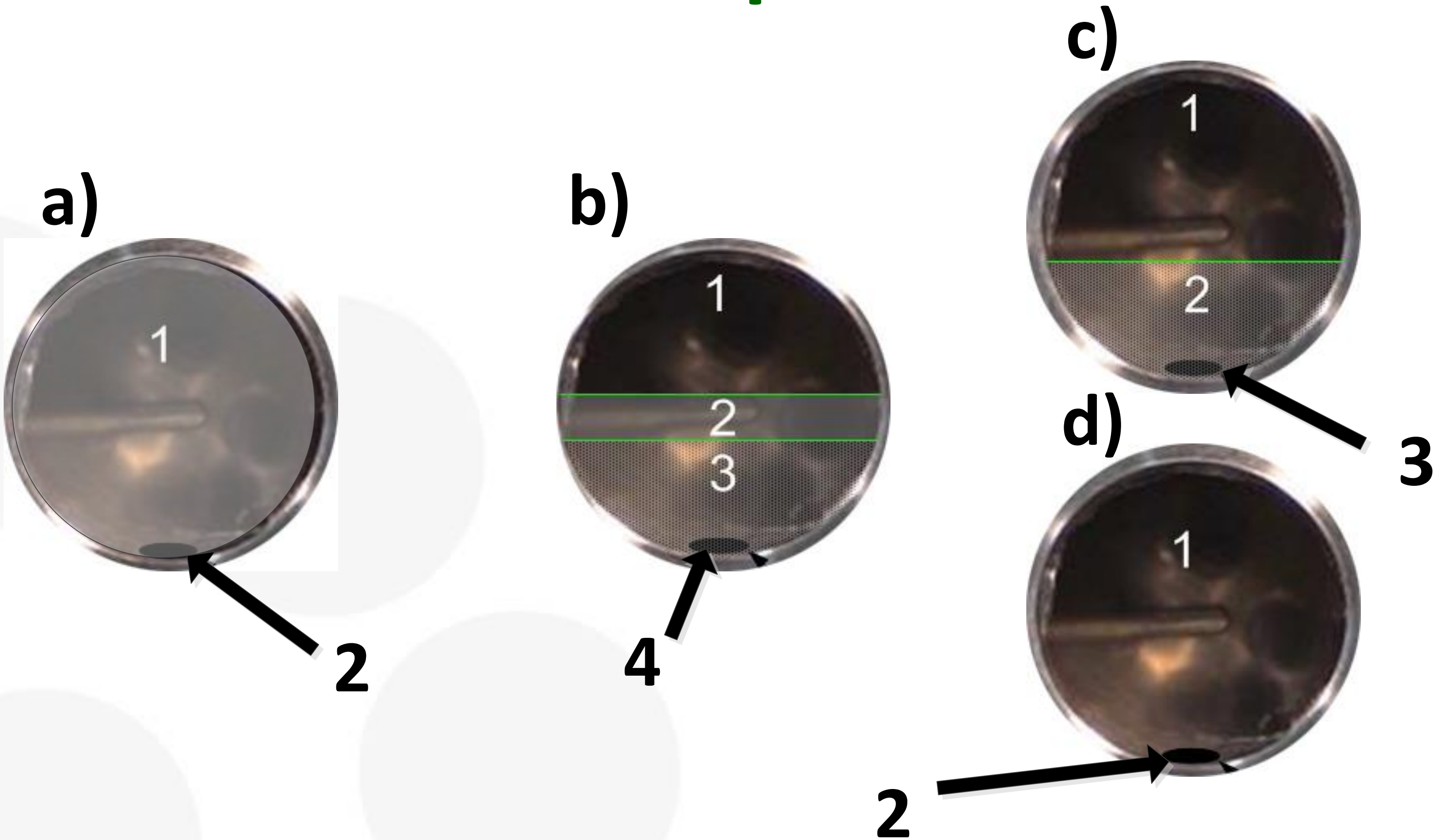
Phase equilibria



a) organic solvent: 1 – organic solvent with all the reagents dissolved, 2 – catalyst;

b) CO_2 at 90 bar: 1 – CO_2-rich phase, 2 – 2,3-dimethylbuta-1,3-diene-rich phase, 3 – mono or polyhydroxy alcohol-rich phase, 4 – catalyst;

c) CO_2 at 120 bar: 1 – fluid constituted by CO_2, 2,3-dimethylbuta-1,3-diene, 2 –1,4-dioxaspiro[4.5]decane-2-methanol or ethylene glycol or glycerol-rich phase, 3 – catalyst;

d) CO_2 at 120 bar: 1 – fluid containing CO_2, 2,3-dimethylbuta-1,3-diene and 1-butanol, 2 – catalyst.

Conclusions

- ✓ A new, facile and efficient method of the heterogeneously catalysed reaction in a sustainable solvent such as carbon dioxide was discovered
- ✓ Carbon dioxide at moderate (90 bar) pressure exhibits the potential for the selectivity's control towards monotelomers
- ✓ By tuning the reaction conditions, a variety of products that can be used for surfactants or defoaming agents' production are formed
- ✓ The catalytic addition of glycerol and mono- and polyalcohols to 2,3-dimethylbuta-1,3-diene is successful with complete avoidance of any volatile organic solvents by their replacement by $scCO_2$

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Acknowledgments

Fundação para a Ciência e a Tecnologia (Portugal) - grants

SFRH/BPD/26356/2006, PEst-C/EQB/LA0006/2011

FCT Fundação para a Ciência e a Tecnologia

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