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PNIPAM-based Polymers with Selective Absorption for Polar Liquid from Non-Polar Liquid

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Needs for Separation of Miscible Liquids

A wide range of practical applications requires liquid separation including:

- Wastewater treatment
- Pharmaceutical engineering
- Petrochemical product refining
- Biofuel production
- Food and beverage industry

Why is separating miscible liquids important?

- It is crucial in these industries to ensure product purity, enhance process efficiency, and reduce environmental impact.

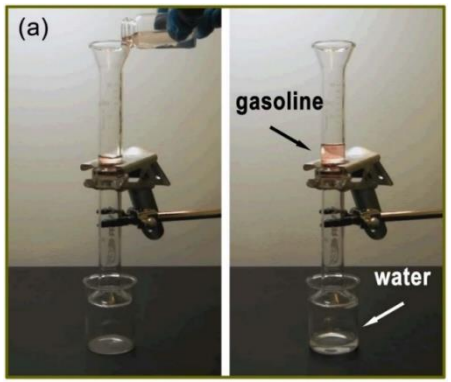
Current limitations of distillation

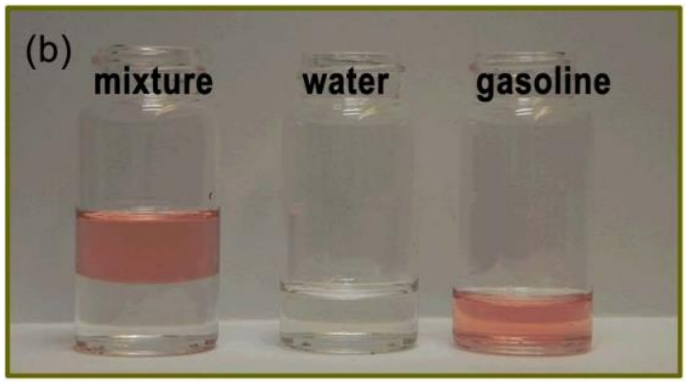
- However, the common method for separating liquids faces challenges: High energy consumption, Lack of ability to separate azeotropes

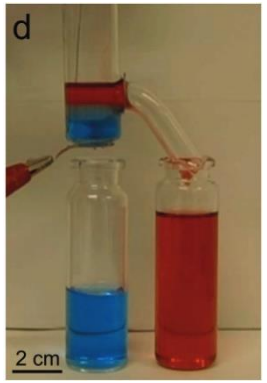
Therefore, there is a need to develop a new solution for **separating miscible liquids.**

Polymer-based (Hydrogel-based) Separation of Miscible liquids

Functional polymers have been used to separate liquids, mostly immiscible liquids such as oil and water.







Limitations of membrane techniques

- Membrane techniques face challenges with separation miscible liquids. Membranes alone are not effective for this. They usually need extra steps like membrane distillation, which makes the process more complex.

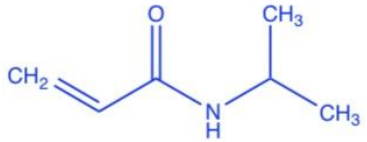
Emerging absorption techniques

- Absorption is a promising method for separating miscible liquids. However, there is no report of polymer absorbent that can separate miscible liquids.

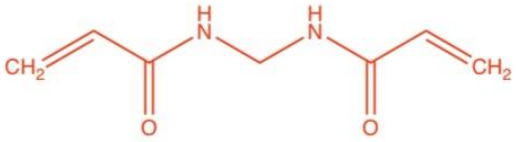
Herein, we present a poly(n-isopropyl acrylamide) (PNIPAM)-based polymer that demonstrates selective absorption for ethanol from n-heptane.

Zhang, L., Zhong, Y., Cha, D., & Wang, P. (2013). A self-cleaning underwater superoleophobic mesh for oil-water separation. Scientific Reports, 3(1), 2326.
Kwon, G., Kota, Arun. K., Li, Y., Sohani, A., Mabry, J. M., & Tuteja, A. (2012). On-Demand Separation of Oil-Water Mixtures. Advanced Materials (Weinheim), 24(27), 3666–3671.

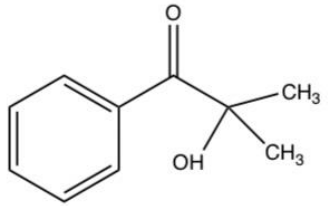
f-PNIPAM Polymer: Synthesis and Chemical Structure



N-Isopropylacrylamide (NIPAM)



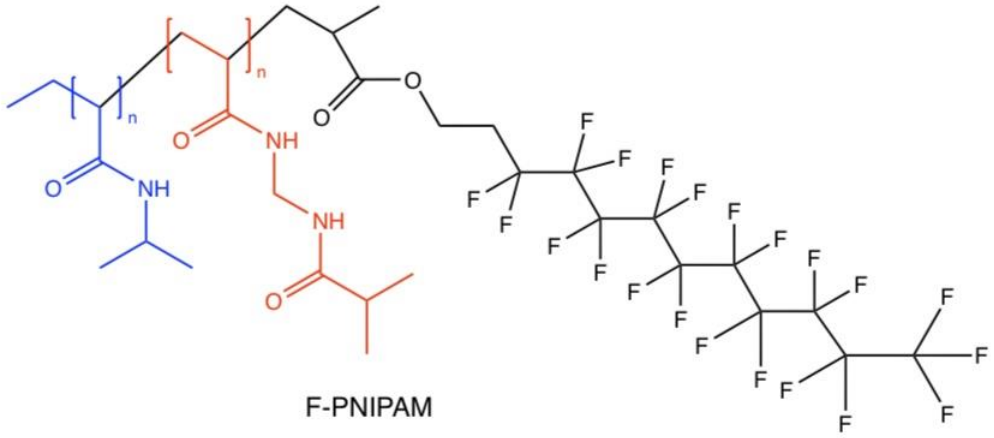
N,N'-Methylenebisacrylamide
(MBAA)



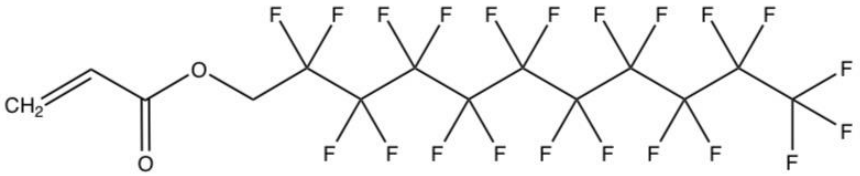
2-Hydroxy-2-methyl-propiophenone
(darocur 1173)

H_2O solvent

UV light

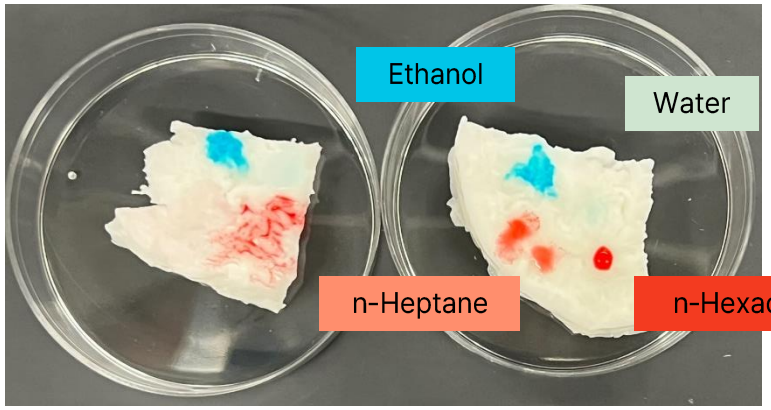


F-PNIPAM



1H,1H,2H,2H-Heptadecafluorodecyl Acrylate
(f-acrylate)

By adding f-acrylate into the well-known PNIPAM structure,
expect its potential for enhanced selective absorption performance.

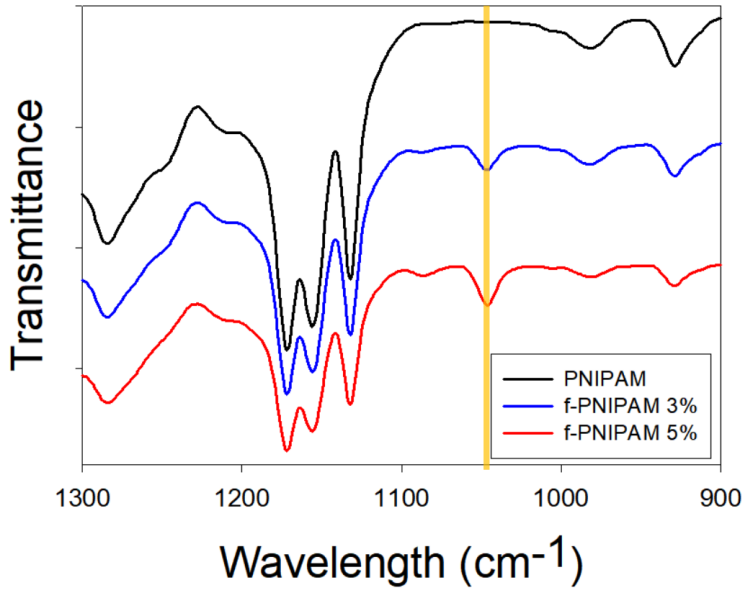


PNIPAM f-PNIPAM

FTIR and DSC Results for PNIPAM and f-PNIPAM

To evaluate the effect of f-acrylate, polymers were prepared with 0%, 3%, and 5% f-acrylate content.

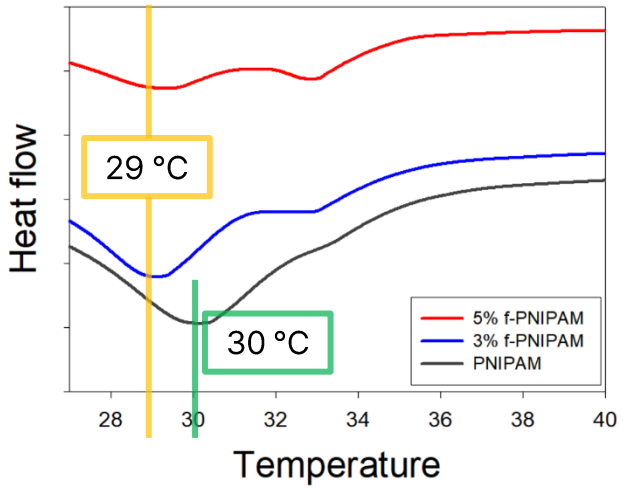
Fourier Transform Infrared spectroscopy (FTIR)



- FTIR results confirm successful synthesis, as evidenced by the C–F bonding peak at 1045 cm^{-1}, which increases proportionally with the f-acrylate concentration.

Differential Scanning Calorimetry (DSC)

- Thermo-responsive Polymer
  - Lower Critical Solution Temperature (LCST)



- The polymer containing f-acrylate showed a lower LCST compared to PNIPAM
- The presence of f-acrylate promotes **liquid release at a lower temperature**, which can help reduce the energy to release absorbed liquid for reuse.

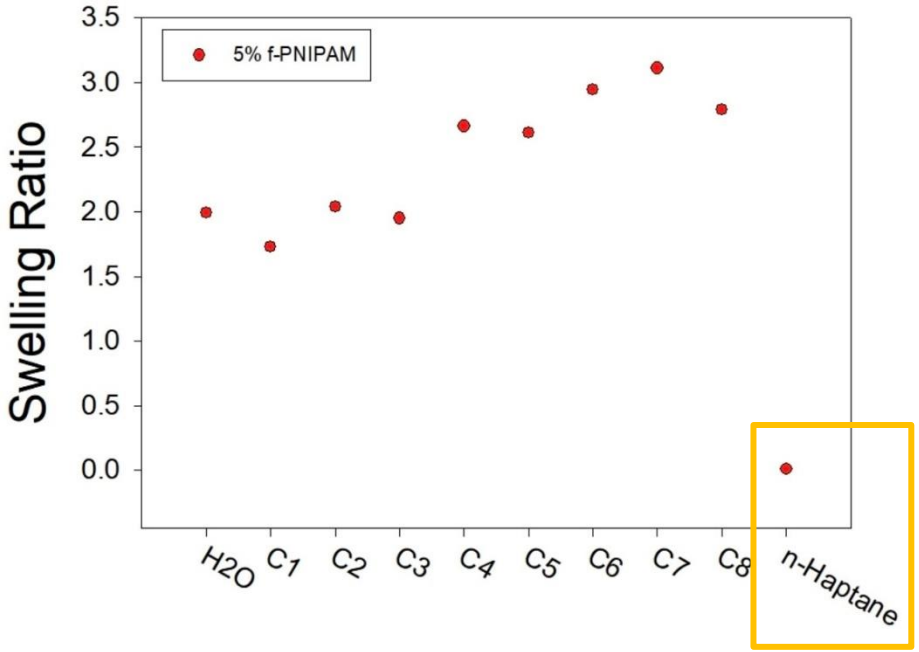
Swelling Ratio of PNIPAM and f-PNIPAM

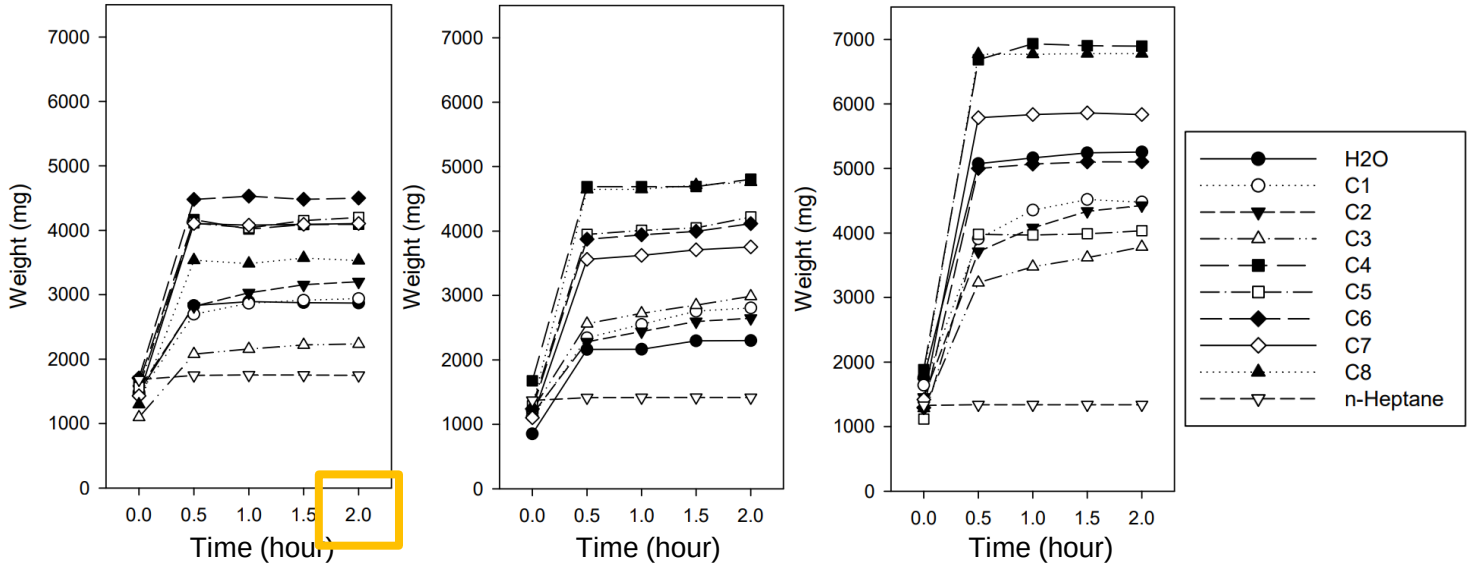
- Swelling tests using various solvents: Water, alcohols with different carbon numbers (C1~C8), and n-Heptane

$$\text{Swelling Ratio} = \frac{W - W_0}{W_0}$$

* W: after swollen weight, W_0: original weight

- The polymers did not absorb the non-polar solvent n-heptane, while they absorbed water and alcohols.
- For alcohol, the swelling ratio increased with the number of carbon.
- The overall swelling ratio was highest in 5% f-PNIPAM, indicating that a **higher f-acrylate** content **enhances absorption capacity**.





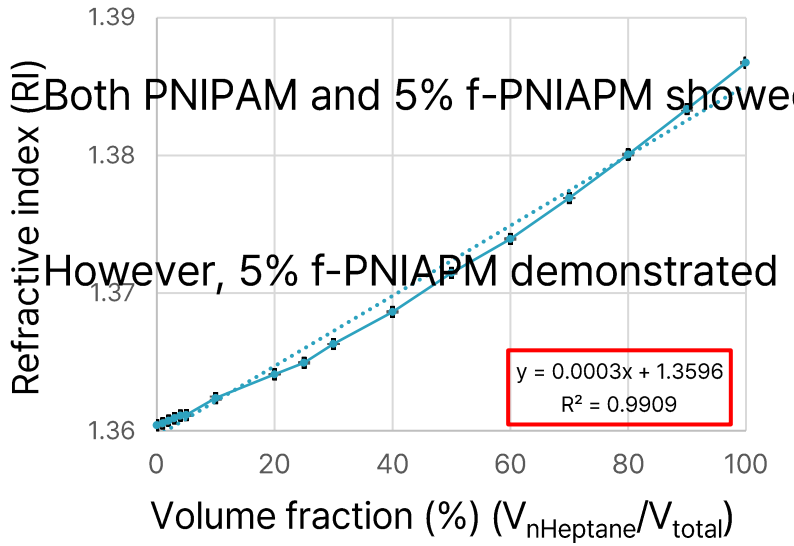
Selective Absorption for Ethanol over n-Heptane

Ethanol w/ methylene blue and n-Heptane w/ oil red o (Ethanol:n-Heptane = 50:50% v/v)

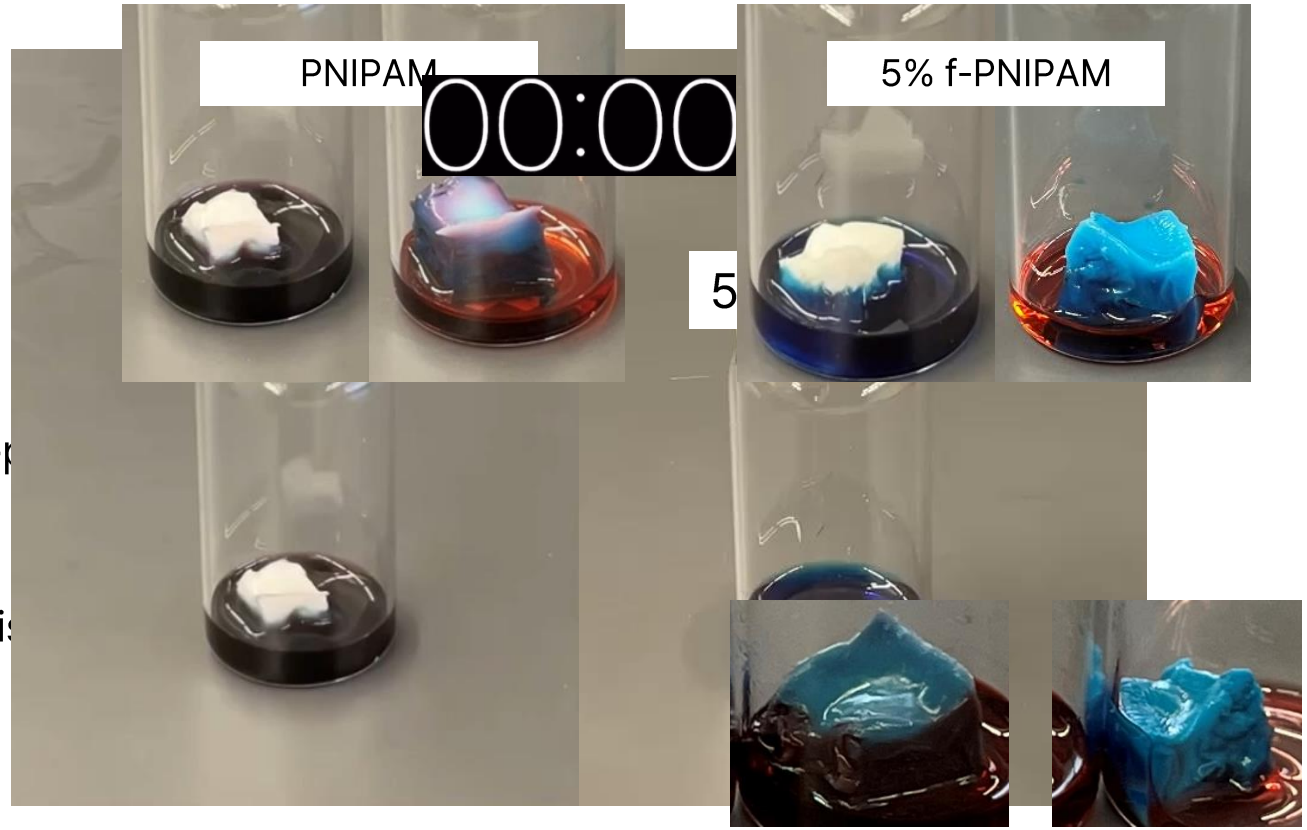
- To achieve a more accurate analysis beyond color observation, refractive index (RI) measurements of before and after separation were conducted.

	RI change
PNIPAM	1.3716 → 1.3867
5% f-PNIPAM	1.3715 → 1.3868

* n-Heptane 90% RI 1.3834
100% RI 1.3870

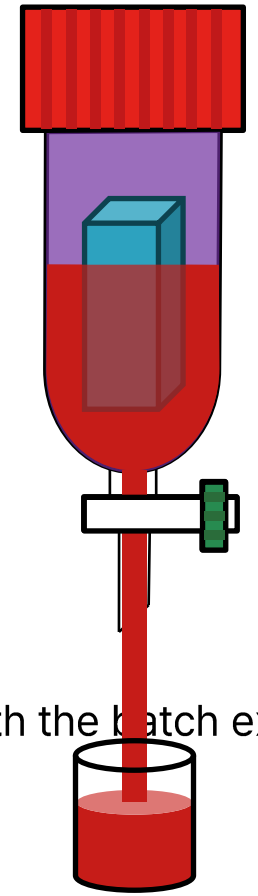


- Both PNIPAM and 5% f-PNIAPM showed great sep
- However, 5% f-PNIAPM demonstrated better resi



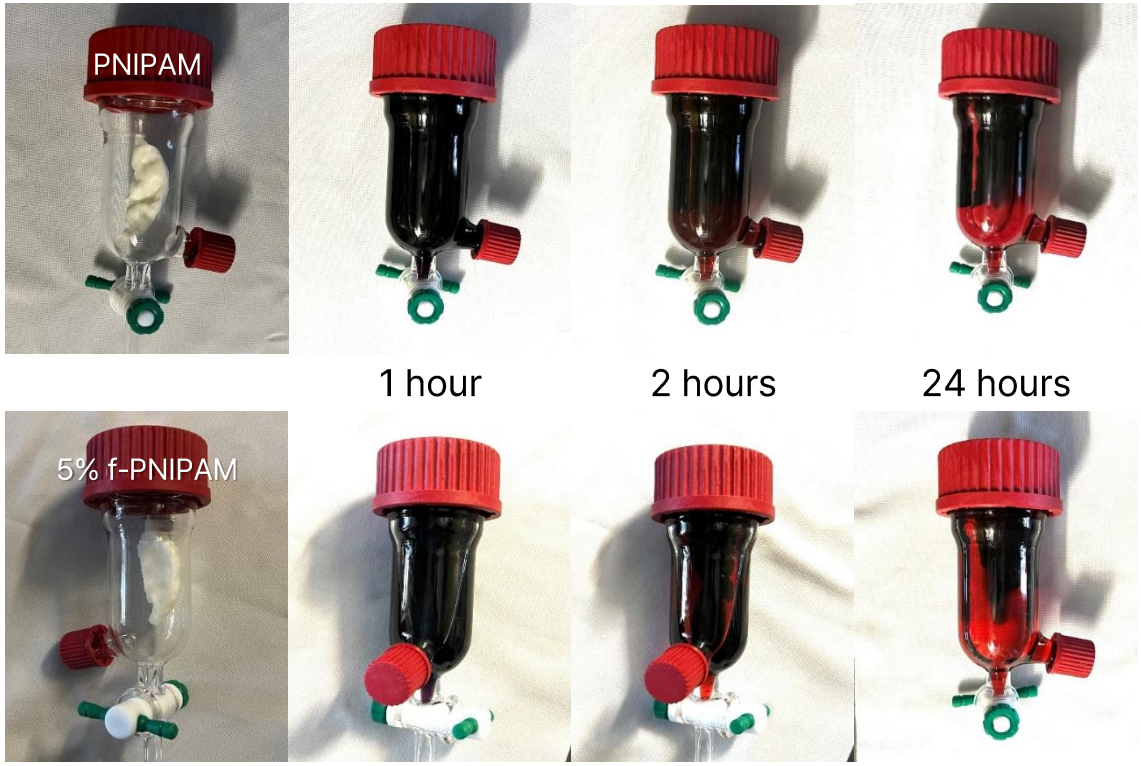
Separation of Ethanol-n-Heptane Mixture

Ethanol w/ methylene blue and n-Heptane w/ oil red o (Ethanol:n-Heptane = 20:80% v/v)



	RI change
PNIPAM	
5% f-PNIPAM	

* n-Heptane 90% RI 1.3834
100% RI 1.3870



- With the batch experiment also showed the same result

Use its thermo-responsive property to recycle it

By heating the swollen polymer, ethanol can be released

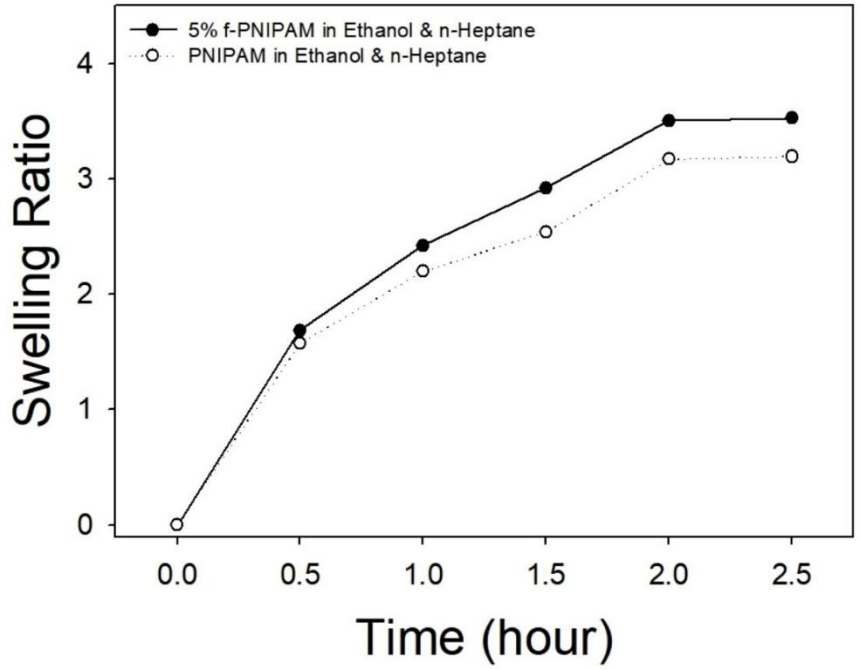
Reusability Test – Dried PNIPAM and f-PNIPAM for separation

PNIPAM & 5% f-PNIPAM dried at 40 °C for 12 hours **to evaluate their recyclability**

The swelling tests were conducted with two solvents: Ethanol & n-Heptane mixture and n-Heptane.

- Dried polymers did not absorb n-Heptane
- But they **cannot** separate miscible polar and non-polar liquids.

Solvent	Polymer	Weight	
		at 0 hour	at 2.5 hours
	PNIPAM	0.42 g	
	5% f-PNIPAM	0.34 g	
	PNIPAM	0.41 g	
	5% f-PNIPAM	0.23 g	



Why dried polymers absorb n-Heptane in the presence of ethanol?

Swelling Ratio of Dried PNIPAM and f-PNIPAM

Swelling tests with dried PNIPAM and 5% f-PNIPAM using various solvents: Water, alcohols with different carbon numbers (C1~C8), and n-Heptane

- The dried polymers showed the opposite trend in alcohols compared to the as-prepared polymers.

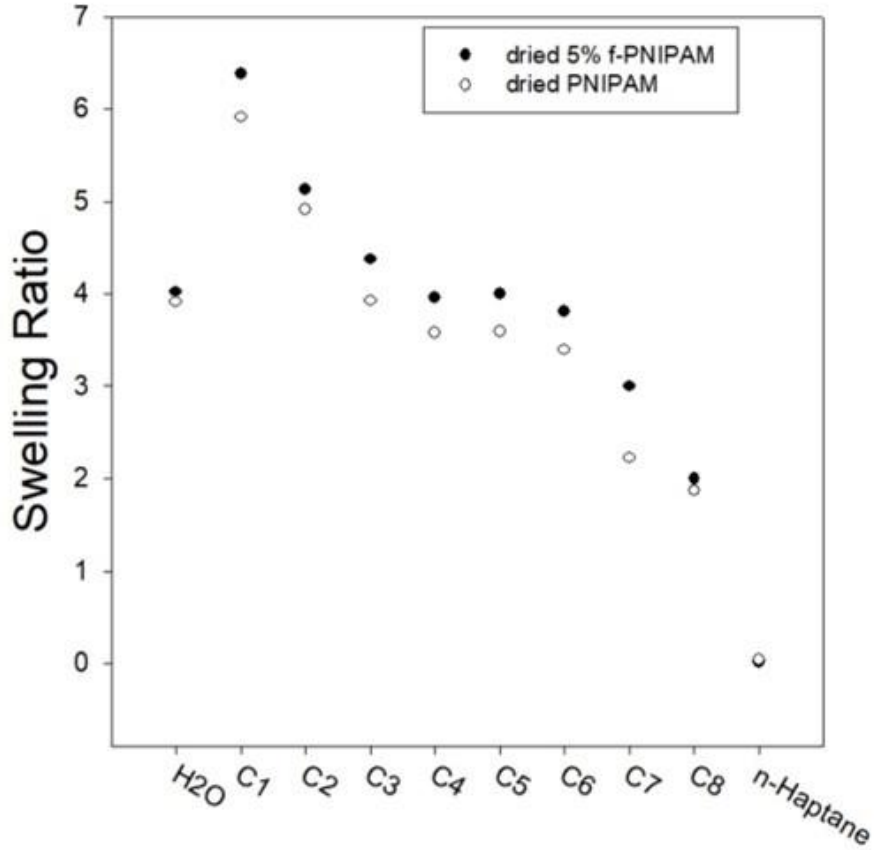
Hypothesis

The liquid absorption of f-PNIPAM is a combination of two mechanisms

- Direct interaction between the liquid and f-PNIPAM
- Interaction between the liquid and the water within f-PNIPAM

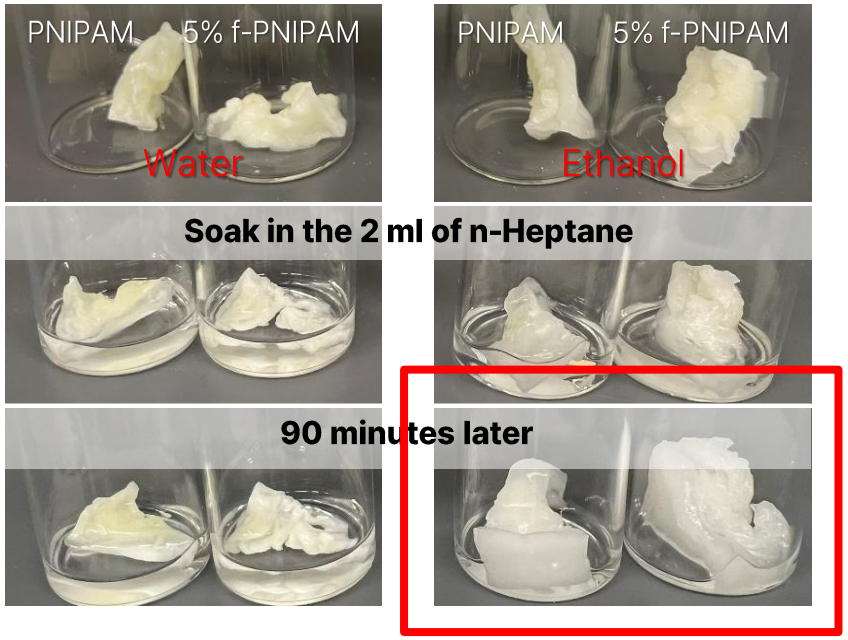
Based on this hypothesis,

- Methanol tends to bind directly to f-PNIPAM due to its structural similarity to water, leading to higher absorption in dried f-PNIPAM.
- In contrast, for octanol, the dominant absorption mechanism involves interaction with the water inside f-PNIPAM rather than with f-PNIPAM itself.



Pre-swollen PNIPAM and f-PNIPAM

Dried PNIPAM and 5% f-PNIPAM absorb each DI water or ethanol for 20 minutes



Solvent Pre-swollen	Polymer	Weight	
		at 0 hour	at 90 mins
	PNIPAM	0.875 g	
	5% f-PNIPAM	0.810 g	
	PNIPAM	0.880 g	
	5% f-PNIPAM	1.246 g	

- Pre-swollen polymers with **water** didn't absorb n-Heptane
- Pre-swollen polymers with **ethanol absorbed n-Heptane** (interaction with the ethanol inside polymers)

Soak these **n-Heptane & ethanol absorbed polymers** in water

- Phase separation: n-Heptane in the top layer, Ethanol & water in the bottom layer
  → Solvent exchange
- However, the top layer's volume was less than 2 ml

Pre-swelling with water to reuse the PNIPAM-based polymers

Conclusion & Summary

To improve the separation efficiency of miscible liquids like ethanol and n-heptane, **f-acrylate** was introduced through **co-polymerization**.

- Enhanced swelling ratios in water and alcohols.
- Lower LCST, enabling absorbed liquid release with lower thermal energy.
- Improved resistance to the non-polar liquid n-heptane.

The **absorption mechanism** of PNIPAM-based polymers

- Direct interaction between the polymer and the liquid
- Interaction with the pre-swollen liquid inside the polymer

Recycling

- For successful polymer reuse, **pre-swelling** the dried polymer with **water** proved effective in minimizing unwanted n-heptane absorption.

These findings suggest that PNIPAM-based polymers have potential applications in efficient miscible liquids separation processes

Acknowledgement

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Thank you