

## project 3.7

**Next generation autonomous analytical platforms for remote  
environmental monitoring:**

**Microfluidic platforms incorporating stimulus-responsive materials  
for Water Quality**

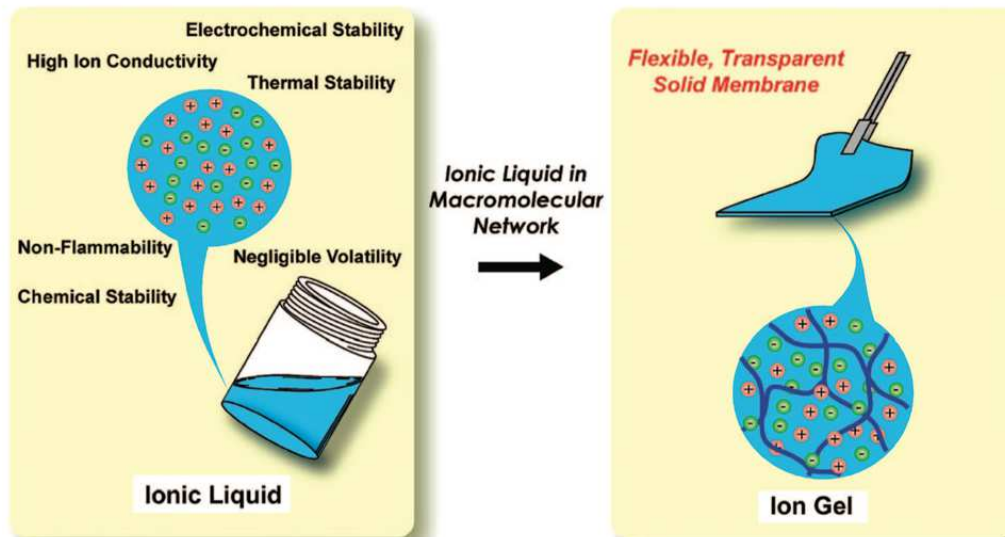
**Bartosz Ziótkowski**

Dermot Diamond

UNIVERSITY COLLEGE DUBLIN • DUBLIN CITY UNIVERSITY • TYNDALL NATIONAL INSTITUTE

- 1. Introduction**
- 2. The recent research focus**
- 3. Training and outputs**

From ionogels to stimulus responsive materials:



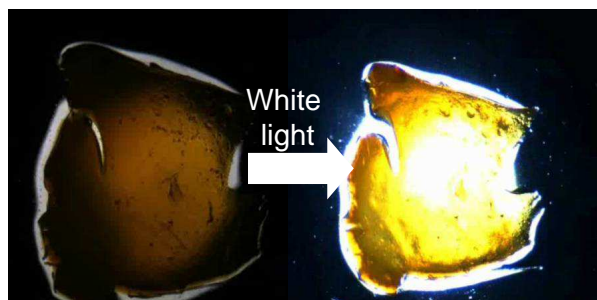
Drying



Soaking (H<sub>2</sub>O)

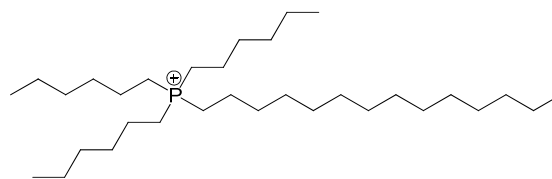
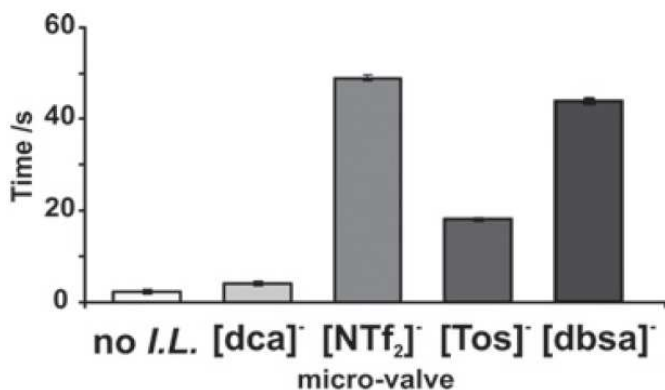
From ionogels to stimulus responsive materials:

From ionogels to stimulus responsive materials:



30% volume decrease in 5 seconds upon irradiation

Benito-Lopez, F. *et al.*  
Lab on a Chip 2010, 10, 195.



Trihexyltetradecylphosphonium cation

Microvalve opening times versus the ionogel composition

Investigation of NIPAM polymerisation in [P<sub>6,6,6,14</sub>] based ionic liquids

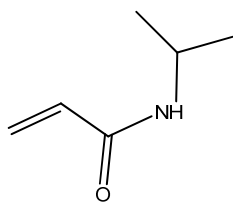


UV curing rheometry of ionogels

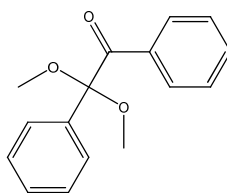


DSC polymerisation kinetics analysis

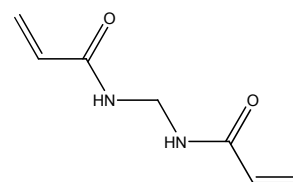
The chemistry:



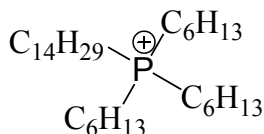
**N-isopropylacrylamide (NIPAM) monomer**



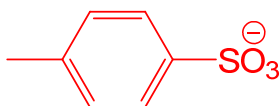
**Dimethoxyphenylacetophenone (DMPA) photoinitiator**



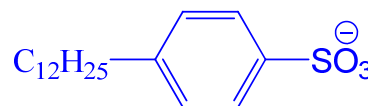
**N,N'-methylenebisacrylamide (MBIS) crosslinker**



**Trihexyl-tetradecyl phosphonium cation [P<sub>6,6,6,14</sub>]**



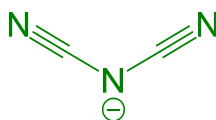
**p-toluenesulfonate [Tos]**



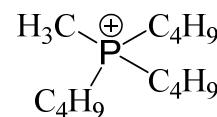
**p-dodecyl benzenesulfonate [dbsa]**



**Chloride [Cl]**



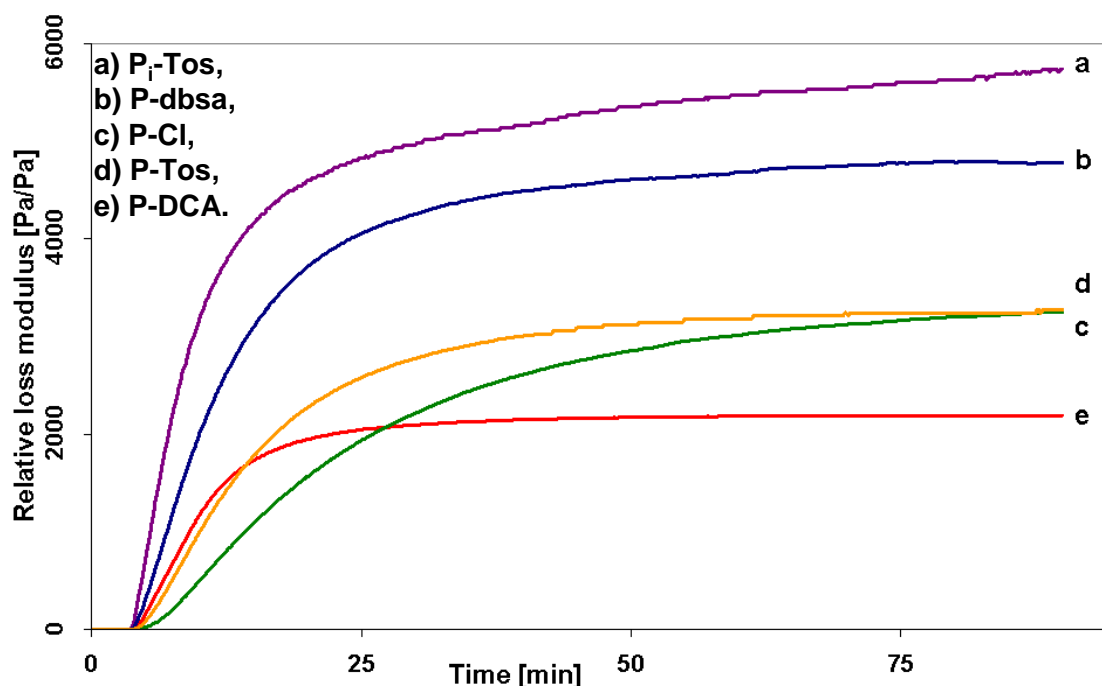
**Dicyanamide [DCA]**



**Tributyl-methyl phosphonium cation [P<sub>1,4,4,4</sub>]**

ATWARM

Rheology of linear polymerisation:



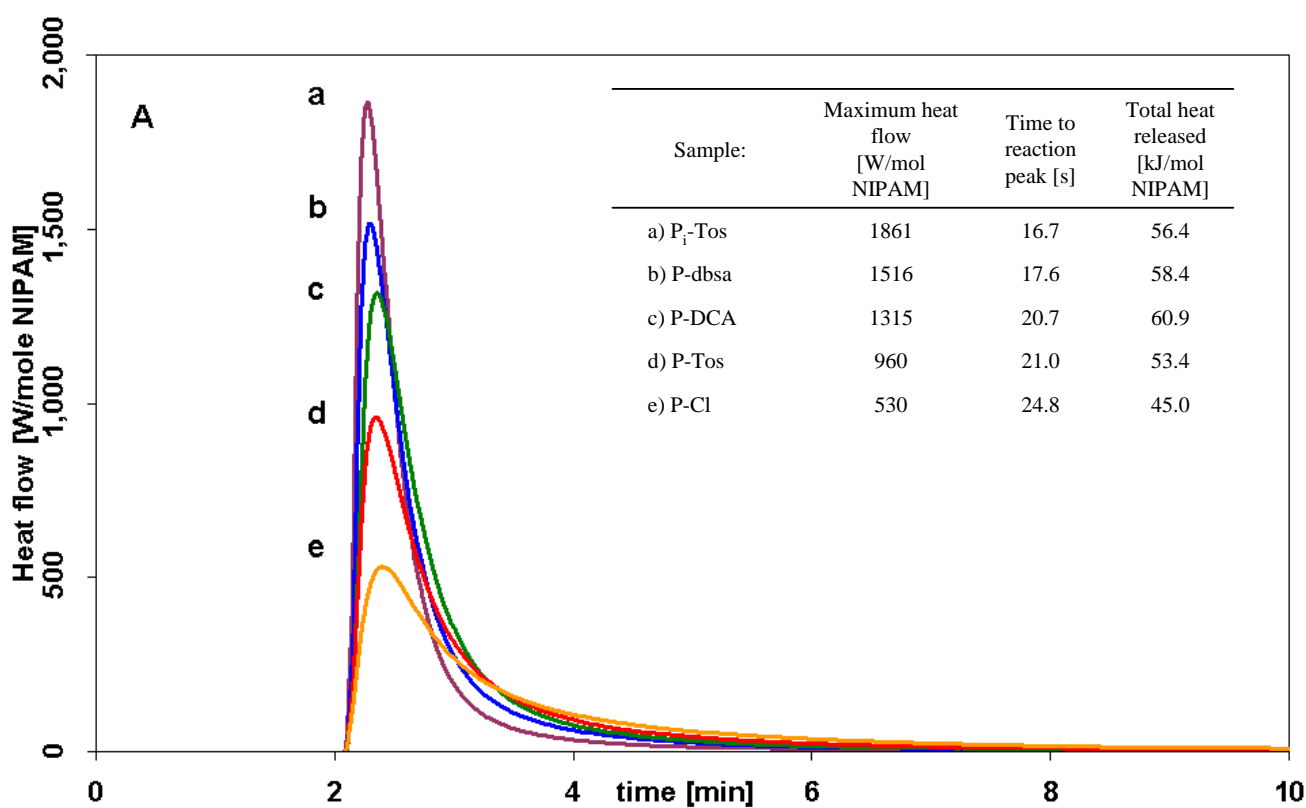
Relative viscous moduli curves during UV polymerisation of a) P<sub>i</sub>-Tos, b) P-dbsa, c) P-Cl, d) P-Tos, e) P-DCA. For each curve, the data was normalised by dividing the initial loss modulus value into the series.

ATWARM

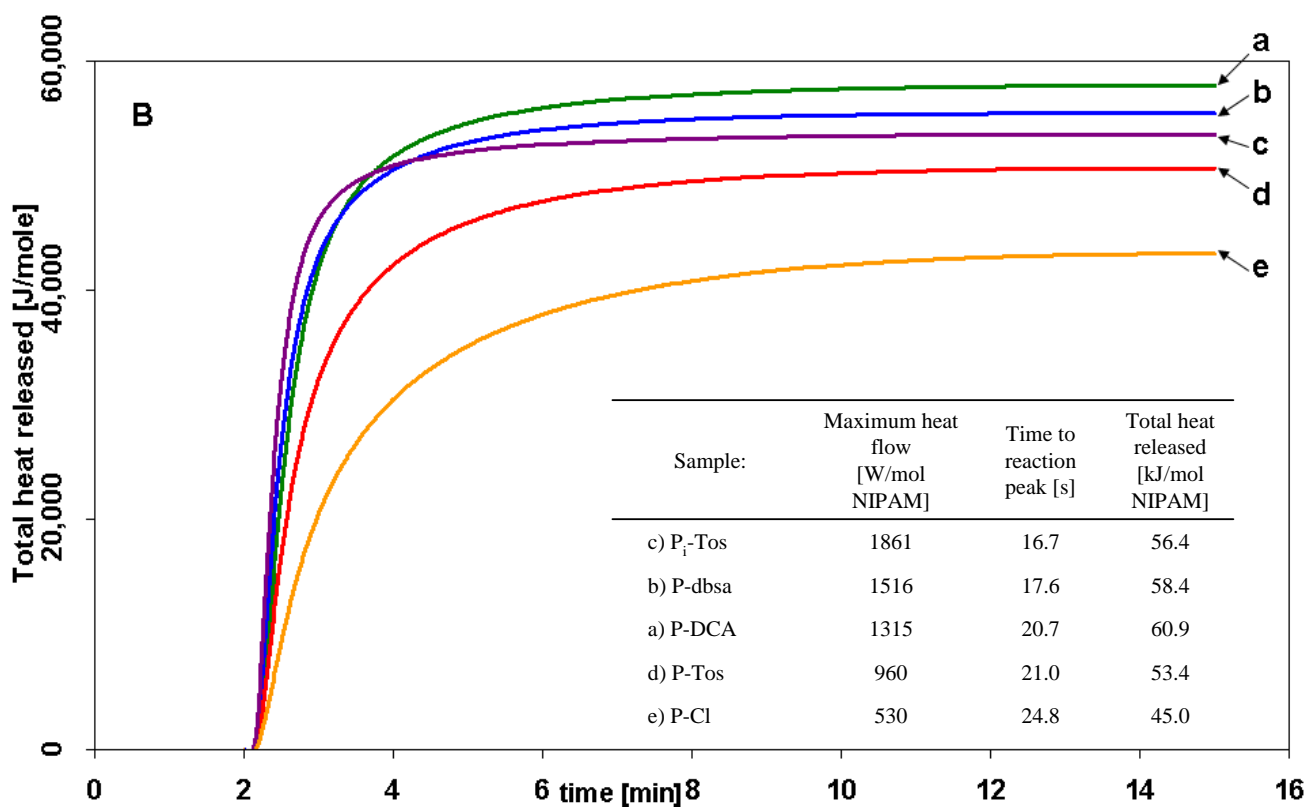
Gel permeation chromatography of linear polymers:

sample	Average molecular weight Mn [g/mol]	Polydispersity index (PDI)
P-dbsa	150 900	2.2
P-DCA	130 600	1.6
P <sub>i</sub> -Tos	117 800	1.76
P-Tos	111 300	1.42
P-Cl	62 650	1.56

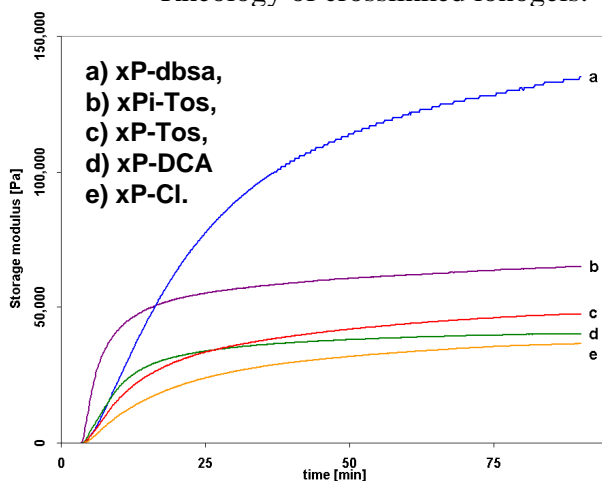
Heat of linear polymerisation:



Heat of linear polymerisation:

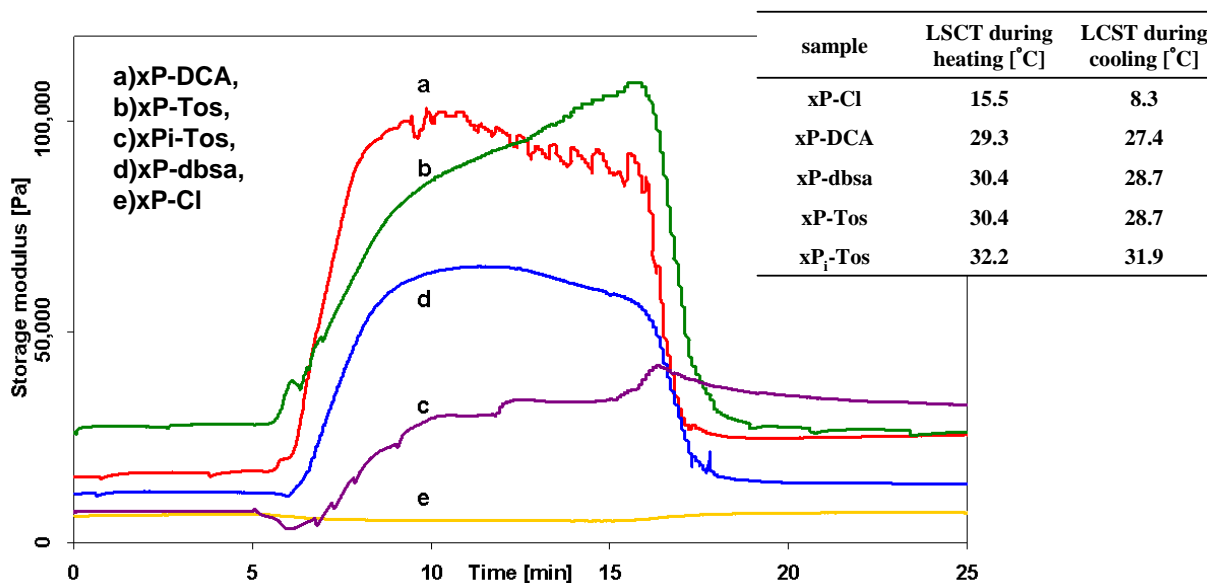


Rheology of crosslinked ionogels:



sample	Viscosity IL 25°C [Pa·s]	G'' (loss modulus) before curing [Pa]	G'' (loss modulus) 90 min. [Pa]	G' (storage modulus) 90 min. [Pa]	Tan δ (G''/G') 90 min.
xP-dbsa	1.8	7.5	200 000	134 000	<b>1.48</b>
xP-Cl	1.955	4.17	42 700	36 700	<b>1.16</b>
xP-Tos	0.96	3.53	38 500	47 700	<b>0.81</b>
xP <sub>i</sub> -Tos	1.36	3.06	52 000	65 170	<b>0.80</b>
xP-DCA	0.256	0.946	6 770	40 400	<b>0.168</b>

Lower Critical Solubility Temperature (LCST)  
behaviour of crosslinked ionogels:



Plots of storage modulus versus time during a temperature step program. The temperature was raised from 25 °C to 45 °C starting at 5th minute and was decreased at 15th minute from 45 °C to 25 °C. a) xP-DCA, b) xP-Tos, c) xPi-Tos, d) xP-dbsa, e) xP-Cl.

Conclusions:

- **Photo-polymerisation of pNIPAM in phosphonium based ionic liquids produces flexible ionogels**
- **Depending on the IL used:**
  - The polymerisation proceed as different rates
  - Produces polymer chains with different lengths and size dispersity
  - The ionogels have different viscoelastic properties (stiffness/stickiness)
- **These ionogels when swollen with water still exhibit polymer LCST transition**
- **The temperature response of the water swollen ionogels is also dependant on the IL used**
- **The best ionogel was obtained with [P<sub>6,6,6,14</sub>][DCA] ionic liquid**

**“Mechanical properties and U.V. curing behaviour of Poly(N-isopropylacrylamide) in phosphonium based ionic liquids”** Bartosz Ziólkowski, Zeliha Ates, Simon Gallagher, Robert Byrne, Andreas Heise, Kevin J Fraser and Dermot Diamond - **submitted to Soft Matter**

**“Integrating stimulus responsive materials and microfluidics – The key to next generation chemical sensors”** Bartosz Ziólkowski, Monika Czugała and Dermot Diamond - review **submitted to Journal of Intelligent Material Systems and Structures**

**“Magnetic iron oxide/poly(N-isopropylacrylamide/ionic liquid hybrid ionogels”** Bartosz Ziólkowski, Kevin J Fraser, Robert Byrne, Dermot Diamond, and Andreas Taubert - being submitted to European Journal of Inorganic Composites

QUESTOR Workshop 28.02.2012 – DCU, Dublin

Analytical workshop 24th - 26th April 2012 – Trinity College Dublin

Talk entitled: “Magnetic ionogels for fluid handling in microfluidic devices” accepted for CIMTEC 2012 conference (10-14 June 2012)

ATWARM

  
NCSR  
National Centre for Sensor Research

Dr. Kevin Fraser  
Dr. Robert Byrne  
Dr. Fernando Benito-Lopez  
Prof. Dermot Diamond

Colleagues from the NCSR

FP7 ATWARM grant (Marie Curie ITN, No. 238273).



**Thank you for attention!**

  
NCSR  
National Centre for Sensor Research