# Characterization of polymer brushes on polyethylene films by fluorescence



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# Overview

- Introduction
  - Films, Synthesis, Pyrene fluorescence
- Results
  - Physical Characterization
  - Photophysical Characterization
- Conclusions

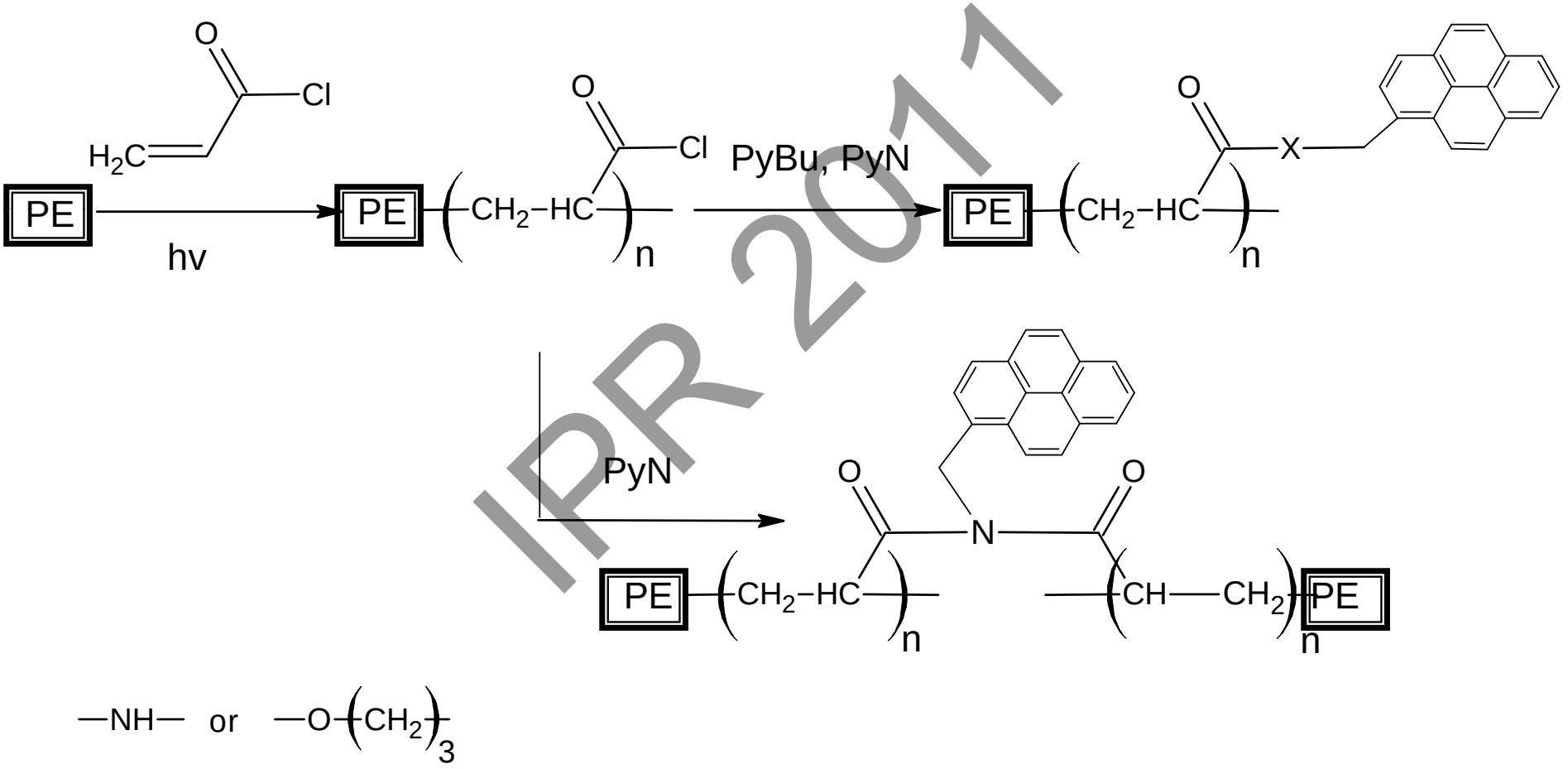
# Background

- Mechanically durable polymer films have desirable physical properties, but often lack functional groups
- Functional polymers allow the incorporation of interesting chemical groups, but may not be physically strong.
- A simple method of combining the best properties of both polymers is to graft a functional polymer from a mechanically durable polymer film.

# Film Composition

- Film samples were synthesized from Polyethylene (PE) plates
- Poly(Acryloyl Chloride) (AC) was incorporated into the plates using ionizing radiation via a grafting-onto scheme.
- The AC groups were capped with either a pyrene derivative or methanol to yield the final product.

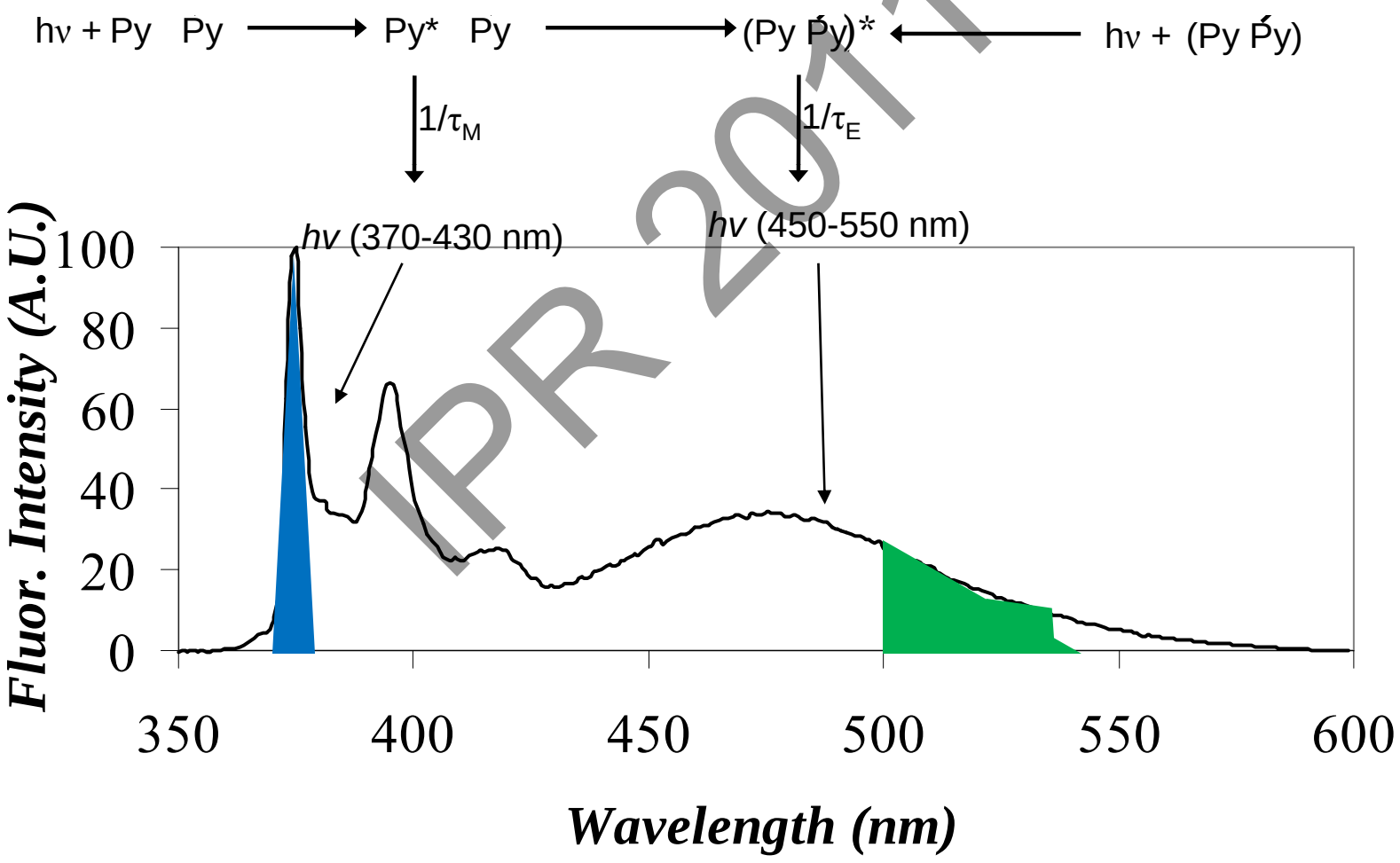
# Synthesis Scheme




—NH— or —O—(CH$_2$)$_3$—

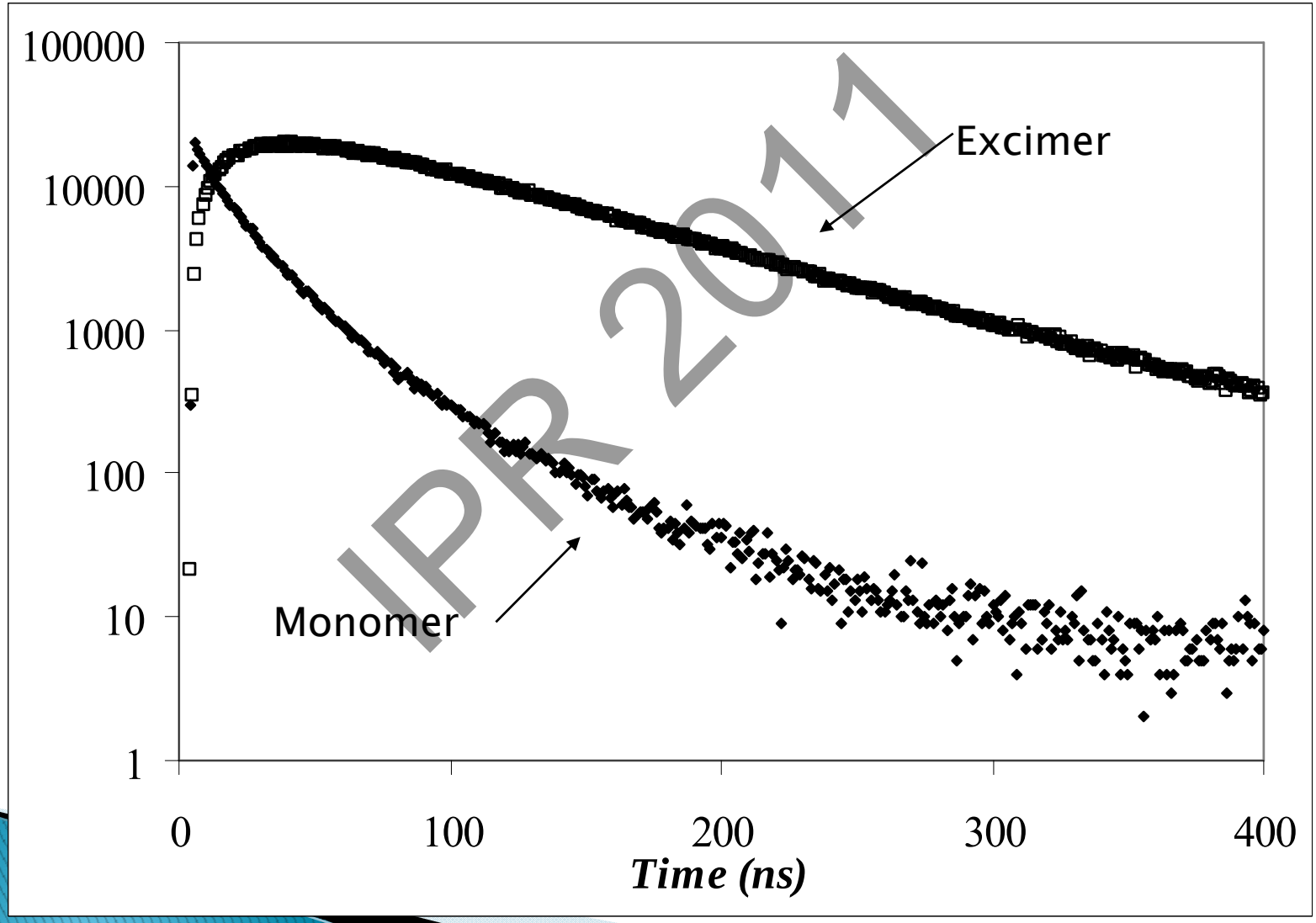
# Pyrene Fluorescence

$$\frac{I_E}{I_M}$$



# Fluorescence Decays

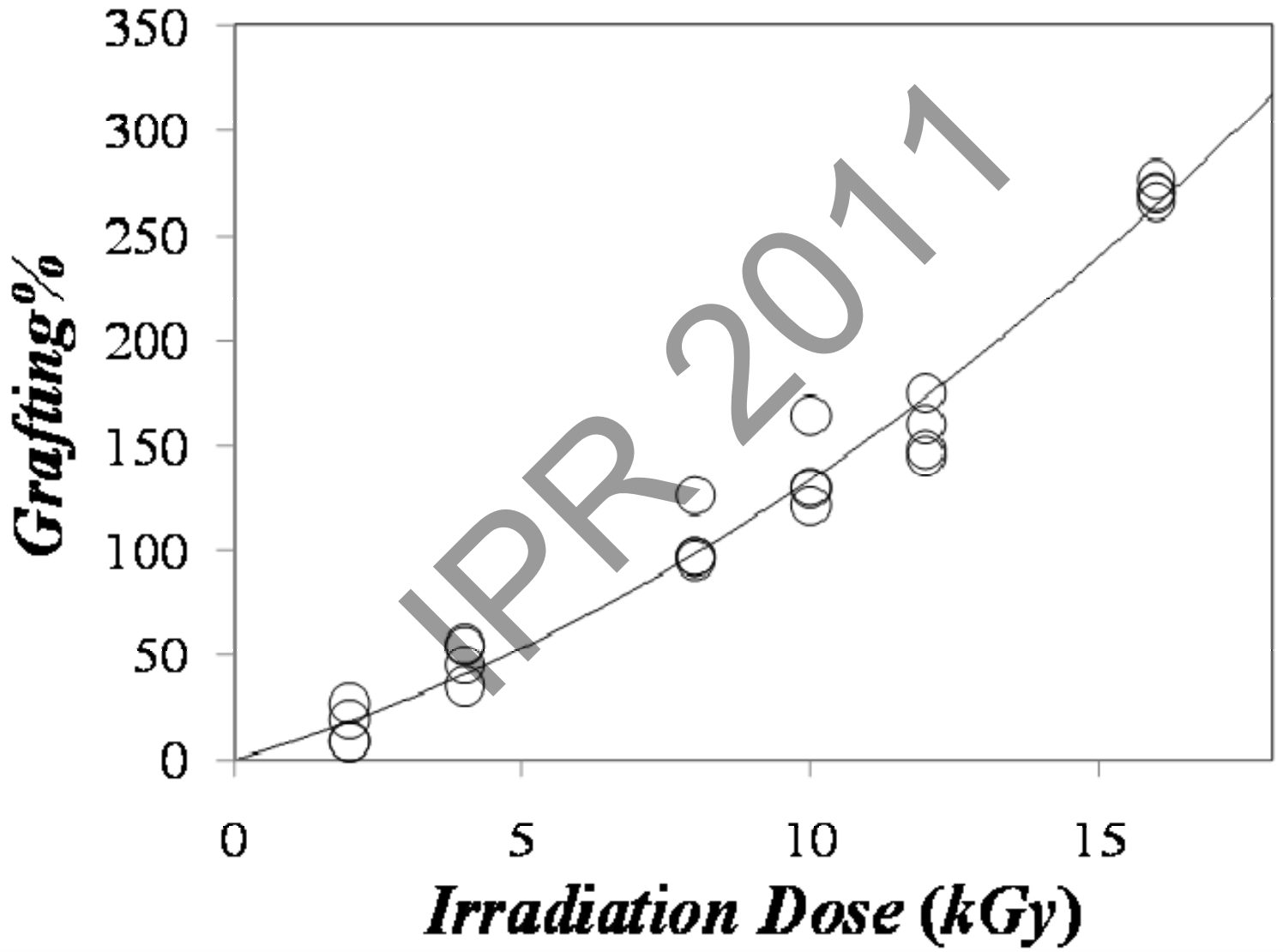
$$I_t = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$



# Results

## Physical Characterization

# Grafting Yield



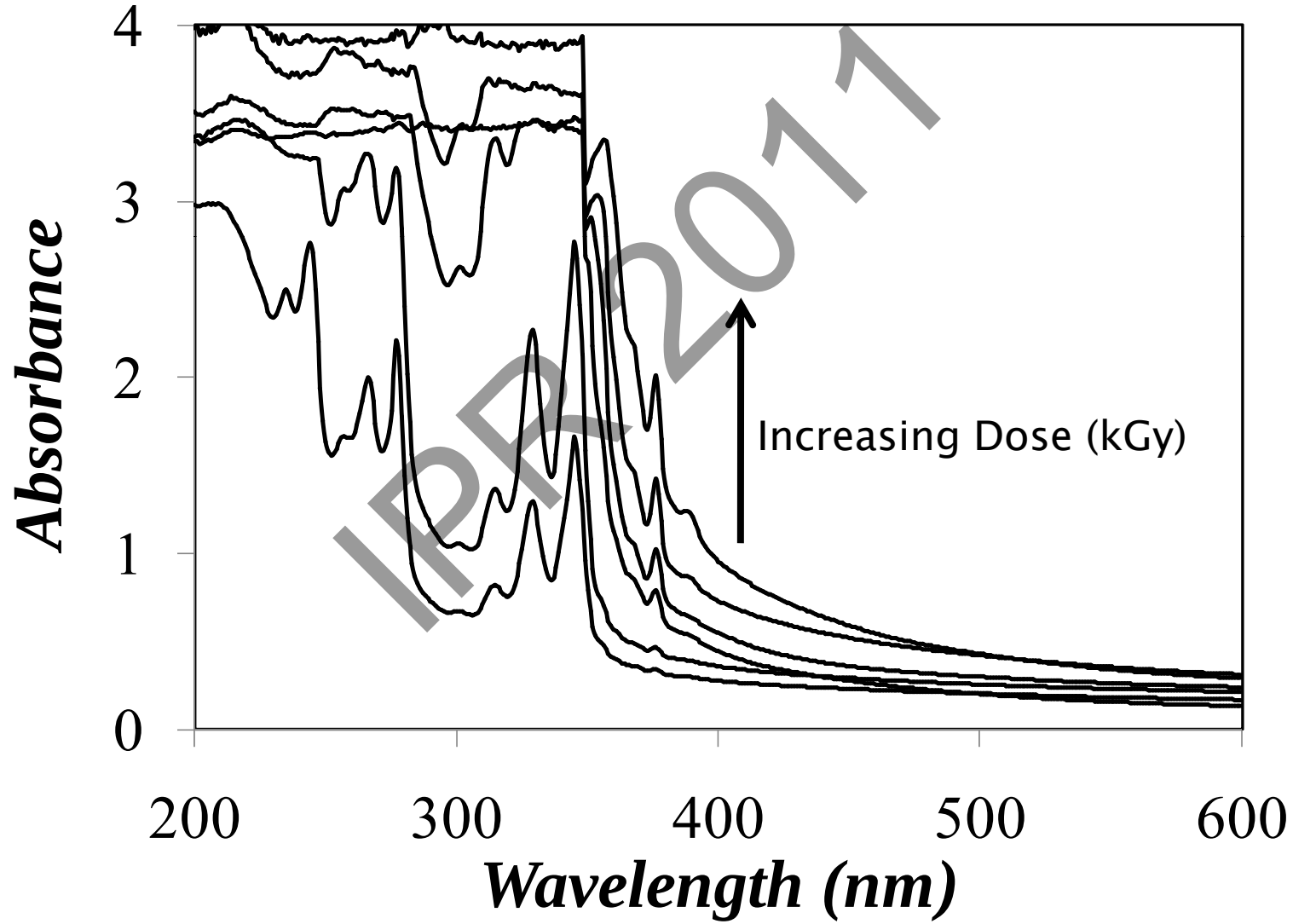
# Pyrene Content

| Sample | *Py-Grafting%* | *x* (without crosslinks) | *x*/2 (with crosslinks) |
|---|---|---|---|
| AC-g-PE-PyBu-2kGy | 46 | 1.00* | |
| AC-g-PE-PyBu-4kGy | 18 | 0.19 | |
| AC-g-PE-PyBu-8kGy | 23 | 0.15 | |
| AC-g-PE-PyBu-10kGy | 30 | 0.17 | |
| AC-g-PE-PyBu-12kGy | 13 | 0.08 | |
| AC-g-PE-PyBu-16kGy | 20 | 0.10 | |
| AC-g-PE-PyN-2kGy | 24 | 0.49* | 0.43 |
| AC-g-PE-PyN-4kGy | 31 | 0.38 | 0.33 |
| AC-g-PE-PyN-8kGy | 36 | 0.32 | 0.28 |
| AC-g-PE-PyN-10kGy | 33 | 0.25 | 0.22 |
| AC-g-PE-PyN-12kGy | 17 | 0.12 | 0.11 |
| AC-g-PE-PyN-16kGy | 38 | 0.23 | 0.20 |

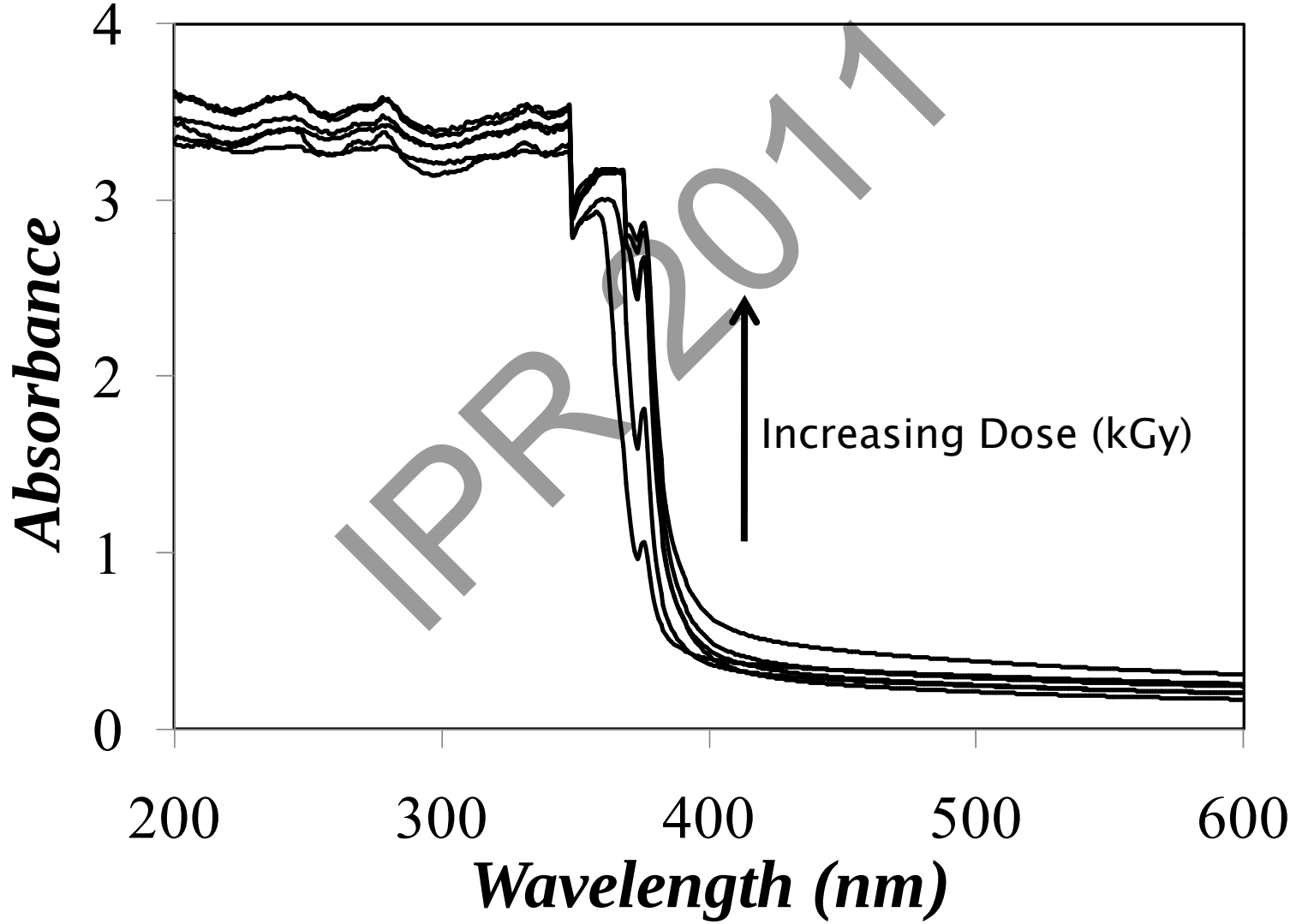
# Results

## Photophysical Characterization

# UV Absorbance – PyBu

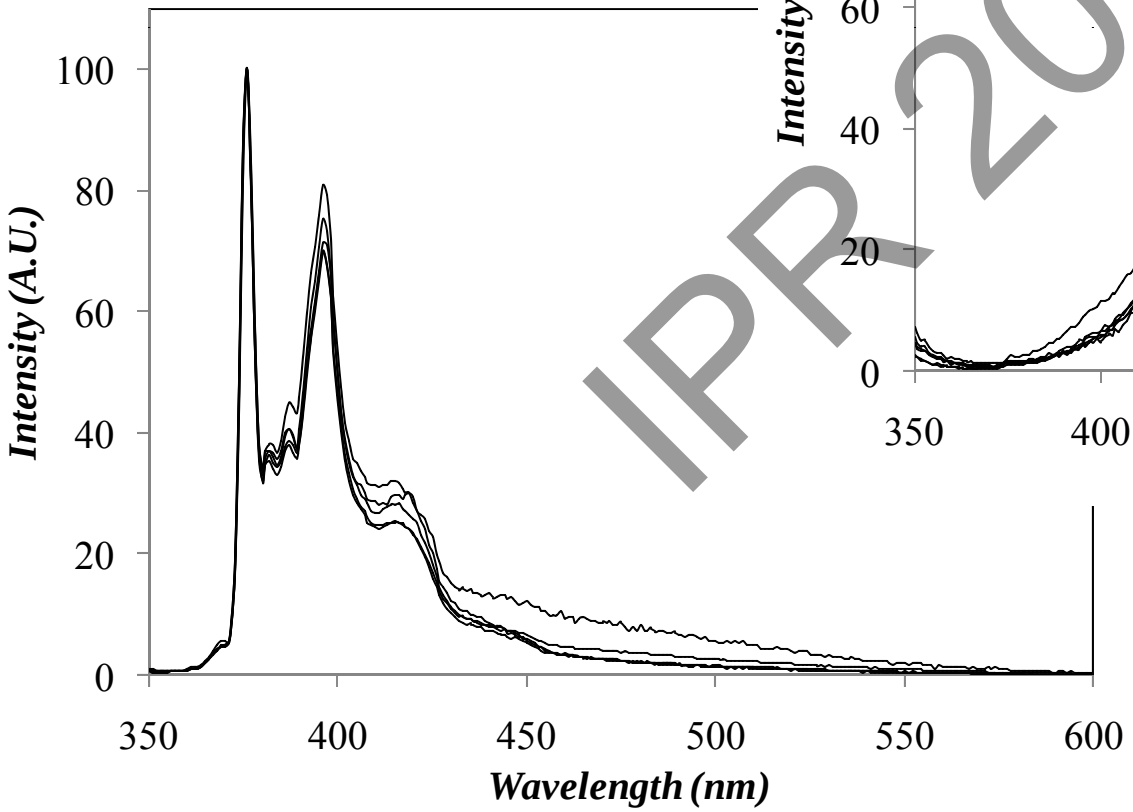


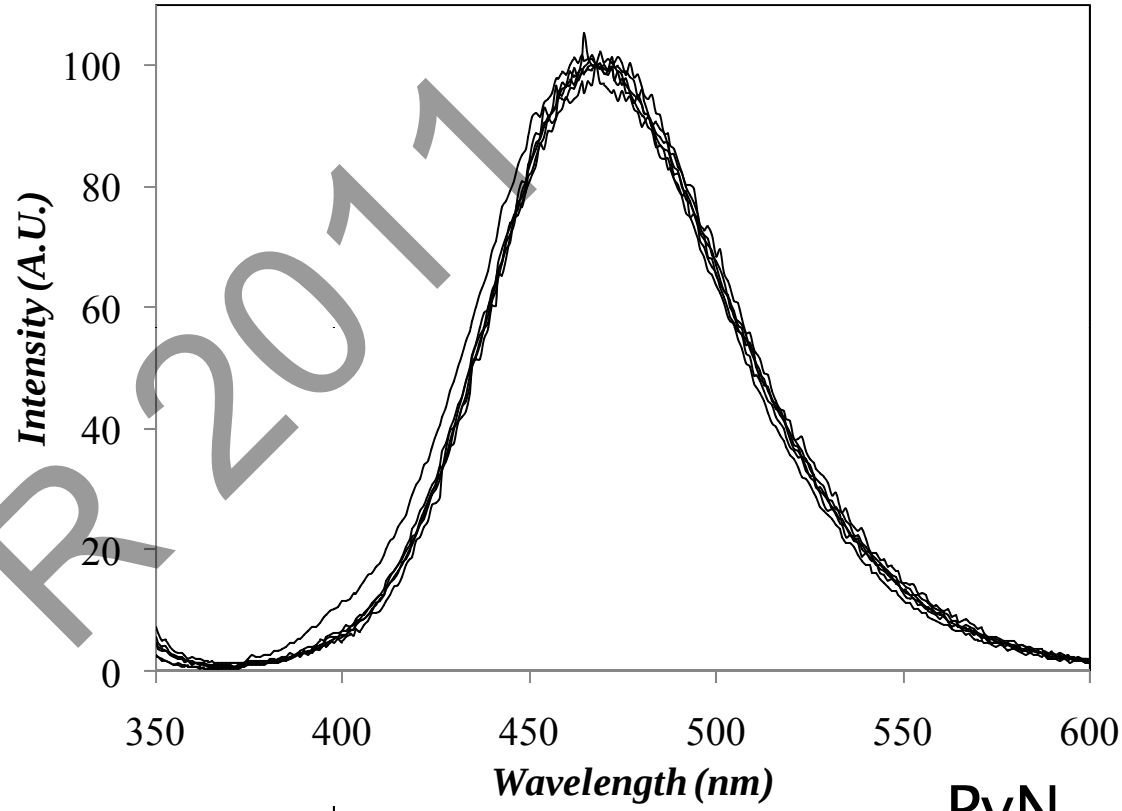
# UV Absorbance – PyN



# Fluorescence Emission –Dry State

PyBu




PyN

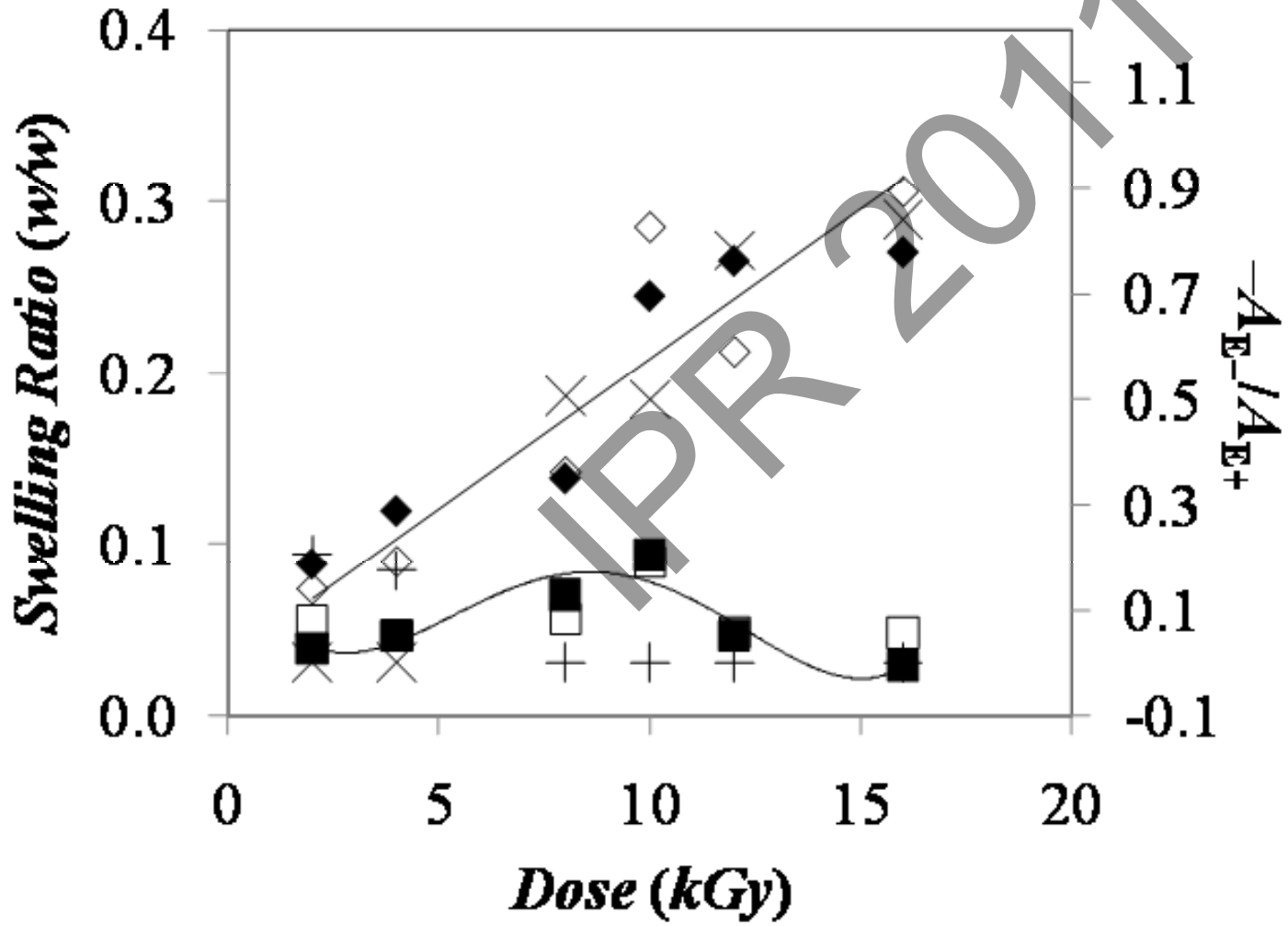


$k_{diff}$ = v. small, constant

$[Py]_{loc}$ = variable

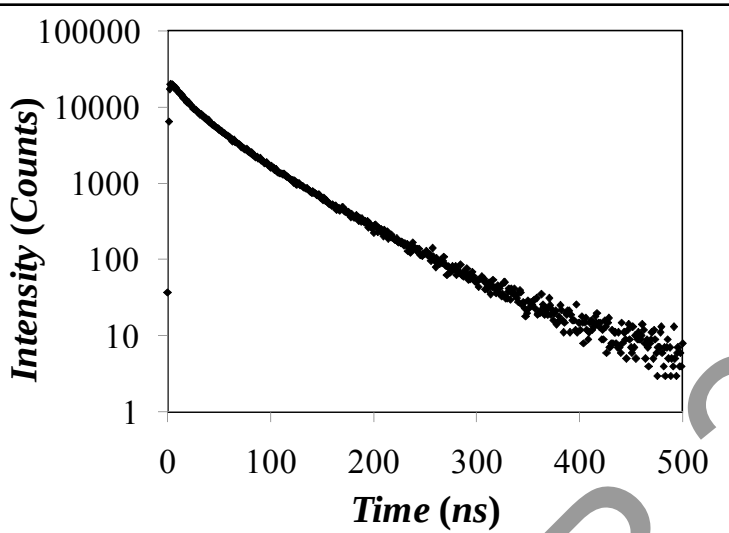
# Swelling Behaviour

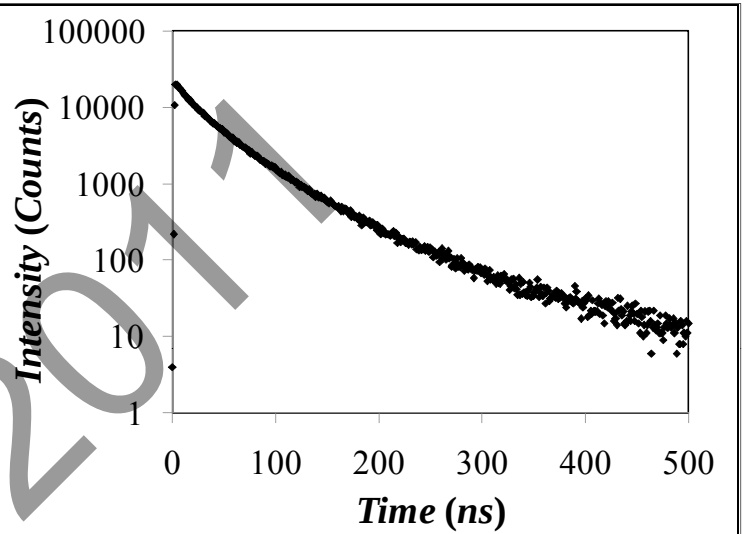
◇◆Swelling, PyBu
□■Swelling, PyN
X $A_{E-}/A_{E+}$ PyBu
+ $A_{E-}/A_{E+}$ PyN



# Excimer Decays (16 kGy)

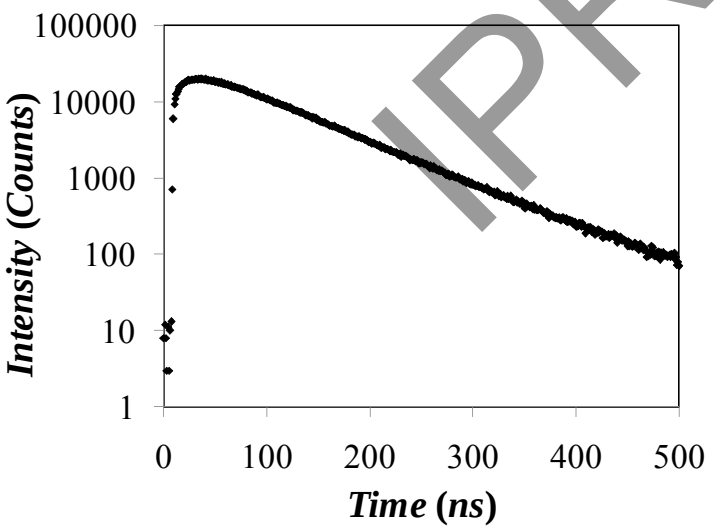
PyBu (Dry)

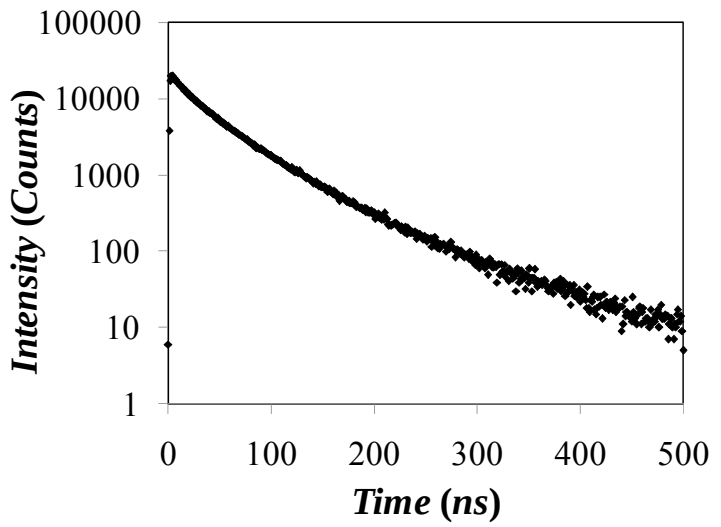



PyN (Dry)

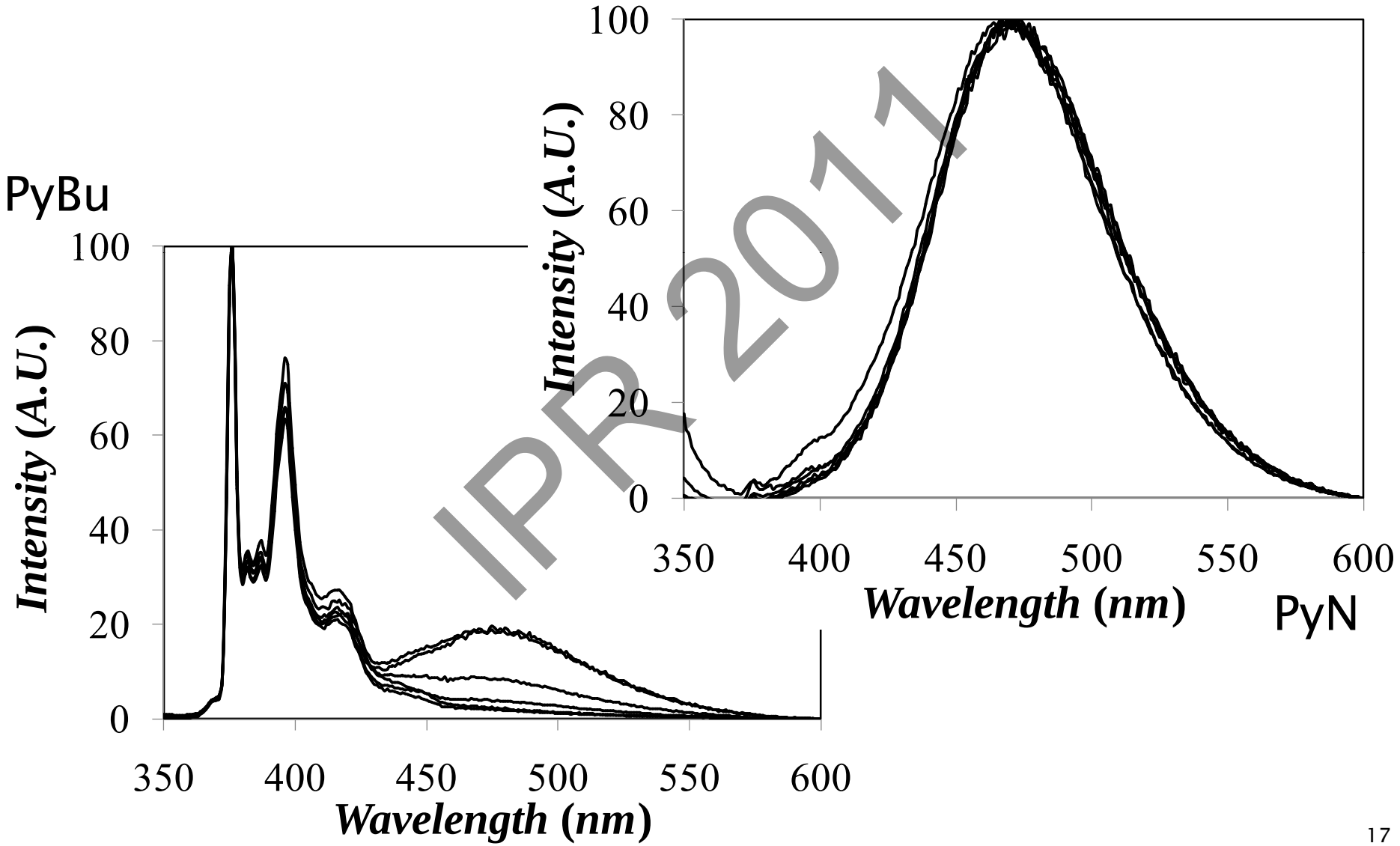
PyBu (Swollen)



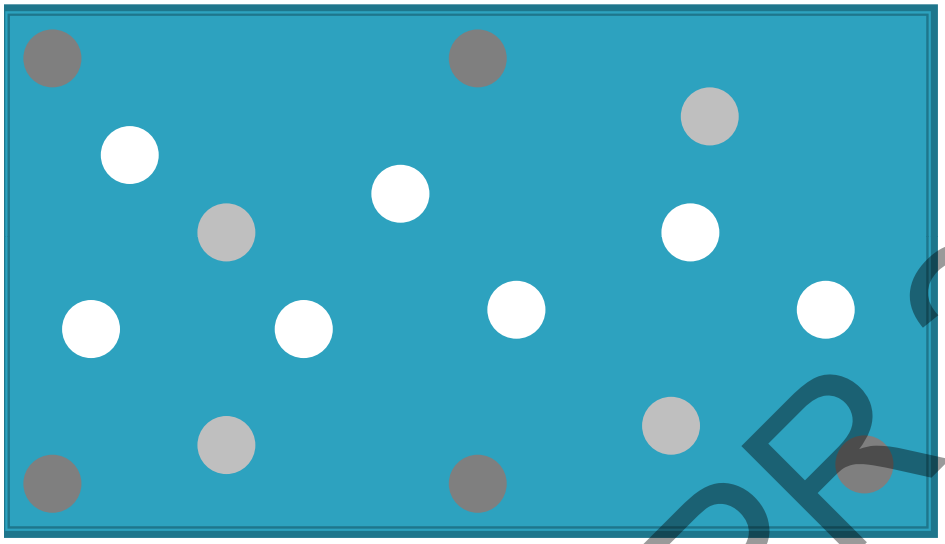




PyN (Swollen)

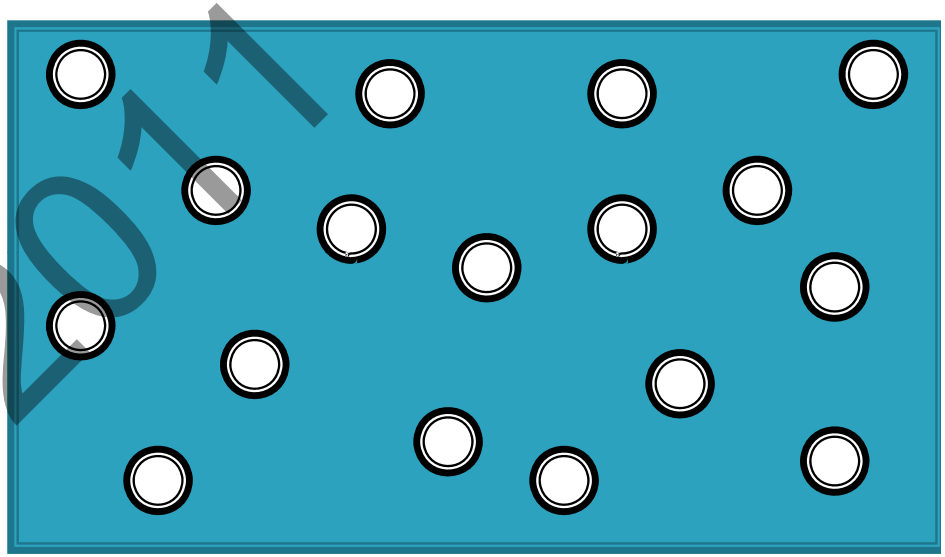
# Fluorescence Emission –Swollen State



# Distribution of Pyrene



PyBu



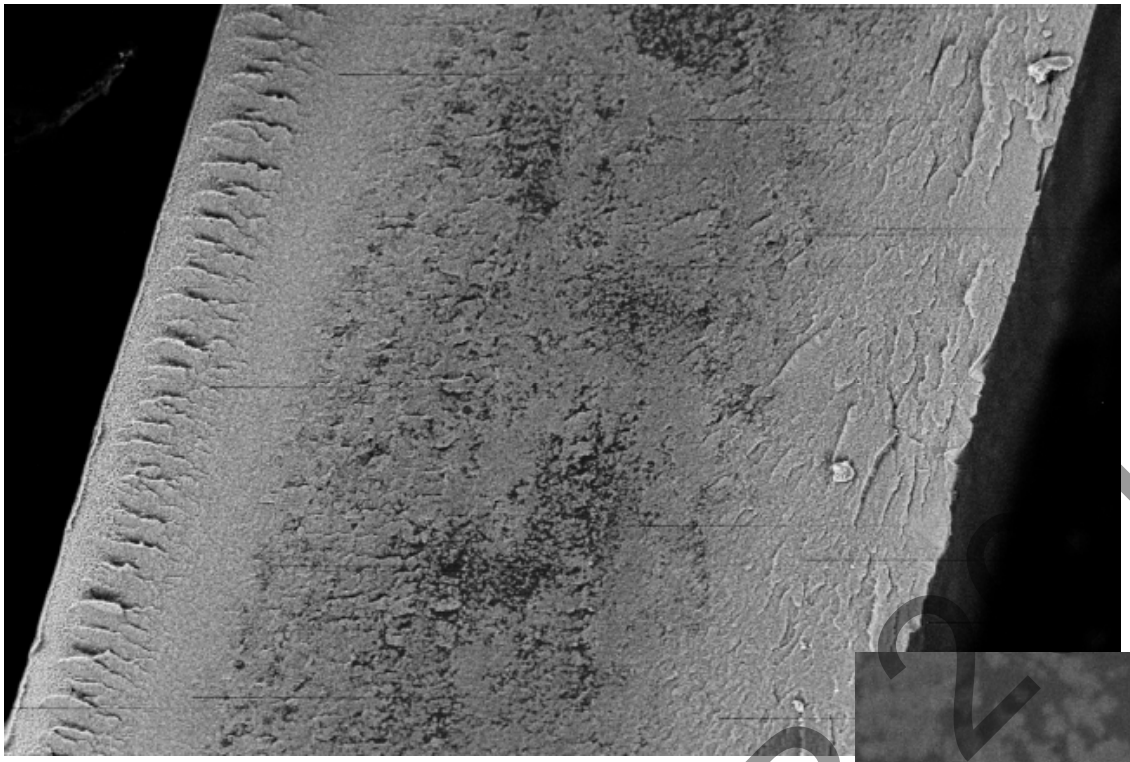
PyN

# SEM Imaging

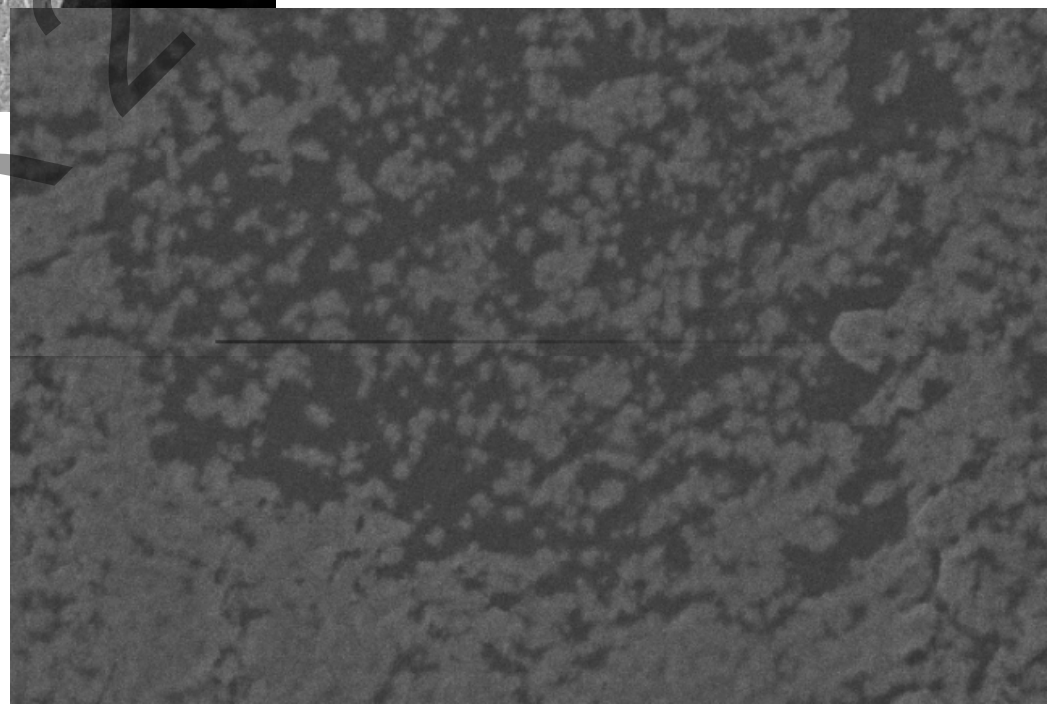
- To better determine the distribution of pyrene and AC within the films, selected samples were prepared for scanning electron microscopy.

- Samples were stained with $RuO_4$ by vapour deposition; $RuO_4$ preferentially stains the aromatic rings of Pyrene increasing the scattering signal.

# SEM – PyN 8k

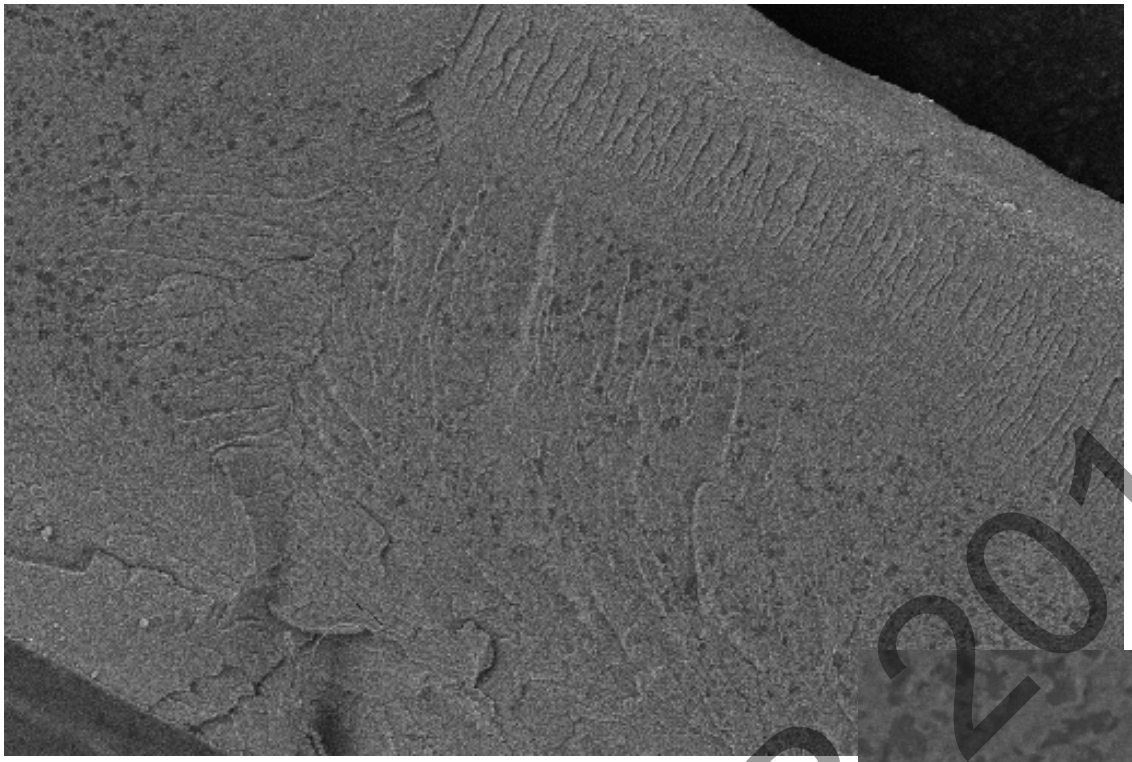


185 μm



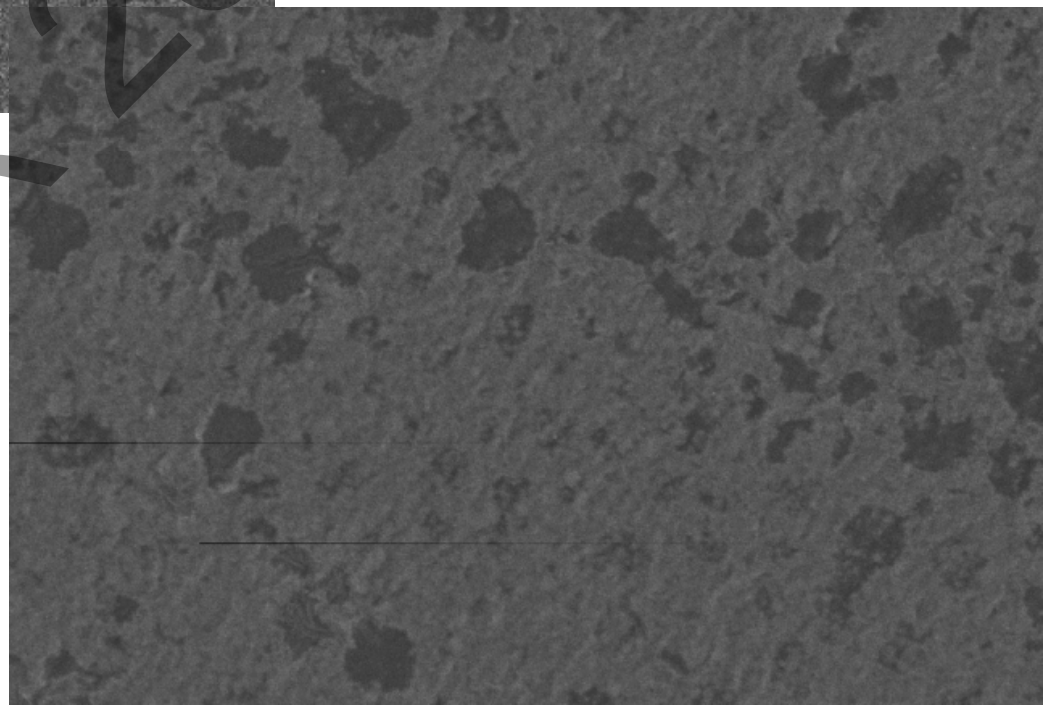
26 μm

# SEM – PyN 12k

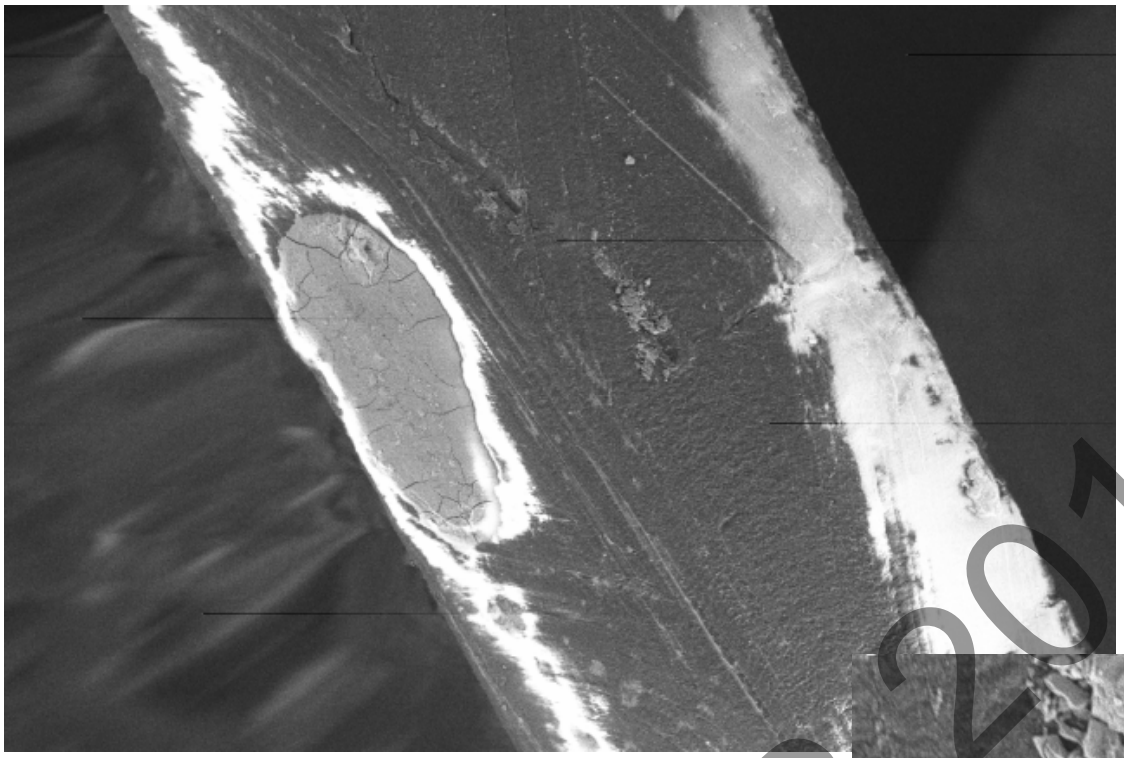


185 μm

26 μm

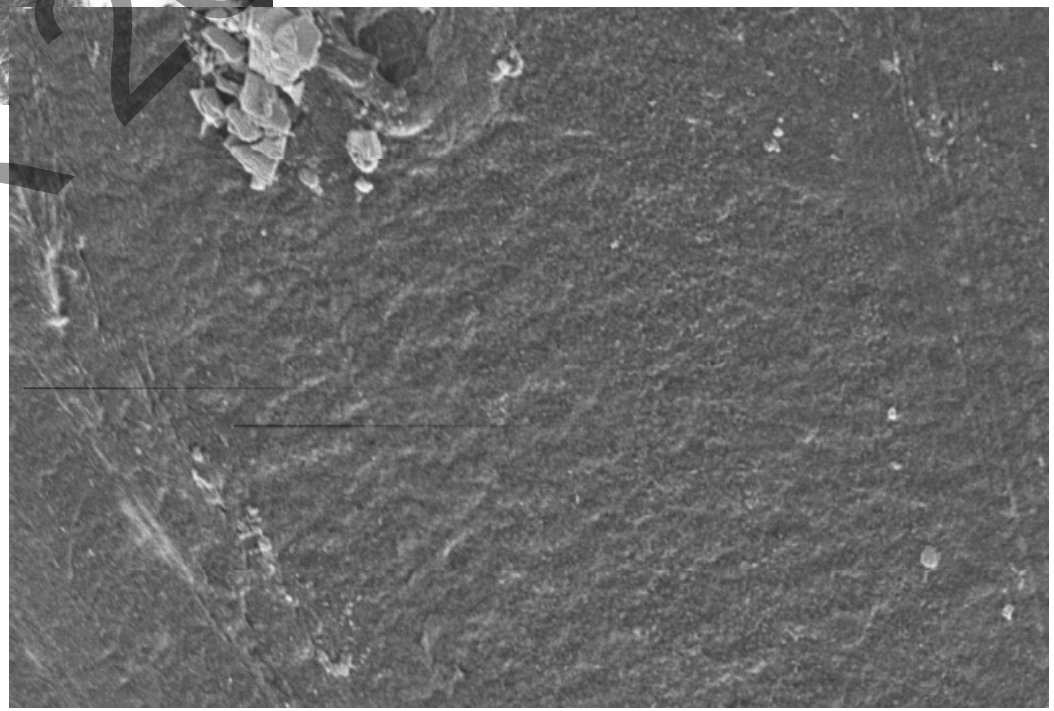


# SEM – PyBu 12k



185 µm

26 µm



# Conclusions

- SS emission shows that the PyBu samples have a much lower $[Py]_{loc}$ than PyN in the dry state, even though their actual pyrene contents are comparable.
- Swelling of the films increases the mobility of the pyrene in the PyBu samples, giving rise to more diffusional excimer formation. The PyN samples are largely unaffected by acetone.
- SEM imaging shows phase separation in the PyN samples but not the PyBu samples.

# Conclusions

- This behaviour is consistent with the PyN label crosslinking the AC phase of the film, as it prevents swelling and alters the visible morphology of the film.

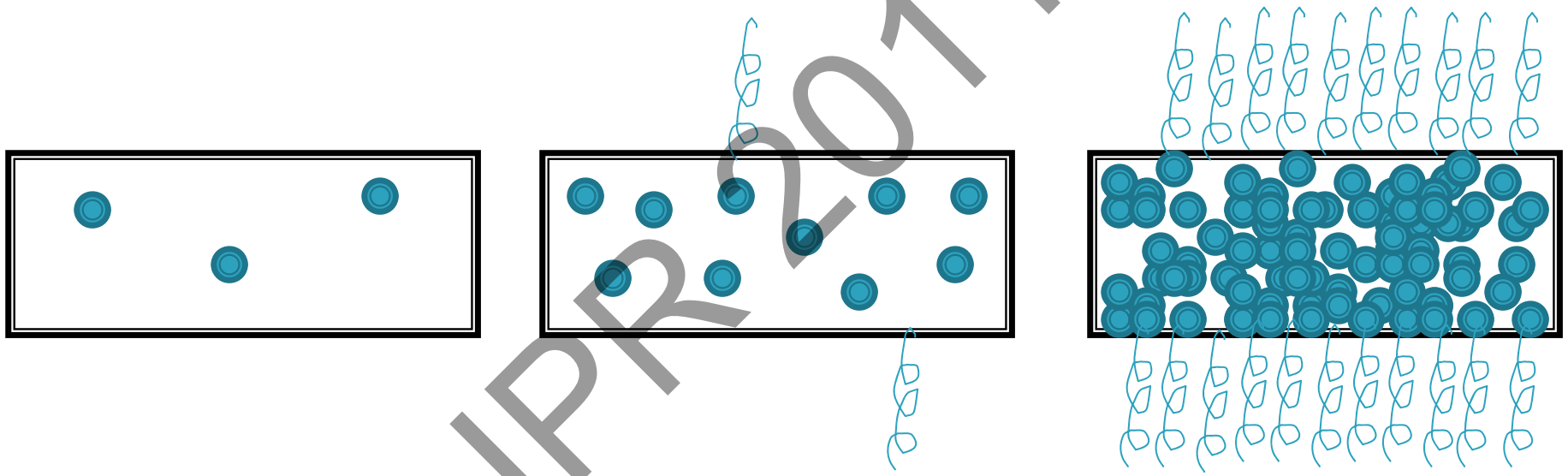
- This work shows that the alteration of a single functional group within a polymer film can have drastic effects on the physical and photophysical properties of the sample

# Acknowledgements


- Jamie Yip
- Jean Duhamel
- Adriana Gelover-Santiago, Guillermina Burillo and Ernesto Rivera
- Duhamel Group
- Gauthier Group
- Nina Heinig

# Questions?

# Distribution of Grafted Polymer



Low Dose

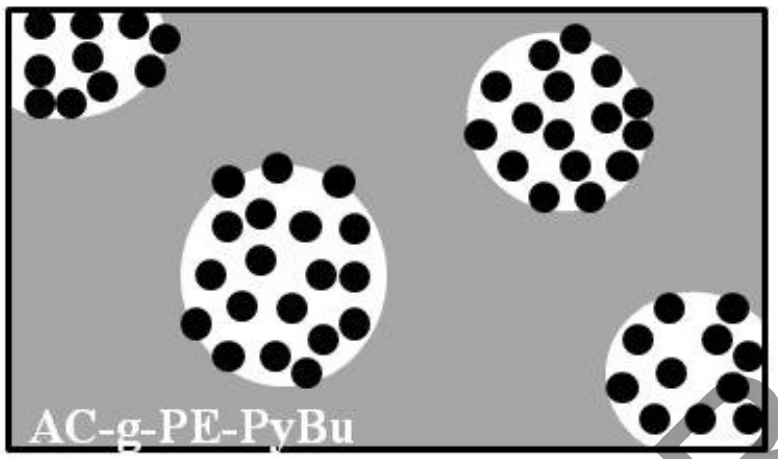
Medium Dose

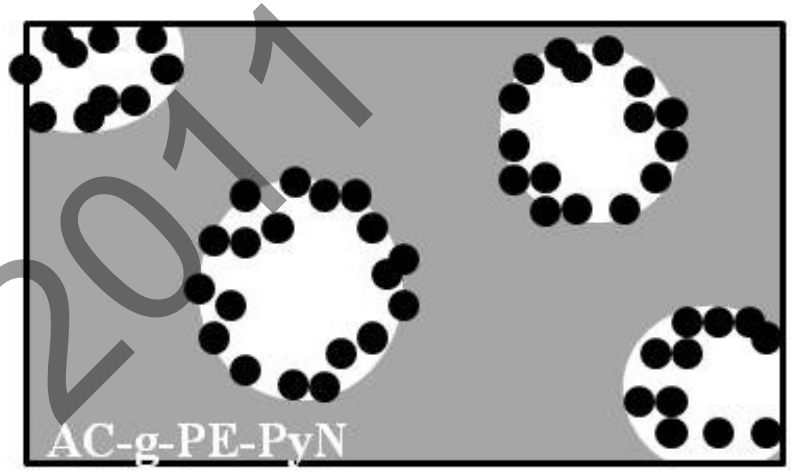
High Dose



Dry Films: Polymer is collapsed against the film!

# Effect of Distribution



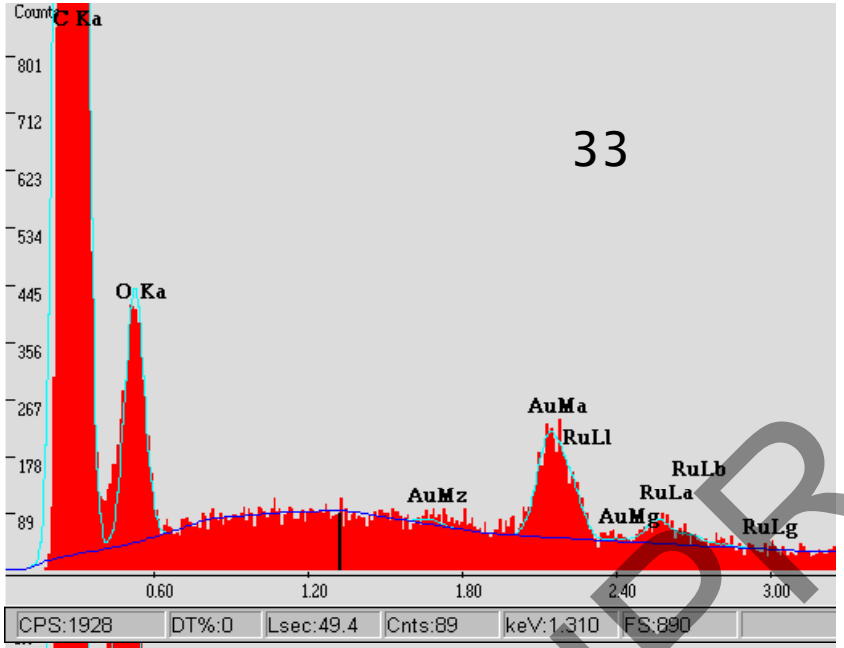



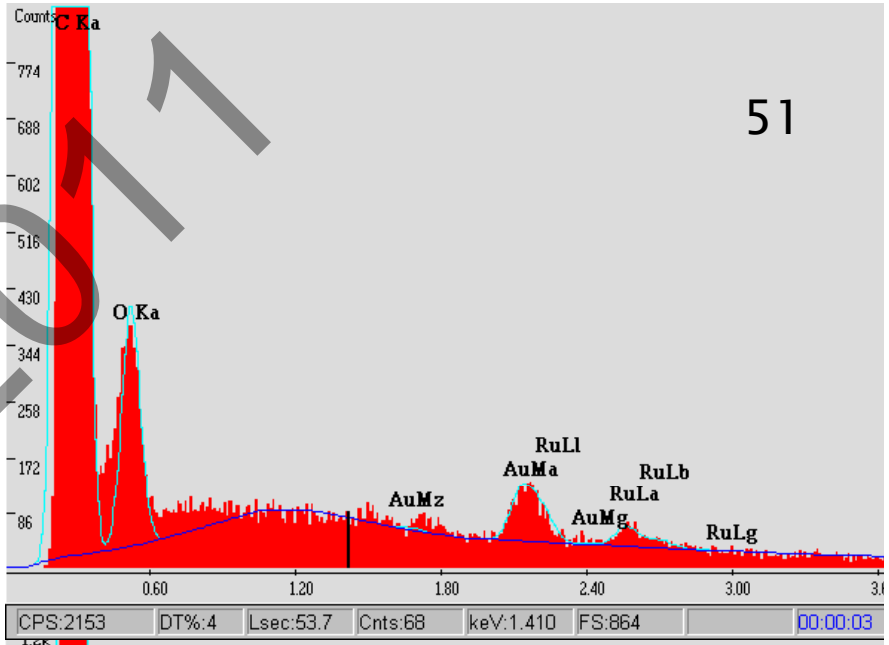


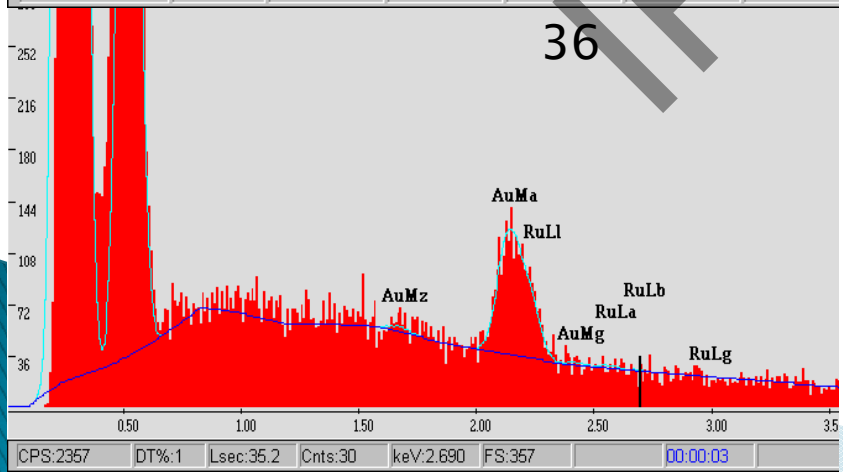

Evenly Distributed Pyrenes
- Less Efficient Absorption/Pyrene

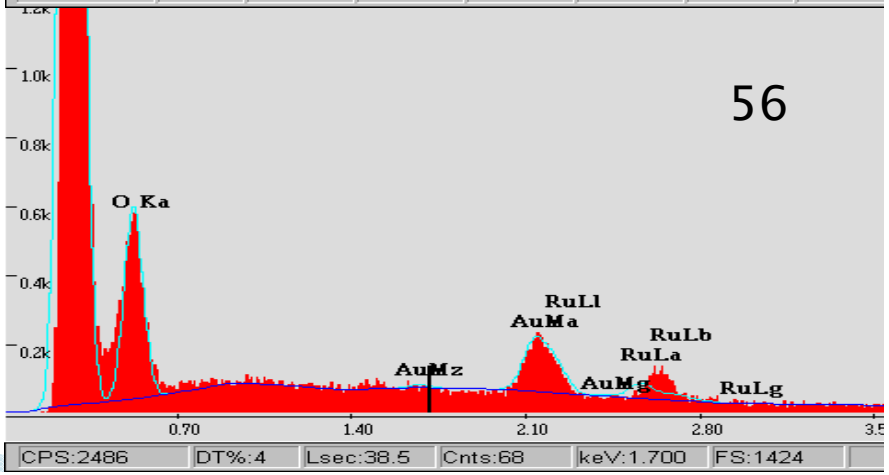
Pyrene localized at interfaces
- Better Absorption/Pyrene

# Elemental Analysis



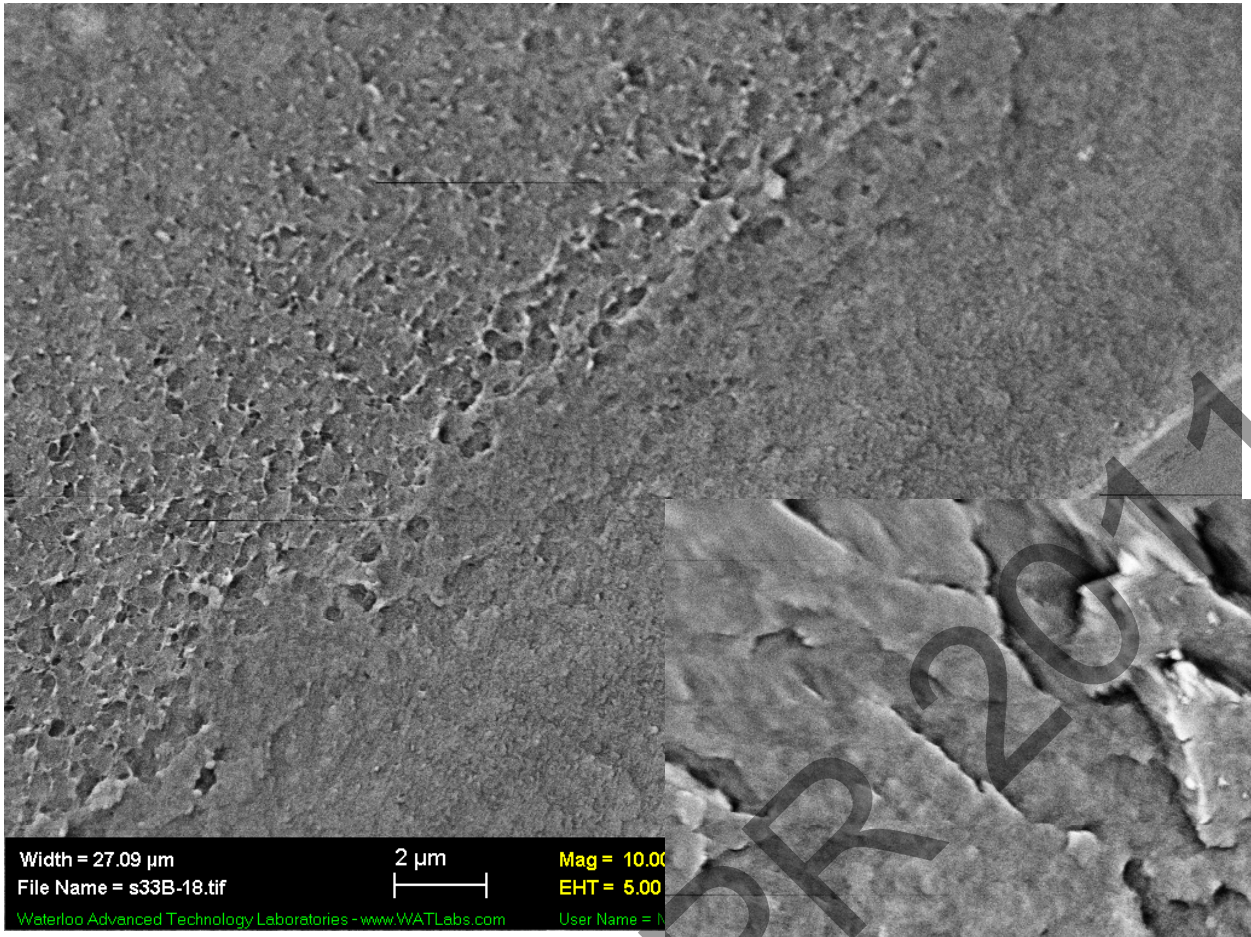



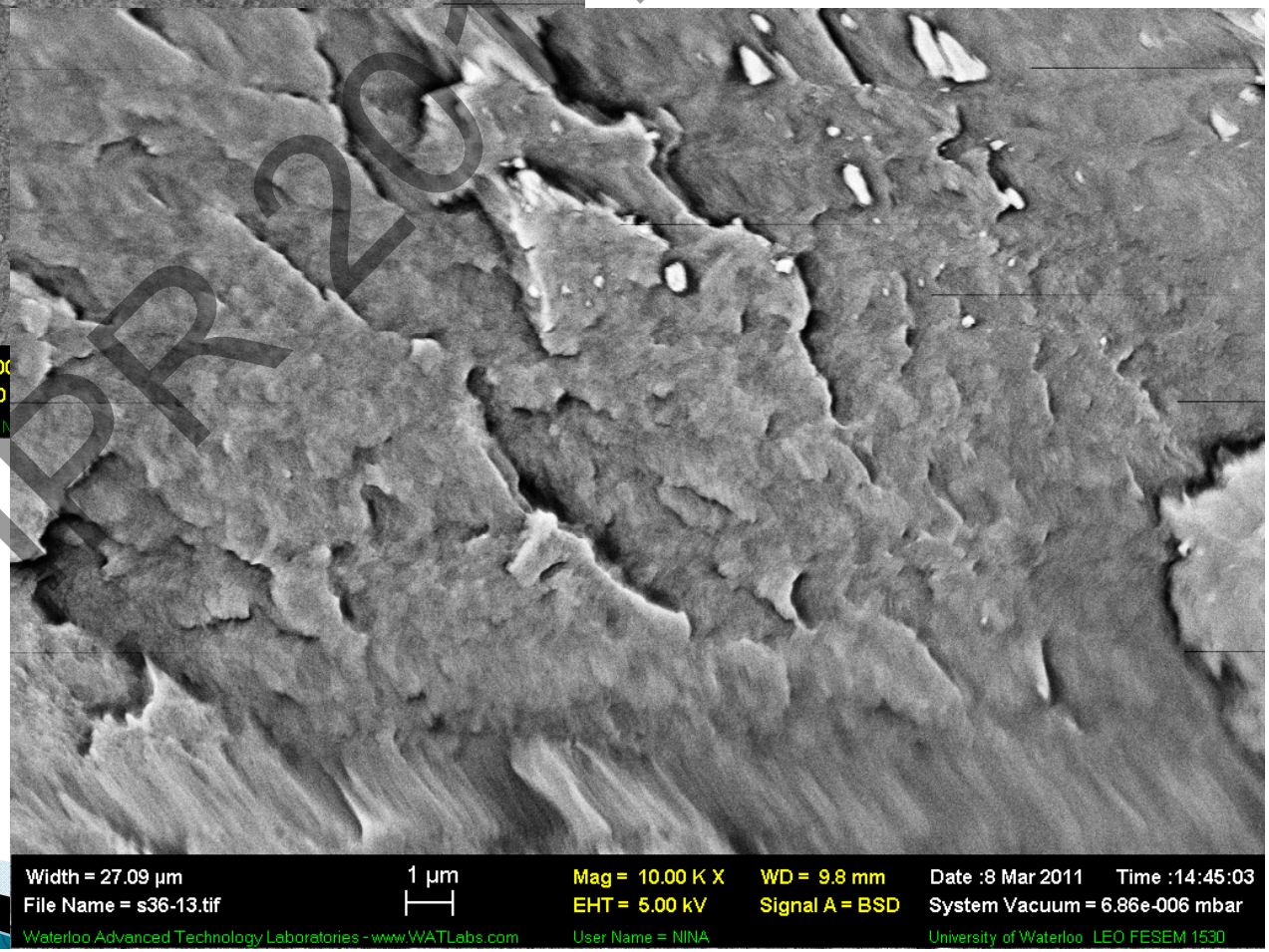



# SEM – PyBu

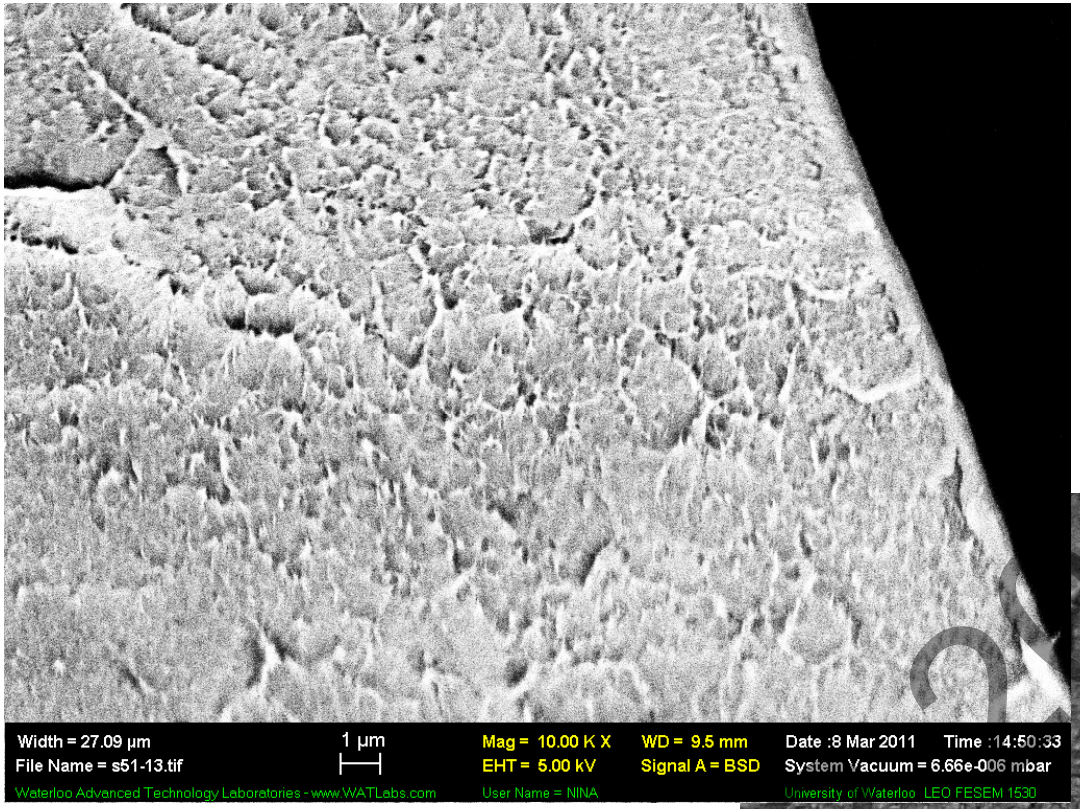
16 kGy




8 kGy

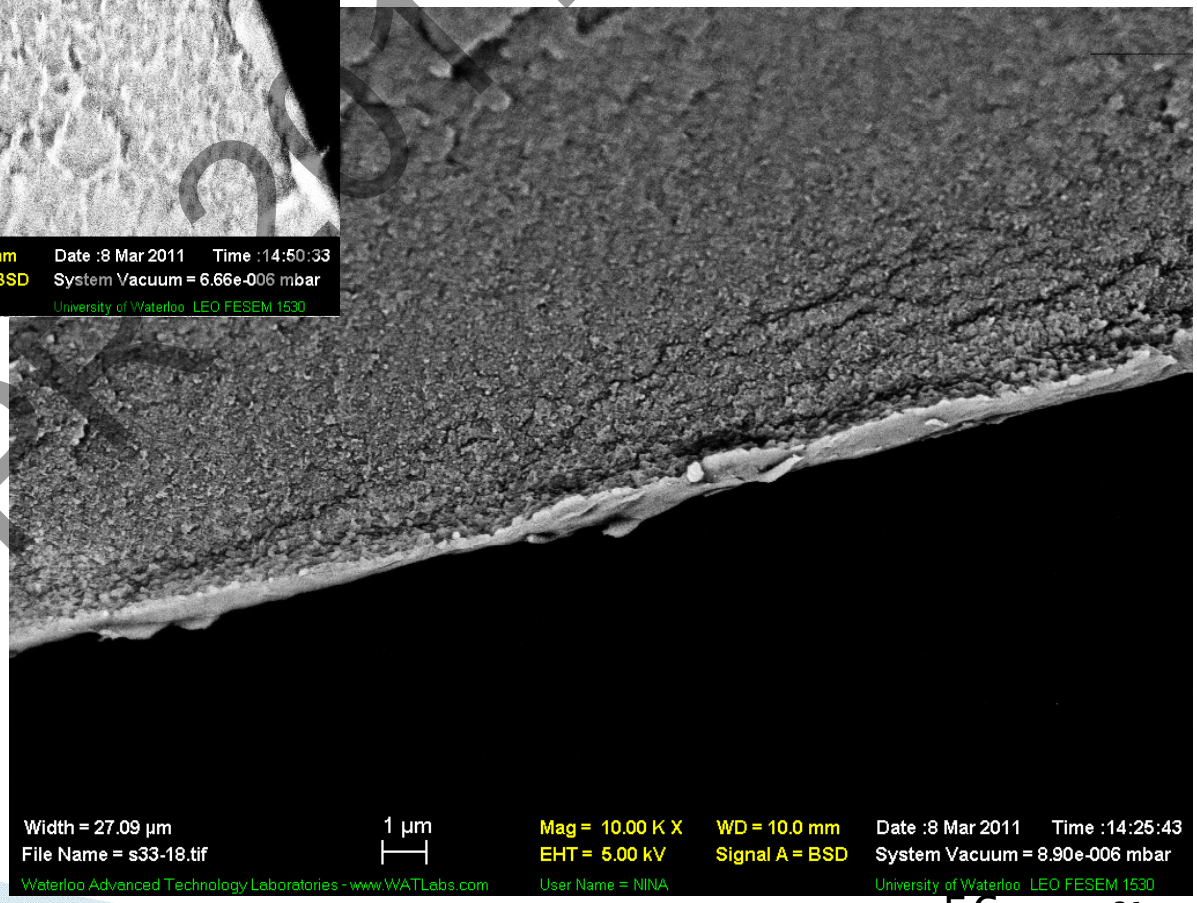


# SEM – PyN



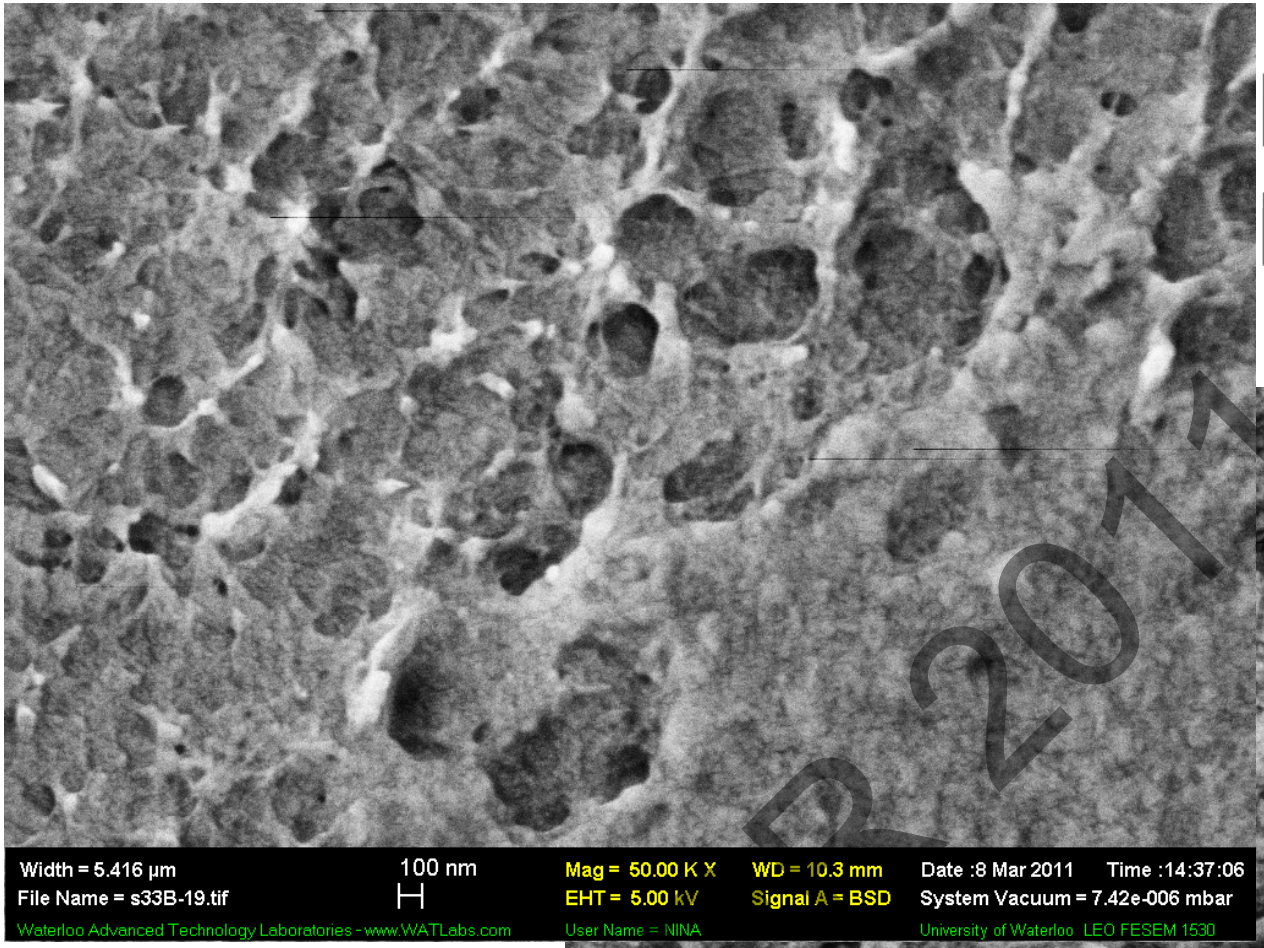

2 kGy

16 kGy



# High Magnification

56

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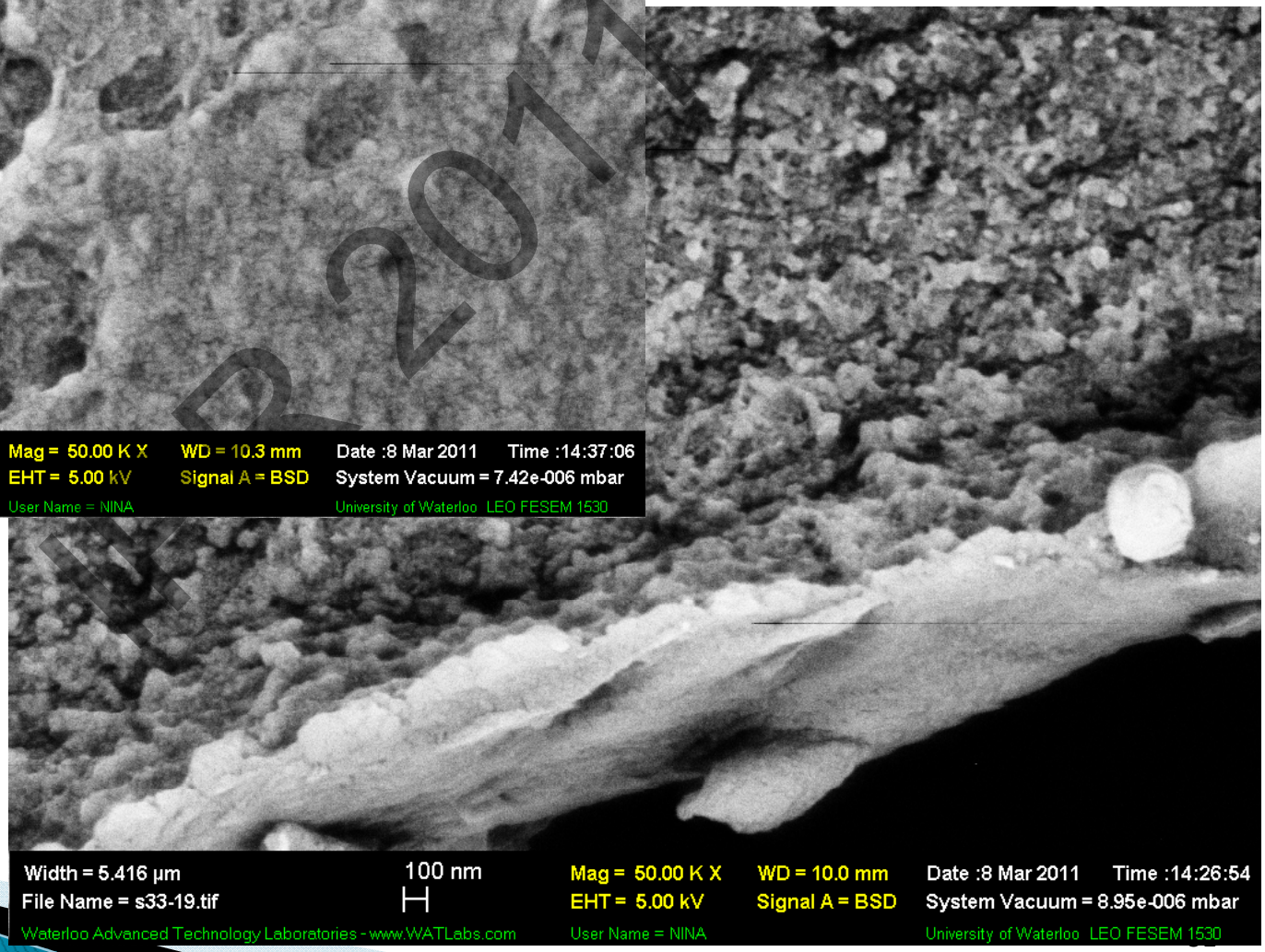

# Conclusions

- films of AC-g-PE labelled with pyrene were successfully synthesized, with AC contents dependent on radiation dose.
- Incorporation of pyrene confirmed by UV absorption
- The grafted AC chains are embedded within the bulk of the PE film, but more AC is found near the edges.