Stable Alkaline Membrane Based on Proazaphosphatranes Organic Super Base

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Project ID: fc179

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline
Project started: Jan. 2018
Project end date: Sept. 2019
Percent complete: 60%

Budget
Total project funding
-DOE share: $150K, 100%
FY18 and FY19 funding $150K

Barriers Addressed
Performance
Durability
Cost

Partners
LBNL
Adam Weber
Daniel Miller
Kraton Corporation

Relevance

Objectives: Develop new alkaline membranes with superb stability and performance to enable PGM-free alkaline membrane based fuel cell. Perform proof-of-concept work on a new class of ultra-stable and high pH proazaphosphatranes super bases for application in alkaline membranes. The ultimate goal is to develop high performance alkaline membranes and fuel cell system that rivals the performance of current Nafion membrane and PEM fuel cell system.

Milestones

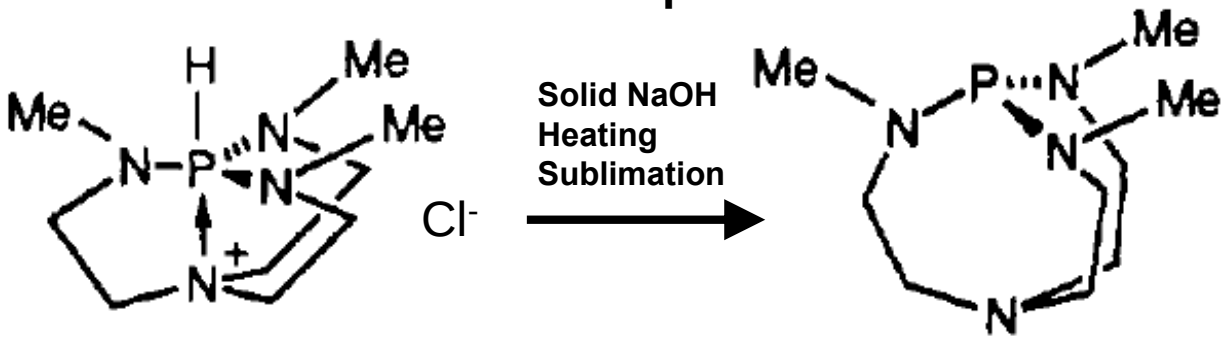
1. Synthesize crosslinking functional group tethered super base (Q1-2. FY18)
2. Study the stability of the polymer matrix (Q3, Q4. FY18)
3. Graft the proazaphosphatrane super base on the polymer matrixes (Q1-3, FY19)
4. Characterize membrane performances (go-no-go as stated in the targets) (Q4, FY19)

Targets for this proof-of-concept project

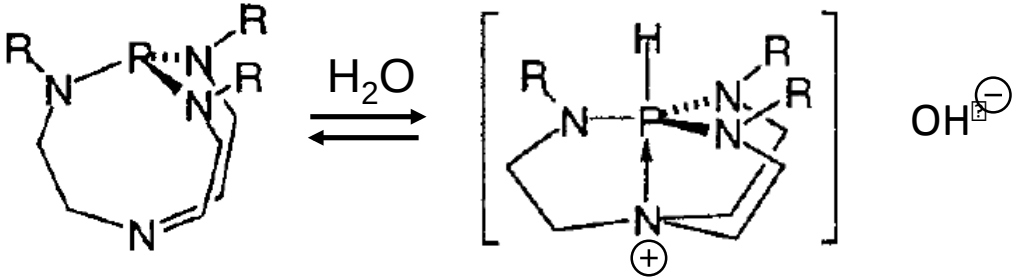
- Initial conductivity should be >100 mS/cm, better than the quats hydroxyl system.
- Membrane stability should be beyond 2000 hours of MEA operation with less than 20% performance degradation.
- Initial performance in a H_2/O_2 fuel cell similar to KOH based system (film at 40 µm) at 50ºC yielding i = 620 mA/cm^2 at V_{cell} = 0.60 V)

Approach: The ultra-stability and high alkalinity of proazaphosphatranes organic super base

Formation of super base



Transformation into high alkaline base



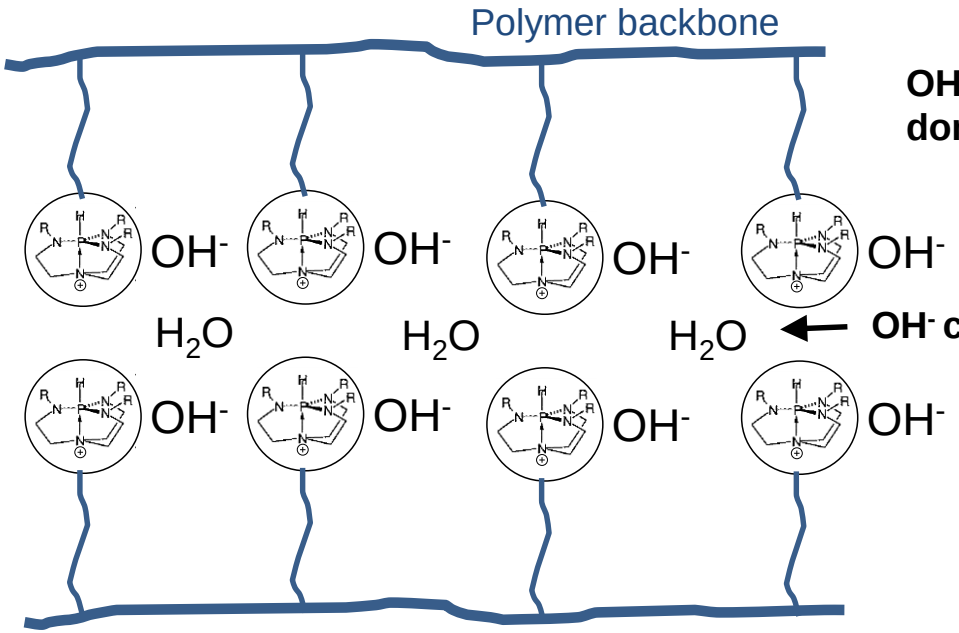
R = Me, *i*-Pr, etc.

Proazaphosphatranes organic super base and its transformation into hydroxide base in aqueous solution. The pH of 1M solution is 14, qualifying it for strong base in aqueous solution. Coupled with the superb thermal stability, it is the ideal choice to be used as base functional groups in OH^- conducting membrane.

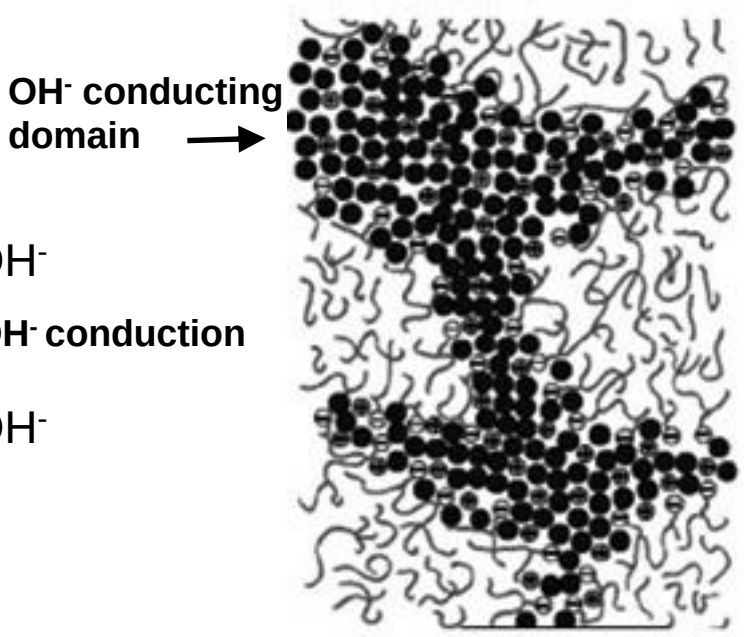
C. Lensink, S. K. Xi, L. M. Daniels, and J. G. Verkade, J. Am. Chem. Soc. 1989, I 1 1, 3478-3479

Approach: Membrane design with proazaphosphatranes super base and a stable polymer matrix

Schematic of the polymer design



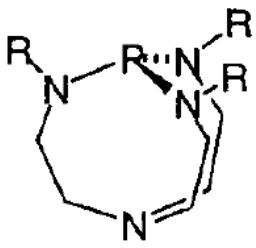
Schematic of the membrane structure

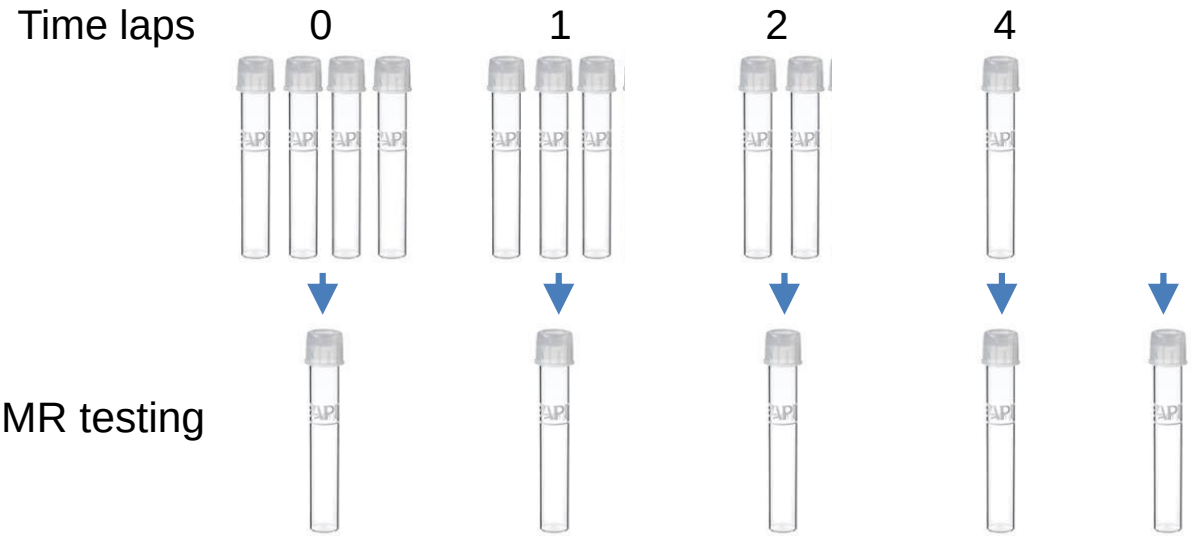


The super base units are grafted to a stable polymer matrix/backbone to achieve a high OH^- conducting polymer as shown in the polymer design. Further design the polymer matrix leads to formation of micro HO^- ion conducting channels in the membrane structure as in the Nafion.

Accomplishments and Progress
Stability study of Proazaphosphatranes and its derivatives 0.1M, pH=13 in D_2O, and 2M KOD in D_2O

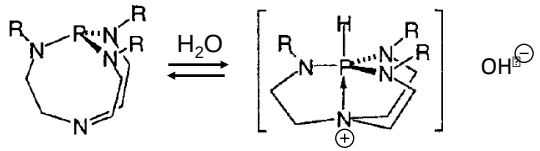
- In case of the pH=13 sample, the super bases are made into 0.1M D_2O solution, and aged at a given temperature in sealed plastic tubes to investigate their stability in a six-months period. Both 25°C and 70°C are chosen, and two types of super base (R is methyl and isopropyl) are chosen. The interval of time laps aging is one month.
- In case of the 2M KOD solution, the concentration of super base derivatives is 0.1M, the R group is methyl, temperature is 75°C and the interval of time laps aging is one week.





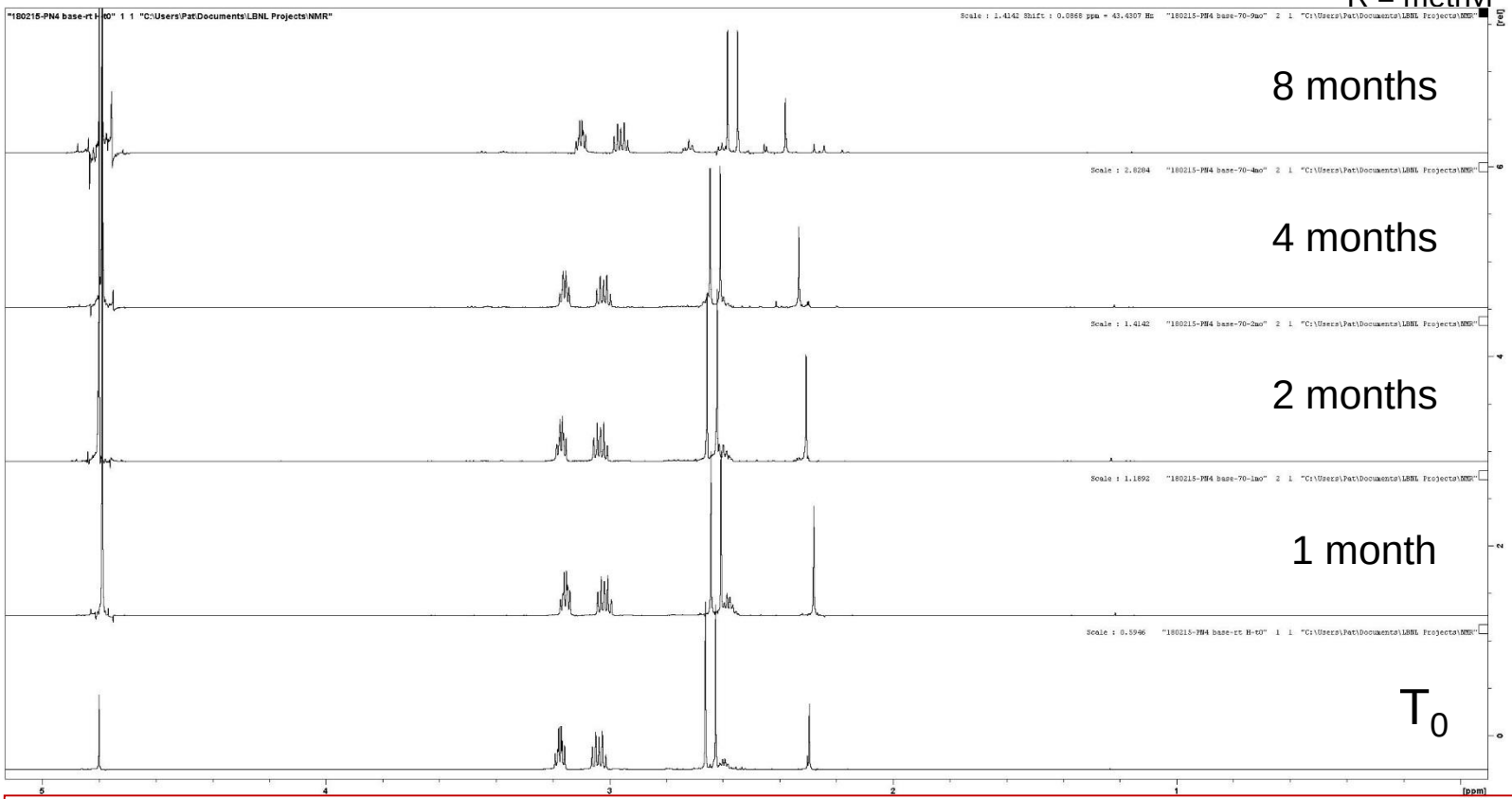
Each sample, both ^{1}H and ^{13}C NMR are performed to study the molecular structure transformation. For 2M KOD solution sample, P^{35} NMR are also performed. The spectra before and after aging are compared.

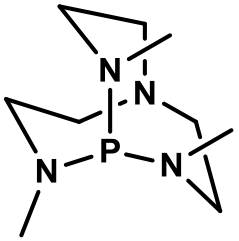
Stability study of Proazaphosphatranes and its derivatives



R = methyl

^{1}H NMR – Stability at **70°C**

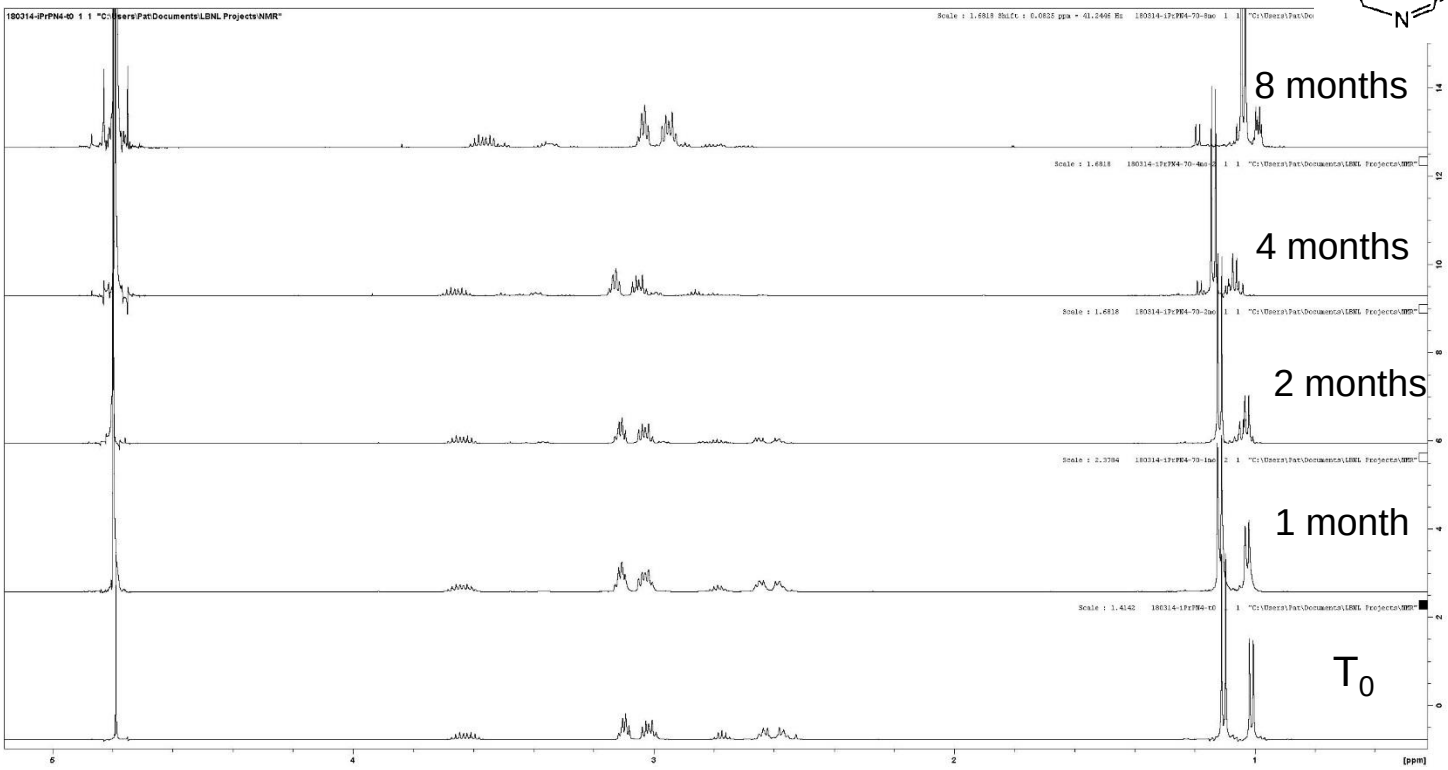


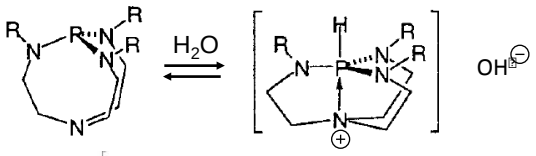


The NMR spectra do not change after aging at 70°C. The methyl group functionalized super base is stable.

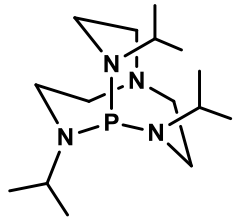
Stability study of Proazaphosphatranes and its derivatives

^{1}H NMR – Stability at **70°C**





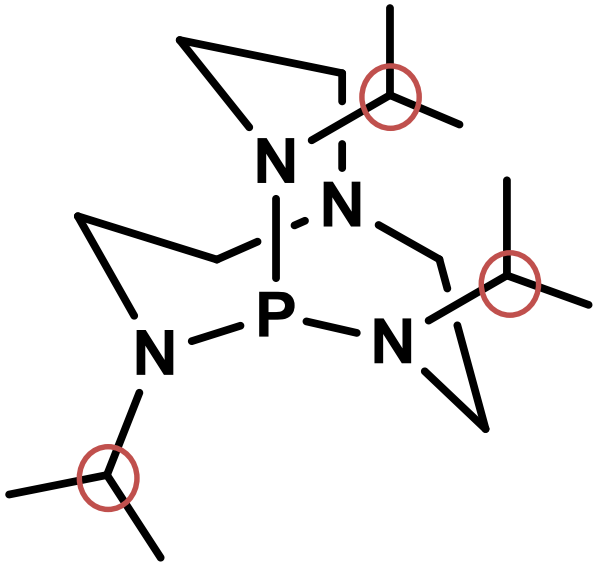
R = isopropyl



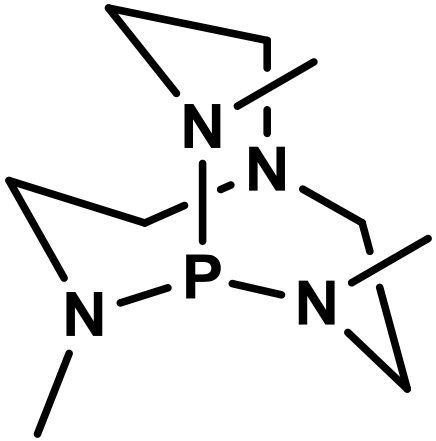
The NMR spectra change at the isopropyl site after 2 months aging at 70°C. The isopropyl functionalized super base is **NOT** stable. Therefore, the 2, 2', 2" connections may not be used to form bonding with the polymer matrix.

Possible degradation sites on proazaphosphatranes derivatives

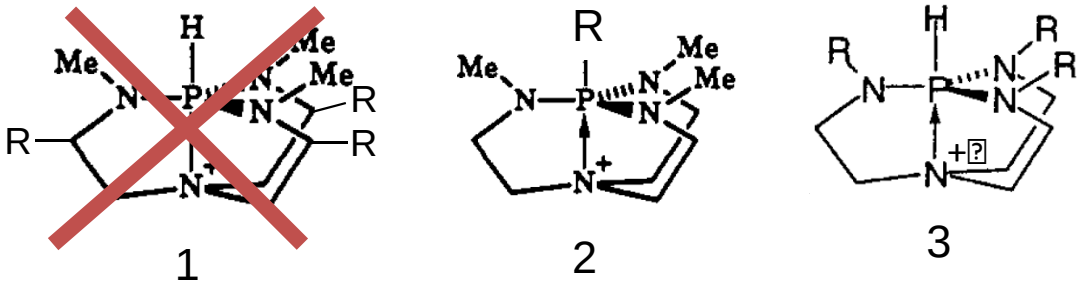
The tertiary carbons next to nitrogen are possible degradation sites



Stable structure



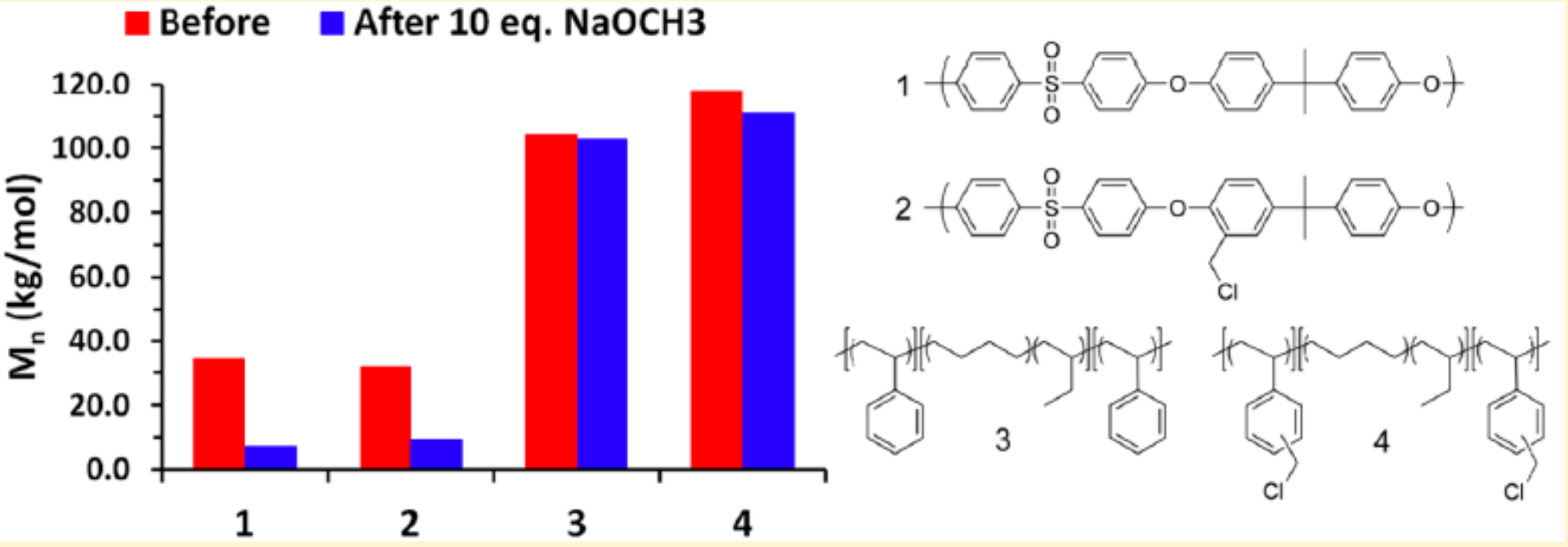
Three types of Proazaphosphatranes with alkyl or alkene derivatives



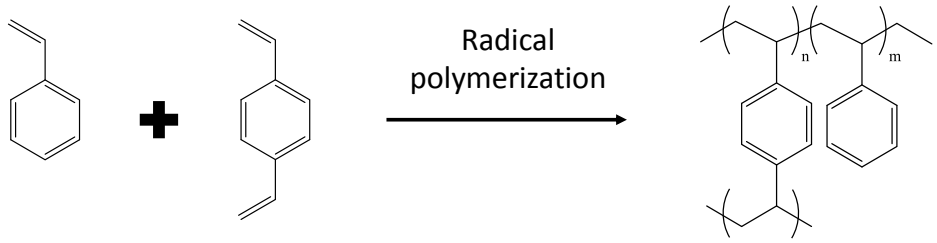
In order to graft the proazaphosphatranes base molecules onto the polymer chains, a connection site will need to be introduced to the super base. The places of R groups are the potential connection sites between the super base and the polymer backbone. However, introduction of the R groups could lead to new reaction sites that can be potentially a degradation point during membrane operation. Structure 1 may not be stable due to the procession of tertiary carbons next to nitrogen. Structure 3 may not have tertiary carbon next to nitrogen.

Identification of a stable polymer matrix

Polystyrene-based copolymers exhibit base stability

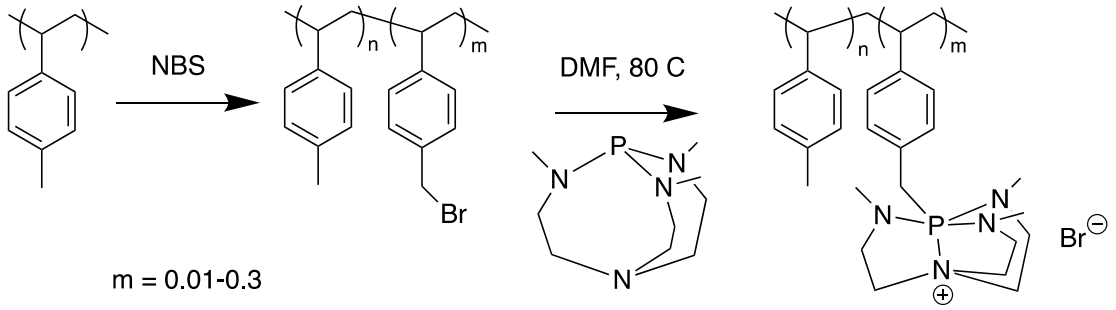


Proposed all hydrocarbon polymer backbone

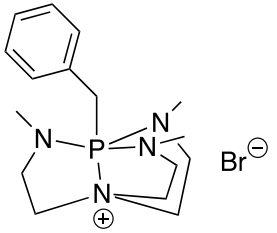


Macromolecules 2016, 49, 3361−3372

Attempted tethering to polystyrene matrix

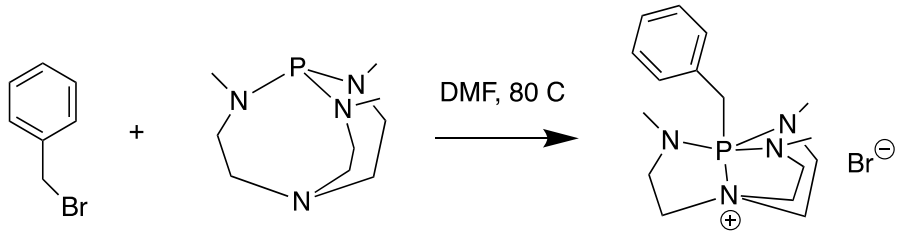


- Bromination of P(4-MeSty) is accomplished with NBS. Degree of functionalization can be easily controlled and a range of materials were synthesized.
- In step two, the proazaphosphatranes is reacted with the brominated P(4-MeSty) derivatives.
- In cases where m > 0.10, gels were formed. Perhaps due to deprotonation/crosslinking with the P(4-MeSty) (non-brominated) repeat units.
- In cases where m < 0.10, gels were not formed, however all films cast from these solutions were extremely brittle and unable to be handled for further testing.
- A suitable copolymer with low Tg flexible block needs to be used to provide mechanical integrity to films.
- Model system as shown can be used to investigate substitution and base stability



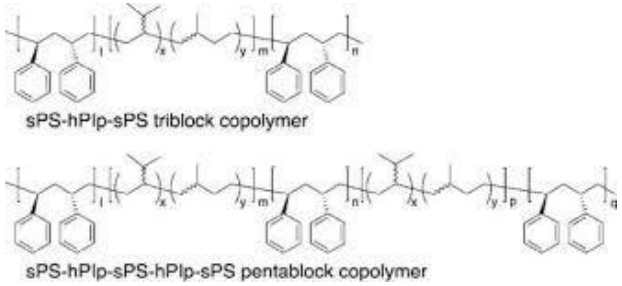
The stability of model compound and Kraton co-polymer

The base stability:



2M KOD in D_2O is made and mixed with 0.1M concentration of the model compound to study the stability at 75˚C.

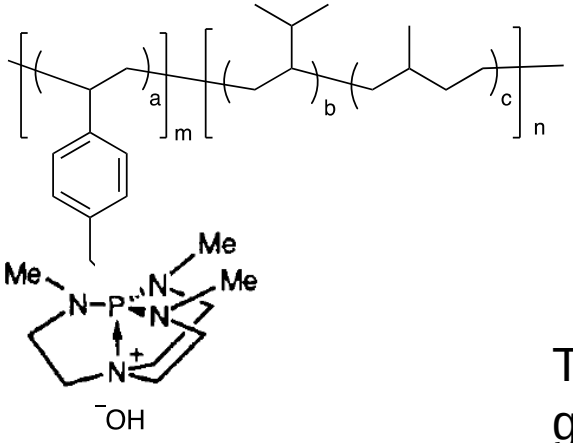
Kraton® hydrogenated polystyrene-co-isoprene polymer provide alkaline stability and flexibility



The copolymer film is emerged in 2M NaOH in H_2O solution to study the long term stability at 75˚C.

Targeted alkaline membrane structures based on super base and Kraton® copolymer

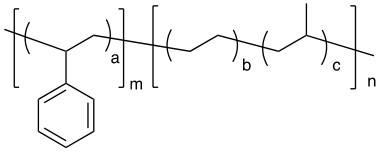
Soft hydrogenated isoprene segment



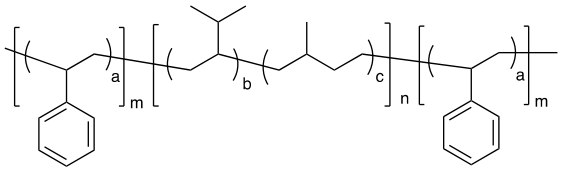
Alkaline functional groups

- High OH^- mobility
- High stability
- Flexible membrane

Two types of KRATON® block copolymers are gifted to LBNL.

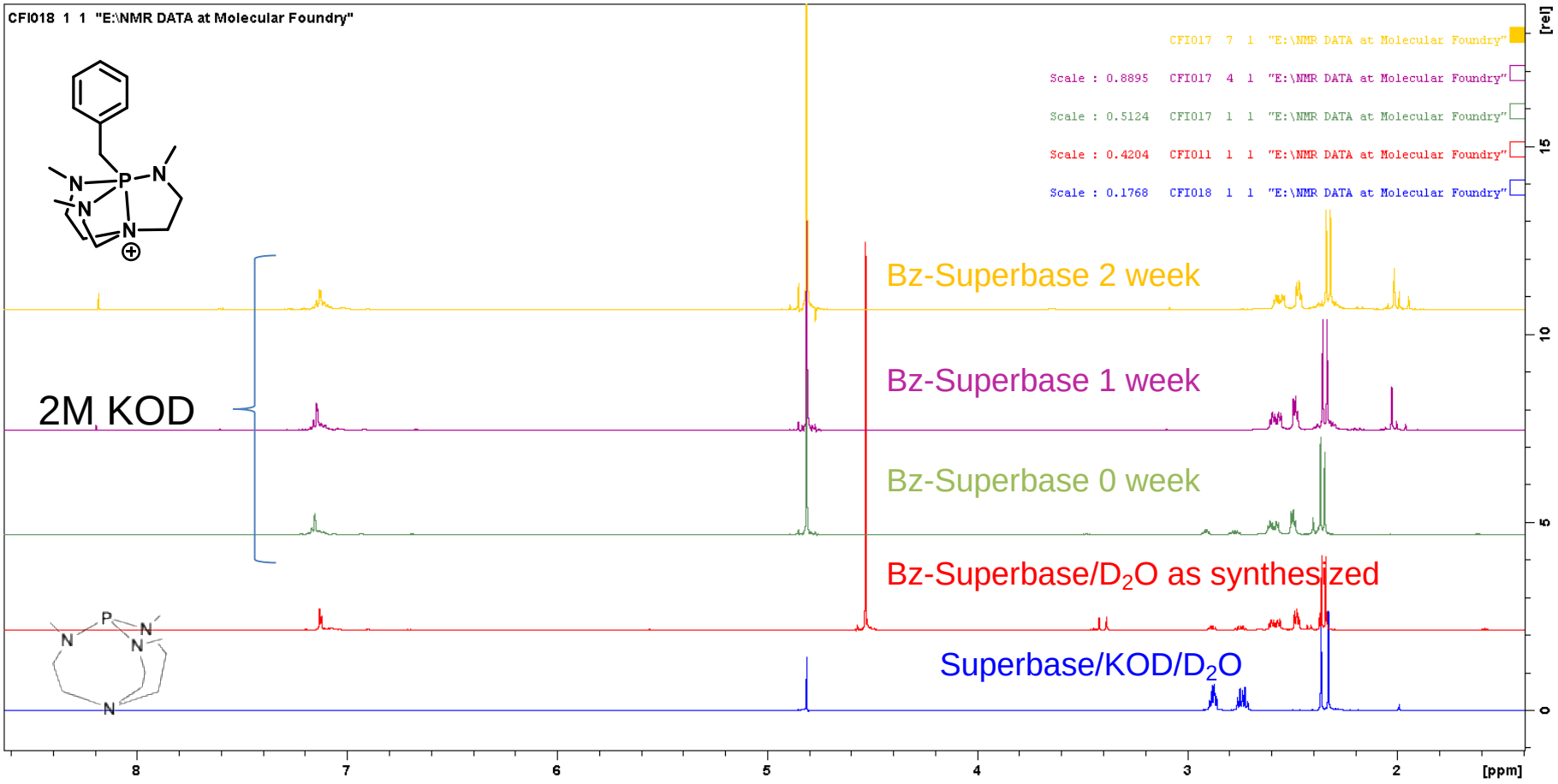


G1730, 20% styrene



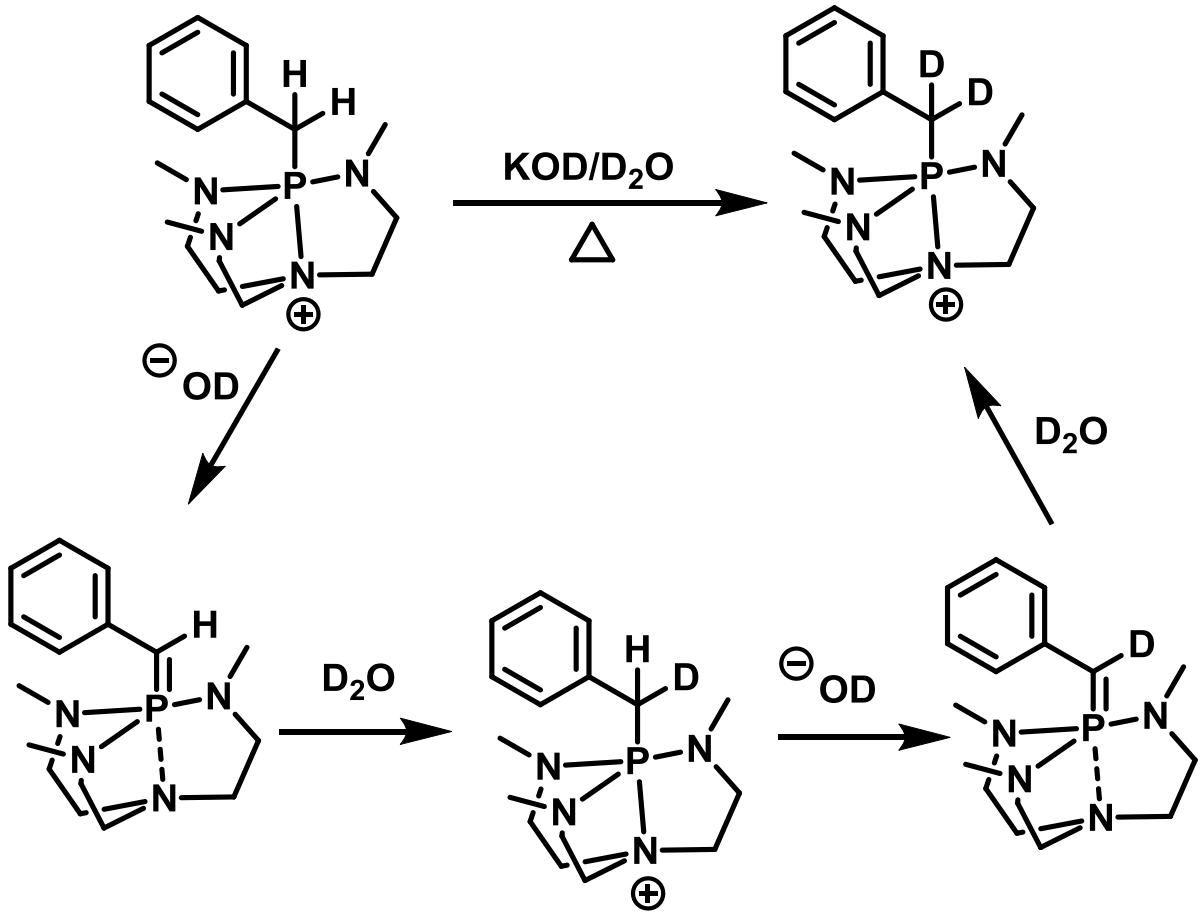
G1650M, 30% styrene

Stability of model base in 2M KOD at 75 ºC – H^1 NMR



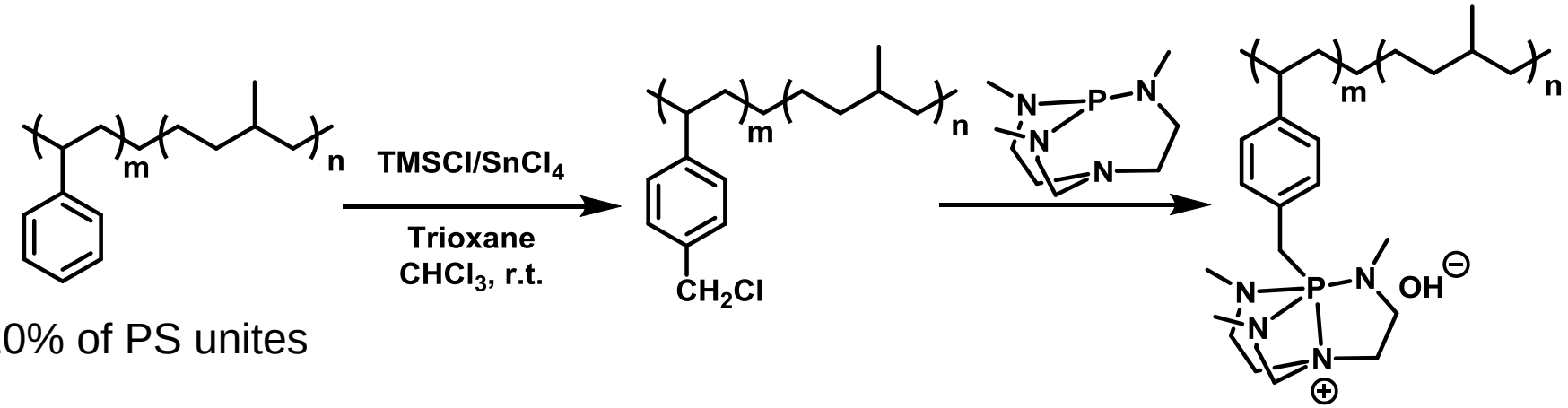
At the maximum, the model base decomposition is 5% in one week.

Possible route of Ylide formation and proton exchange for the model compound

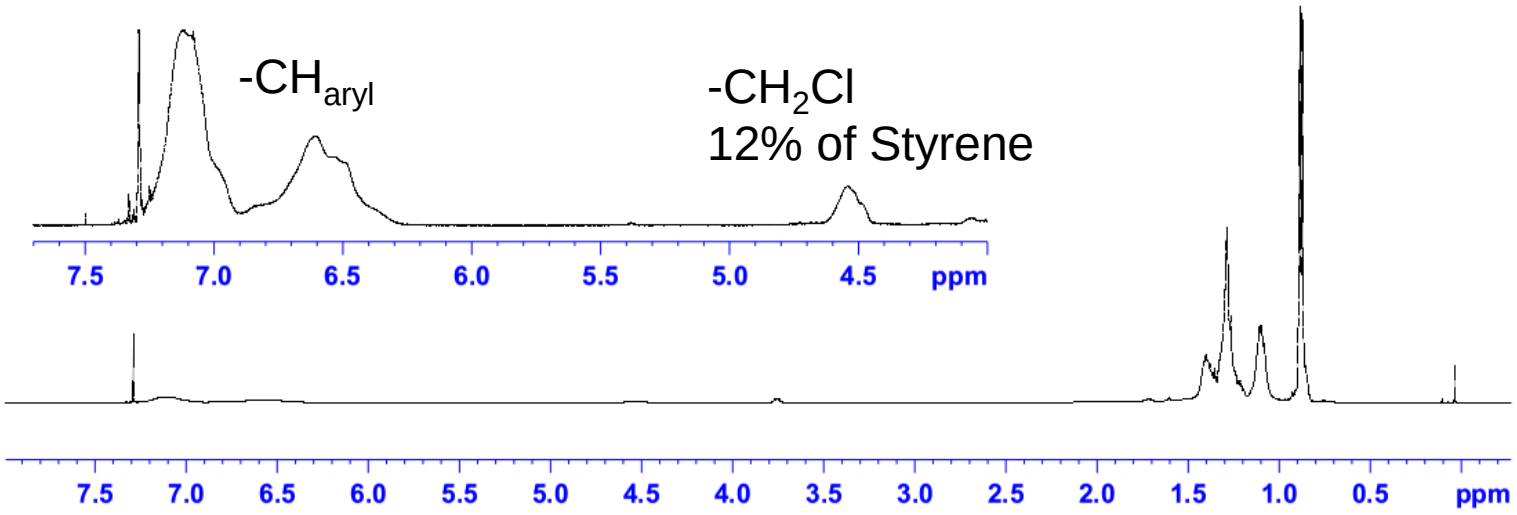


The higher electron negativities of super base prevent formation of the Ylide and increase the overall structure stability in alkaline conditions.

Ionomer synthesis based on Kraton® copolymers



20% of PS unites



The methylene chloride modification to the Kraton polymer is successful. The grafting of super base is forthcoming.

Responses to Previous Year Reviewers' Comments

This project was not reviewed in FY18.

Collaboration & Coordination

This project is a collaboration among three teams at LBNL and Kraton Co..
1. Gao Liu's team: Proazaphosphatranes stability investigation, and derivative synthesis, and membrane integration.
2. Daniel Miller's team: Member development and integration and stability study.
3. Adam Weber's team: AEM development and testing, and water management investigation and modeling.
4. Kraton® provided gift materials to this project.

Remaining Challenges and Barriers

1. Perform ionomer synthesis and MEA testing.
2. Increase super base functional group loading to 30%.
3. Further quantify Ionomer stabilities through model compound and MEA operation.

Proposed Future Work

1. Continue the stability investigation of the super base and its derivatives in 2M KOD in D_2O solution.

2. Stability investigation of the Kraton® polymer matrix in alkaline condition.

3. Accomplish the super base polymer development based on polystyrene-co-polyisoprene (hydrogenated) backbone structures

4. Finish all the tasks and milestones of remaining of the years

5. Develop more robust connections between super base and polymer matrix

Technology Transfer Activities

1. Works with polymer materials companies to explore possible collaborations in the future.

2. One provisional patent application is under consideration at LBNL.

3. Interacted with large energy companies and startups for possible collaborative technology development.

Summary

1. Quantified and understood the superb alkaline stability of the organic super base via model compounds synthesis and characterization.

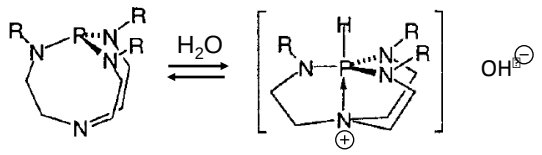
2. Identified a stable and flexible polymer matrix in high alkaline conditions.

3. Developed a feasible process to synthesize the super base grafted ionomers.

4. Membranes synthesis, MEA development and testing are under way.

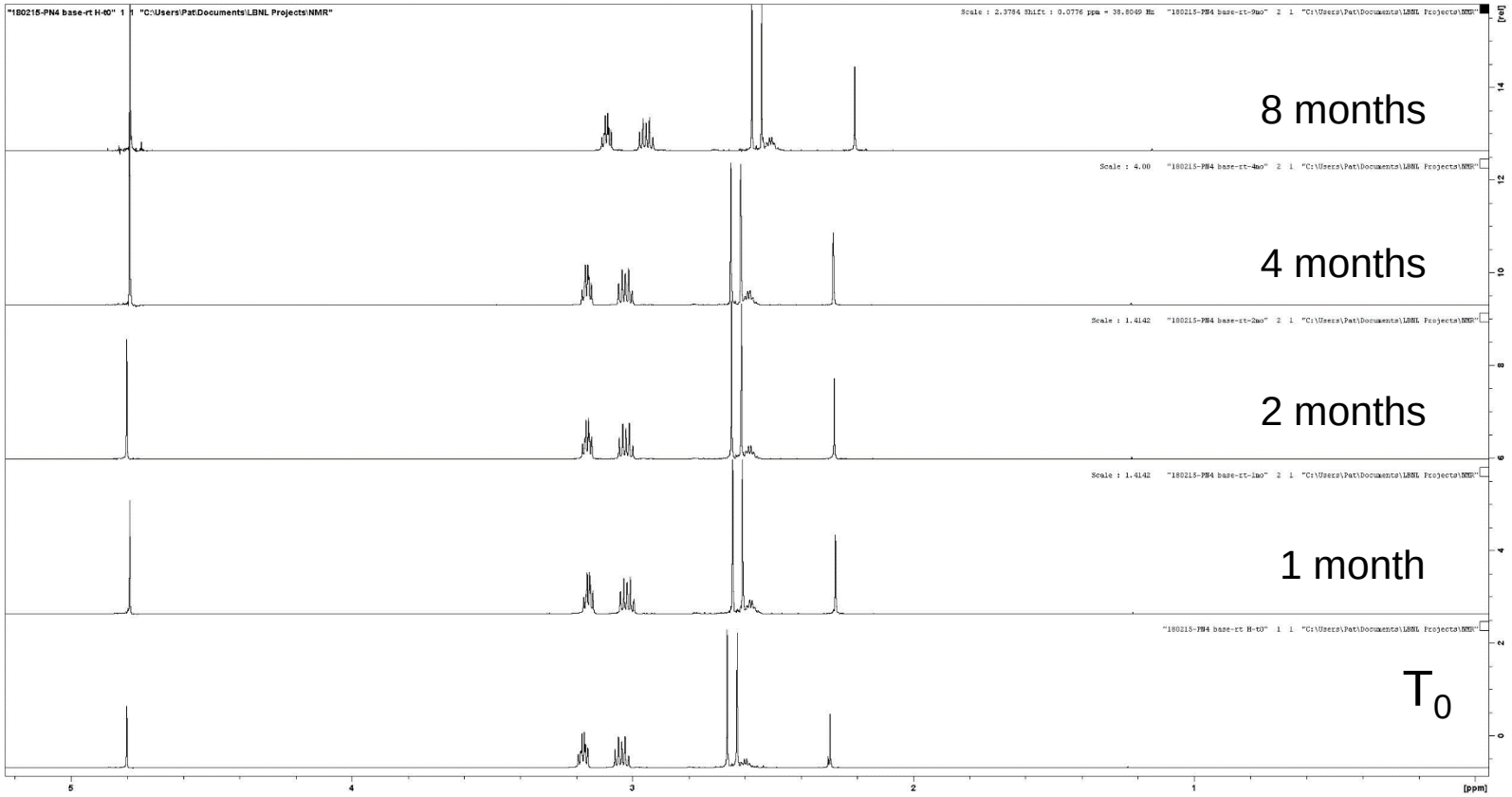
Technical Back-Up Slides

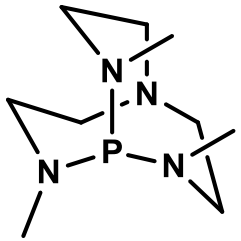
Stability study of Proazaphosphatranes and its derivatives



R = methyl

^{1}H NMR – Stability at **25°C**





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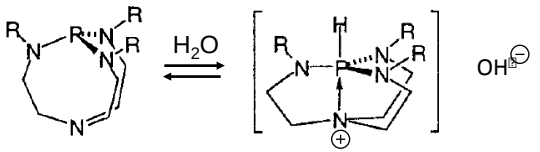

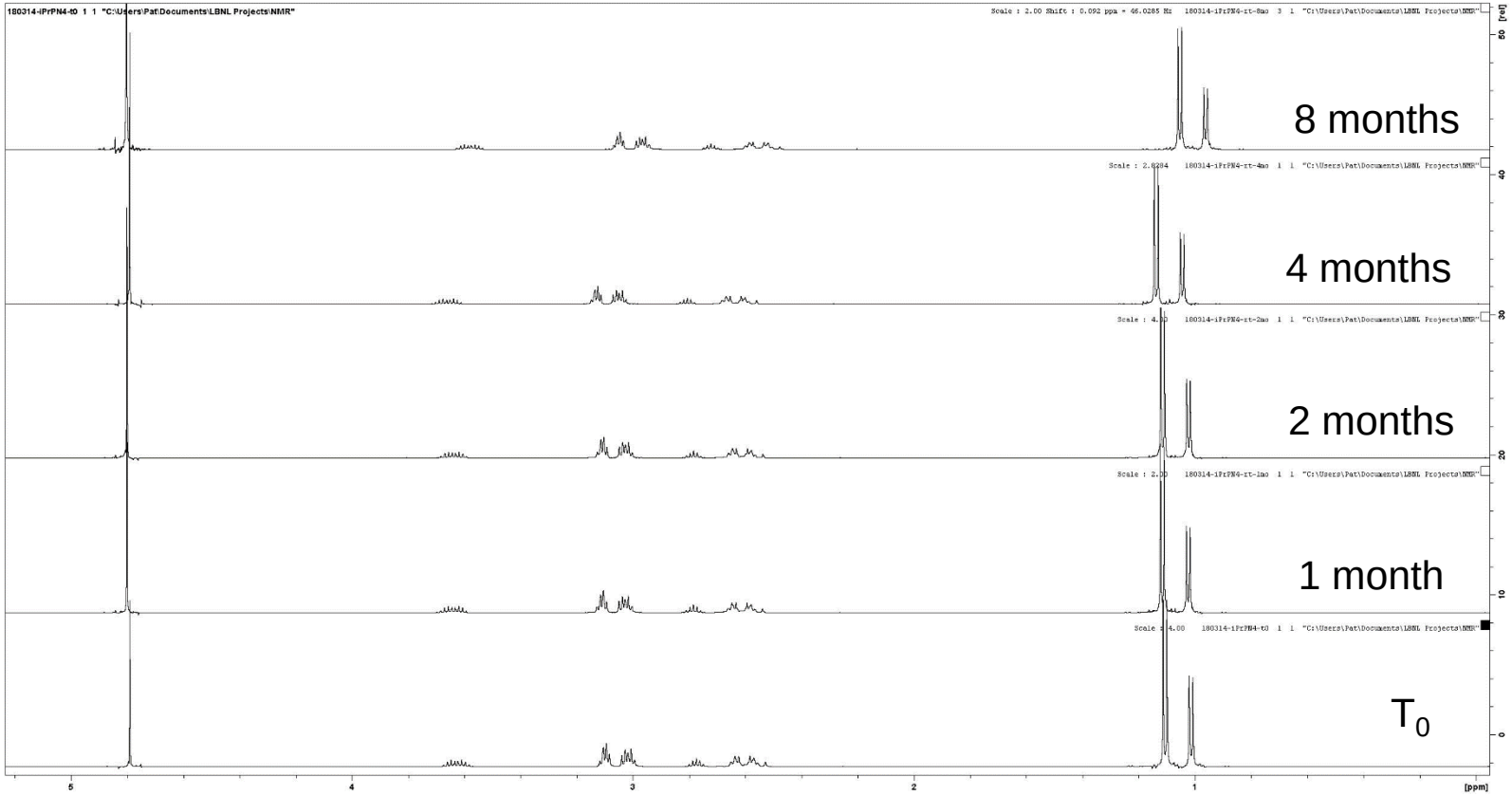

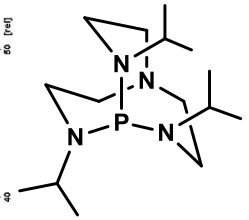

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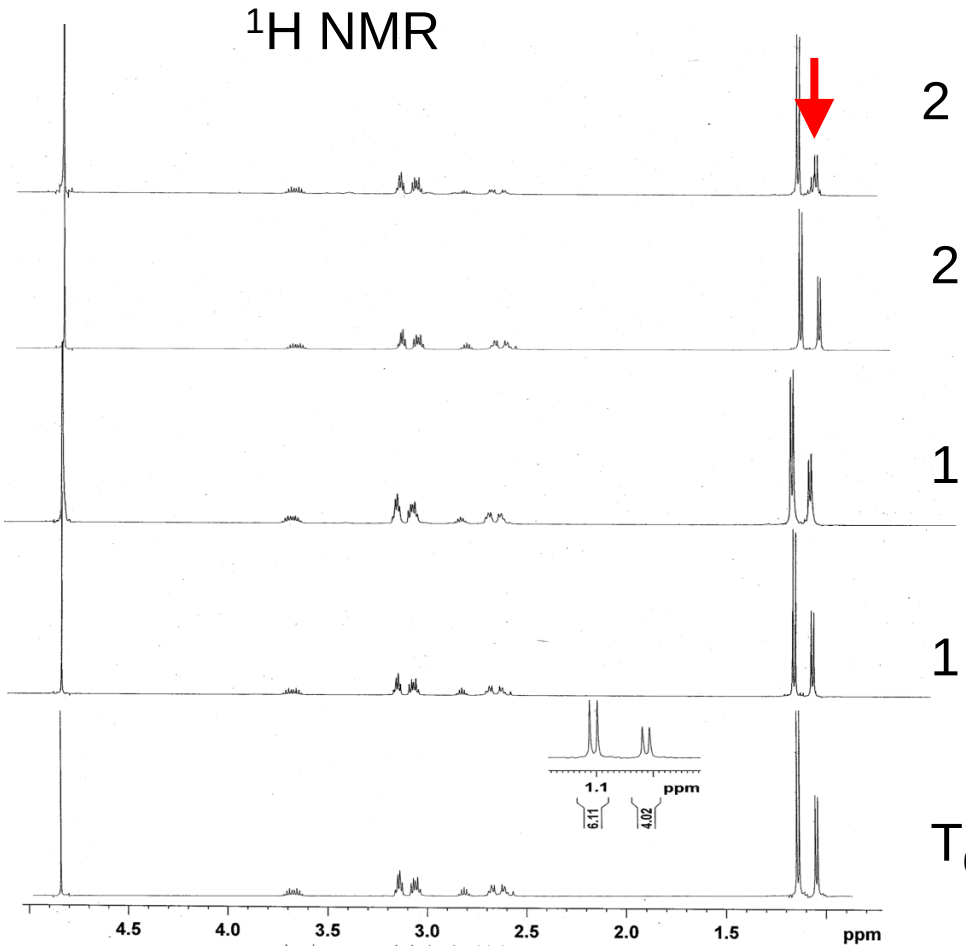
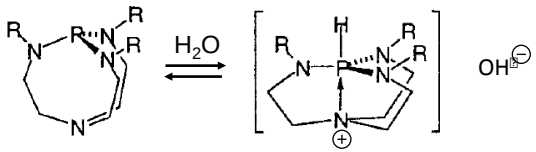
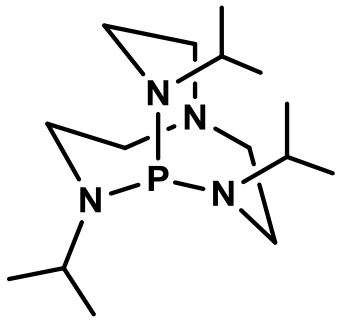


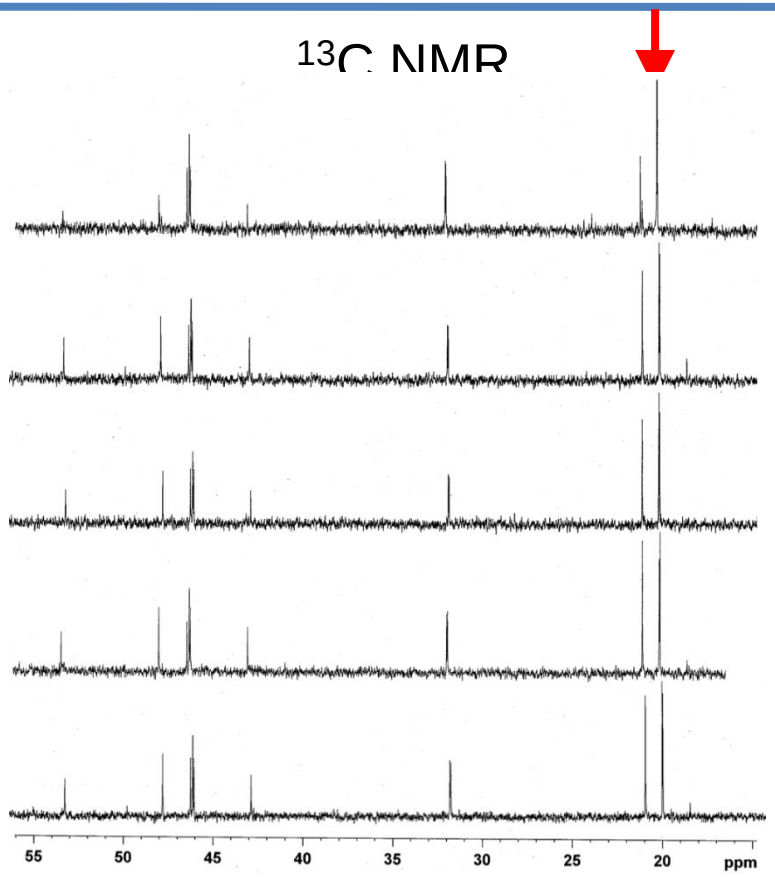


R = isopropyl



The NMR spectra change at the isopropyl site after 2 months aging at 70°C.
The isopropyl functionalized super base is **NOT** stable.

Stability study of Proazaphosphatranes and its derivatives



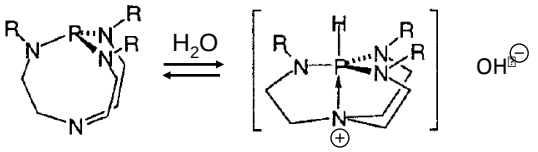
2 Mon, 70°C

2 Mon, 25°C

1 Mon, 70°C

1 Mon, 25°C

T_0, 25°C



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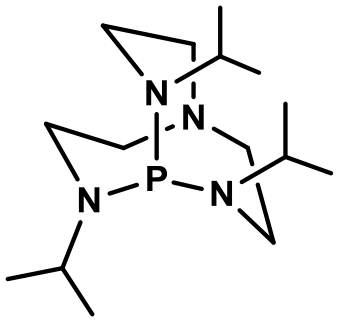
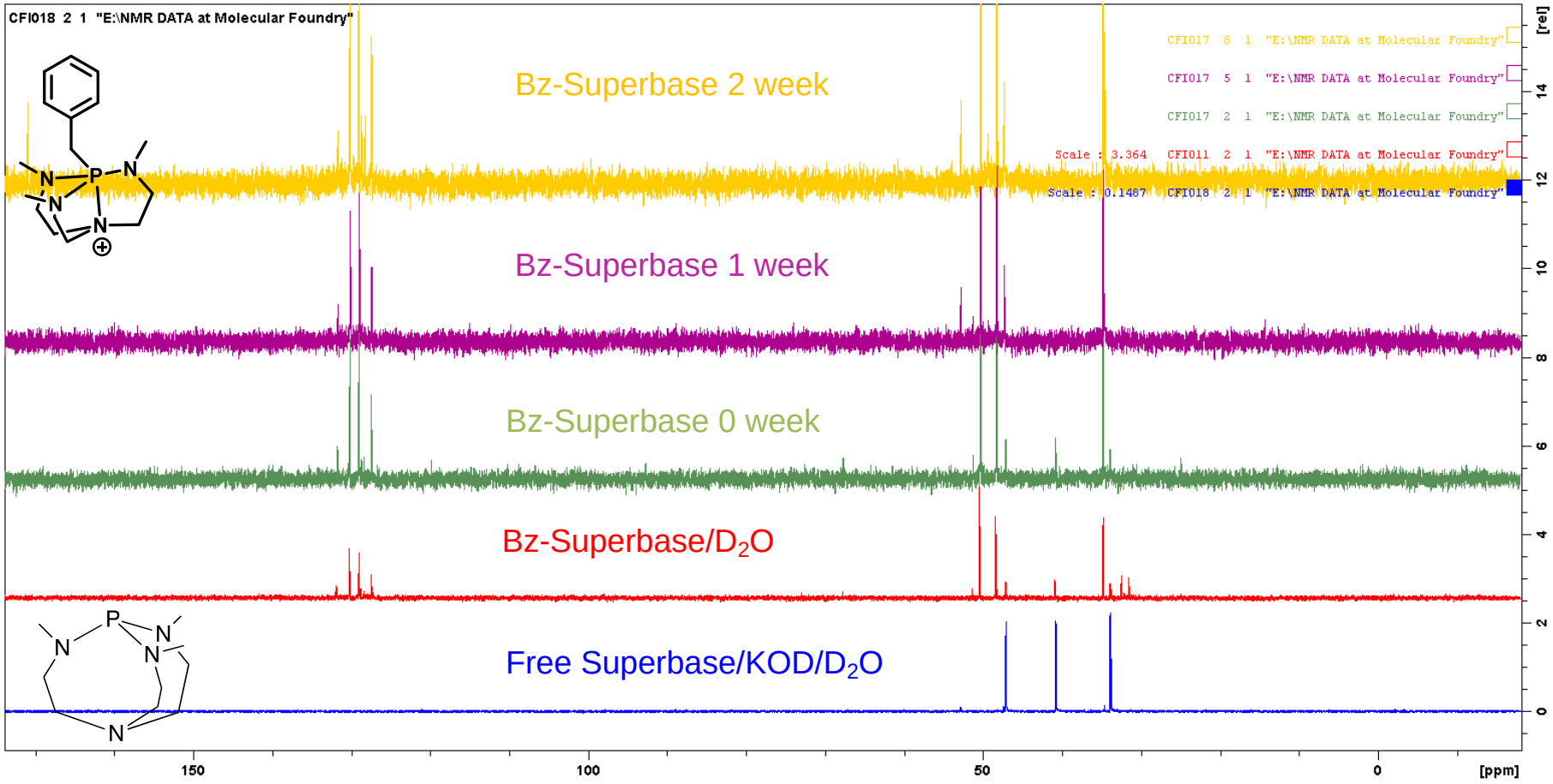


The NMR spectra change at the isopropyl site after 2 months aging at 70°C. The isopropyl functionalized super base is **NOT** stable. Therefore, the 2, 2', 2" connections may not be used to form bonding with the polymer matrix.

Stability of model base in 2M KOD at 75 ºC – C^{13} NMR



Stability of model base in 2M KOD at 75 ºC – P^{35} NMR