

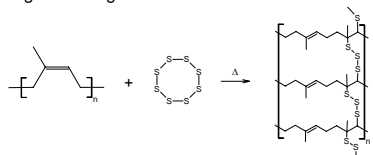
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## Abstract

Bipyridyl (bpy) groups are attached to the ends of poly(dimethylsiloxane) (PDMS) chains. When ruthenium is introduced to a solution of the bpy-PDMS, the bipyridyl groups can complex with Ru creating effective Ru(bpy)<sub>3</sub> cross-links. These materials should offer interesting optomechanical properties which can be utilized to make sensors or to study stress in elastomeric materials on the molecular level.

## Chain Architecture

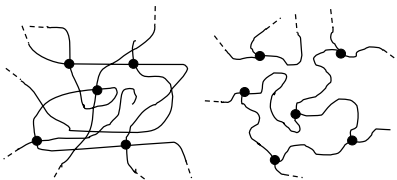
- Charles Goodyear invented the process for cross-linking natural rubber, poly(isoprene), with sulfur.
- Cross-linking increases stiffness and prevents material from dissolving or melting.



- Covalent cross-linking method, typical of most modern elastomer syntheses, creates a 3-D "haphazard network."<sup>11</sup>

## Covalent Cross-Linking

- The "haphazard network" has dangling chain ends and a highly variable molecular weight between cross-links.<sup>1</sup>



- Studies have shown ideal networks have superior mechanical properties.<sup>1</sup>
- We propose to use metal-ligand binding to cross-link polymer chains and create "ideal" elastomeric networks.

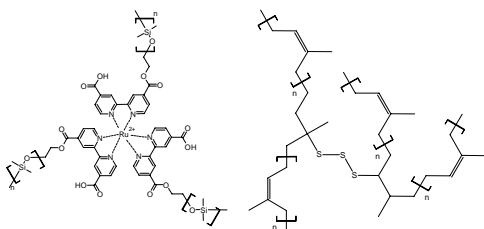
## Network Formation

To create a 3-D network (elastomer), three or more polymer chains must be joined at a single point.

- Ru<sup>2+</sup> can bind to six ligands
- Bipyridine (attached to polymer chain ends) is bidentate: three can attach to a single Ru<sup>2+</sup> atom

Trifunctional Ru(bpy)<sub>3</sub> cross-link (proposed)

Tetrafunctional Sulfur cross-link (Goodyear)

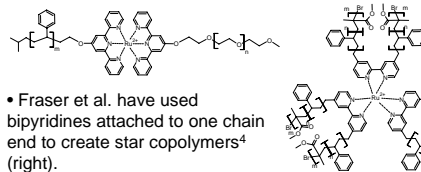


## Why metal-ligand cross-links?

- Metal-ligand binding leads to the formation of highly colored complexes.
  - If complexes are broken through mechanical or chemical stress, material should change color
  - Indicator of stress on the molecular level (sensor applications)
- Introducing a ligand that binds more strongly to Ru<sup>2+</sup> than bipyridine means cross-links can be broken, and the material can be recycled.
- Elastomers can be synthesized wherein the cross-links can be severed through the application of light or perhaps electrical charge.
  - Studies have shown certain Ru(bpy)<sub>2</sub>L<sub>2</sub> complexes can release ligand upon light exposure.<sup>2</sup> This allows for materials wherein cross-linking can easily be "turned on" or "shut off".

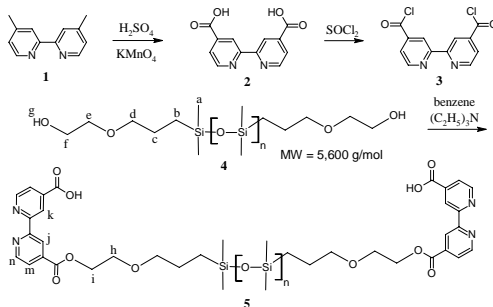
## Will it Work?

- Schubert et al. have demonstrated that terpyridine groups can be used for chain extension and block copolymer formation<sup>3</sup> (below).

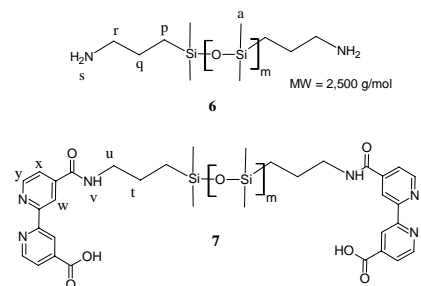


- Fraser et al. have used bipyridines attached to one chain end to create star copolymers<sup>4</sup> (right).

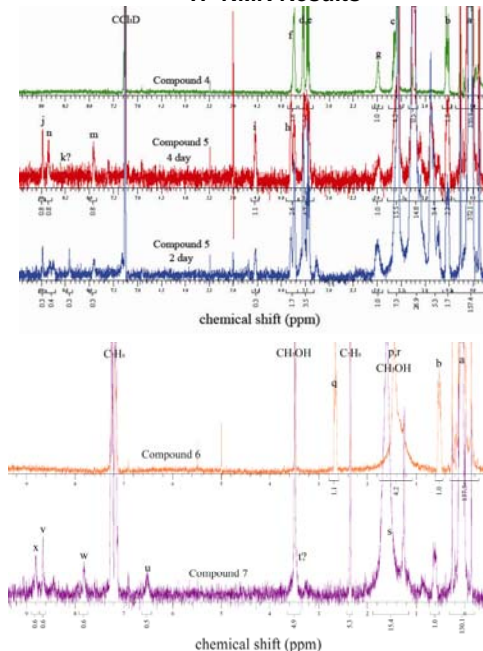
## Versatile Synthetic Scheme<sup>5</sup>



## Amine Starting Material and Product

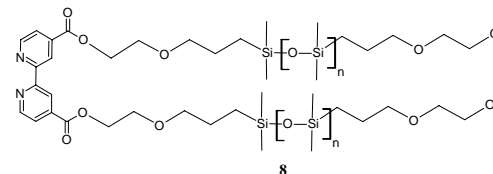


## H<sup>1</sup> NMR Results



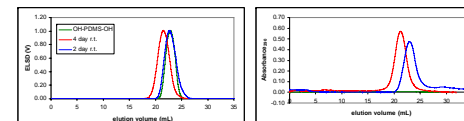
- Peak assignments were made based upon spectral comparisons to available data for several similar compounds.

- 4,4'-dimethyl-2,2'-bipyridyl successfully converted into 2,2'-bipyridine-4,4'-dicarboxylic acid.
- End-group analysis is quite challenging
  - Large fraction of protons lie in backbone



Structure caused by chain coupling

## GPC Results



- The ELSD detector (left) serves as a universal detector and should show a response for PDMS regardless of the end group.

- The UV detector (right) is set to measure absorbance at 290 nm, the absorbance maximum of bipyridine.

For the 2 day reaction:

- UV peak appears at the same elution volume as the ELSD peak for the starting material
- This indicates successful attachment of the bipyridine to the PDMS chain without increasing the size of the polymer

For the 4 day reaction:

- The GPC peaks shift to a small elution volume
- This indicates a larger molecular size (due to chain coupling)

## Results

	% Attachment	MW (g/mol)	Elution Time (min)
-OH s.m.	--	5,600	23.0
4 day -OH	35%	>5,600	21.5
2 day -OH	13%	5,600	23.0
-NH <sub>2</sub> s.m.	--	2,500	--
4 day -NH <sub>2</sub>	100%	-5,400 - 5,600	22.5

## Conclusion To Date

- Ligands with two or more attachment functional groups will lead to chain coupling despite the use of reaction conditions that favor chain termination.

- The shorter the reaction time, less bipyridine attachment occurs with very little chain coupling.

- The longer the reaction time, more bipyridine attachment occurs with more chain coupling

- Best Solution: use ligands with single attachment functionalities, which is where future work is heading

## Future Synthetic Options

- Polymer repeat unit and molecular weight can easily be varied.

- 4,4'-dimethyl-2,2'-dipyridyl can be replaced with another ligand, like 2,2'-bipyridyl-4-carboxylic acid or phenanthroline (left).

- Poly(ethyleneoxide), a water-soluble polymer, may be used.

## References

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## Acknowledgements

Dr. Al Schwab for the answers to the questions

Ryan Kincer for his previous work

Appalachian State University and Pfizer, Inc. for funding