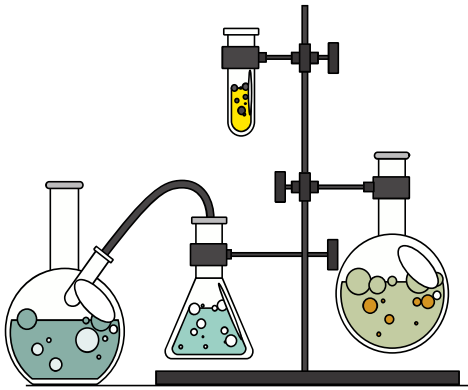
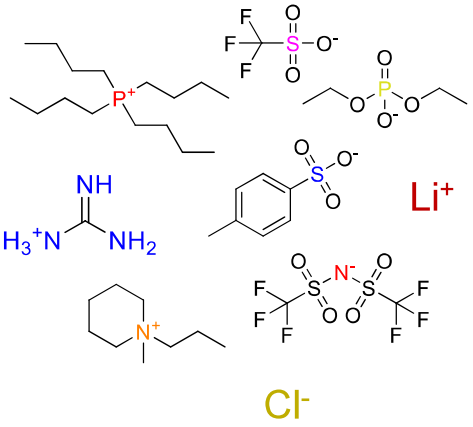
Long-Term Thermal Stability of Ionic Liquids for High-Temperature Applications

João Fabian, Murilo Alcantara, Filipe Sosa and João Coutinho

Universidade de Aveiro, CICECO – Aveiro Institute of Materials, Portugal





HOW DO YOU DEFINE THERMAL STABILITY OF YOUR IONIC LIQUID?

HOW DO YOU DEFINE THERMAL STABILITY OF YOUR IONIC LIQUID?

WHAT IS THE METRIC YOU USE TO EVALUATE?

Thermal energy storage

3.2. Thermal stability

Thermal stability was evaluated in terms of thermogravimetric analysis (see Supporting information S3). It is an important parameter for the final applicability of a PCM because the temperature gap between the transition and decomposition temperature must be enough to ensure the PCM integrity during the heating/cooling cycles. In this sense, the decomposition temperature gives us essential information about the maximal operational temperature of a given PCM. In Fig. 3 are depicted the onset decomposition temperatures determined according to the ISO 11358-1 [33] of the six ionic liquids prepared and their melting points.

Thermal fluids

3.6. Thermal Stability

The thermal degradation due to high heat conditions in thermal systems is one of the main reasons for the failure of heat transfer and lubrication fluids. In order to overcome this, thermal analysis was done to determine the thermal decomposition of the as-prepared samples. As such, the as-prepared samples were subjected to Thermogravimetric analysis (TGA) from 30 °C to 650 °C with a heating rate of 10 °C/min under 20 mL/min flow rate

Thermal fluids

Table 3. Summary of Ionic Liquid Properties

Property	Ionic Liquid	
	[EMIM][BF_4]	[BMIM][BF_4]
Density at 60° C	1.2187 g cm^3	1.1811 g cm^3
Freezing point	4° C	-88° C (T_g)
Thermal decomposition onset	434° C	424° C

Lubrication

Table 1
Thermal stability of the lubricants determined by TGA in air.

Lubricant	Temperature (°C)		
	Onset	50% weight loss	Endset
Mineral oil MO	263.1	300.3	339.5
AM-101	219.1	236.2	336.4
L-108	370.9	400.6	436.2
L-P106	322.0	355.5	393.0

Polymers

2.2. Thermogravimetric Analysis of Allyl-Based Ionic Liquids

To determine the thermal stability of the ionic liquids, Thermogravimetric Analysis was employed, as it is the most used tool for the determination of such properties. All obtained results are presented in Table 3.

Table 3. Thermal decomposition temperatures obtained with TGA measurements for all ionic liquids presented in this study.

IL Number	T_{onset} (°C)	$T_{onset5\%}$ (°C)	T_1 (°C)
1	208.08	179.38	309.92

Thermal energy storage

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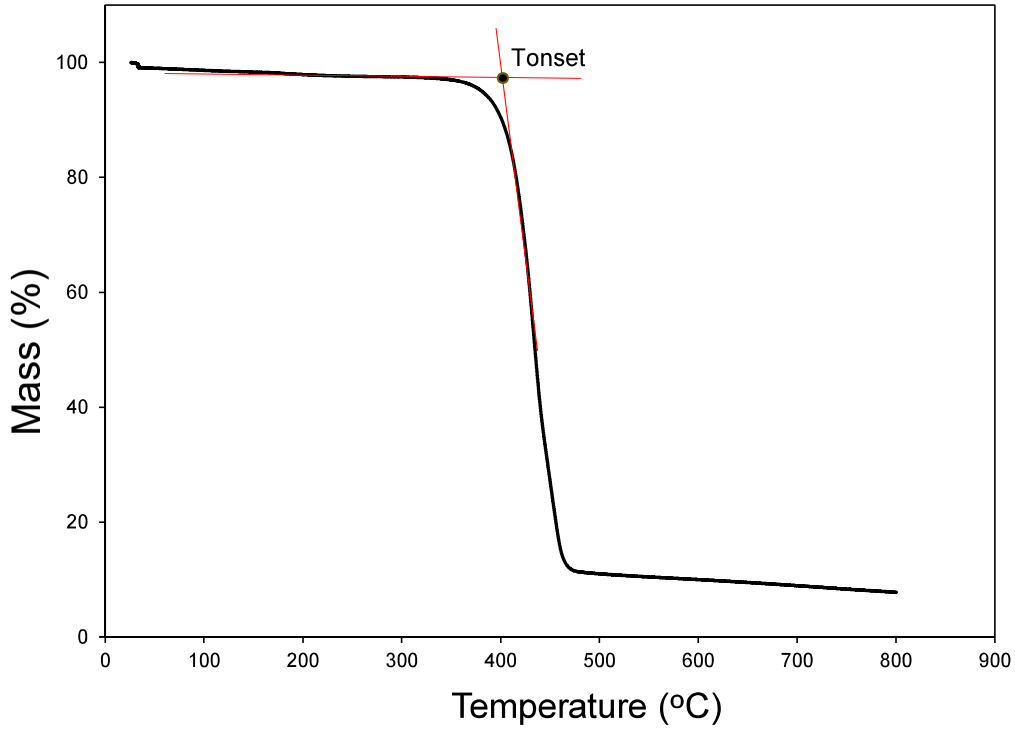
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Tonset is convenient but it is a dynamic measurement

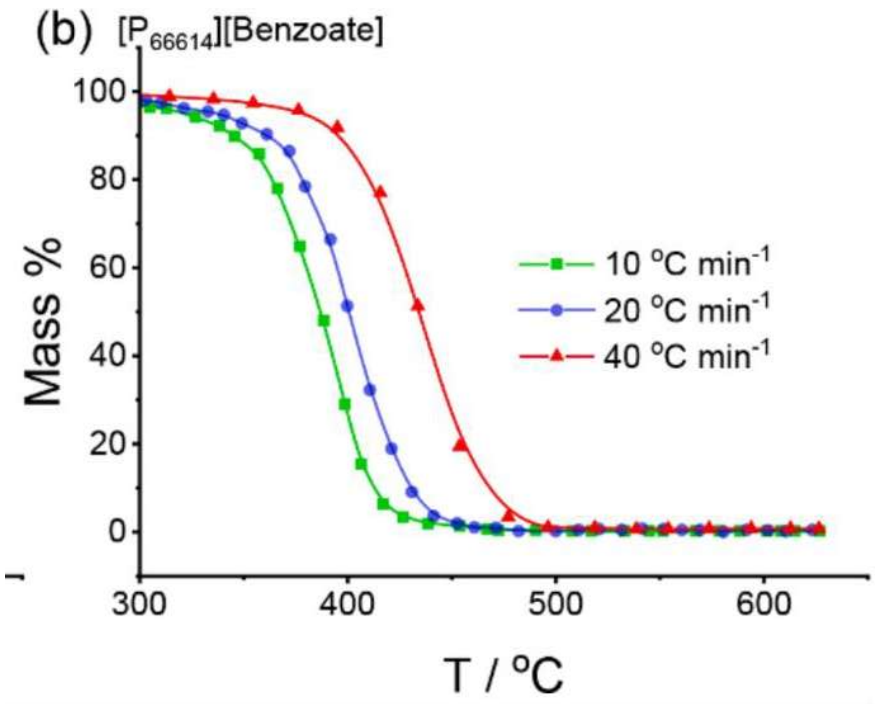
Intersection of the starting-mass baseline with the tangent to the TGA curve at the point of maximum gradient.

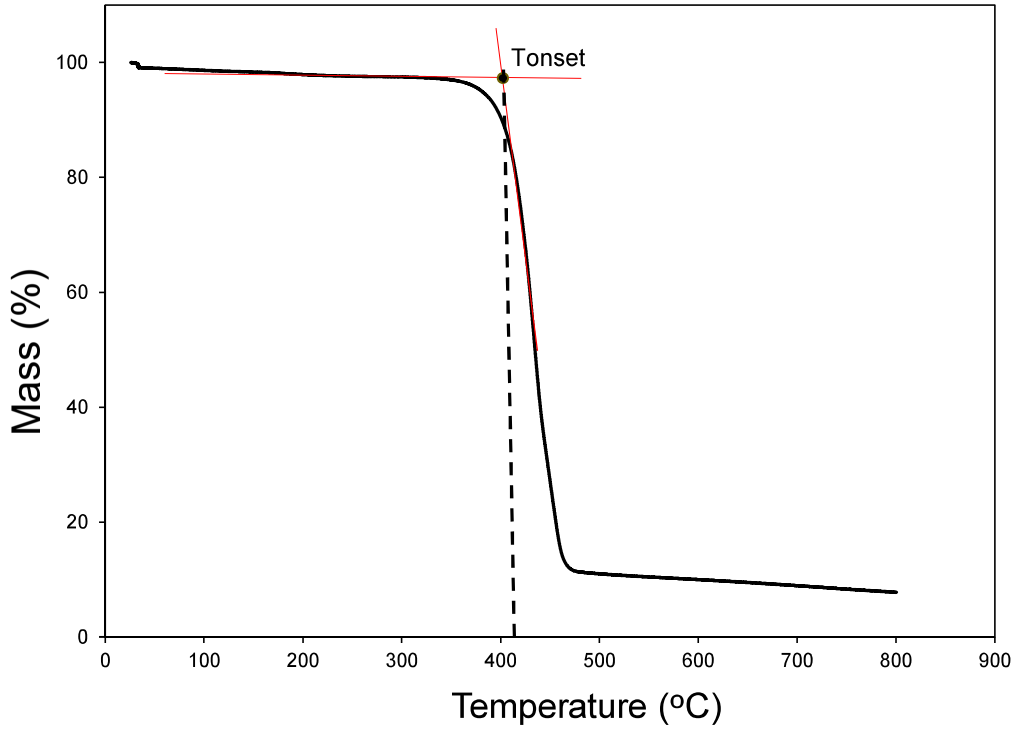
WHY TONSET CAN **MISLEAD**?



Tonset is convenient but it is a dynamic measurement

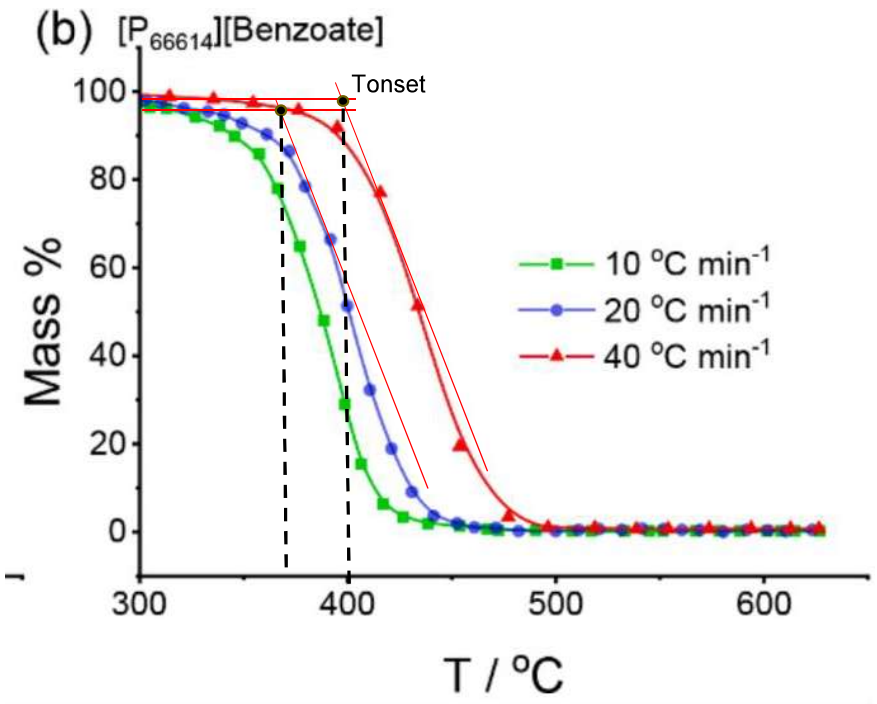
WHY TONSET CAN MISLEAD?

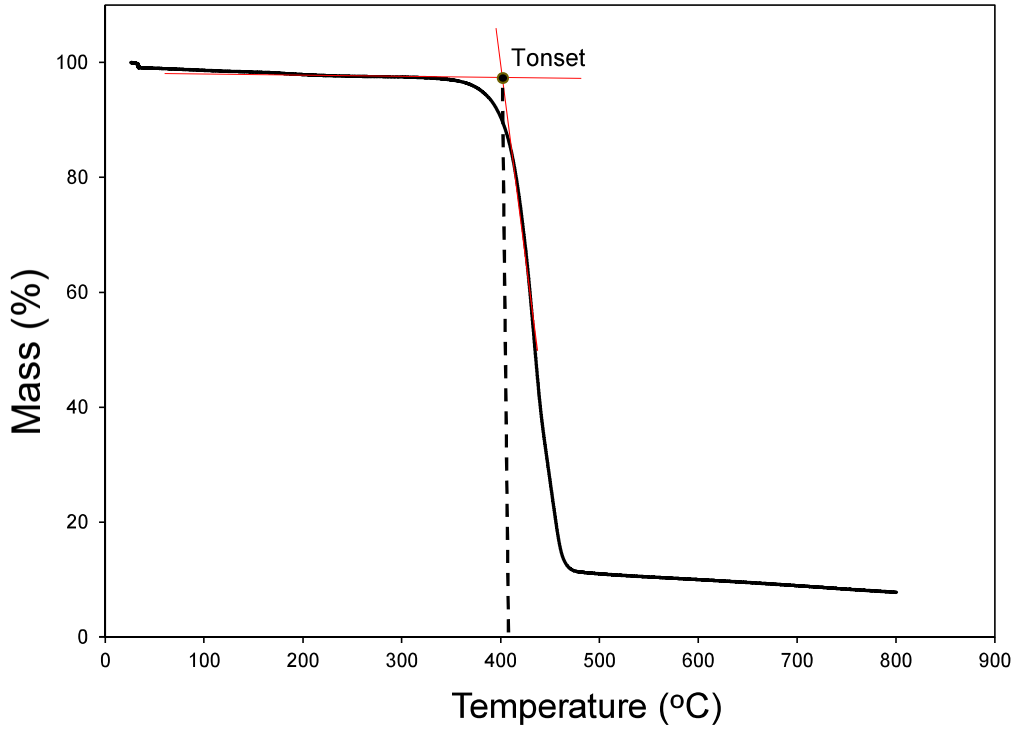




Tonset is convenient but it is a dynamic measurement

WHY TONSET CAN MISLEAD?





Thermal degradation of cyano containing ionic liquids

Tim J. Wooster,†[a] Katarina M. Johanson,[b] Kevin J. Fraser,[b] Douglas R. MacFarlane[b] and Janet L. Scott*[a]

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$T_{0\text{-}01/10h}$

METRIC SUGESTED BY WOOSTER et al.

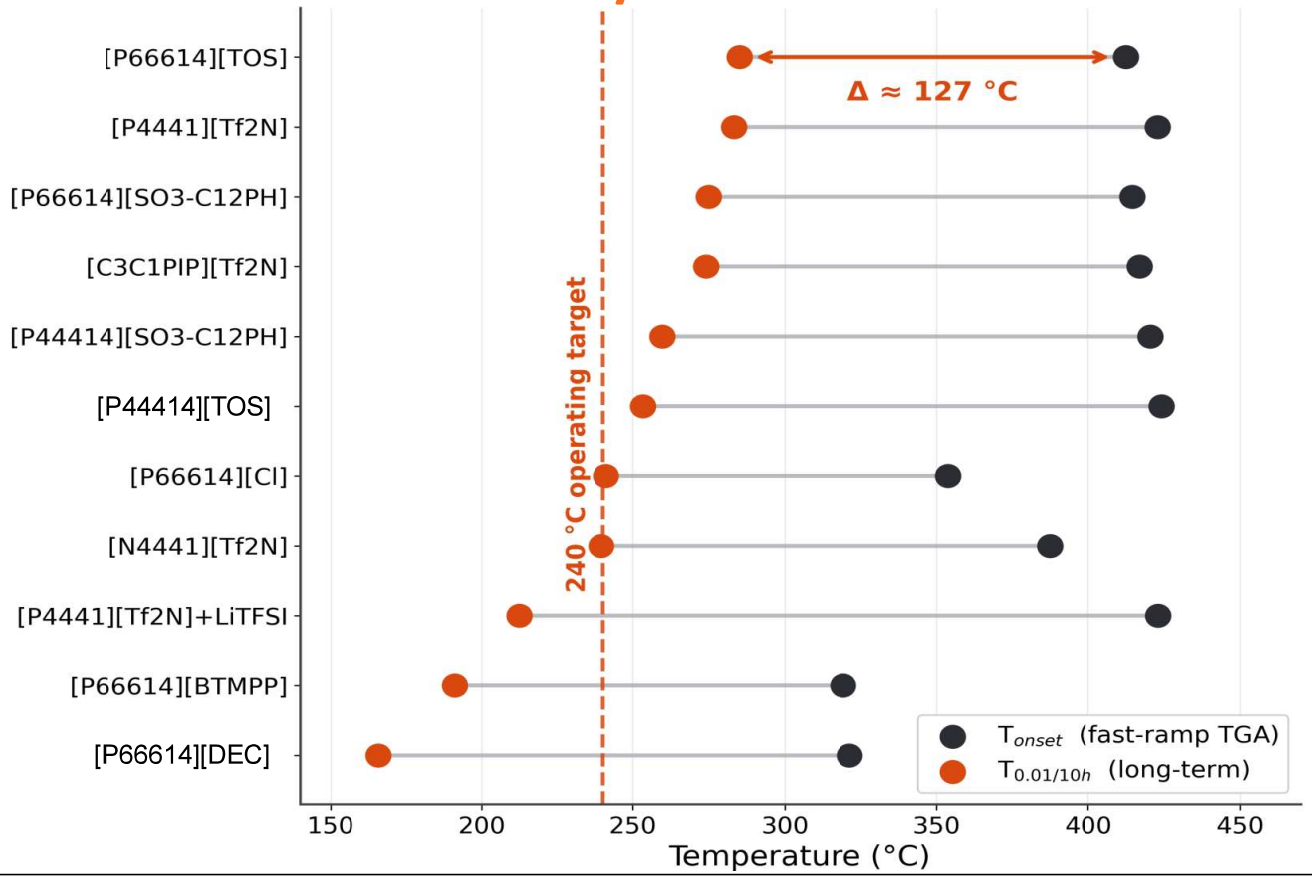
1% mass loss — Criterion

in

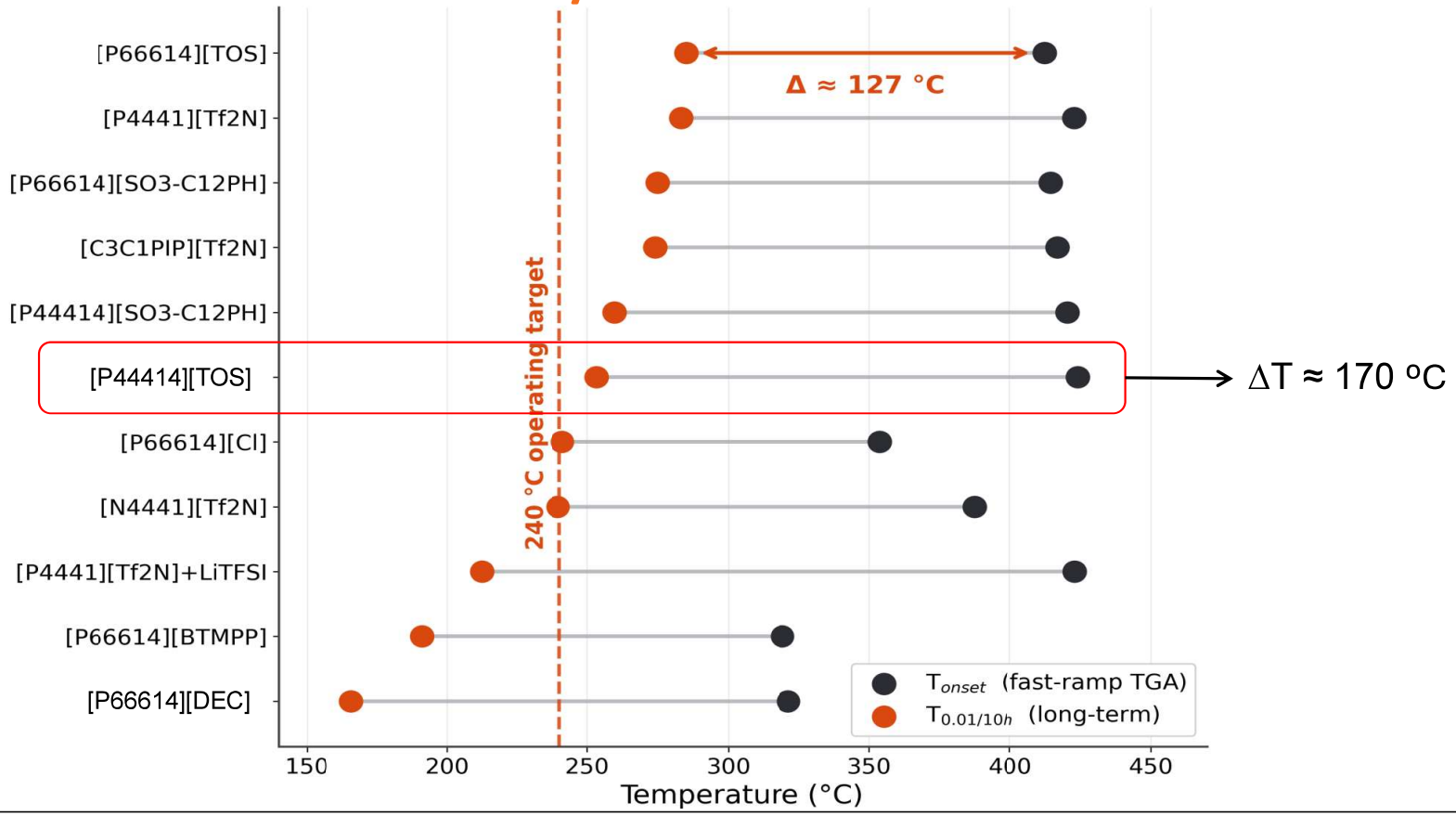
10 h isothermal exposure — Time

Unlike Tonset, the metric states both the tolerated change and the duration.

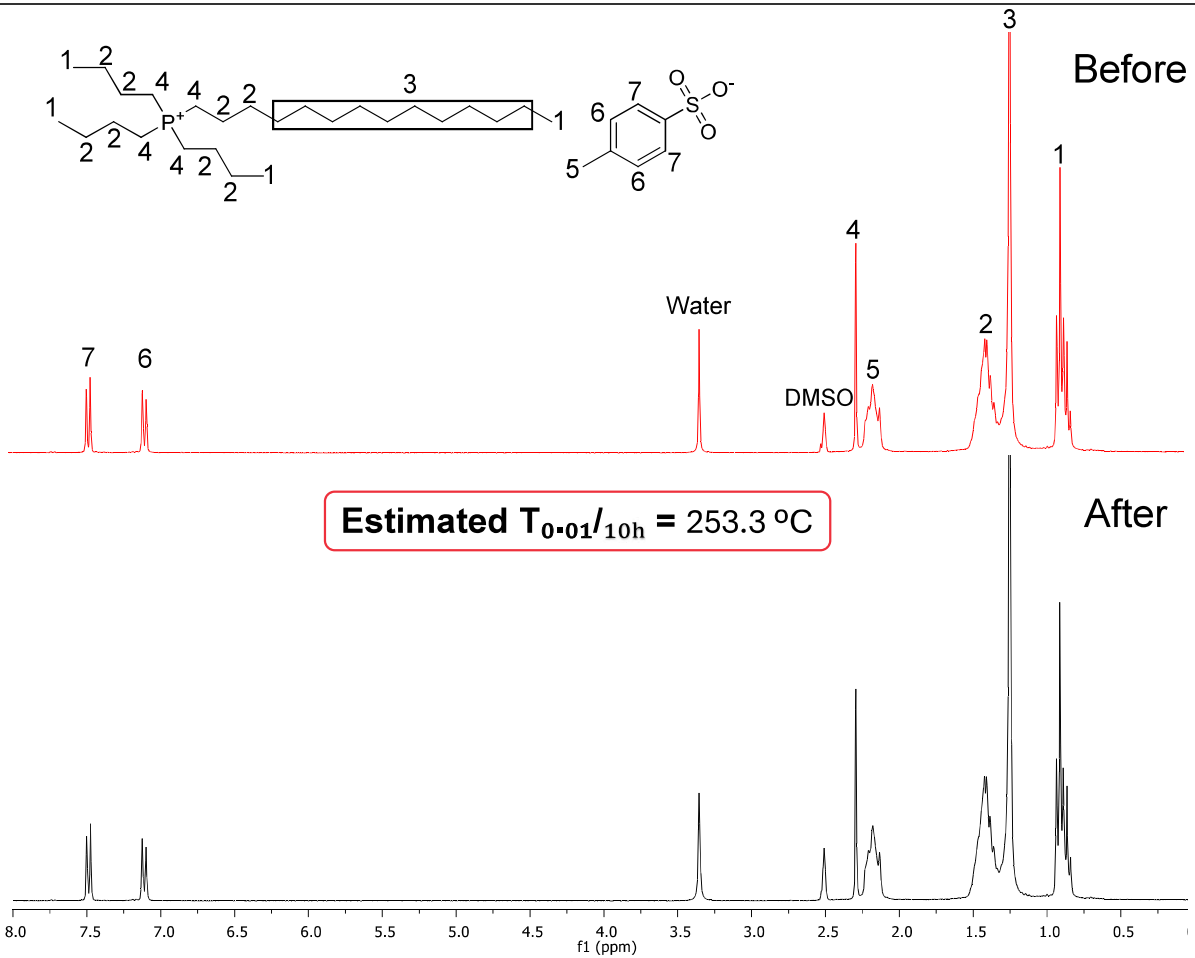
$T_{0.01/10h}$ x T_{onset}



$T_{0.01/10h}$ x T_{onset}



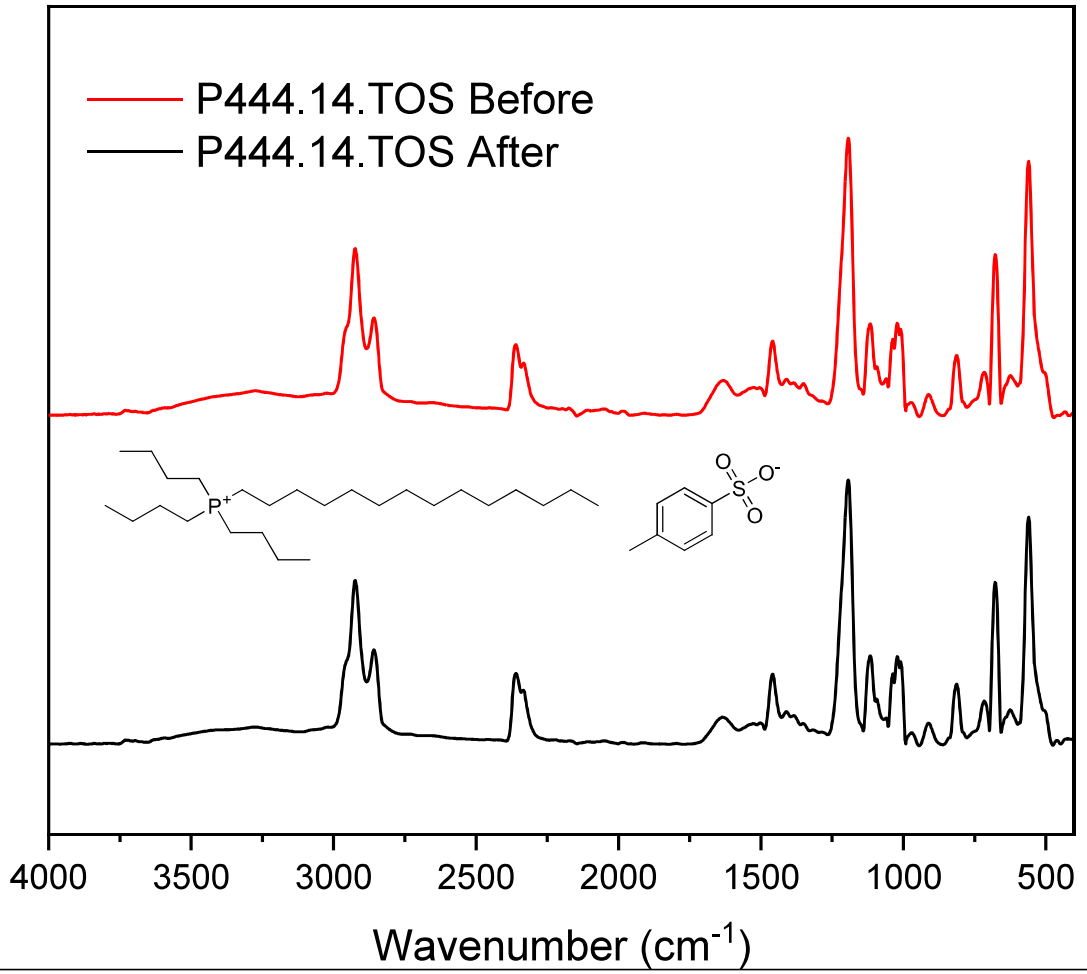
H-NMR [P44414][TOS] 10 days Thermal Stability at 240 ºC







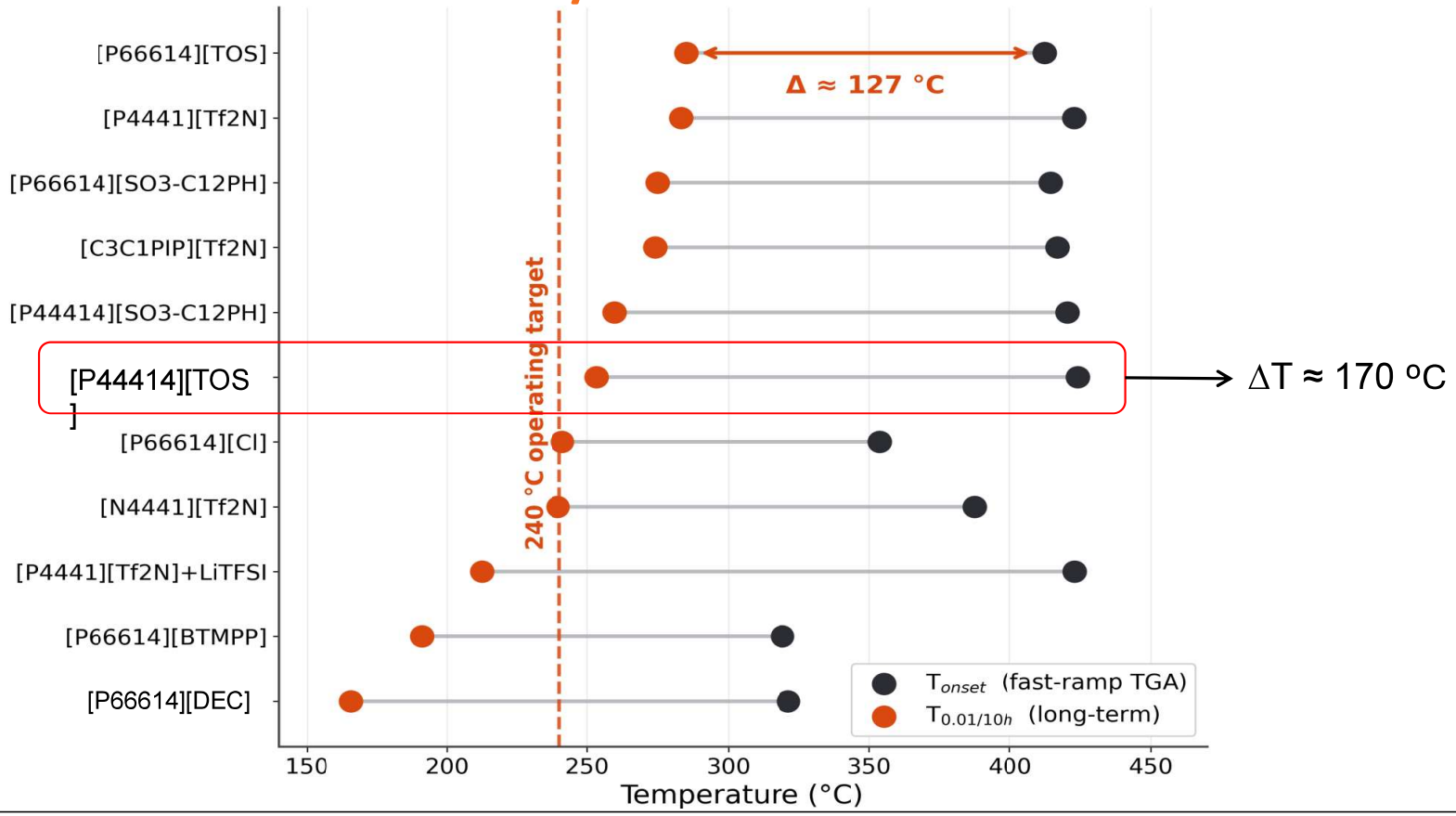
P44414.Tosylate 10 days Thermal Stability - FTIR



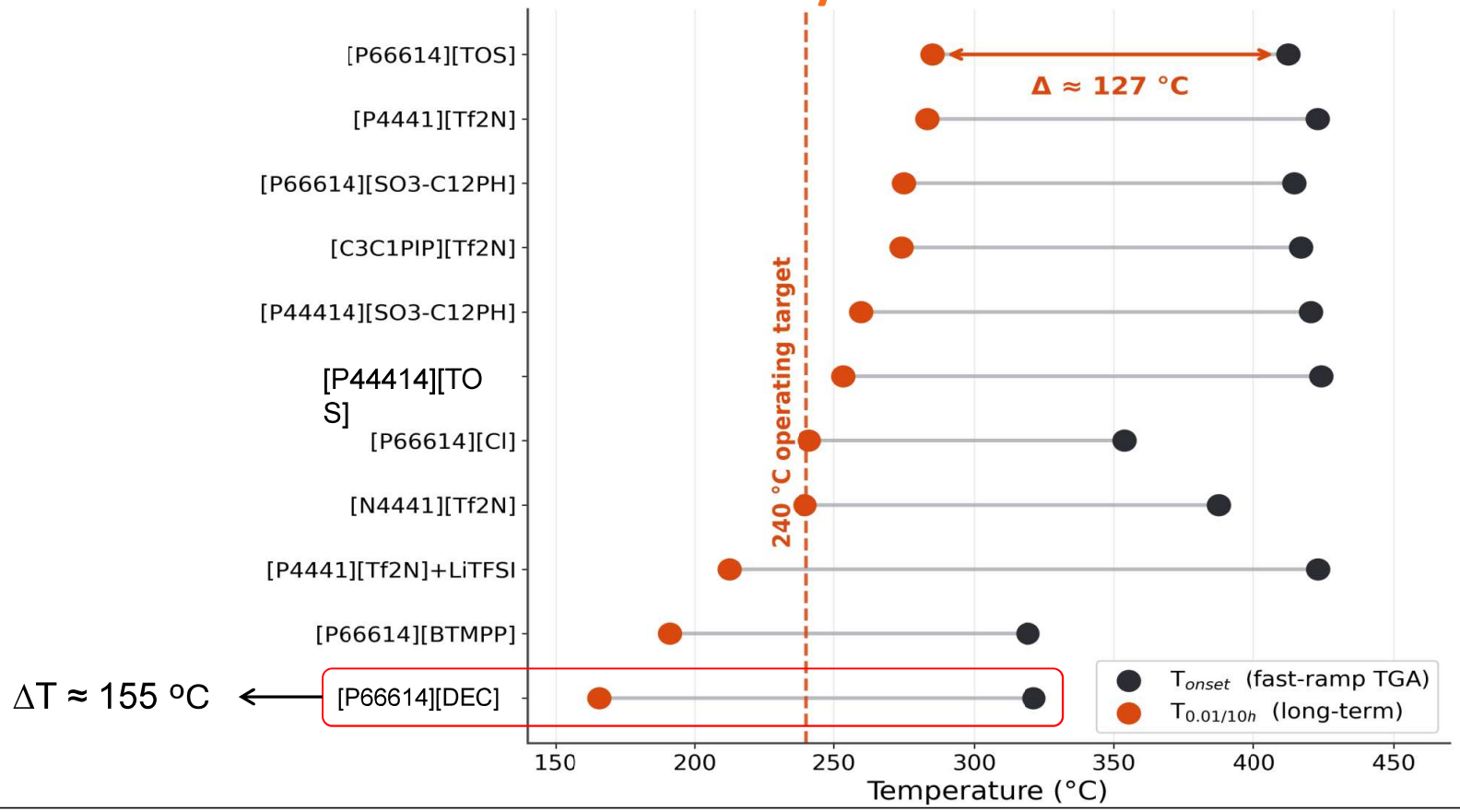




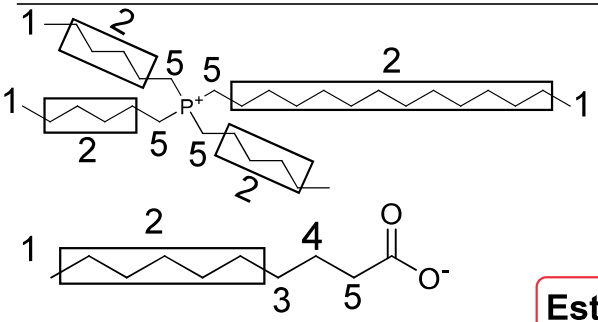
$T_{0.01/10h}$ x T_{onset}



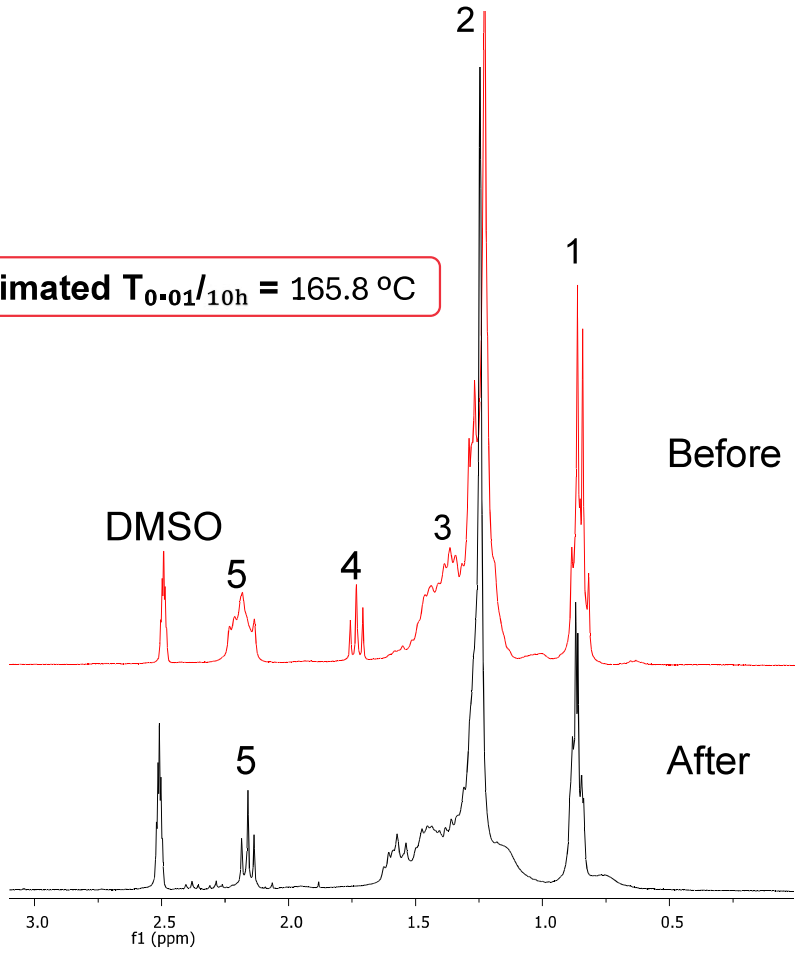
$T_{0.01/10h}$ x T_{onset}



H-NMR [P66614][DEC] 10 days Thermal Stability at 240 ºC



Estimated $T_{0.01}/_{10h}$ = 165.8 ºC



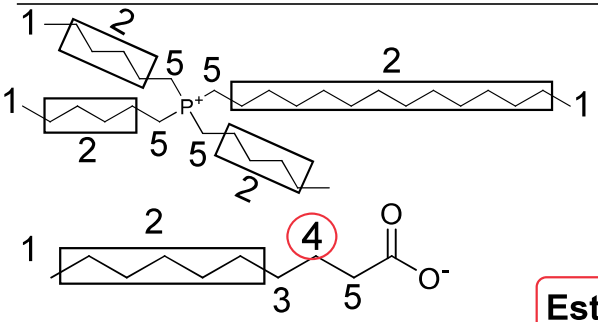
Before



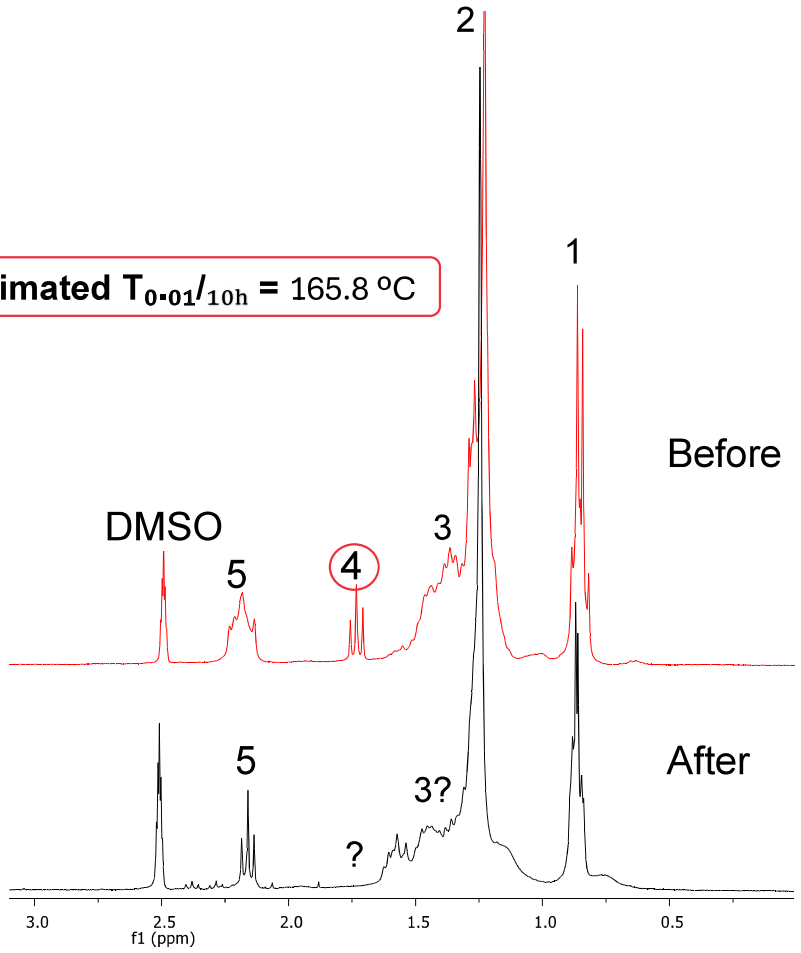
After



H-NMR [P66614][DEC] 10 days Thermal Stability at 240 ºC



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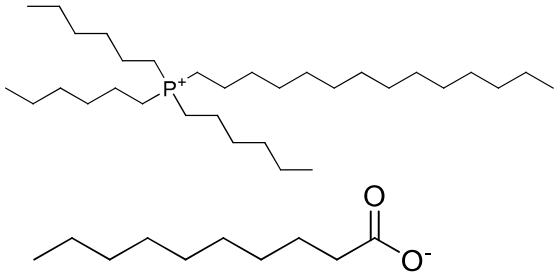
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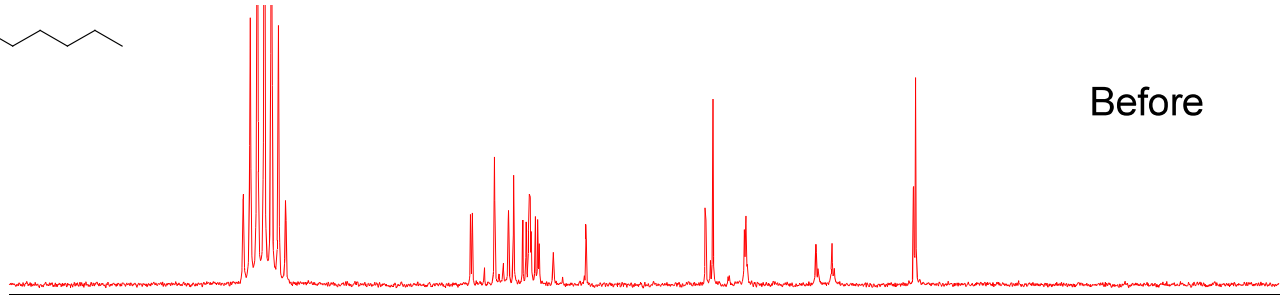


After



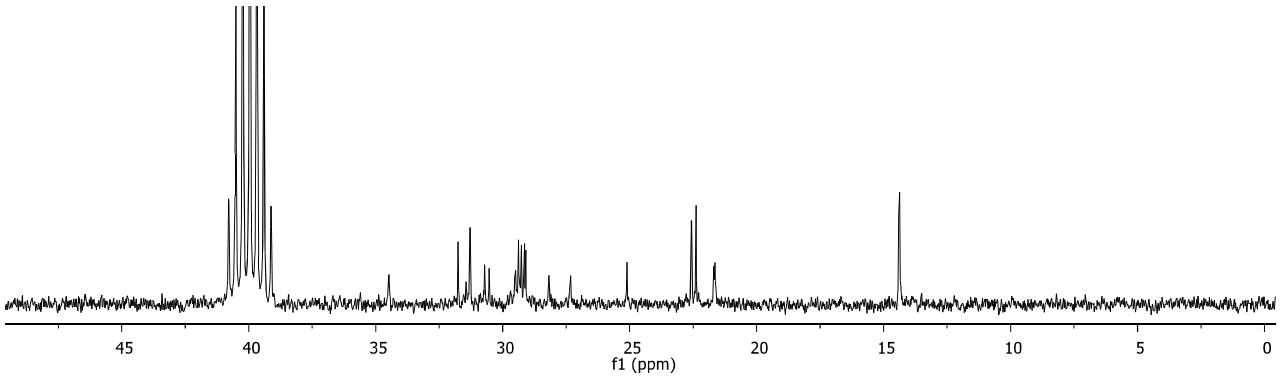
C-NMR [P66614][DEC] 10 days Thermal Stability at 240 ºC





Before

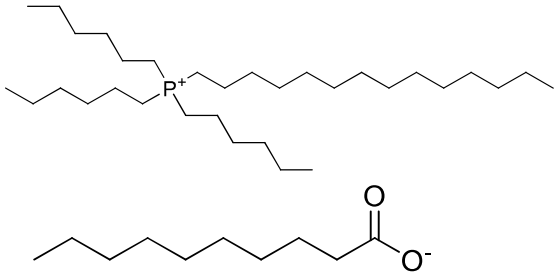


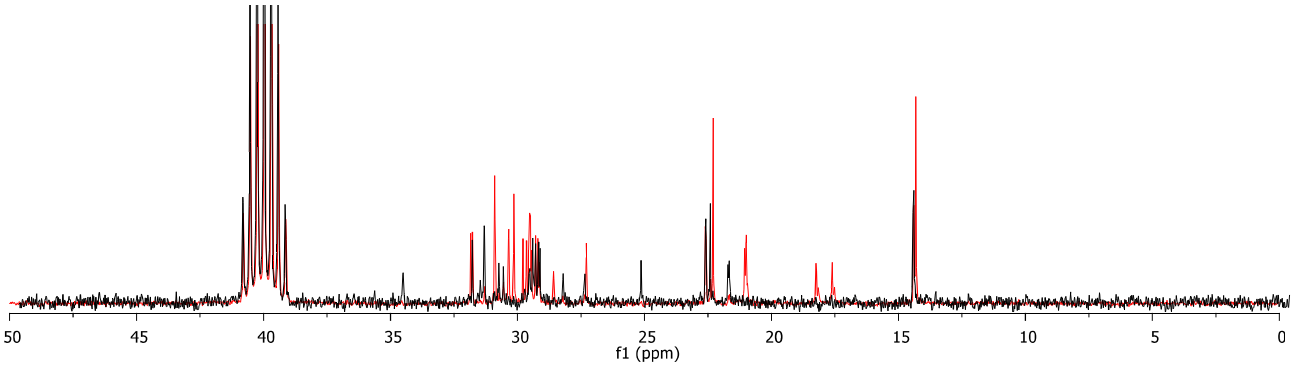


After



C-NMR [P66614][DEC] 10 days Thermal Stability at 240 ºC





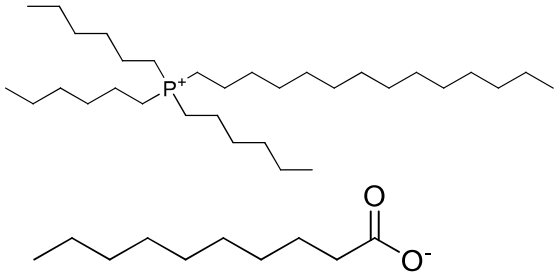
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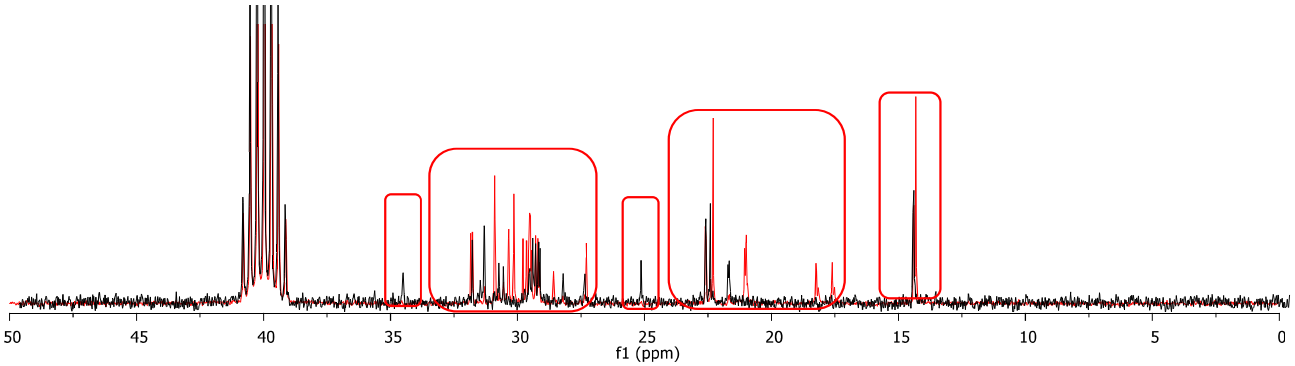


After



C-NMR [P66614][DEC] 10 days Thermal Stability at 240 ºC





Before



After



Thermal degradation of cyano containing ionic liquids

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Received 8th May 2006, Accepted 19th June 2006
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journal homepage: www.elsevier.com/locate/jct

Thermal stability of ionic liquids in nitrogen and air environments

Yong Huang [a], Zhichao Chen [b], Jacob M. Crosthwaite [c], Sudhir N.V.K. Aki [d], Joan F. Brennecke [b,*]

[a] Amyris, 5885 Hollis St. Suite 100, Emeryville, CA 94608, USA
[b] McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E Dean Keeton St, Austin, TX 78712, USA
[c] The Dow Chemical Company, Analytical Science, Building 1897-F11, Midland, MI 48667, USA
[d] Invista, Sabine River Laboratory B568, 3055 A FM Road, Orange, TX 77630, USA

2014

Largest published dataset of $T_{0.01/10h}$

First publication on $T_{0.01/10h}$

2006

Recent study of $T_{0.01/10h}$

2021

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Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis

Yuanyuan Cao and Tiancheng Mu*

Department of Chemistry, Renmin University of China, Beijing 100872, P. R. China

First publication on $T_{0.01/10h}$ **2006**

1 Dynamic TGA
10 °C min⁻¹ to 700 °C

2 5–8 isotherms
20 °C spacing within each family

3 Kinetic fit
Pseudo-zero order fit

4 Prediction
Estimate $T_{0.01/10h}$

Largest published dataset of $T_{0.01/10h}$ **2014**

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High experimental cost

1 Dynamic TGA
10 °C min^{-1} to 800 °C

2 1 Isothermal TGA
Temperature defined by Dynamic TGA

3 Kinetic fit
N order fit
Auto-catalytic fit

4 Prediction
Estimate $T_{0.01/10h}$

Proposed Methodolgy

Fn – n=0 → Used in previous studies

$$\frac{dm}{dt} = \mathrm{A}\exp\left(-\frac{E_a}{RT}\right)$$

Fn

$$\frac{d\alpha}{dt} = \mathrm{A}(1-\alpha)^n\exp\left(-\frac{E_a}{RT}\right)$$

Cn

$$\frac{d\alpha}{dx} = \mathrm{A}(1-\alpha)^n(1+k_{auto}b)\exp\left(-\frac{E_a}{RT}\right)$$

Cnm

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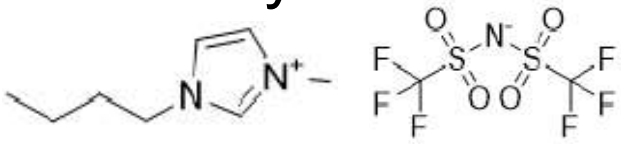
Cn

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Cnm

$$\frac{d\alpha}{dx} = \mathrm{A}(1-\alpha)^n (1 + k_{auto} b^m) \exp\left(-\frac{E_a}{RT}\right)$$

Only **2** TGAs?



1-butyl-3-methylimidazolium.Tf2N

Cao et. al

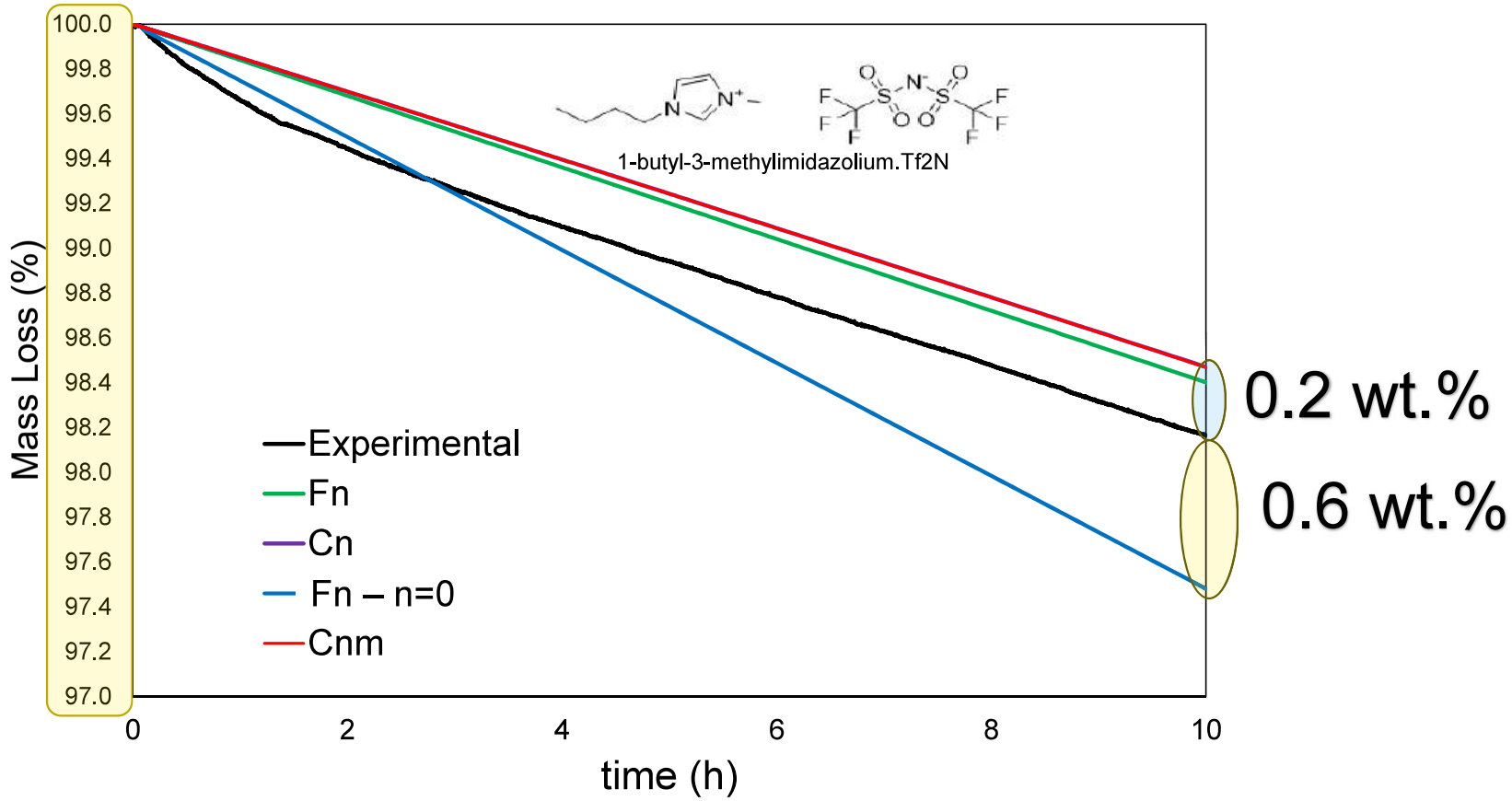
$$E_a = 126.4\ \frac{kJ}{mol}$$

Cao et. al

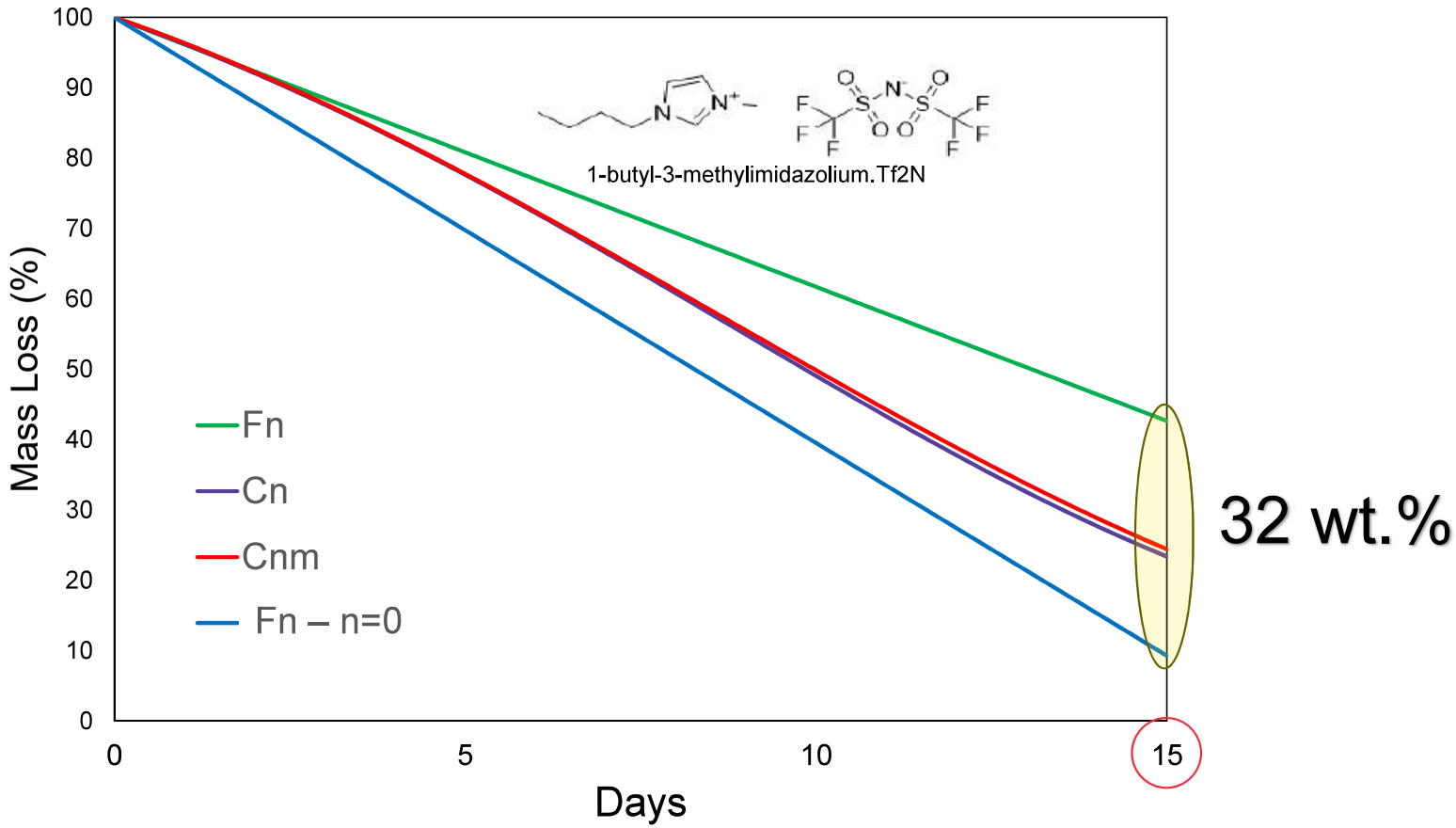
$$T_{0.01/10h} = 227.00\ °C$$

Isotherms	1 ramp (10 C/min - 800C)	**1 ramp (10 C/min - 800C) and Isotherm (300)**	1 ramp (10 C/min - 800C) and Isotherm (220 - 300)
N of TGA	1	**2**	6
Best Model	Cnm	**Cnm**	Cnm
$T_{0.01/10h}$ (UAv)	267.40	**236.40**	236.10
$T_{0.01/10h}$ (UAv)	160.40	**234.52**	234.36
Activation Energy (UAv)	154.23	**108.018**	109.71
Activation Energy (UAv)	65.37	**120.785**	120.87

Bmim.Tf2N 10 hours isotherm at 240 ºC



Bmim.Tf2N 15 days (prediction) isotherm at 240 ºC



1 METRIC

Tonset is not an operating limit

above $T_{0.01}$/10 h in the examples shown

Dynamic ≠ long-term stability

2 EXPERIMENTAL LOAD

Two TGAs reproduced the six-TGA fit

6 → 2 TGAs

$T_{0.01}$/10 h: 236.10 vs 236.40 °C

Difference: only 0.30 °C

3 EXTRAPOLATION

Model influence grows with prediction horizon

≤0.6 → 32 wt%

model spread: 10 h → 15 days (predicted)

Cnm gave the best fit

Thank You, Questions?



CIRCECO

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