CO_2 Sequestration: Thermally Programmable pH Buffers

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Dara Van Gough, Jill S. Wheeler, and Erik D. Spoerke

Sandia National Laboratories, Albuquerque, NM

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Outline

- Motivation
  - Obama goal/DOE goal (1 slide)
    - Point out the targets
- Approach
  - Bioinspiration: comment on plants/animals
  - Show the CO2 solubility with pH
  - Then show our approach: A way to reversibly adjust the pH without the addition of acid/base
- Background/meat
  - What is NIPAM?
  - Comment about pH shift in different dielectric environments?
  - Easy schematic about what's going on
  - Show the chemical equilibria – only what's important
  - Data time. Focus on preliminary data then show the CO2 capture. Emphasize limitations, possible solutions
- Summarize

Motivation & Targets

"To prevent the worst effects of climate change, we must accelerate our efforts to capture and store carbon in a safe and cost-effective way. This funding will both create jobs now and help position the United States to lead the world in CCS technologies, which will be in increasing demand in the years ahead."[1]

- Energy Secretary Steven Chu

"Rapid commercial development and deployment of clean coal technologies, particularly carbon capture and storage, will help position the United States as a leader in the global clean energy race."[1]

- President Obama

Burning of fossil fuels introduce 6 x 10^9 metric tons (6 GT) of CO_2 into the air each year.

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Targets for CO_2 Sequestration

Prevent Global Warming associated with the burning fossil fuels.
(Fuels introduce 6 x 10^9 metric tons (6 GT) of CO_2 into the air each year.)

Remove CO_2 from air.
(Atmosphere = 5.1 x 10^{15} metric tons)

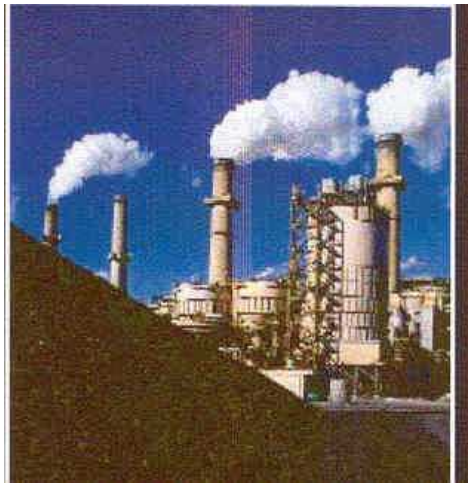
Current CO_2: 377 ppm
(2 x 10^{12} metric tons)

Removal Goal: 10^9 metric tons/yr
(1 km^3 of liquid CO_2)

Disposal: underground

Desired Cost: $10/metric ton
(4 kcal/mole)

Alternate: treat coal exhaust
(10-15% CO_2)



Processes must be selective, reversible, cheap, and capable of handling billions of tons of CO_2, preferably from air.

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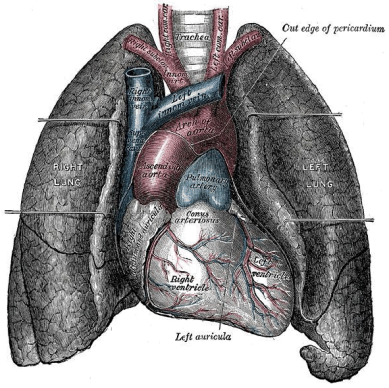
Natural process for dealing with CO_2



Release CO_2

Capture CO_2

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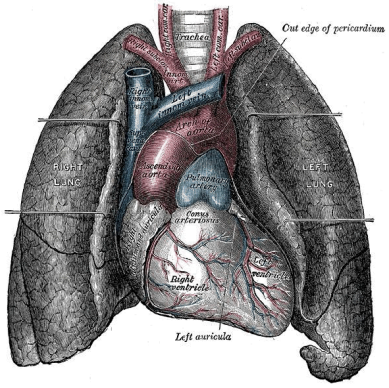
Natural process for dealing with CO_2



Release CO_2

Capture CO_2

Natural processes for CO_2 capture and release all involve water.

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What happens to CO_2 in water?

$$CO_2\,(g) + H_2O \leftrightarrow CO_2\,(l) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$K_{Henry} = \frac{[CO_2(l)]}{[CO_2(g)]} = 0.33M/atm$$

$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O$$

$$K_{deprot} = \ldots\ldots\ldots$$

$$K_{hydrolysis} = \frac{[H_2CO_3]}{[CO_2(l)]} = 2.6x10^{-3}$$

Aqueous CO_2 capture is a matter of tracking protons!

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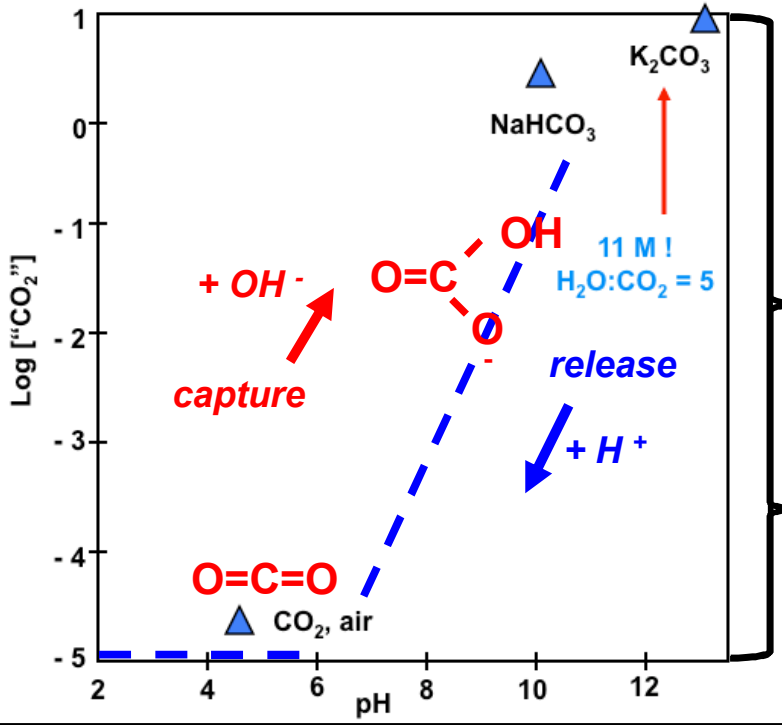

Aqueous CO_2 capture is a matter of tracking protons!

Δ["CO_2"] of 100,000 is possible.
Requirement: Δ"pH" = 4-5.

Carbonates for capture ←→ CO_2 for release

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Nature Currently Mediates Atmospheric CO_2 Levels

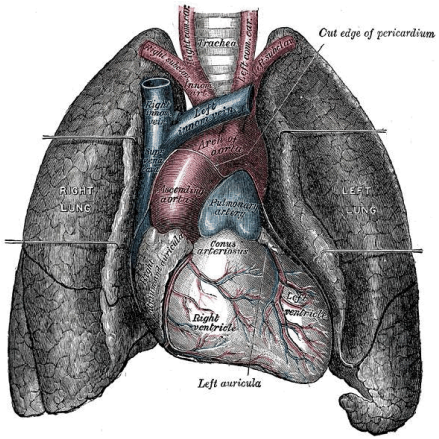
Natural processes for CO_2 capture/release all involve water.

Plants (Capture)

Land Biomass =
11,000 GT

β-carbonic
anhydrase

Animals (Release)



100 kg/yr/liter blood
(Humans exhale 6 GT/yr)

α-carbonic
anhydrase

Oceans (Capture/Release)

Ocean Volume =
2×10^9 GT
2×10^9 km^3

"Dissolved C"
(solubility + biomass) =
37,000 GT

Question: Can we adopt Nature's processing schemes in artificial systems?

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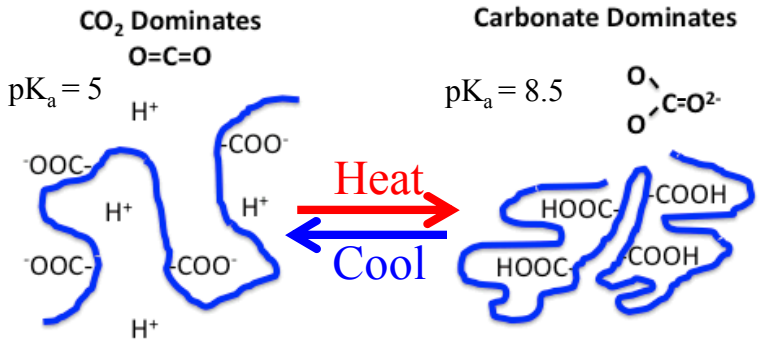
Thermally Programmable pH Buffers

pH Control: enabled by a reversible, thermally-activated swelling transition

N-isopropylacrylamide (NIPAM) → provides programmability
Acrylic acid (AA) → provides acid-base activity

Hydrophilic:
AA ionization promoted →
Low pK_p for CO_2 unloading
HA → A^-
HCO3- → H_2CO_3 → CO_2(g)



Hydrophobic:
AA ionization suppressed →
High pK_p for CO_2 loading
A^- → HA
CO_2(g) → H_2CO_3 → HCO_3^-

Below T_c: PNIPAM is swollen and hydrophilic.
Above T_c: PNIPAM is collapsed and hydrophobic.

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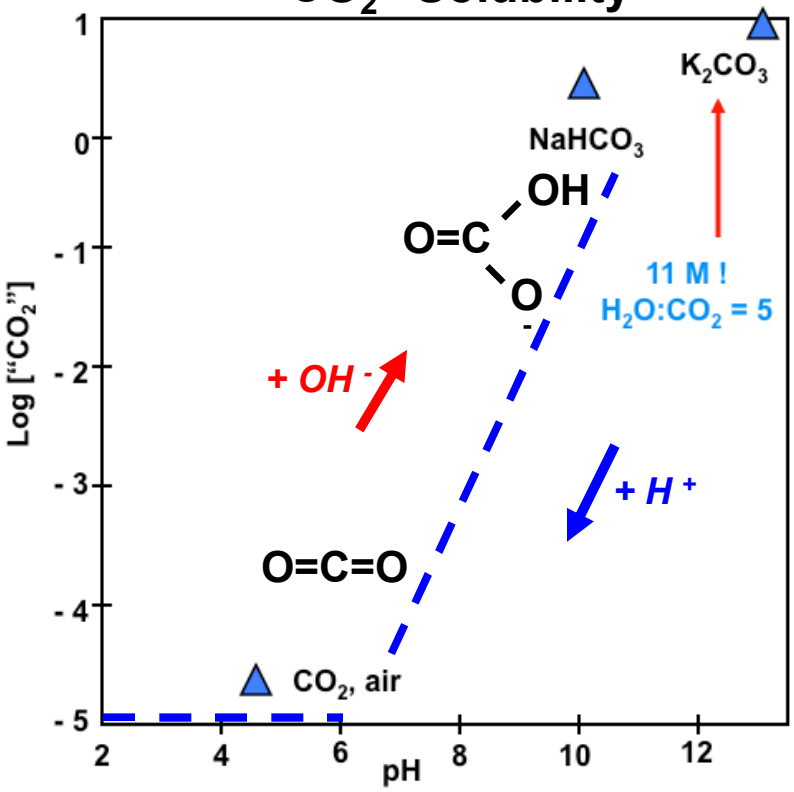
Interconversion from Soluble to Insoluble "CO_2"

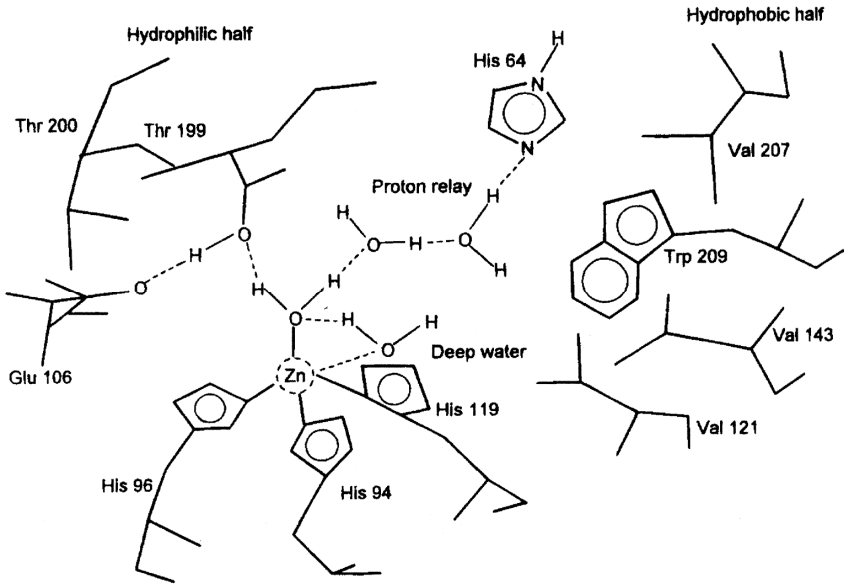
Carbonates for capture ←→ CO_2 for release

"CO_2" Solubility



Δ["CO_2"] of 100,000 is possible.
Requirement: Δ"pH" = 4-5.

Catalytic Enzymes (carbonic anhydrase)



Same enzyme used for loading/unloading.
Rapid, diffusion-controlled kinetics.
Requirement: ΔpH = 2 (around pH 7).

Goal: Develop programmable pH buffers that can be used to promote CO_2:carbonate inter-conversions via pH control.

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Chemical Equilibria

Carbon Dioxide in Water

CO_2 (gas) + H_2O ←→ CO_2 (l) $\quad K_{Henry} = 0.033$ M/atm

CO_2 (l) + H_2O ←→ H_2CO_3 $\quad K_{hyd} = 2.6 \times 10^{-3}$

H_2CO_3 ←→ $H^+ + HCO_3^-$ $\quad K_{a1} = 1.7 \times 10^{-4}$ M^{-1}

$H_2CO_3 + OH^-$ ←→ HCO_3^-

Programmable Buffers in Water

HA ←→ $H^+ + A^-$ $\quad K_p$ = programmable

$pK_p = -\log K_p$

Programmable Buffer + CO_2

$H_2CO_3 + A^-$ ←→ $HCO_3^- + HA$

loading → $\quad pK_p > 8.5$

← unloading $\quad pK_p < 5$

To reversibly load and unload CO_2 in water, a programmable pH buffer is required that can reversibly switch its acid dissociation constant by a factor of over 3000.

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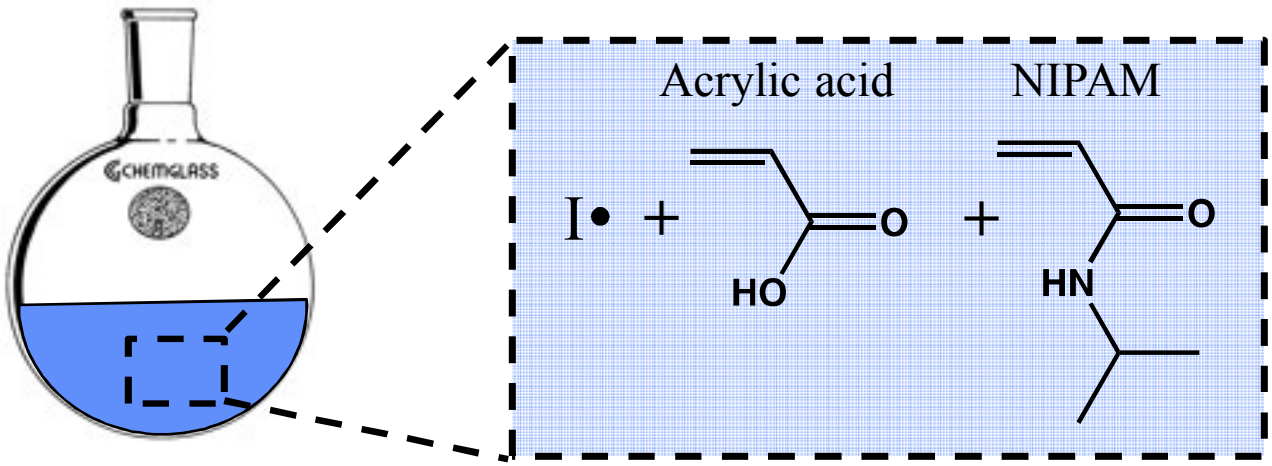
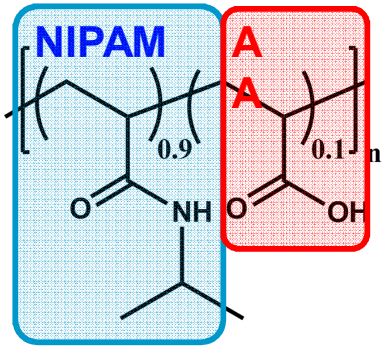
Synthesis of Programmable Materials

pH Control: enabled by a reversible, thermally-activated swelling transition

N-isopropylacrylamide (NIPAM) → provides programmability
Acrylic acid (AA) → provides acid-base activity





Synthesis: free radical polymerization (MW = 25,000 g/mole)
N-isopropylacrylamide (NIPAM) content: 65 – 99 mole%
Acrylic acid (AA) content: 1 – 30 mole%

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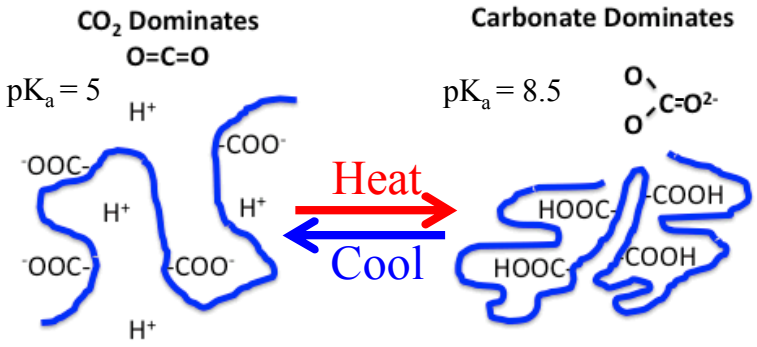
Programmable pH Buffers: P(NIPAM-AA)

Switching mechanism: a reversible, thermally-activated swelling transition

Below T_c: PNIPAM is swollen and hydrophilic.
Above T_c: PNIPAM is collapsed and hydrophobic.

Hydrophilic:
AA ionization promoted →
Low pK_p for CO_2 unloading
HA → A^-
HCO3- → H_2CO_3 → CO_2(g)



Hydrophobic:
AA ionization suppressed →
High pK_p for CO_2 loading
A^- → HA
CO_2(g) → H_2CO_3 → HCO_3^-

The dissociation constant for acrylic acid is sensitive to the local polymer environment, facilitating reversible programming of the pH buffer system.

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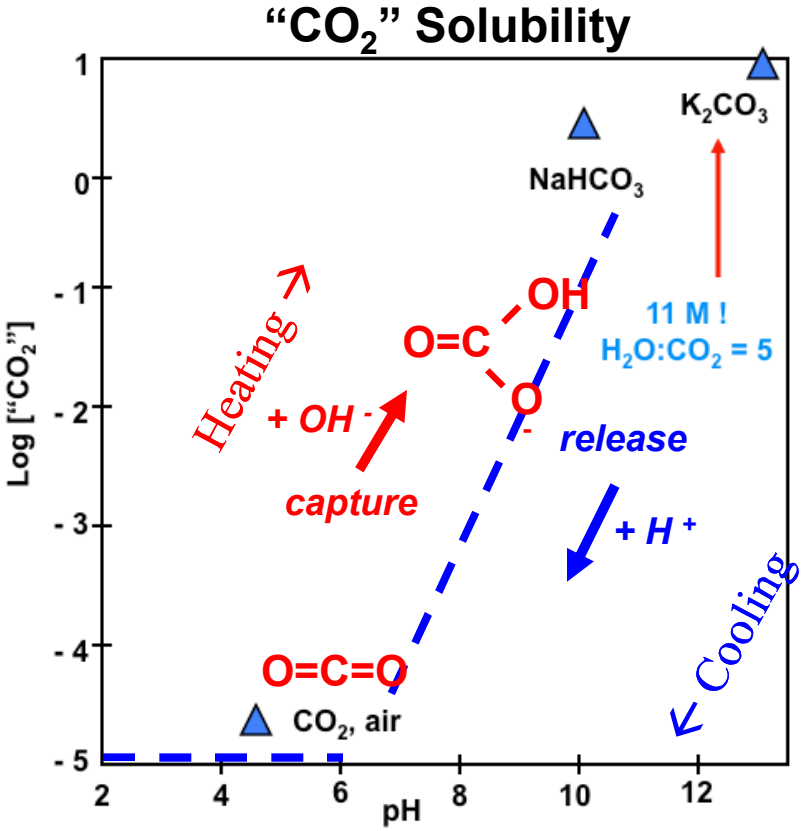
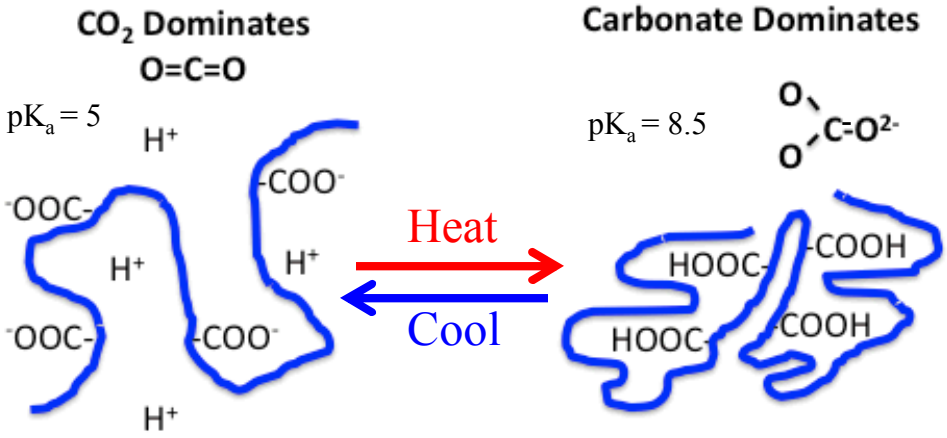
CO_2 Behavior with Polymer

$$H_2CO_3 + A^- \leftrightarrow HCO_3^- + HA$$



Low T: PNIPAM is swollen and hydrophilic

High T: PNIPAM is collapsed and hydrophobic



Carbonates for capture ←→ CO_2 for release

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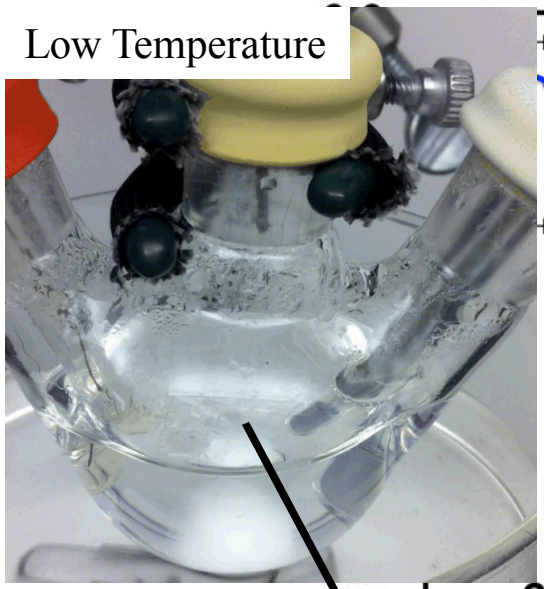
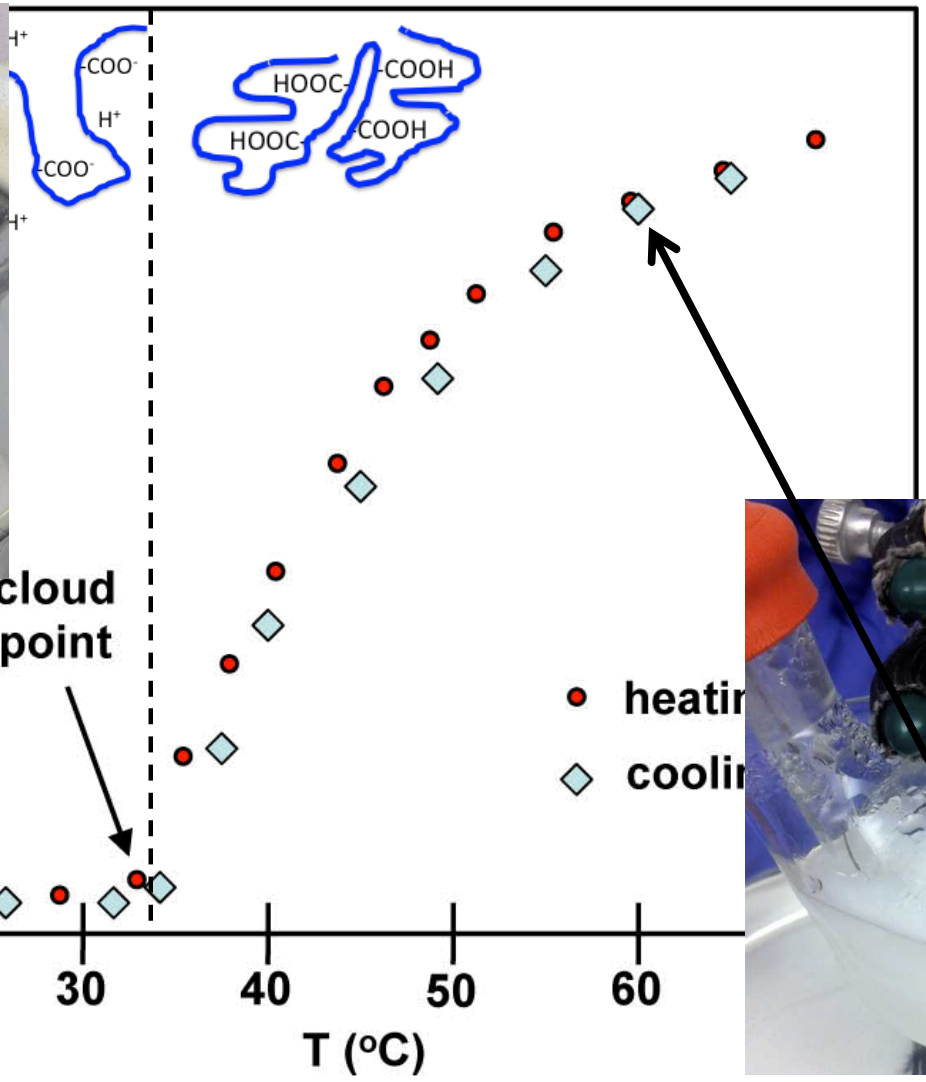
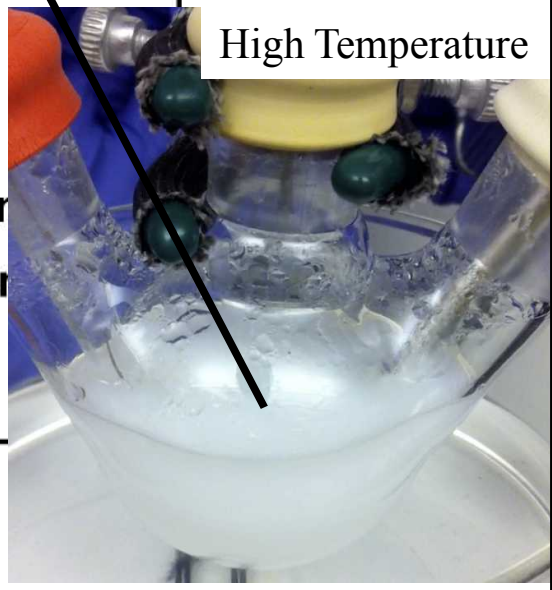
Programming pH with Temperature

1 wt % solution of P(NIPAM-AA)







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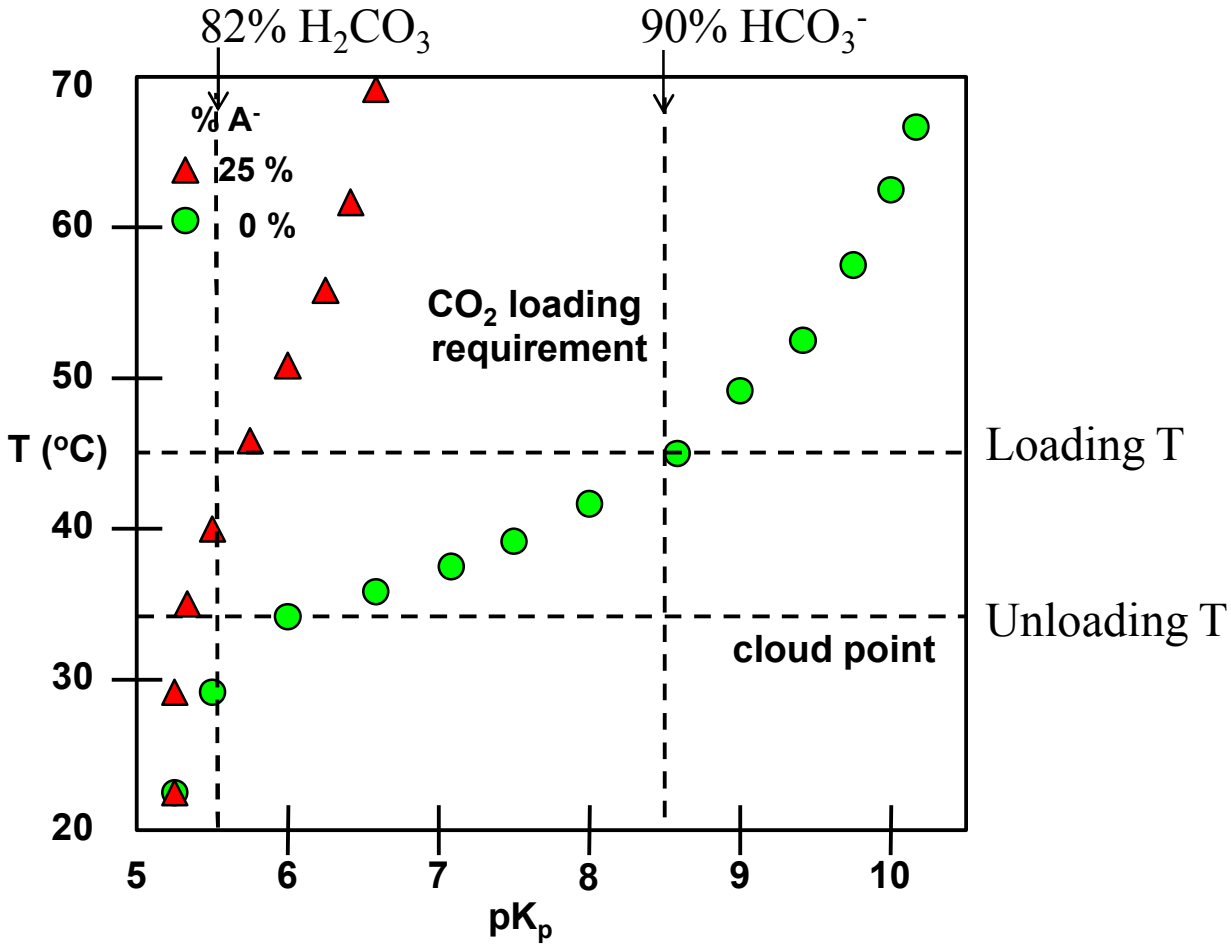
Programming pK_a with Temperature



1) The polymer transition temperature in water is 33°C.
2) The transition induces large, reversible changes in solution pH, pK_p.
3) *Programming of the polymer should suffice for loading/unloading of CO_2.*

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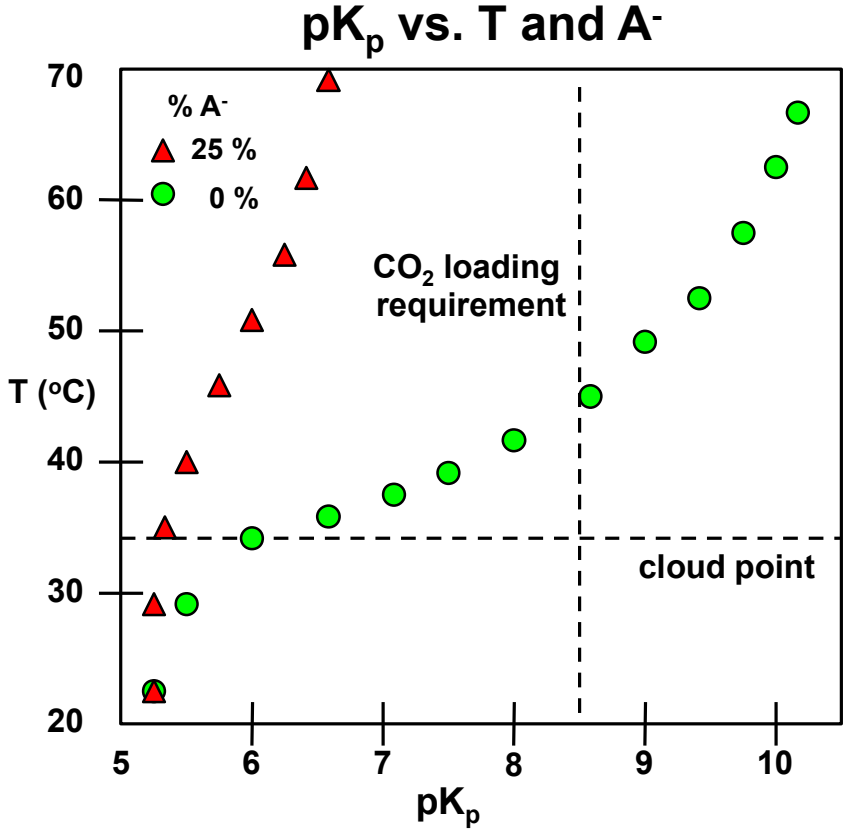
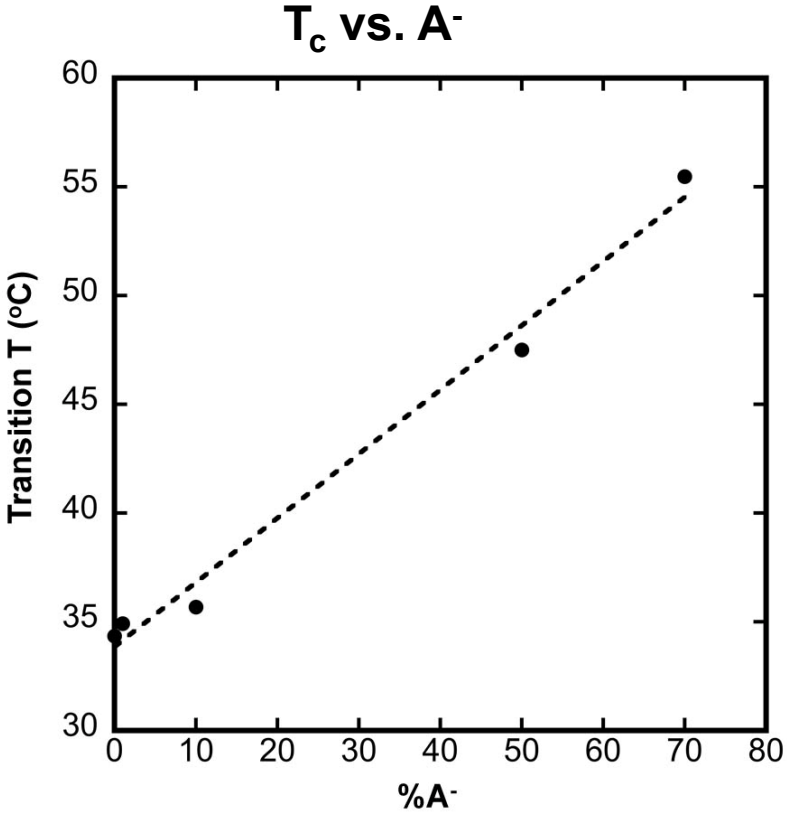
Mechanism for Irreversible Polymer Behavior

Introduction of A^- into the polymer makes the environment more hydrophilic. Hydrophilic groups suppress the phase transition and pK_p changes.





Loading/unloading is reversible if only a fraction of the buffer capacity is used. The maximum HCO_3^- attainable on loading scales with usable buffer capacity (A^-).

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Summary

- Polymer-based programmable pH buffers have the potential for promoting the reversible loading and unloading of CO_2 from water.
- Our initial P(NIPAM-AA) provides complete unloading of HCO_3^- to CO_2.
- CO_2 loading is limited by the maximum anion content the buffer can maintain and still support the required thermal phase transition.
- The current buffer will require modifications to achieve a buffer capacity that is sufficient to deploy in a practical process for the reversible capture and release of CO_2 from air.

Ongoing Work

- Determination of CO_2 capture capacity and kinetics
- Varying polymer properties through composition
- Exploring properties of grafted copolymers

Acknowledgements

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- Bruce Bunker
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- Holly Zarick
- Mariah Austin

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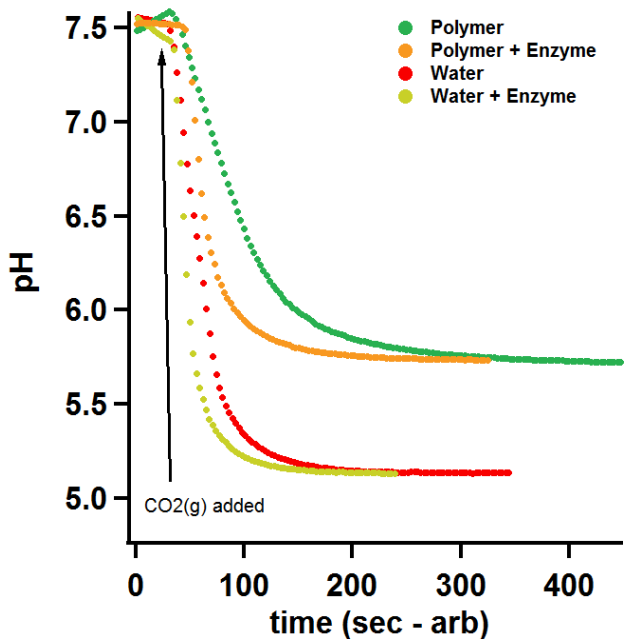
Solution pH with CO_2 added



2% CO_2 bubbled into the indicated solutions at room temperature. Curves are normalized to the time of CO_2(g) addition.

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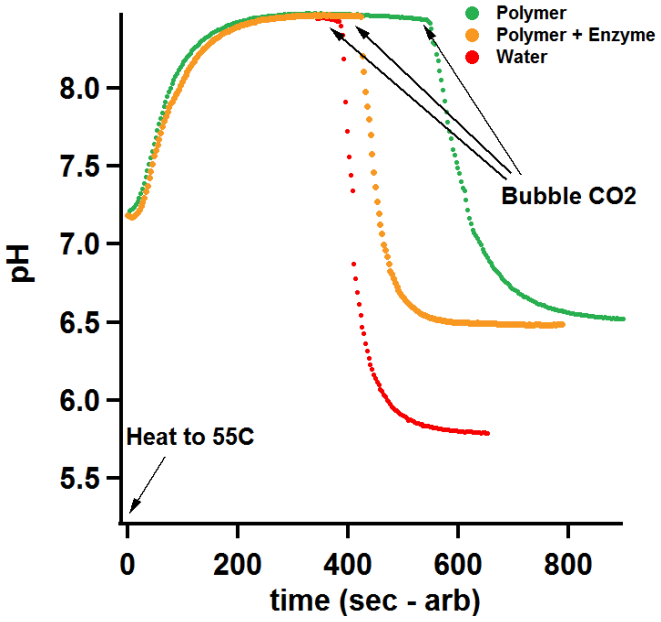
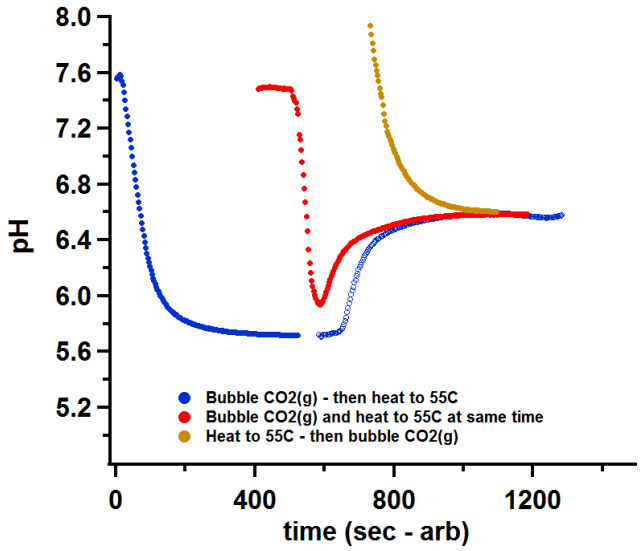
CO_2 capture comparison



CO_2 capture for polymers in high temperature configuration



Step wise processing compared to simultaneous processing of heat and CO_2(g) addition

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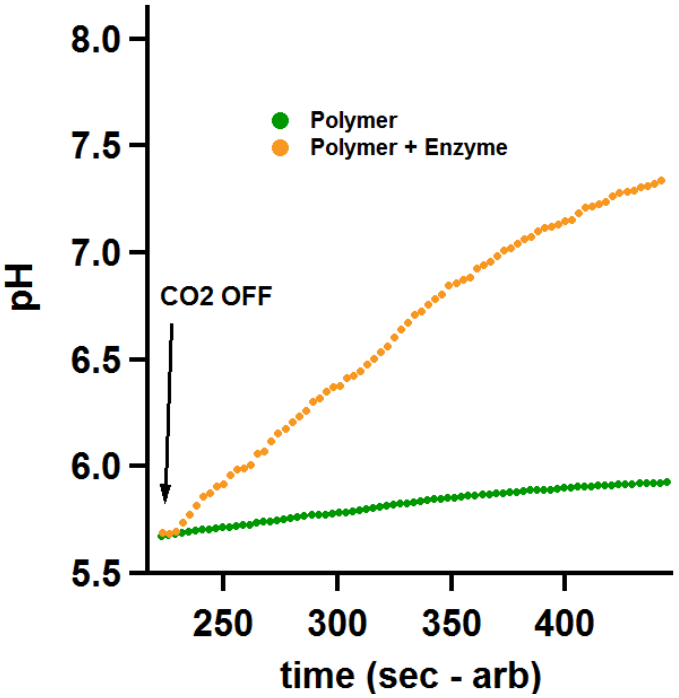
Release of CO_2 gas from solution



Liberation of CO_2(g) from saturated solutions of polymer and polymer + enzyme

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Initial Experiments on CO_2 Unloading

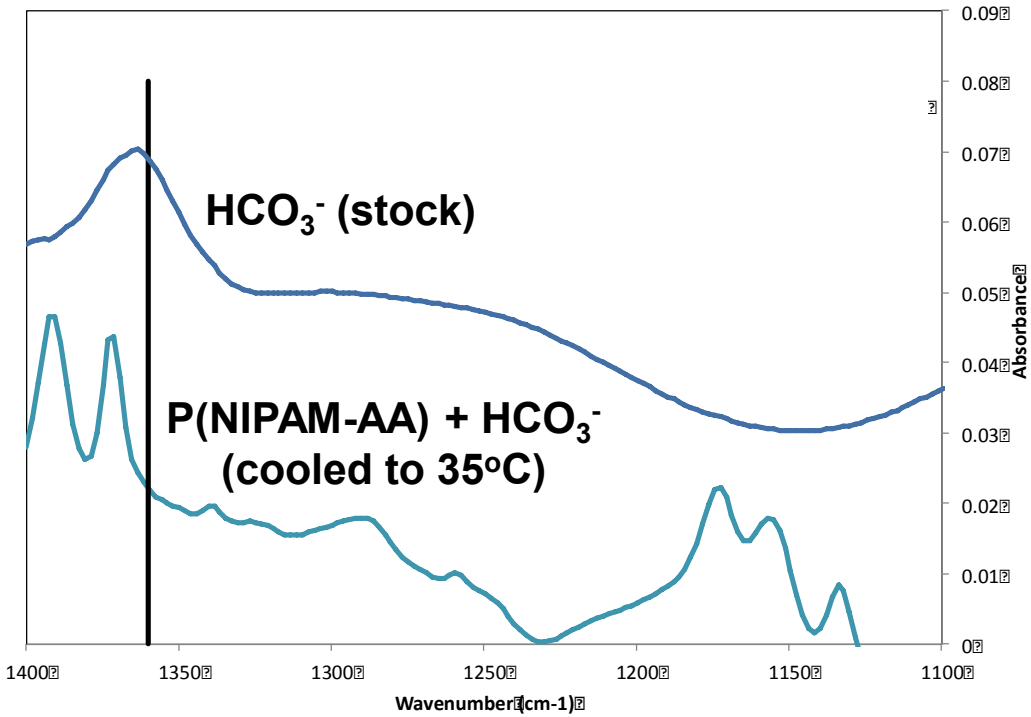
T = 63°C, 100% HCO_3^-

T = 50°C

T = 47°C, 65% HCO_3^-

T = 45°C, 0% HCO_3^-

Infrared Spectra for HCO_3^- Unloading



Good News → Programmed CO_2 unloading is successful.

HCO_3^- is stable in contact with P(NIPAM-AA) above T_c.

HCO_3^- completely decomposes to release CO_2(g) as T drops below T_c.

Bad News → Extensive reloading with CO_2 does not occur.

After complete unloading, P(NIPAM-AA) does not exhibit a phase transition.

Reheating "used" P(NIPAM-AA) does not result in significant pH or pK_p increases.

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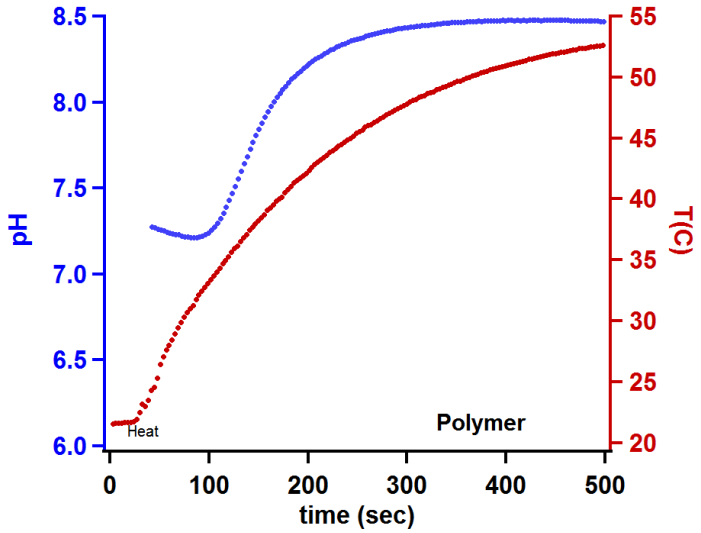

Thermal response of the polymer solution monitored by pH.