

Use of CO₂ to Trigger Reversible Volume Phase Transition in Hydrogels

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Abstract

Smart materials are often inspired by natural processes that are responsive to environmental stimuli. CO₂ has garnered interest as a stimulus as it is abundant, inexpensive, and non-toxic. Swelling, or the process of absorbing water, is a fundamental property of hydrogels yet is often not controlled using an environmental stimulus. In this work, CO₂ is used to trigger pronounced, reversible swelling of a crosslinked hydrogel. Specifically, CO₂ responsiveness was conferred to hydrogels with a volume phase transition temperature (VPTT), which demarcates the transition from a collapsed to swollen state. We show that these gels display a CO₂-switchable volume phase transition that enables gas-triggered swelling at a constant temperature. To tune the VPTT, compositional studies were conducted to evaluate the effect of varying co-monomer content on the resulting VPTT shifts in these samples. Increasing the concentration of the CO₂-responsive moiety resulted in an increase in the initial VPTT as well as a greater shift in the VPTT after CO₂ exposure. Isothermal swelling studies conducted at a temperature between the VPTTs before and after CO₂ exposure show that CO₂ triggers a reversible volume transition and controls swelling. The results presented here demonstrate the promise of CO₂ as a stimulus for the design and study of smart materials, which may find applications in drug delivery, microfluidics, and soft actuators.

Composition Dependent VPTT Shift

Hydrogels with varying NIPAM:VI comonomer ratios were synthesized to demonstrate the effect on the VPTT shift. The VPTT is measured as the temperature at which the gel displays a transmittance of 50%.

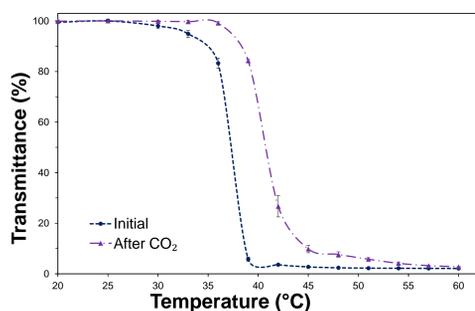


Figure 3: VPTT Shift for 95:5 NIPAM:VI Hydrogel

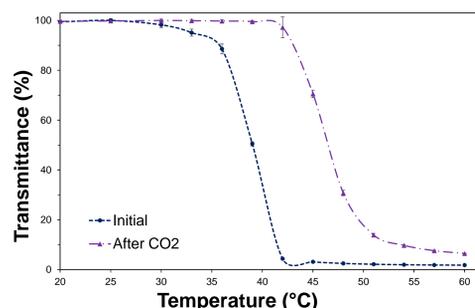


Figure 4: VPTT Shift for 90:10 NIPAM:VI Hydrogel

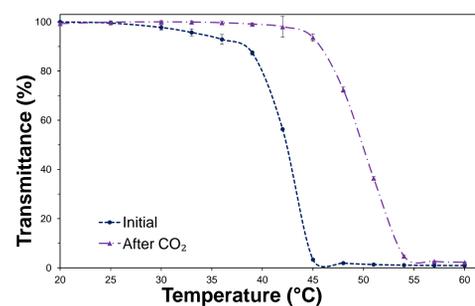


Figure 5: VPTT Shift for 85:15 NIPAM:VI Hydrogel

Table 1: VPTT of each composition before and after CO₂.

| NIPAM:VI Ratio | Initial VPTT (°C) | VPTT After CO ₂ (°C) |
|----------------|-------------------|---------------------------------|
| 100:0 | 34.5 ± 0.0 | 34.8 ± 0.1 |
| 95:5 | 37.2 ± 0.3 | 40.8 ± 0.4 |
| 90:10 | 38.8 ± 0.1 | 46.5 ± 0.1 |
| 85:15 | 42.0 ± 1.1 | 49.7 ± 0.2 |

It was observed that increasing the imidazole concentration in the gels resulted in a higher initial VPTT as well as an increased shift after exposure to CO₂. Hydrogels synthesized without VI displayed no shift in the VPTT. This demonstrates the compositional dependence of the VPTT and shift.

Hydrogel Design

The hydrogel was designed at the molecular level to include:

- 1) A monomer displaying an LCST in water when polymerized.
- 2) A monomer that is responsive to CO₂ in water.

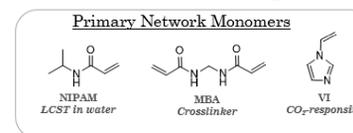


Figure 1: Monomers in CO₂ Responsive Hydrogel

Poly(NIPAM) has a known LCST of 32 °C in water. VI is a known pH responsive monomer. CO₂ in water forms carbonic acid, a weak acid capable of protonating VI and triggering a switch from a neutral to protonated state without the accumulation of byproducts.

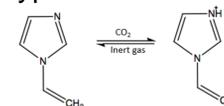


Figure 2: Protonation of VI under acidic conditions.

Hypothesis: When VI is incorporated into a NIPAM network, CO₂ can be used to trigger a reversible volume phase transition isothermally and without the accumulation of byproducts. It is expected that the initial VPTT and its shift can be tuned by network composition and will enable CO₂-induced swelling.

Reversible CO₂-Triggered Swelling

The shift in the VPTT results in enhanced swelling of the hydrogels at a constant temperature. Exposure to CO₂ results in the expansion of the gas-responsive network.



Figure 6: Gas-responsive network swelling and collapse.

The transition from cloudy to clear is indicative of the shift in the VPTT of the gel. The protonation of the VI groups within the network can be reversed with an inert gas. The degree of swelling of the hydrogel is measured by the swelling ratio.

$$\text{Swelling Ratio} = \frac{\text{Mass}_t - \text{Mass}_{t=0}}{\text{Mass}_{t=0}}$$

The swelling ratio quantifies the increase in the mass of the hydrogel as it absorbs and expels water in response to the gas.

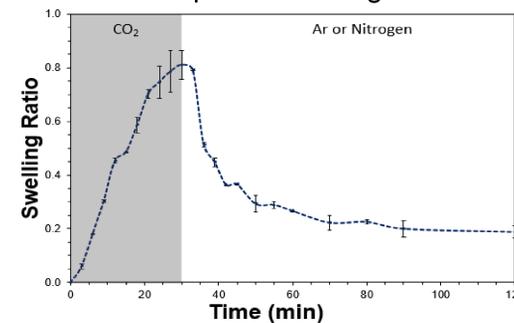


Figure 7: Swelling and Deswelling of 95:5 NIPAM:VI Hydrogel

Future Work

- Characterize swelling as a function of comonomer ratios.
- Measure the mechanical properties of the hydrogels before and after the VPTT shift.
- Explore the potential drug delivery applications associated with the isothermal VPTT shift.

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