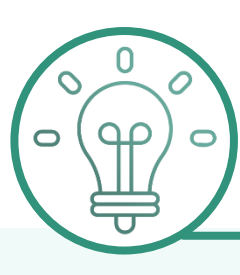


# Fluorinated Block Copolyesters via Switchable Ring-Opening Alternating Copolymerization: Reactivity and Self-Healing Insights

○ Chun-Yao Ke<sup>1,4</sup> · Mei-Nung Chen<sup>5</sup> · Yu-Xin Hsu<sup>5</sup> · Takuya Isono<sup>2</sup> · Feng Li<sup>2</sup> · Takuya Yamamoto<sup>2</sup> · Guey-Sheng Liou<sup>4</sup> · Yu-Cheng Chiu<sup>5</sup> · Toshifumi Satoh<sup>2,3</sup>


<sup>1</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, <sup>2</sup>Faculty of Engineering, Hokkaido University, <sup>3</sup>ICReDD List-PF, Hokkaido University, <sup>4</sup>Institution of Polymer Science and Engineering, National Taiwan University, <sup>5</sup>Department of Chemical Engineering, National Taiwan University of Science and Technology.



## INTRODUCTION


### — Why Sequence Matters —

**ABS**  
Acrylonitrile-Butadiene-Styrene  
(Stiffness and Toughness)




Random copolymer

**SMA®**  
Styrene-Maleic Anhydride  
(Transparent)



Alternating copolymer

**SEBS**  
Styrene-Ethylene-Butylene-Styrene  
(Elastic and Soft)

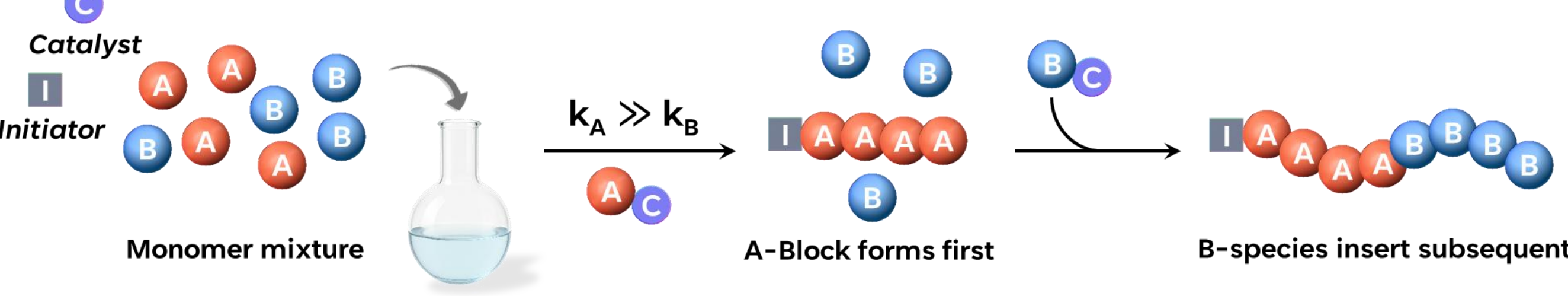


Block copolymer

“Sequence determines structure.  
Structure defines function.”

### — In this research —

**Intrinsic-Reactivity-Driven Sequence Control via ROAC**



Monomer mixture

A-Block forms first

B-species insert subsequently

Cyclic Anhydrides

PA

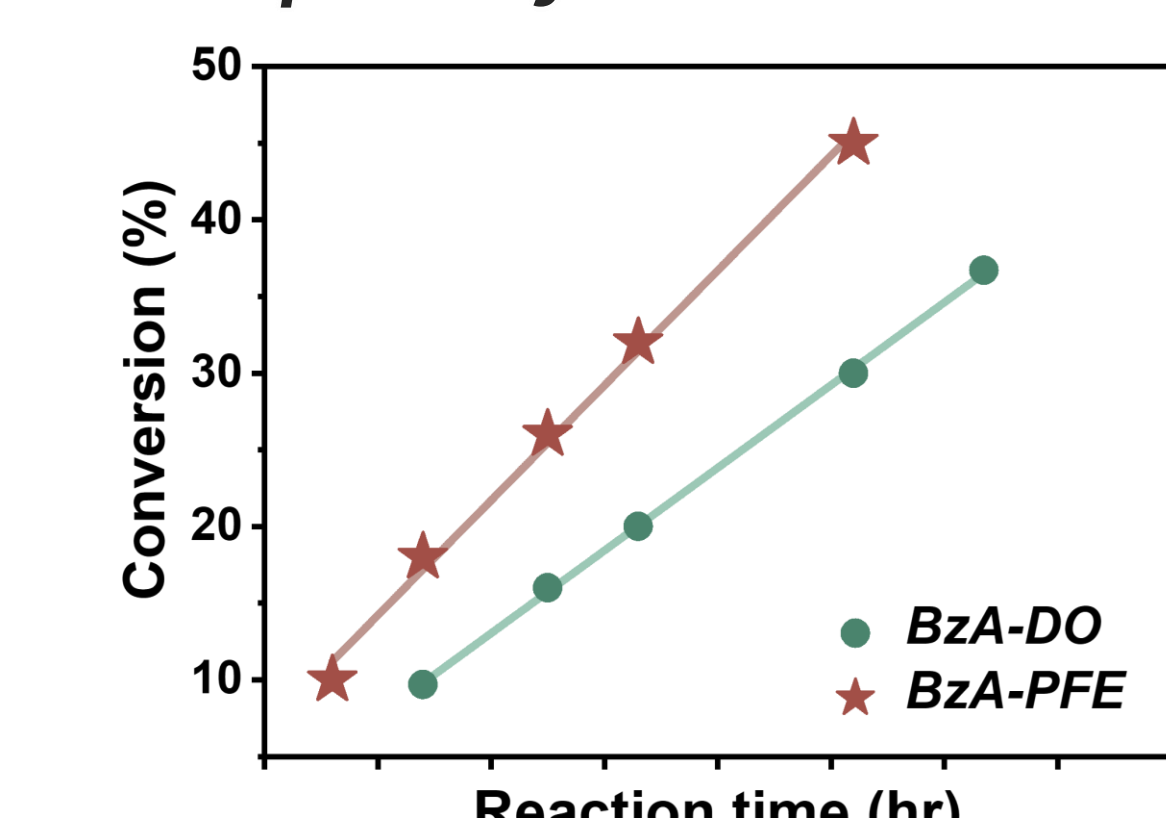
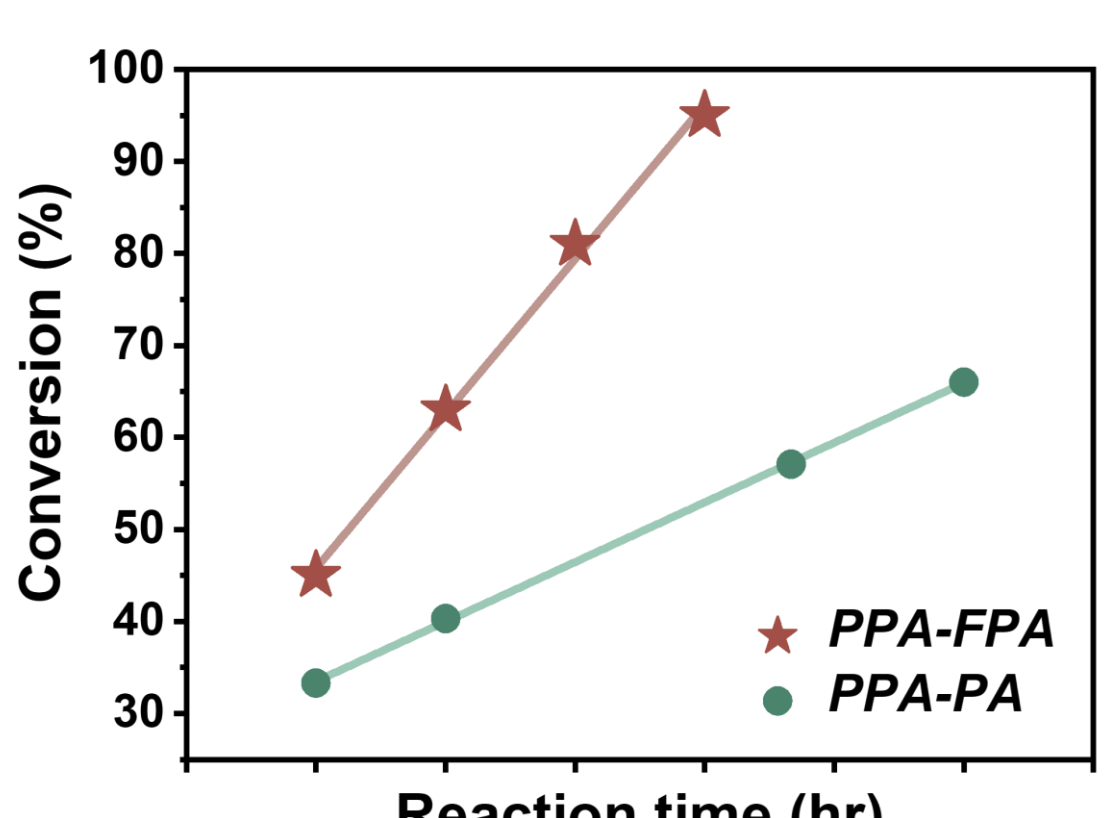
FPA

Electron density: **with F** > **without F**

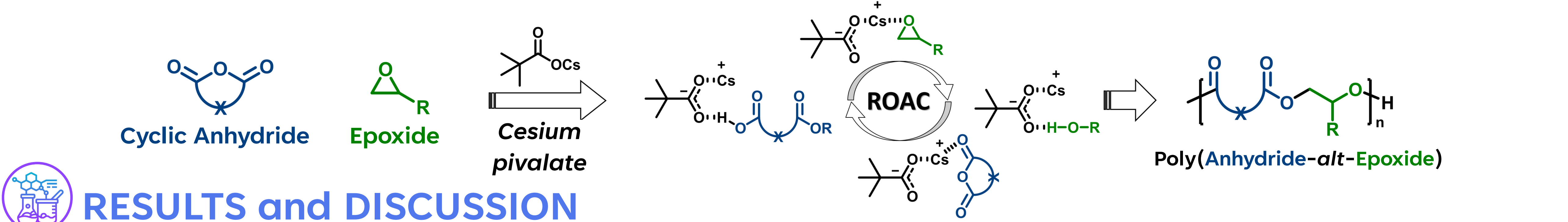
Electrophilicity: **with F** < **without F**

DO

PFE



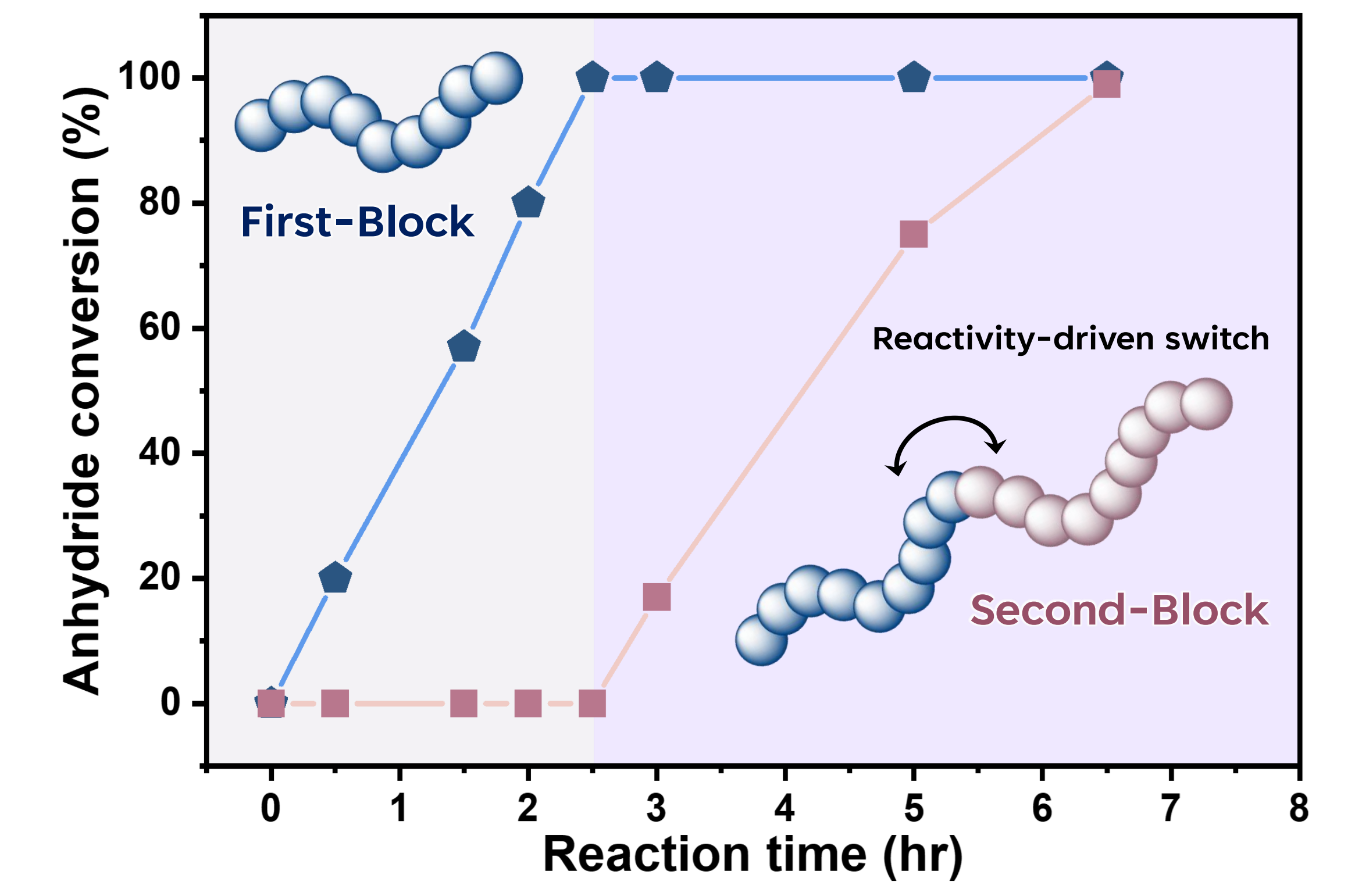
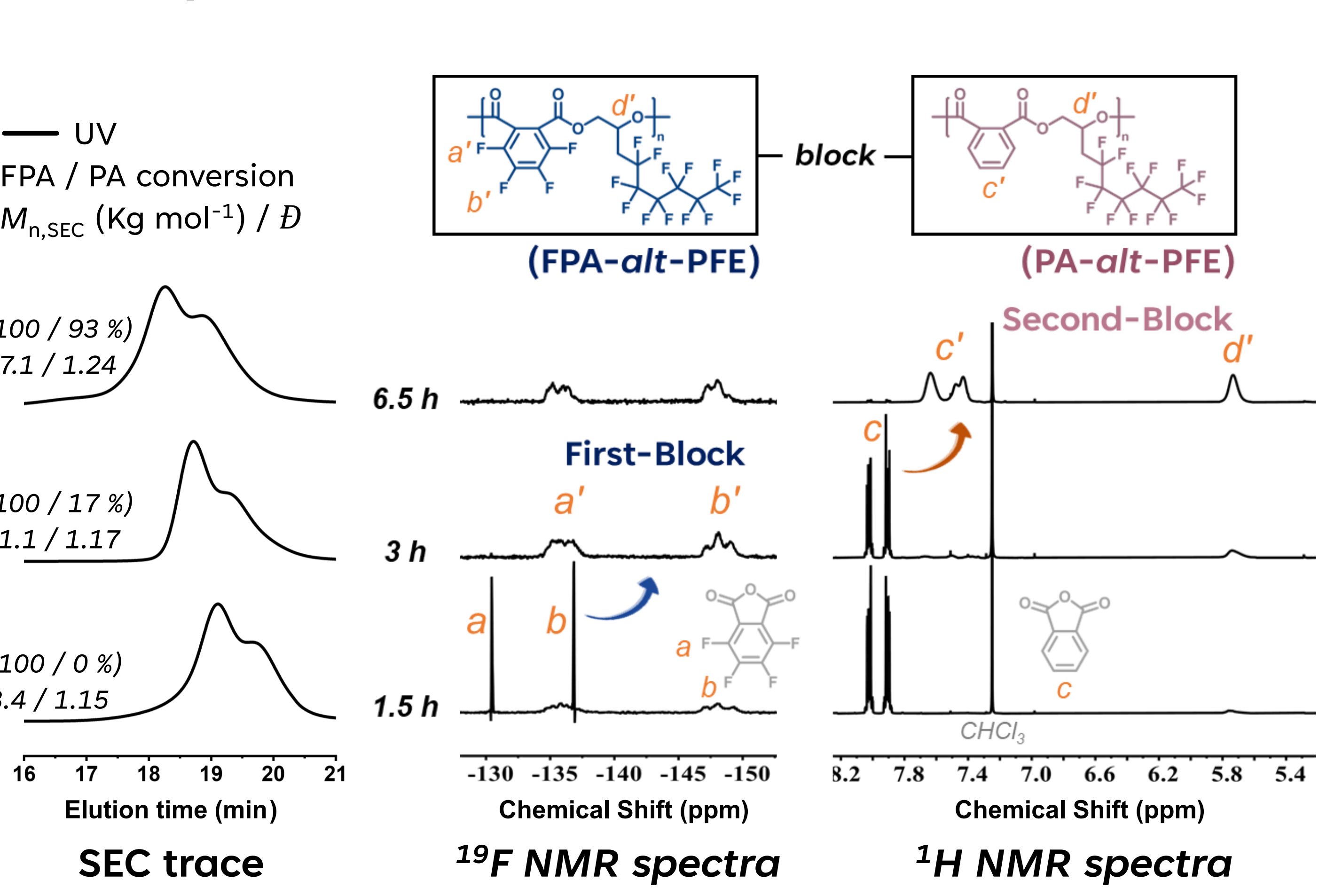
### Ring-Opening Alternating Copolymerization (ROAC) of Epoxides with Cyclic Anhydrides



## RESULTS and DISCUSSION

### — Sequence-Controlled Block Formation —

◆ Fluorinated Anhydride (FPA) —■ Non-fluorinated Anhydride (PA)

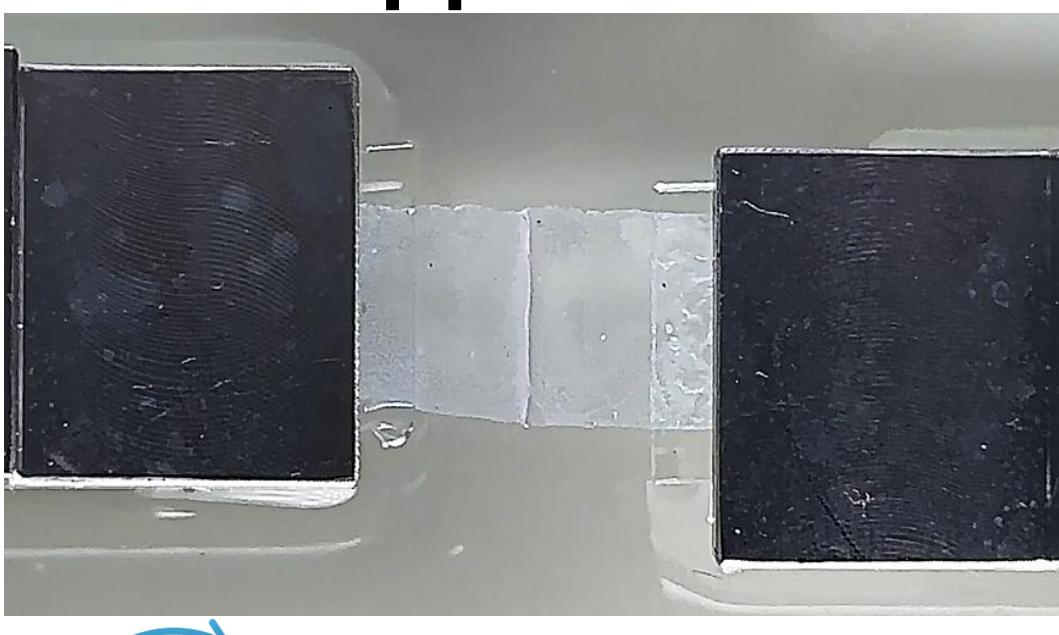


Segment-A entirely consumes  
→ Then Segment-B starts.

### — Self-Healable Block Copolymer —

Under OM observation

Approach

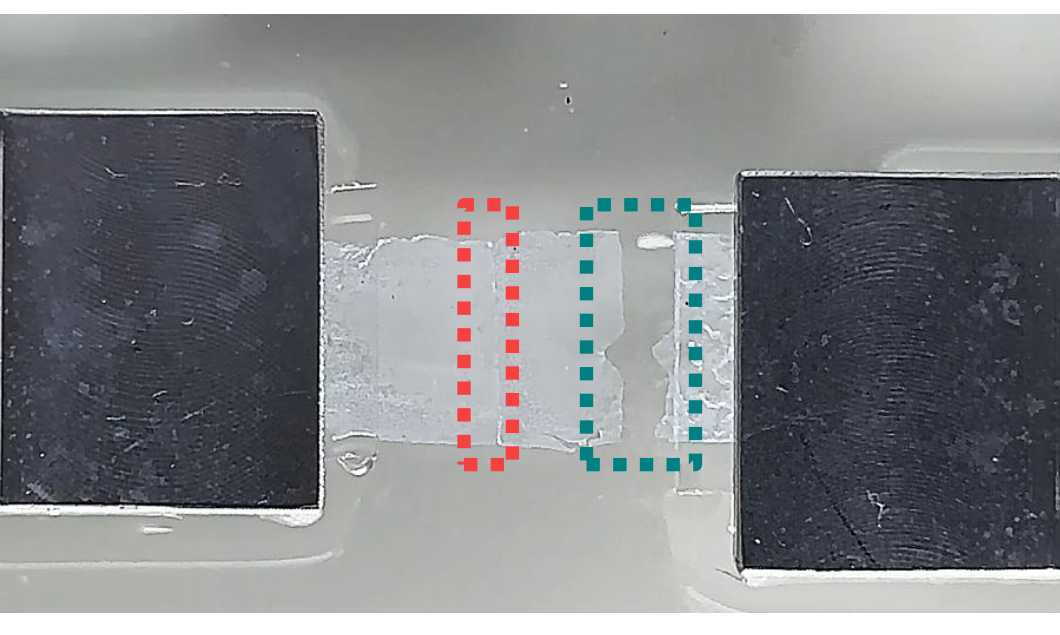


120 mins

Healing

Ambient  
No force  
No heat  
No solvent

Detachment



Before healing: clear fracture line

Healed: merged into a single piece

Fracture occurs at a new location



## KEY TAKEAWAYS



### Design & Mechanism

- Fluorine induces reactivity contrast in ROAC by modulating both monomers and chain ends.
- Segment control is achieved in one pot via intrinsic kinetic selectivity.

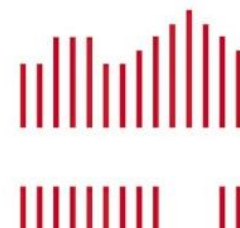


### Function & Application

- Self-healing films recover at room temperature with no solvent or external force.
- Additive blending promotes cohesive healing and soft-material potential.



北海道大学  
HOKKAIDO UNIVERSITY



National Taiwan University  
國立臺灣大學

高分子化学  
Polymer Chemistry

Google Scholar



LinkedIn



Manuscript in preparation...