Solvato-morphologically controlled photo-actuated hydrogels

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Background

- p(NIPAAm) based hydrogels that incorporate a spiropyran photochromic unit

- Drawback: These hydrogels function only in acidic conditions (HCl, pH~3)
Background

- Recent work: co-polymerised Acrylic Acid inside p(NIPAAm) in the hydrogel

![Chemical structures showing hydrophilicity change](image)

- Advantage: These hydrogels function in water.

(B.Ziolkowski et al, Soft Matter, 2013, 9, 8754-8760)
Background

- Changing the polymerisation solvent can control the hydrogel morphology.

(Zhang et al., Langmuir, Vol. 18, No. 7, 2002, 2538-2542)
Photo-responsive hydrogels

less hydrophilic

more hydrophilic

spontaneous in H₂O

white light

Spontaneous in H₂O

White light
Hydrogel fabrication

View of the free standing gels under microscope
Hydrogel microstructure

200 mg NIPAM
5 mol % Acrylic acid
1 mol % acrylated-Spiropyran
3 mol % MBIS
1 mol% PBPO
Polymerization solvent
Polymerisation solvent:

THF : Water
THF: Water

Under White light

before 60s 120s 180s 240s

1:1 THF: DI Water

In the Dark

300s 420s 540s 660s 840s
1st irradiation cycle

![Graph showing shrinking (% vs. time (s)) with different solvent ratios (1:1, 2:1, 4:1 THF:Water) and time points (n = 3). The graph includes error bars for each data point. The solvent ratios are differentiated by symbol and color: 1:1 THF:Water is represented by orange triangles, 2:1 THF:Water by green circles, and 4:1 THF:Water by purple diamonds. The graph indicates that the shrinking percentage decreases over time, with 1:1 THF:Water showing the highest percentage of shrinkage. The time scale ranges from 0 to 900 seconds, and the shrinking percentage ranges from 0 to 100%. The graph is labeled as 'Dark' in the center.]

- 1:1 THF:Water polymerisation solvent
- 2:1 THF:Water polymerisation solvent
- 4:1 THF:Water polymerisation solvent

n = 3
Multiple irradiation cycles

![Graph showing shrinking over time for different solvent ratios in dark conditions.](image-url)
SEM Imaging

Polymerisation solvent
4:1 THF: Deionised Water

Polymerisation solvent
2:1 THF: Deionised Water

Polymerisation solvent
1:1 THF: Deionised Water
Rheology, Curing tests

- Storage modulus [Pa]
- Time (s)

- 4:1 THF: WATER
- 2:1 THF: WATER
- 1.1 THF: WATER

DARK
Polymerisation solvent:

Dioxane : Water
Dioxane: Water

1:1 Dioxane: DI Water

Before 60s 120s 180s 240s

300s 420s 540s 660s 840s

In the Dark

500μm

White Light
1st irradiation cycle

- 1:1 Dioxane:water polymerisation solvent
- 2:1 Dioxane:Water polymerisation solvent
- 4:1 Dioxane:Water polymerisation solvent

Shrinking (%)

Time (s)

n = 3

Dark
Multiple irradiation cycles

Shrinking (%) vs. Time (s)

1:1 Dioxane:Water polymerisation solvent
2:1 Dioxane:Water polymerisation solvent
4:1 Dioxane:Water polymerisation solvent

Dark
SEM Imaging

Polymerisation solvent
4:1 Dioxane: Deionised Water

Polymerisation solvent
2:1 Dioxane: Deionised Water

Polymerisation solvent
1:1 Dioxane: Deionised Water
Rheology, Curing tests

Storage modulus [Pa]

Time(s)

4:1 DIOXANE : WATER
2:1 DIOXANE : WATER
1:1 DIOXANE : WATER
Polymerisation solvent:

Acetone : Water
Acetone : Water

1:1 Acetone: DI Water
1st irradiation cycle

Shrinking (%) vs. Time (s)

4:1 Acetone : Water polymerisation solvent
2:1 Acetone : Water polymerisation solvent
1:1 Acetone : Water polymerisation solvent

n = 3
Multiple irradiation cycles

- 4:1 Acetone : Water polymerisation solvent
- 2:1 Acetone : Water polymerisation solvent
- 1:1 Acetone : Water polymerisation solvent

Shrinking (%) vs. Time (s)

Time (s)

Shrinking (%)

Dark
SEM Imaging

Polymerisation solvent
4:1 Acetone: Deionised Water

Polymerisation solvent
2:1 Acetone: Deionised Water

Polymerisation solvent
1:1 Acetone: Deionised Water
Rheology, Curing tests

Graph showing storage modulus [Pa] vs. Time(s) for different acetone:water ratios in dark conditions.
Solvent comparison

- 4:1 THF: Water
- 4:1 Dioxane: Water
- 4:1 Acetone: Water

DARK

Shrinking (%) vs. Time (s)
Conclusion

• Successful demonstration of how different polymerisation solvents effect the morphology of the hydrogel.

• Possibility to control the photo-actuation of the hydrogels by varying the polymerisation solvent.

• Providing faster and repeatable shrinking and reswelling kinetics.
Thank You

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