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Ruthenium-Poly(Vinyl Pyridine) (RuPVP) Metallopolymers for Catalyzing Self-Oscillating Gels

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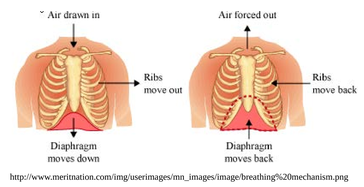
MOTIVATION

- Polymer gel is a research field that has made a rapid progress during the past 20-30 years. The soft, absorbent qualities of polymer gels make them extremely useful for biologically related applications such as soft contact lenses.
- In these stimuli responsive polymer gels, a single stimulus (external trigger) is required to cause a change in volume. Therefore, a periodic external change has to be created for periodic oscillations.
- Stimuli responsive gels change volume when induced by an external trigger such as changes in temperature or pH.

PNIPAM/PAA IPN microgel

http://onlinelibrary.wiley.com/store/10.1002/pi.4192/asset/image_m/mgra001.jpg?v=1&s=4256da7364b2e1b7c13fe583b7040e1a5ac5734b

- Many biological systems maintain periodic oscillations under constant environmental conditions by converting chemical energy into mechanical work.

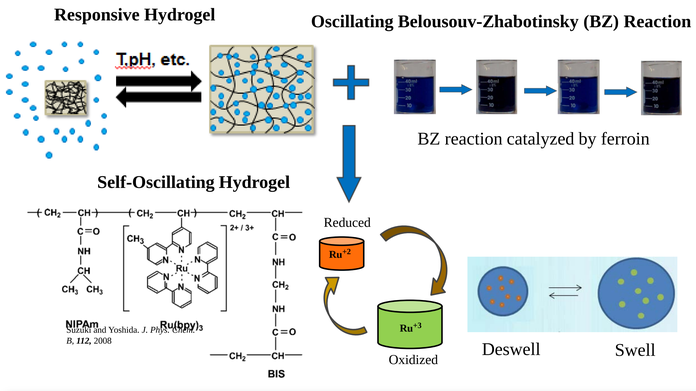


http://www.meritnation.com/img/userimages/mn_images/image/breathing%20mechanism.png

- What if a synthetic material could be developed that similarly converts chemical energy to autonomous mechanical motions

BACKGROUND

- Autonomous, coupled chemical-mechanical oscillations can be achieved by the oscillating Belousov-Zhabotinsky (BZ) reaction within gels in which the BZ catalyst has been covalently bonded.



Suzuki and Yoshida. *J. Phys. Chem. B, 112*, 2008

Features

- Displays autonomic behavior (without external control)
- Converts chemical to mechanical energy
- Responds to internal stimulus

Key Challenges

- Lack of options for BZ catalysts
  - i) Cost-prohibitive
  - ii) Overly difficult to synthesize

} → Suppresses high-throughput experimentation

PRIMARY AIM

Develop an alternate ruthenium complex, produced through a facile, inexpensive synthesis, that can be incorporated into a hydrogel to catalyze chemical-mechanical oscillations - autonomously converting chemical energy to mechanical work

APPROACH

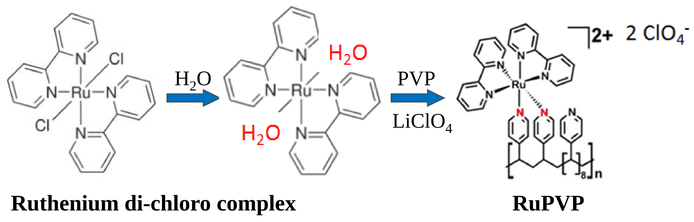
- A procedure for the facile synthesis of a ruthenium metallopolymer for study of electrochemiluminescence was adopted.[1]
- The procedure was followed using readily available precursors, *cis*-Dichlorobis(2,2'-bipyridine)ruthenium(II) and poly(4-vinylpyridine) to produce a ruthenium-poly(vinylpyridine) (RuPVP) metallopolymer.

[1]G. Jensen, E. Hvastkovs, *Facile One Pot Preparation of [Ru(bpy)$_2$PVP$_{10}$]$^{2+}$ (RuPVP) Metallopolymer,* 2008

EXPERIMENTAL / PROCEDURE

Procedure Summary

- Ruthenium di-chloro complex was heated with minimal amount of water for 45 minutes.
- After sufficient time to displace the chlorines, $LiClO_4$ was added to the reaction vessel.
- After an hour of heating under reflux, poly(4-vinylpyridine) (PVP) dissolved in ethanol was slowly added.
- After heating for 48 hours, the ethanol/water solvent was removed.
- After being re-dissolved in ethanol, the product was precipitated in ether, then collected via gravity filtration.



Ruthenium di-chloro complex **RuPVP**

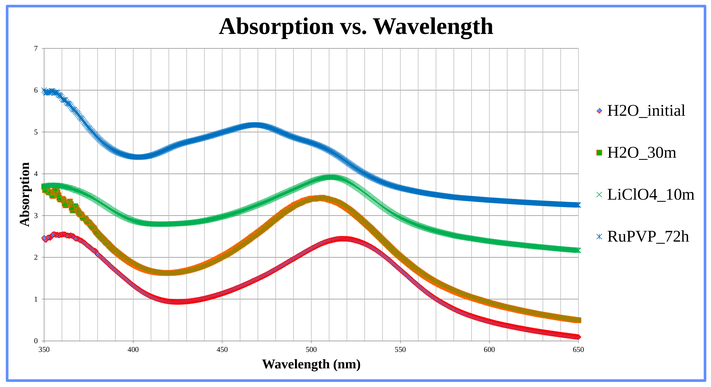
- Color changes indicated reactions occurring throughout the synthesis

Precipitation

- The ratio of the amount of PVP added in the reaction to the amount of the solvent was found to be important.
- The optimal ratio was determined to be **0.24g PVP : 3mL Ethanol**.
- With a ratio higher than the above, solids resulting from precipitation were sticky and not useable.
- With a lower ratio, no solids were precipitated.

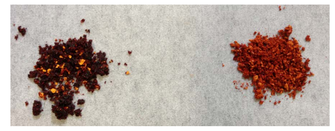
- Ultraviolet-visible spectroscopy (UV-Vis) was used to monitor the reaction.

- As reported in a coordination polymer literature, max. absorption (λ_{max}) shifted from 530nm to 505nm as water replaced chlorines from ruthenium di-chloro complex, and to 465nm as reaction occurred between PVP chain and ruthenium.[1]



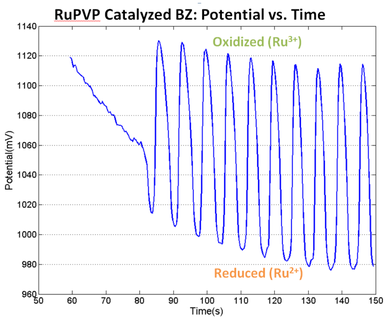
RESULTS

- Depending on the amount of $LiClO_4$ used, different types of solids were obtained as product.
- While ensuring more ruthenium become coordinated with PVP, too much $LiClO_4$ yielded insoluble, unusable product.



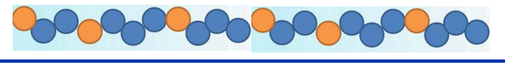
2.2x molar excess $LiClO_4$ **1.8x $LiClO_4$**

- BZ reaction was successfully catalyzed by RuPVP. Change in potential in the reaction solution was measured by a redox potential probe.



CONCLUSIONS / FUTURE WORK

- Synthesis of an alternate ruthenium complex capable of catalyzing BZ reaction was successful.
- Next step is to vinyl-functionalize PVP so that the product can be copolymerized with the hydrogel chain by radical polymerization.



Orange represents Ru
Blue represents hydrogel

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