Poster session 2 | Room 1

Eco-friendly synthesis polyimide via water-borne poly(amic acid) salt using organic base catalyst

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INTRODUCTION & OBJECTIVES

Introduction

[Polyimide]

- Polyimide was developed as an aerospace material in the 1960s.
- Its use has expanded to include microelectronics, membranes, and composites due to its excellent thermal stability, chemical resistance, and mechanical properties.

[Synthesis]

- Polyamid acid(PAA) precursor is prepared in aprotic polar solvent such as N-methyl-2-pyrrolidone(NMP), N,N'-dimethylformamide (DMF), N,N'-dimethylacetamide (DMAc) or m-cresol.

[This Study]

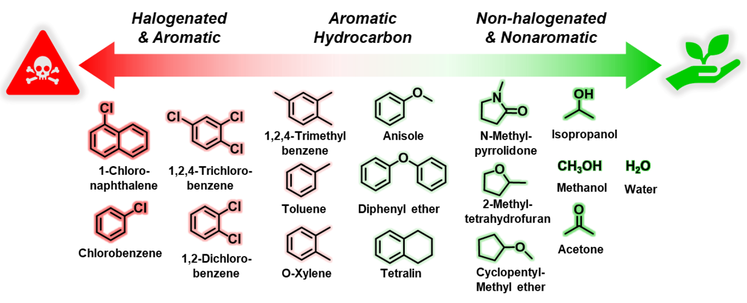
- We report the reaction mechanism of W-PAAS polymerization in the presence of organic bases in aqueous medium.

[Mechanism]

- The reaction begins with the functional groups being intimately exposed to form an acid base salt between the organic base and the aromatic dianhydride.
- Our findings reveal that polymerization occurs at the interface of the dianhydride particles in water.

Green Solvent & Solution Process

Environmental issue



Solution process

- ✓ Low cost
- ✓ Rapid manufacturing
- ✓ Large area
- ✓ Mass production
- ✓ High feasibility of customization

Objectives

Research Goal

Mechanistic investigation of aqueous polymerization for poly(amic acid) salts (PAAS)

Promising Benefits

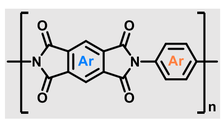
Providing novel guidelines for the PAAS synthesis

Possible to design the materials with various structures

[Compatibility of aromatic monomers / Kinetic study / Confirming possibility of expanding chemical diversity]

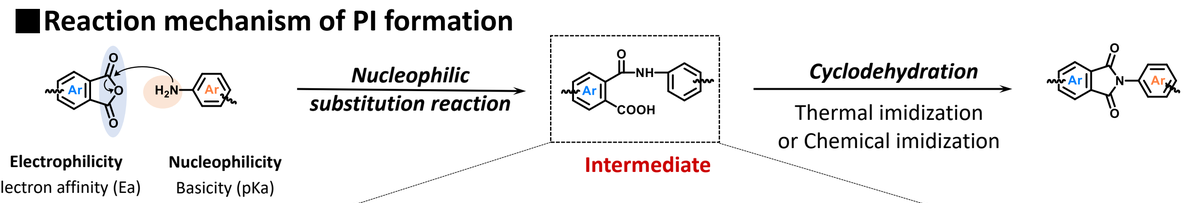
Poly(amic acid) salts (PAAS)

Aromatic Polyimide



Rigid planar aromatic & heteroaromatic structure
→ **Infusible & insoluble**
→ **PI prepared by PI precursors**

■ Reaction mechanism of PI formation

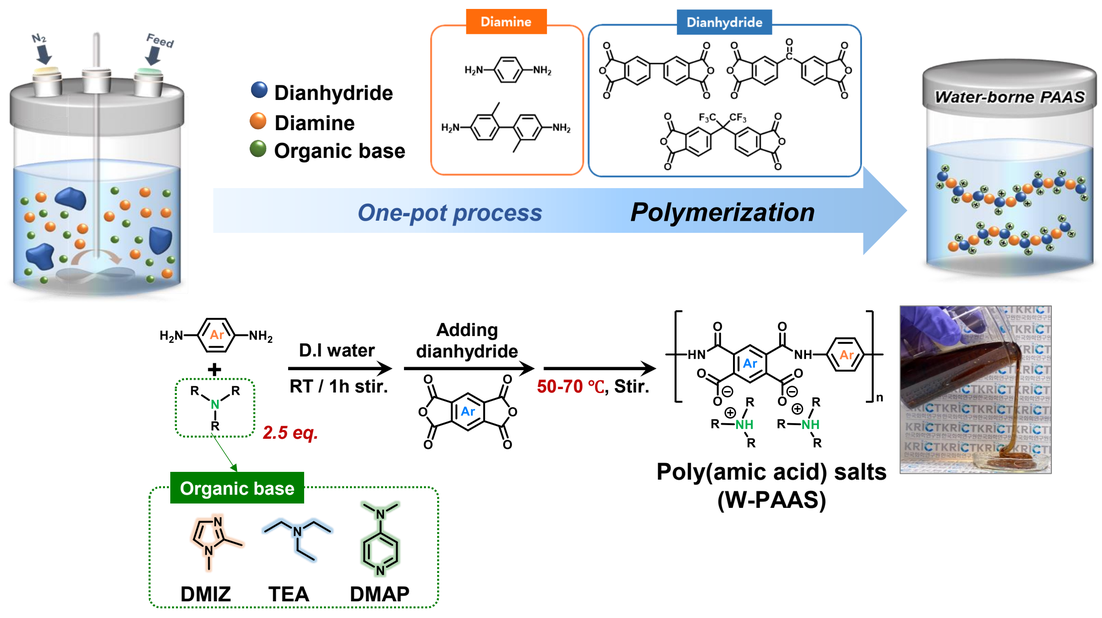


■ Advantages

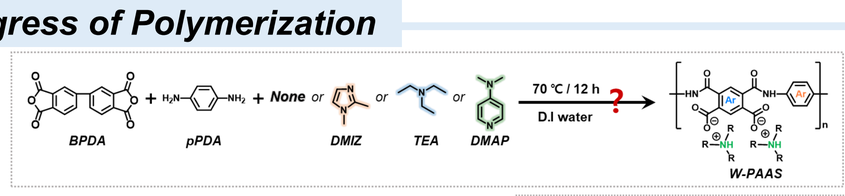
1) High solubility in ethanol or water
2) High hydrolytic stability
3) Low imidization temperature

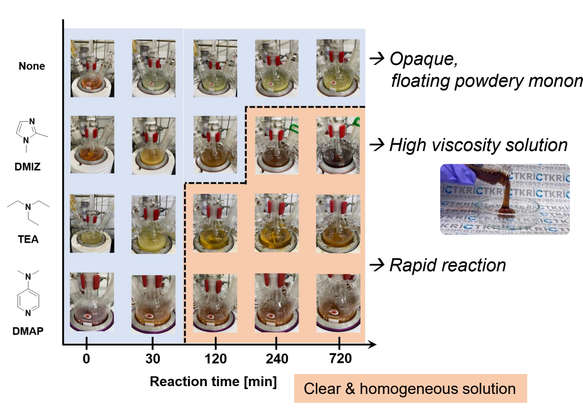
RESULTS & DISCUSSION

Synthetic Method & Approach

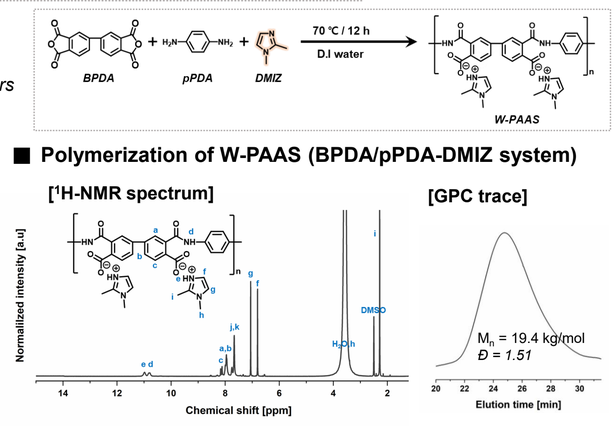


Progress of Polymerization





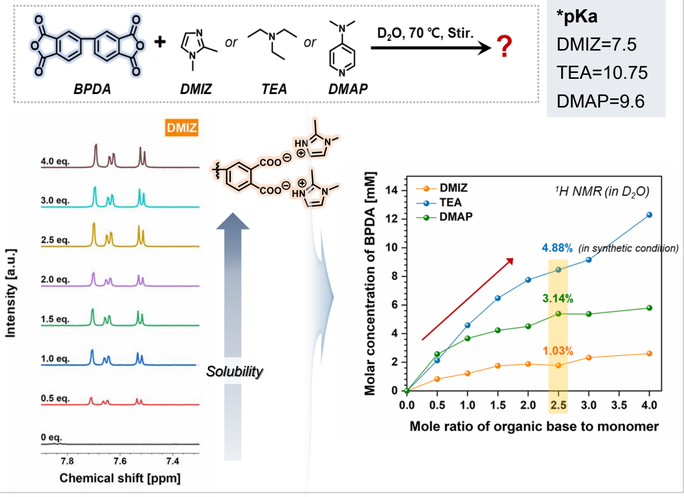
✓ Difference of reaction progress (type of organic bases)



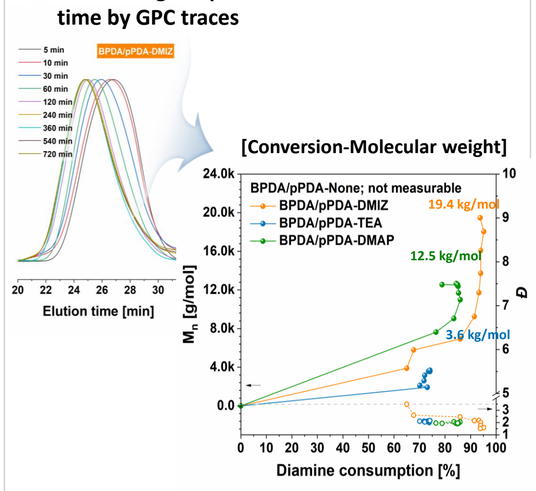
✓ W-PAAS polymerization with high-molecular weight

Compatibility of an Aromatic Dianhydride in Aqueous Medium

■ Solubility of BPDA with organic base



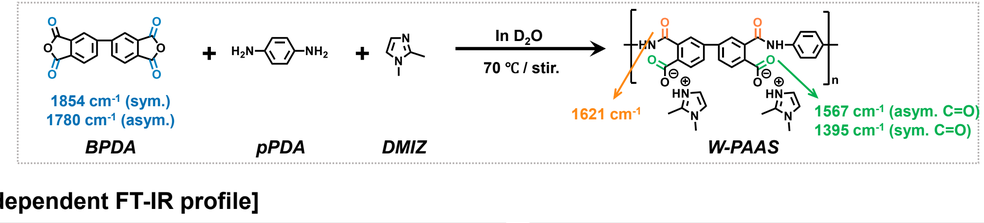
■ Monitoring the products with the reaction time by GPC traces



✓Carboxylate-ammonium salt complexes ➔ Exposed interface to the aqueous medium ↑

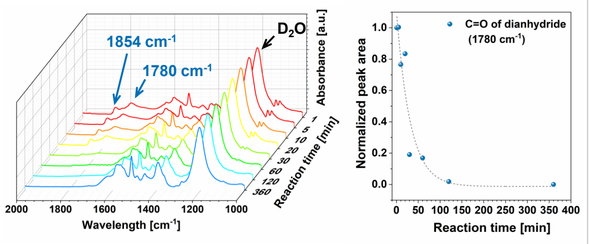
✓Organic base ➔ Effect on initial reaction rate / Degree of polymerization (growth of polymer chain)

The Reaction Kinetics of W-PAAS Polymerization

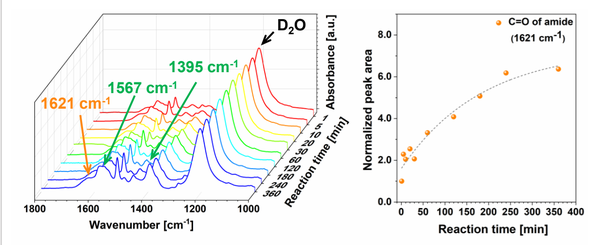


[Time-dependent FT-IR profile]

Reactant: BPDA (dianhydride)



Product: -CONH / -COO⁻ (Amic acid salt)



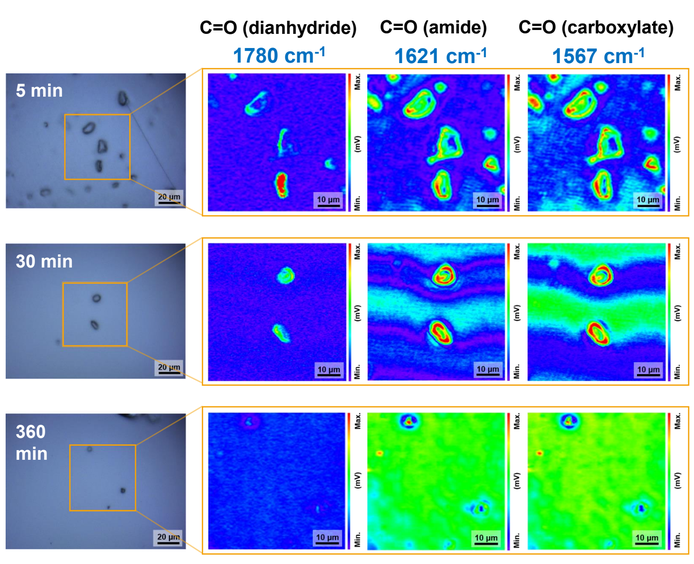
✓Logarithmic decay/growth curve: step-growth

✓Amide bond & carboxylate salt ➔ Products: Poly(amic acid) salt (PAAS)

The Reaction Kinetics of W-PAAS Polymerization

*O-PTIR; Photothermal Spectroscopy

■ Mechanistic investigation by O-PTIR analysis [Optical images & O-PTIR absorbance maps]



C=O (dianhydride)

Strongly detected inside particles

C=O (amide, carboxylate)

More concentrated on the periphery of the BPDA particles

➔ Polymerization is initiated close by the dianhydride particles

Particles are smaller

The boundary is more ambiguous and diffuse to the surrounding

➔ *Quasi-interfacial polymerization* could be conducted compared to the organic-based polyimide precursor

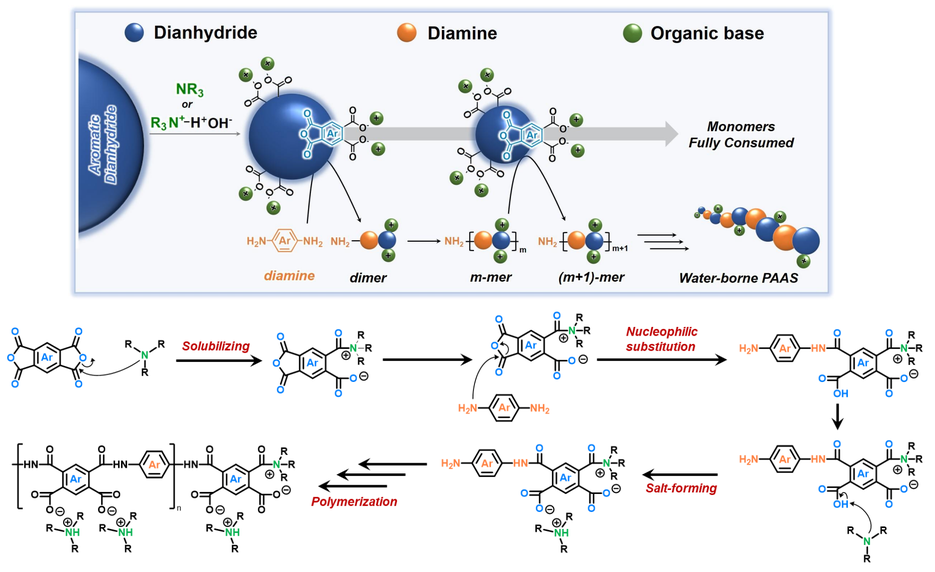
BPDA particles are barely observed

Homogeneous dispersion without any phase features

➔ Complete polymerization of PAAS in an aqueous system

Proposed Mechanism of W-PAAS Polymerization

■ Quasi-interfacial Polymerization



CONCLUSIONS

- ✓ The mechanism of polymerization with aromatic dianhydride and diamine in aqueous system is proposed as Quasi-interfacial Polymerization.
- ✓ The organic base with moderate basicity such as DMIZ enabled the production of a stable polymer chain in an aqueous solution leading to W-PAAS with high-molecular weight.
- ✓ The solubility of dianhydride in the presence of an organic base showed the compatibility between the insoluble monomer and aqueous phase.
- ✓ We demonstrated via mechanistic investigations, the accelerated nucleophilic substitution reaction via an increase of reactive functional group density followed by salt-forming of the W-PAAS chain.
- ✓ The exponential growth with monomer consumption in the obtained polymer molecular weight suggests the polymerization proceeds through step-growth addition polymerization.

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