

# Establishing On-line NMR to Supplement Size Exclusion Chromatography of Polyester Polyurethane

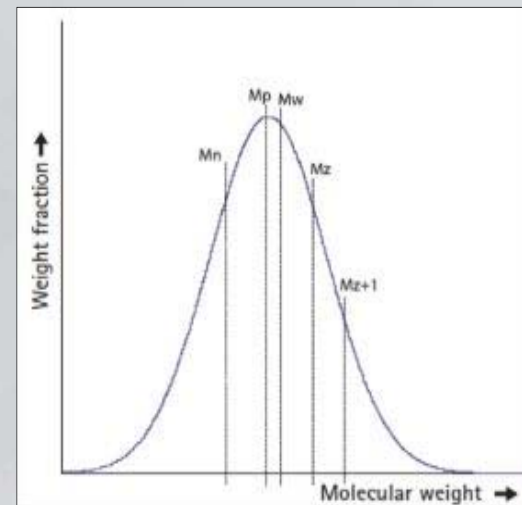
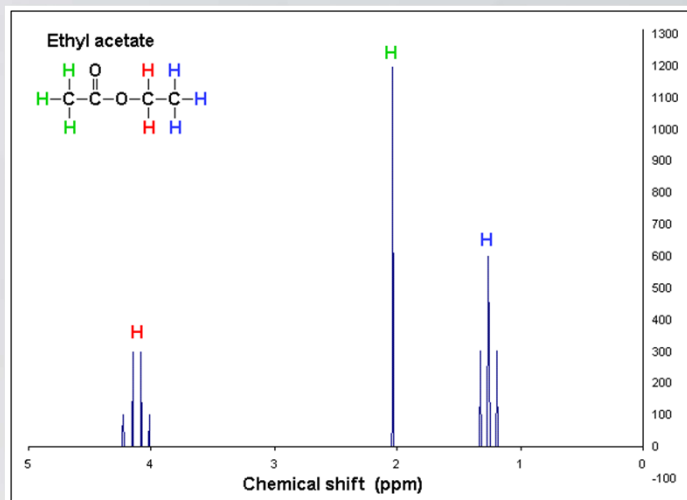
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# Introduction and Background

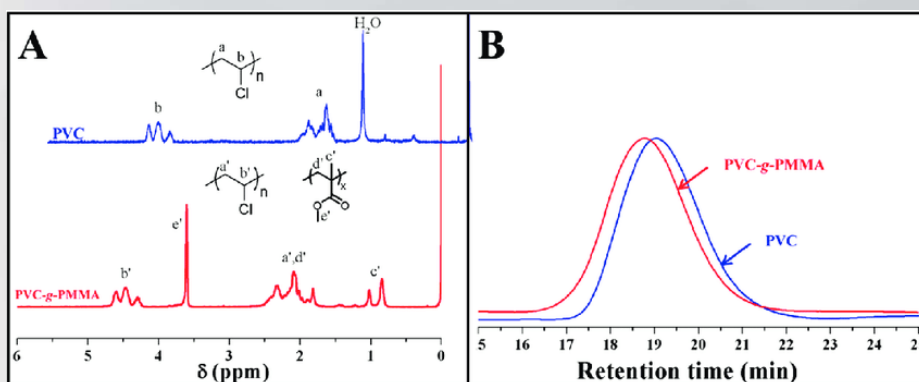
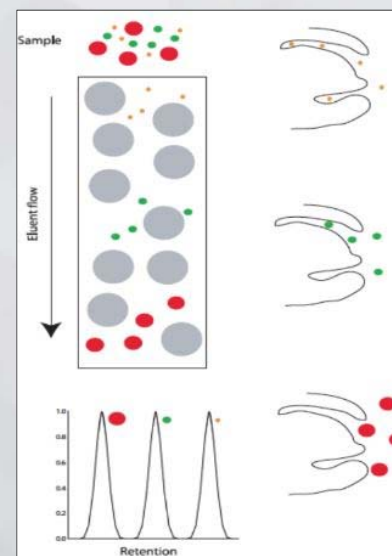
The purpose of this project is to use a hyphenated technique to combine **Nuclear Magnetic Resonance (NMR) spectroscopy** and **Gel Permeation Chromatography (GPC)** to evaluate the *chemical composition* and *molecular weight distribution* of the polymer Estane with an emphasis on determining if the technique is sensitive enough to evaluate the aging of Estane.

- **NMR:** concentrates on both the chemical composition of a compound and molecular weight analysis
- **GPC:** focuses on the molecular weight distribution of a compound.



# NMR-GPC Coupling

- GPC is the only effective technique used to differentiate molecular weight distribution.
- GPC:
  - Stationary and mobile phase
  - Separate particles by **size**
- By separating the polymer particles by size, each monomer unit can be analyzed at the same time.



- The particle groups of **comparable mass** and **size** are analyzed by NMR for the evaluation of **chemical composition** through molecular weight analysis.
- This coupled technique will then aid in effective polymer characterization.

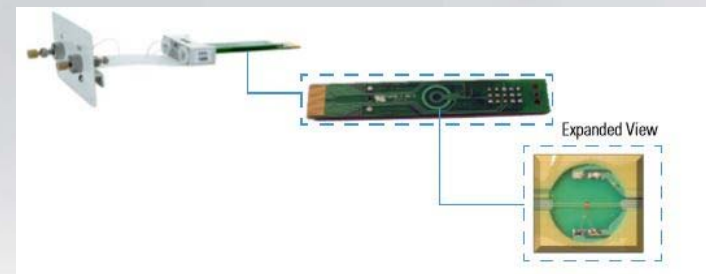
# The Rise of Benchtop NMR



- Larger in size
- Higher in cost
- Requires regular maintenance involving cryogenic liquids
- Requires training to use
- Cannot be used in-line with other detectors
- More sensitive and high resolution



- More portable
- Cost effective
- Service free, rare Earth magnet
- Easy to operate
- Can be used in-line with other detectors
- Less sensitive and lower resolution

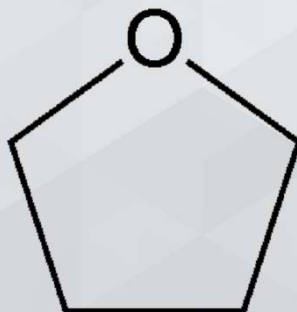


## Parameter Experiments

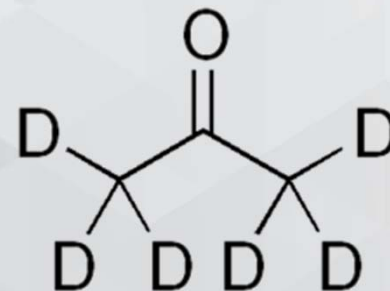
This research performed baseline experiments to evaluate potential solvents, concentrations of Estane, and flow rates of the solution for further experiments incorporating GPC.

### Solvents:

- Tetrahydrofuran (THF)
- Deuterated Acetone
- Ethyl Acetate



THF



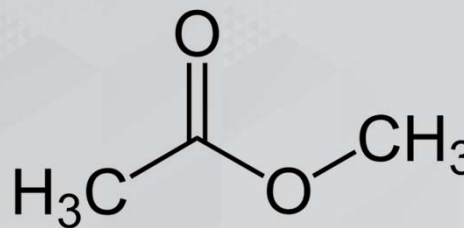
Deuterated Acetone

### Concentrations:

- 0.7 mg/ml (typical for GPC)
- 13.5 mg/ml (pristine)
- 6.2 mg/ml (aged)

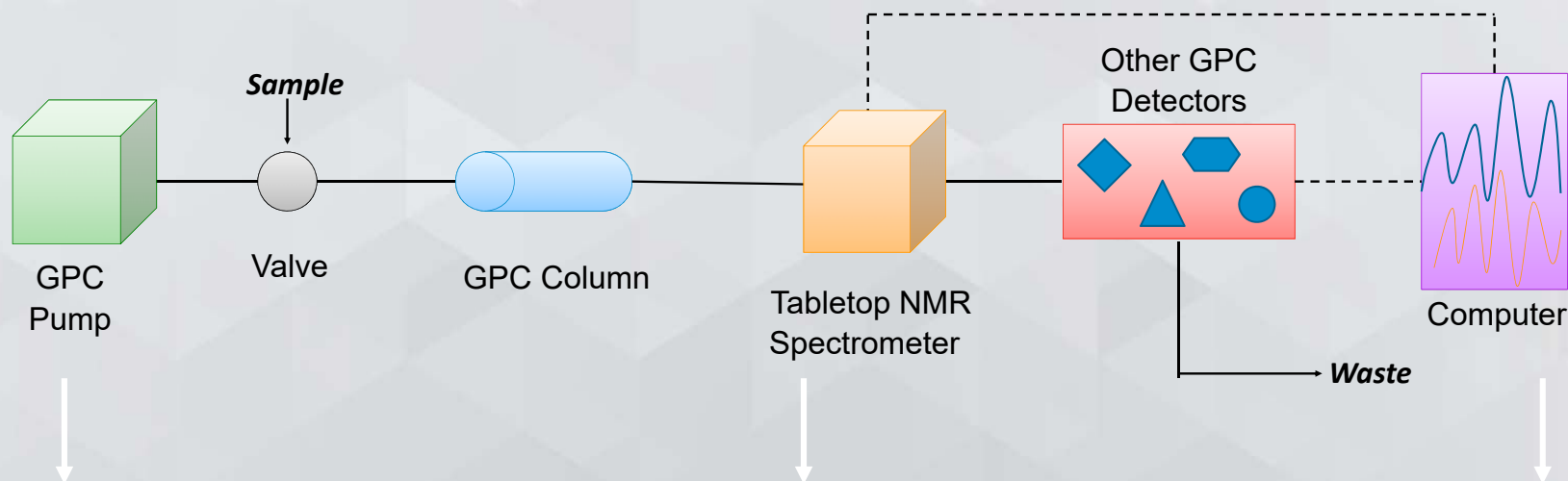
### Flow Rate:

- Normal GPC 0.1 – 5 ml/min
- Consider 1 ml/min based on research



Ethyl Acetate

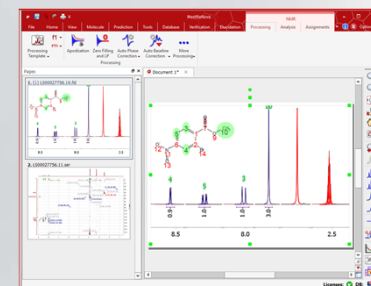
# Instrumentation and Experiment



- M1 Class Pump, Scientific Systems, United States



- 82 MHz,  $^1\text{H}$ -NMR Spectrometer, Picospin 80 Series II, Thermoscientific, United States

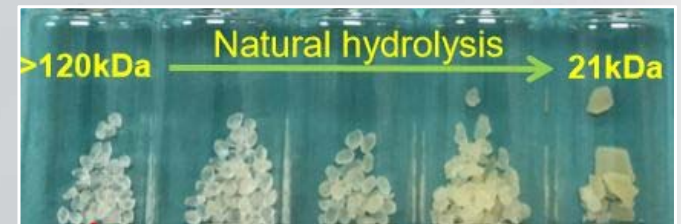
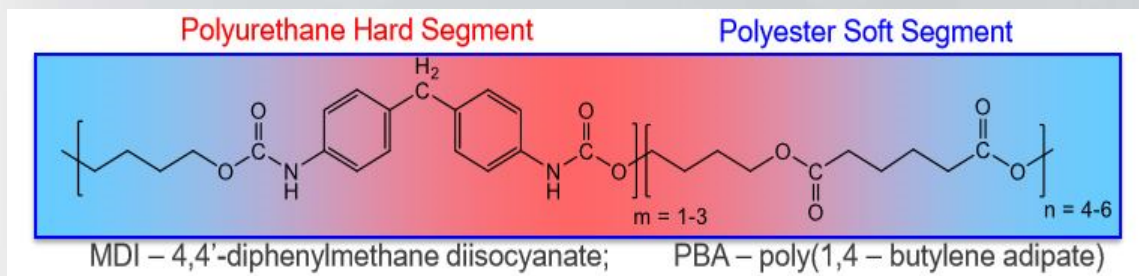


- MNova Software, Mestrelab



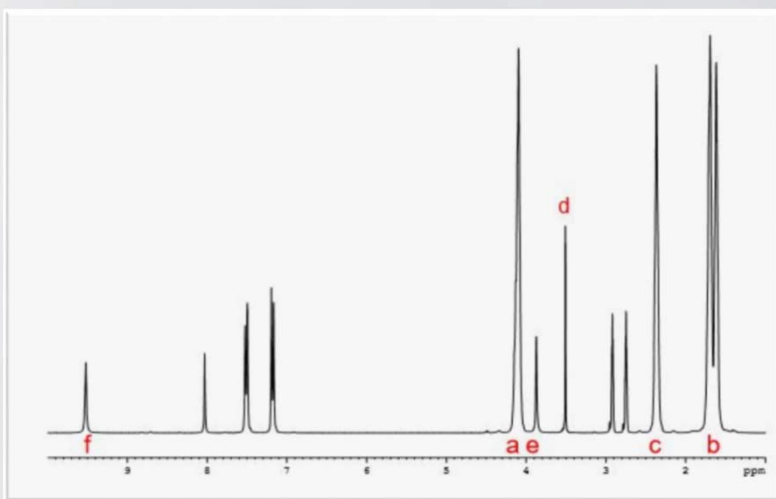
# Polyester Polyurethane

- Random Copolymer
- Variation in hard and soft segments,
  - Hard: 4,4-diphenylmethane diisocyanate (MDI) and
  - Soft: poly(1,4-butylene adipate) or PBA
- Ratio of hard to soft fluctuates depending on manufacturing conditions and aging
  - Literature reports show **1-3** hard with **4-6** soft per repeating unit
- Freshly manufacture sample is approximately 23% hard segment



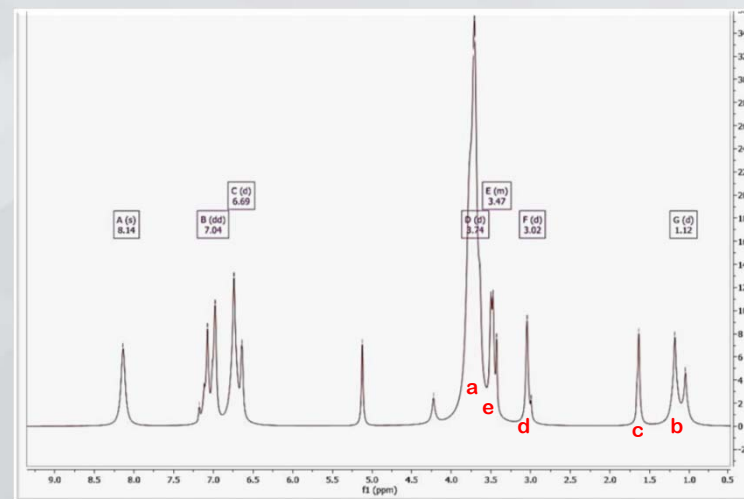
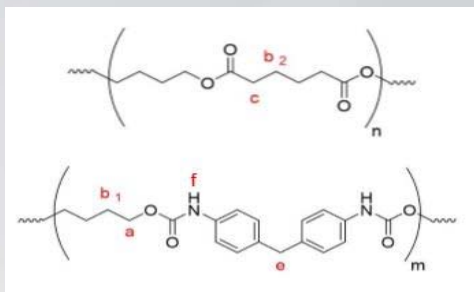
## Data and Discussion

Graphs 1 and 2 were compared for similarities to evaluate the Picospin. Slight chemical shifts were expected due to the size of the magnet as well as the type of solvents used. The data in Graphs 1 and 2 are similar in spectra despite the use of Estane samples with differing molecular weight.



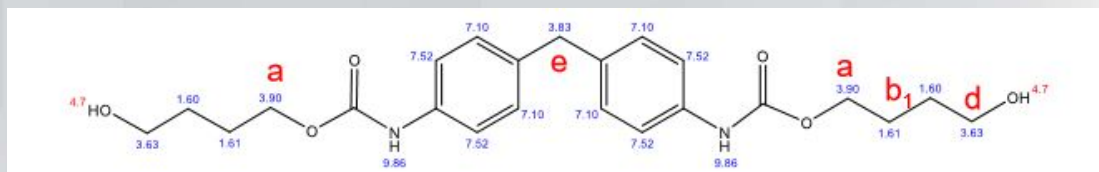
Graph 1. NMR data of pristine Estane in deuterated DMF by Conventional NMR.

- A 120kDa sample was analyzed by LANL at approximately 100 mg/ml concentration.



Graph 2. NMR data of pristine Estane in protonated THF by Tabletop NMR.

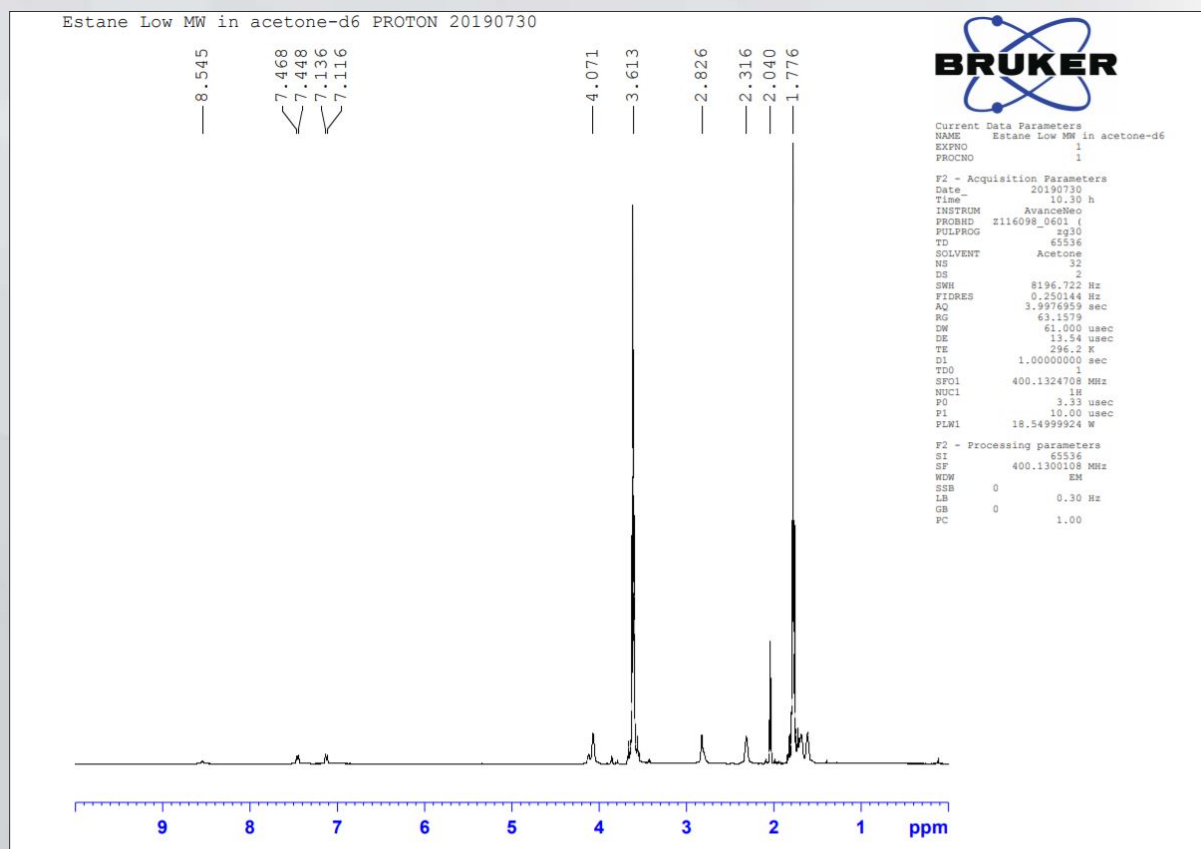
- A 140kDa sample was analyzed by Pantex with approximately 100 mg/ml concentration.





# Deuterated Solvents

- Higher in cost, less prevalent in labs
- Allows for a stronger signal of the solute molecules and in turn, more distinguishable peaks.
- 99.9% deuterated, .1% protonated
  - Visible at peak 2.04 ppm
- Will aid in differentiating significant peaks apart from noise of the tabletop NMR.



Deuterated Acetone and Estane 6.2 mg/ml by conventional NMR.

## What's Next?

- Evaluation of aged samples of Estane
- Exploration of other deuterated solvents
- Identify best parameters for GPC and NMR, such as:
  - similar concentration
  - 15 s scans vs. 12 hr scans
  - pressure < 500 psi (vs. 1200 for typical GPC)
- Evaluation of multiple NMR scans on one sample to determine homogeneity of Estane sample
- Evaluation of best solvent suppression techniques in the lab as well as within the software

## Acknowledgement and References

- CNS for providing the internship and the SAFE group for providing mentoring and laboratory space.
  - CMD for providing funding for the purchase of the NMR.
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- Yang, Dali; Edgar, Alexander; Wu, Ruilian. (2019). *Hydrolysis Studies of Naturally and Accelerated Aged Poly(Ester Urethane)*. ISPAAC, (pp. 1-29). Sendai, Japan
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  - [https://www.researchgate.net/figure/H-NMR-spectra-A-and-GPC-curves-B-of-pristine-PVC-and-PVC-g-PMMA\\_fig1\\_300374138](https://www.researchgate.net/figure/H-NMR-spectra-A-and-GPC-curves-B-of-pristine-PVC-and-PVC-g-PMMA_fig1_300374138)

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