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Organocatalytic Synthesis of Bio-Based Thermoplastic Polyester Elastomers

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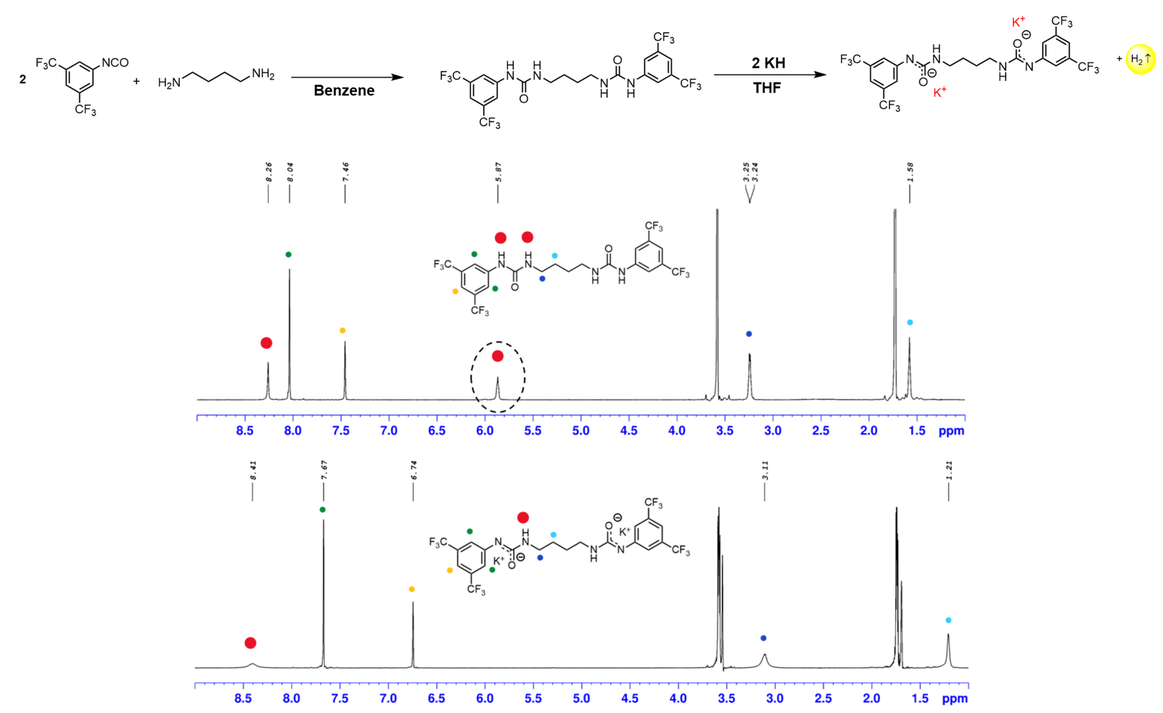
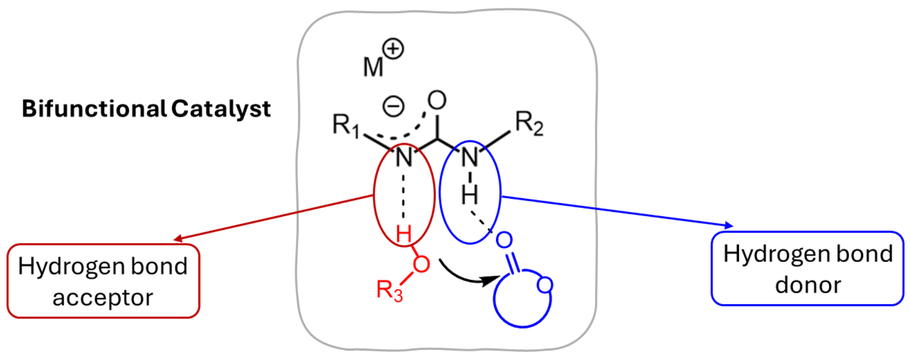
UREATE: BIFUNCTIONAL CATALYST

The organocatalytic system is based on a ureate anion species with two complementary functions. The deprotonated site, carrying a negative charge, acts as a hydrogen-bond acceptor that interacts with and activates the alcohol initiator. In parallel, the neutral urea group acts as a hydrogen-bond donor, enhancing the electrophilicity of the monomer carbonyl group (such as in lactones) and thereby facilitating the ring-opening process [1]. In this study, bis-urea precursors were deprotonated with KH to generate the corresponding bis-ureates. The cooperative interaction between the two ureate sites leads to a marked increase in catalytic activity compared to the corresponding mono-urea species.

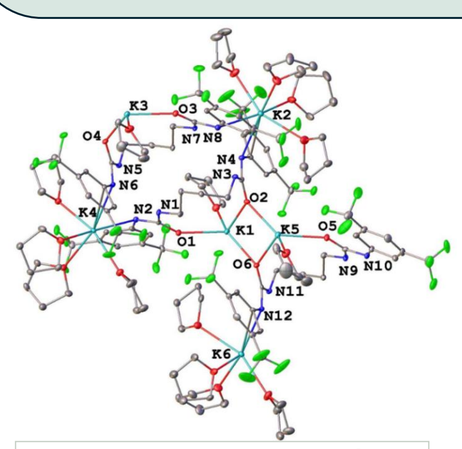


600 MHz, THF-d_8, 298 K

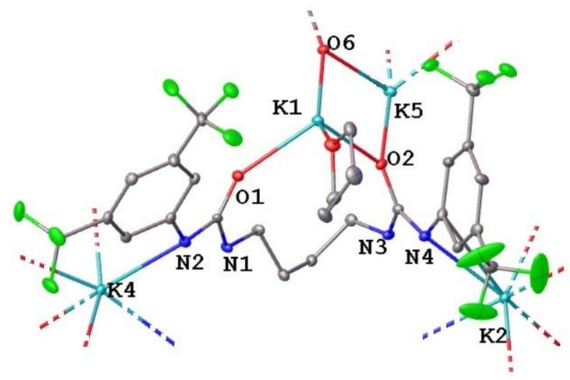


X-RAY STRUCTURE OF THE BISUREATE ORGANOCATALYST

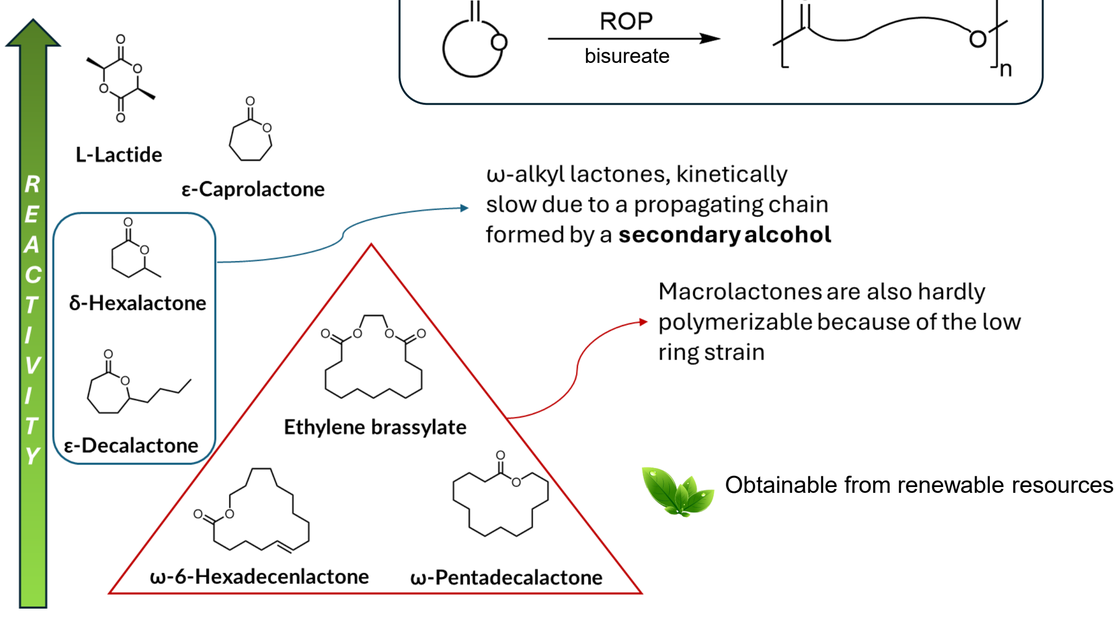
The X-ray structure highlights how the metal ions, through their templating role, organize the bis-ureate units so as to prevent self-conjugation and promote cooperative interaction between the two active sites. This arrangement leads to the formation of a true "catalytic pocket", able to simultaneously accommodate both the monomer and the growing chain, stabilizing them through multiple hydrogen bonds. The bis-ureate anions bridge the potassium ions, forming an extended framework stabilized by five coordinated THF molecules, which reinforces the well-defined catalytic pocket.



ORTEP drawing of compound **K^+_2U2b^{2-}-5THF**



ORTEP drawing of K1 ion coordination site of compound **K^+_2U2b^{2-}-5THF**

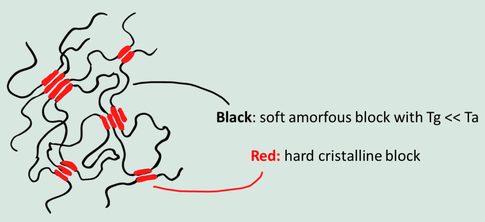


The **homopolymerizations of different lactones** demonstrated that bisurea anions act as active and versatile catalysts, providing good conversions and narrow dispersities. Even less reactive macrolactones can be polymerized in high yields, particularly at elevated temperatures, due to the stability of the catalytic system. Overall, the catalyst exhibits a "living/immortal" behavior, minimizing side reactions and enabling the synthesis of well-defined polymers. In particular, the activities achieved in the ROP of lactide are among the highest reported so far, comparable only to those obtained with urea catalysts bearing an anionic pendant group [2].

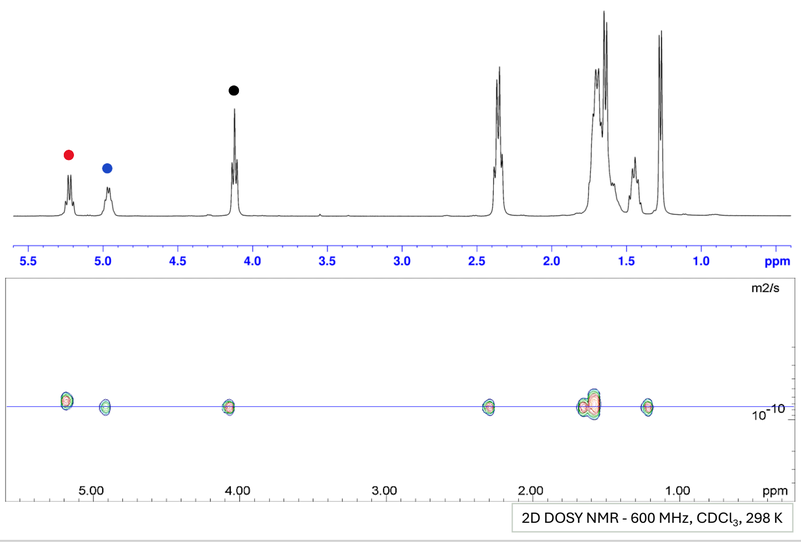
[a]Entry	Monomer	Time	Temperature	[b]Conversion	[c]Mn_{theo} (kDa)	[d]Mn_{GPC} (kDa)	Đ	TOF (h^{-1})
1	[e]LLA	10 sec	25°C	88 %	9.2	8.8	1.15	250 k
2	ε-CL	30 sec	25°C	77 %	7.0	8.5	1.13	37.5 k
3	ε-DL	9 h	25°C	69 %	9.4	10.1	1.17	62.2
4	δ-HL	5 min	25°C	80 %	7.3	10.2	1.14	4.0 k
5	HDL	12 h	25°C	40 %	20.2	10.7	2.19	27.3
6	EB	3 min	110°C	92 %	19.9	33.3	2.00	15.0 k
7	PDL	20 min	110°C	82 %	-	-	-	2.0 k

[a]All reactions were carried out in 0.2 mL of THF with [U2]:[base]:[BnOH]$_0$: [M]$_0$= 0.5:1:10:800 [b]Determinated by ^{1}H NMR. [c]Mn_{theo} = [Mon]/([KH]+[BnOH]) × conv × MM mon. [d]Experimental M_n and Đ values were determined by GPC analysis in THF using polystyrene standards. [e]Polymerization with LLA (1600eq) were carried out in 2mL of THF.

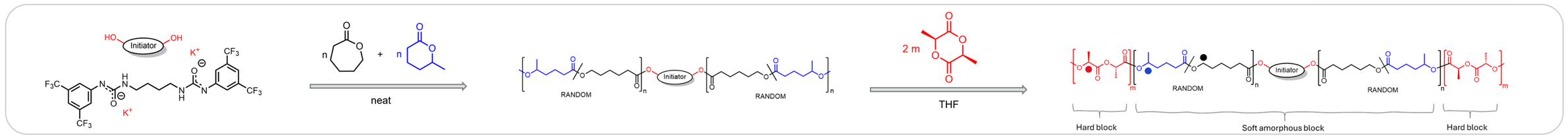
SUSTAINABLE THERMOPLASTIC ELASTOMERS



A sequential, one-pot, two-step methodology was developed at room temperature for the synthesis of renewable ThermoPlastic Elastomers (TPEs). The strategy involves the initial random copolymerization of ε-caprolactone (ε-CL) and δ-hexalactone (δ-HL) to form a soft, amorphous block, followed by the polymerization of L-lactide (LLA) to create hard, crystalline domains [3]. This approach successfully produced triblock copolymers (confirmed by 2D DOSY NMR) with both linear and star-shaped architectures (2, 3, and 4 arms). DSC showed the expected T_m of PLA blocks, supporting the formation of well-defined hard domains while TGA revealed good thermal stability with degradation onset above 250 °C.



2D DOSY NMR - 600 MHz, $CDCl_3$, 298 K



[a]Entry	Initiator	[b]Conversion	[c]Mn_{theo} (kDa)	[d]Mn_{GPC} (kDa)	Đ
1	**MPD** (5 eq)	**δ-HL**: 96% **ε-CL**: 98 % **LLA**: 97%	23.4	36.2	1.14
2	**TEOA** (5 eq)	**δ-HL**: 91% **ε-CL**: >99 % **LLA**: 98%	23.2	34.1	1.14
3	**PET** (5 eq)	**δ-HL**: 90% **ε-CL**: >99 % **LLA**: 97%	23.1	47.0	1.16
4	**MPD** (1 eq)	**δ-HL**: 88% **ε-CL**: 96% **LLA**: 98%	103.6	79.1	1.24

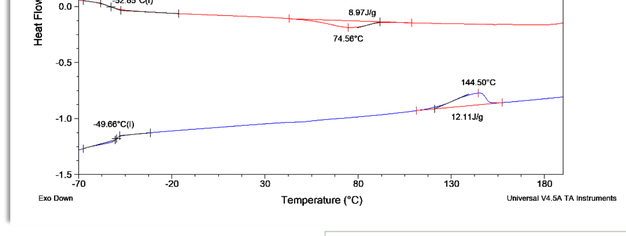
[a]All reactions were carried out in 0.2 mL of THF. [b]Determined by ^{1}H NMR. [c]Mn_{theo} = [Mon]/([KH]+[BnOH]) × conv × MM mon. [d]Experimental M_n and Đ values were determined by GPC analysis in THF using polystyrene standards. Polymerization step with LLA were carried out in 2mL of THF

INITIATORS:

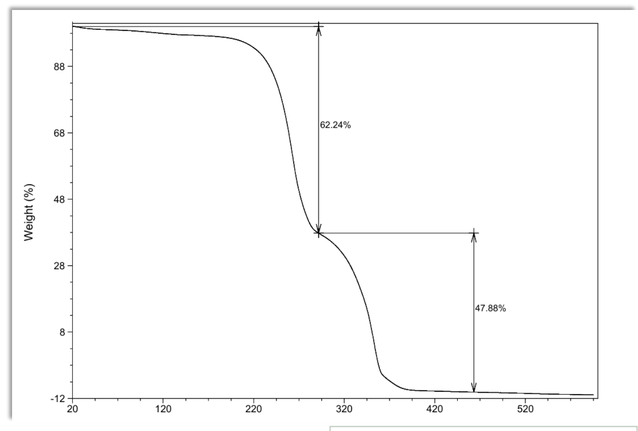
MPD 2-methylene-1,3-propanediol

TEOA triethanolamine

PET pentaerythritol



DSC thermogram of the triblock copolymer



TGA thermogram of the triblock copolymer

[1] Lin, B.; Waymouth, R. M. Urea Anions: Simple, Fast, and Selective Catalysts for Ring-Opening Polymerizations. *J. Am. Chem. Soc.* **2017**, *139* (4), 1645–1652
[2] Li, C.; Wang, L.; Yan, Q.; Liu, F.; Shen, Y.; Li, Z. Rapid and Controlled Polymerization of Bio-sourced δ-Caprolactone toward Fully Recyclable Polyesters and Thermoplastic Elastomers. *Angew. Chem. Int. Ed.* **2022**, *61* (16), e202201407
[3] Geng, X.; Liu, X.; Yu, Q.; Zhang, C.; Zhang, X. Advancing H-Bonding Organocatalysis for Ring-Opening Polymerization: Intramolecular Activation of Initiator/Chain End. *J. Am. Chem. Soc.* **2024**, 146 (37), 25852–25859
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