Amino-Functionalized Polyester Synthesis via Ring-Opening Alternating Copolymerization of Glycidylamine with Cyclic Anhydride

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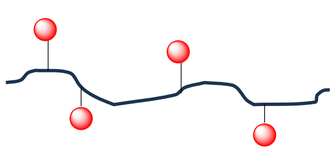
Introduction

1. Amino-functionalized polyester

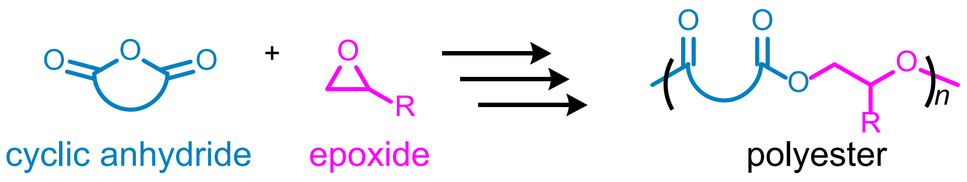


◎ bio-degradable, cationic polymer

useful for biomaterial applications
(drug delivery system, antibacterial coating…)

Synthesis strategy have several challenge
- Multi-step synthesis
- Poor structural diversity
- Difficult to polymerization control

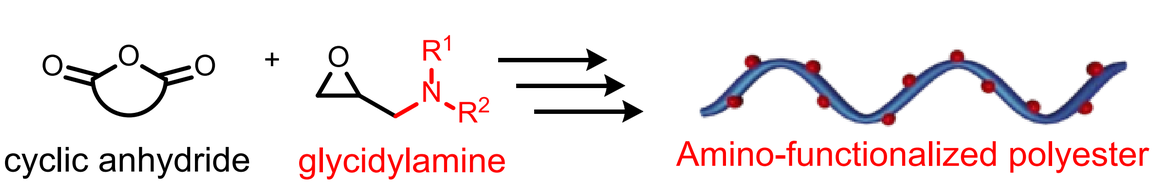
2. Ring-opening alternating copolymerization (ROAC)



X. Xia *et al., ACS Catal.*, **2021**, *11*, 5999; X. Xia *et al.*, *Nat. Comm.*, **2022**, *13*, 1;
X. Xia *et al.*, *J. Am. Chem. Soc.*, **2022**, *144*, 17905.

◎ Simple ◎ Broad structural diversity ◎ Highly controllable

3. This work



***This work*:**
Establish new method for amino-functional synthesis

Results and Discussions

1. Catalyst Screening

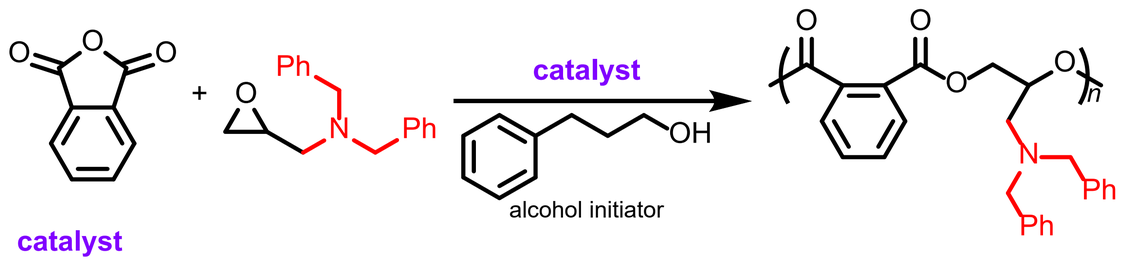
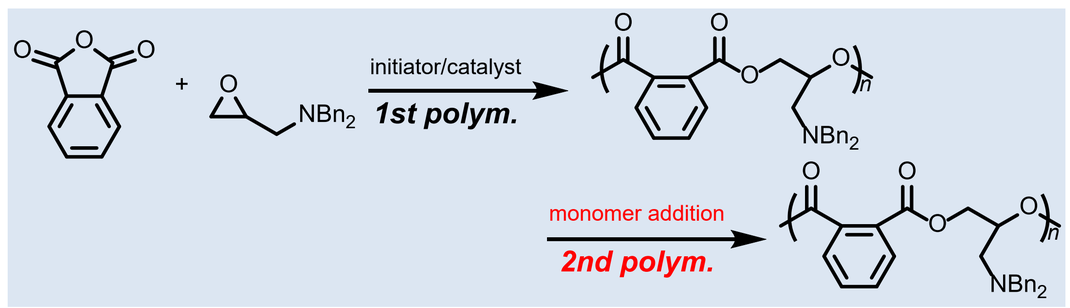


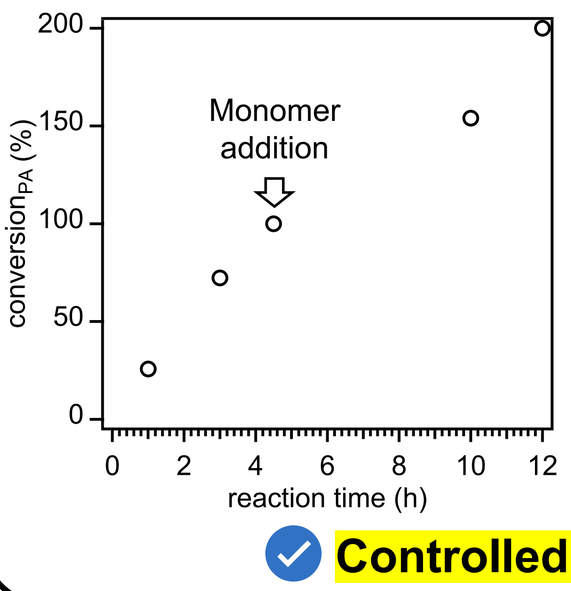
Table 1. ROAC of PA and BMGA using various catalyst [a]

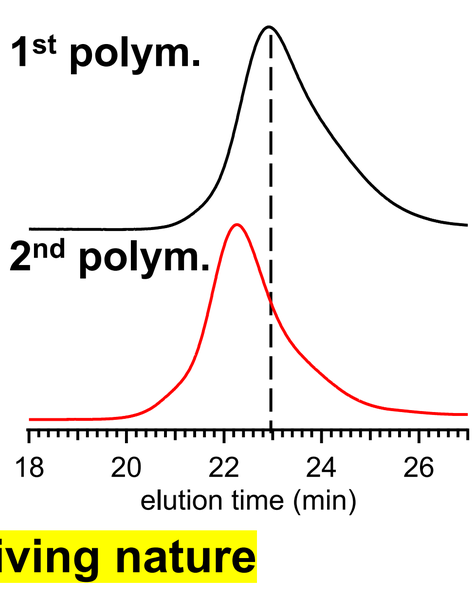
Run	Catalyst	Time (h)	Conv.$_{PA}$ [b] (%)	$M_{n,theo.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ$ [d]
1	CsOPiv	9.0	77	7,800	7,100	2,670	1.62
2	NaOAc	6.5	68	6,900	11,700	3,380	1.19
3	*t*-BuP$_1$	2.5	80	6,900	8,000	3,760	1.10
4	*t*-BuP$_2$	1.5	86	8,700	8,000	2,560	1.20
5	*t*-BuP$_4$	0.8	88	9,000	8,300	3,330	1.35

[a] Polymerization conditions: atmosphere, Ar; temp., 80 °C; $[PPA]_0/[catalyst]/[PA]_0/[DBGA]_0$ = 1/1/25/75. [b] Determined *via* ^{1}H NMR spectroscopy in $CDCl_3$. [c] Calculated from (M.W. of PPA) + $[PA]_0/[PPA]_0$ × ((M.W. of PA) + (M.W. of DBGA)) × (conv.$_{PA}$). [d] Determined by SEC in DMF containing 0.01 M LiCl using polystyrene standard.

2. Chain Extension Experiment



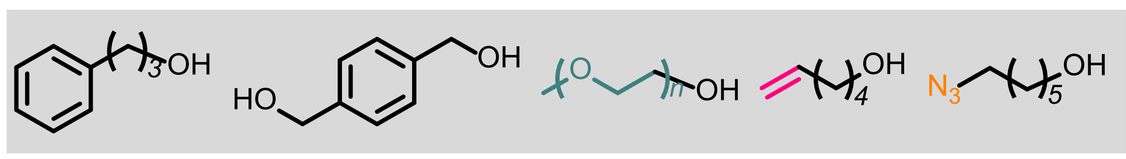




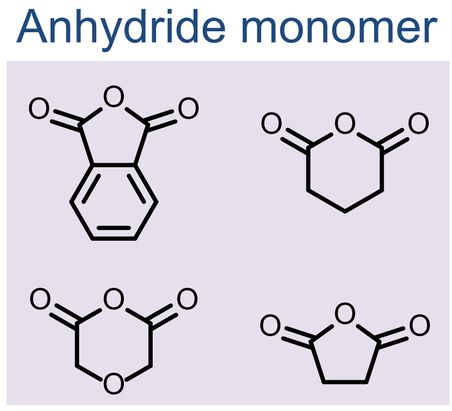
Controlled / living nature

4. Structure diversity

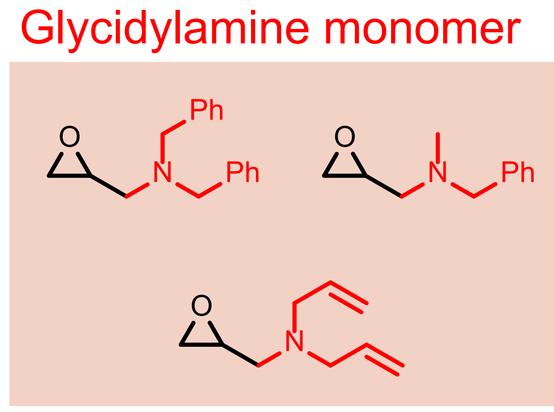
Alcohol initiator



Anhydride monomer



Glycidylamine monomer

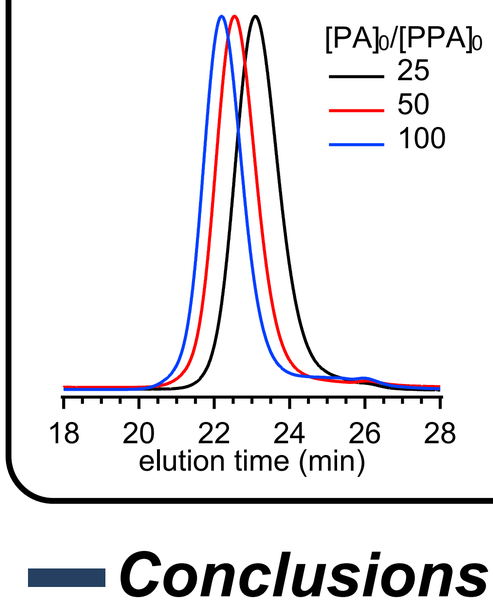


Accessible to specific architecture
(ex. Star, Block, End-functional)

Tunable properties
(T_g, hydrophilicity)

3. Molecular weight controlled

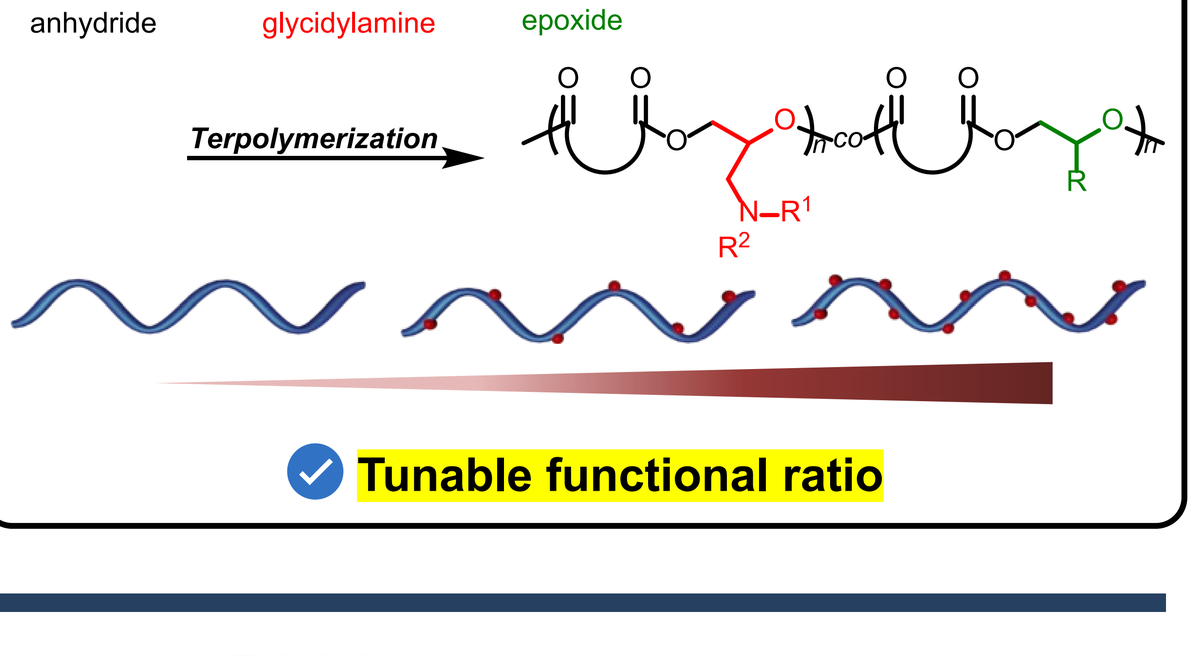
- Changing the initiator/monomer ratio



Successful control over M.W.

Achieved to high M.W.
(21,000 g mol^{-1})

5. Controlled functional ratio



Tunable functional ratio

Conclusions

✔ We successfully **synthesized amino-functional polyester** via ROAC using glycidylamine.
✔ Our polymerization demonstrates **high controllable** and **broad diversity** of accessible structure.
✔ These polymers are expected to be used as antimicrobial materials, biodegradable systems, and nanocarriers for drug delivery.

European Polymer Congress (EPF) 2025 @Martiniplaza, Netherlands