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Investigations into Ring-Opening Polymerization of Functionalized ϵ-Caprolactones

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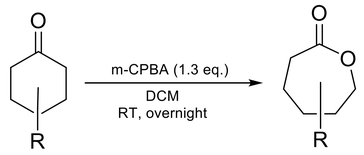
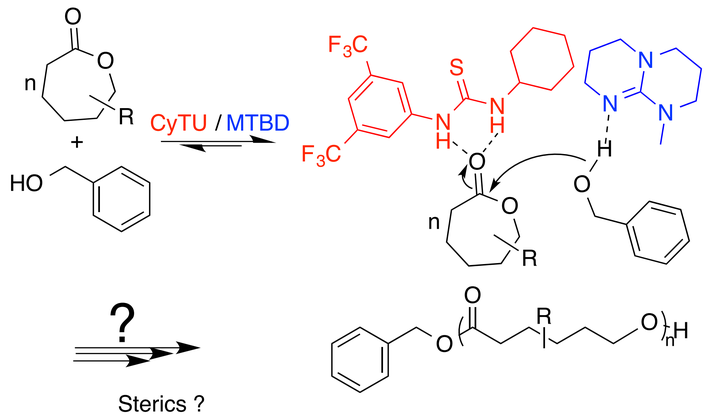
Abstract

Polymers are large molecules constructed from small, repeating units (monomers) which make up a variety of everyday items. H-bonding urea (U) or thiourea (TU) catalysts paired with base cocatalysts used for organocatalytic ring-opening polymerization (ROP) of cyclic esters have been shown to exhibit fast rates of polymerization, result in polymers with controlled molecular weights (M_n) and low polydispersity indexes (PDI), and are tolerant of the incorporation of functional groups into the monomer feed. Variation of the substituent position on the monomer allows for optimization of the material properties. This research investigated the kinetics of H-bonding organic catalysts for the ROP of the functionalized monomers of interest (5-MeCL, 6-MeCL, and TOSUO). Until this point, these new monomers have only been polymerized to approximately 7% conversion after 8 days with a commonly used guanidine base. Using the dual H-bonding catalysts, whose electronics can be modified, along with different commercially available bases, provides a more tunable approach for the ROP of functionalized lactones.

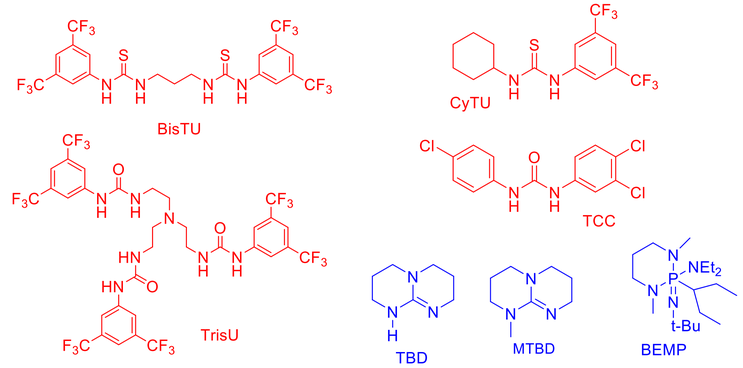


Substituent Effects on ROP

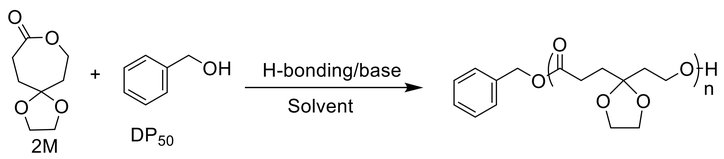


Sterics ?
Alcohol/Chain end Nucleophilicity ?
Ring Strain / Monomer Eq.Conc. ?

ROP Cocatalysts



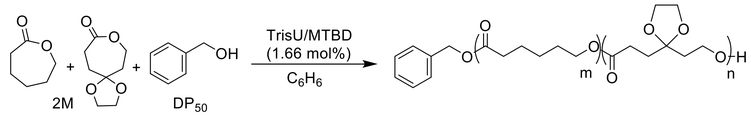
TOSUO ROP



H-Bonding	Mol %	Base	Mol %	Solvent	% Conv.	Time (min)	Rate Constant	PDI
CyTU	5	MTBD	5	C_6D_6	82	11208	0.0014	n/a
BisTU	2.5	MTBD	2.5	C_6D_6	92	1059	0.0024	1.15
TCC	5	MTBD	5	C_6D_6	93	102	0.0263	n/a
TrisU	1.66	MTBD	1.66	C_6H_6	97	30	0.1446	1.08
TrisU	1.66	DBU	1.66	C_6D_6	93	224	0.1190	1.06
TrisU	1.66	BEMP	1.66	C_6H_6	97	3	1.4329	1.07
TrisU	1.66	MTBD	1.66	Acetone-d_6	97	18	0.2185	1.13

Reaction Conditions: TOSUO (0.871 mmol), Benzyl alcohol (0.0174 mmol), Benzoic acid (0.0871 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.

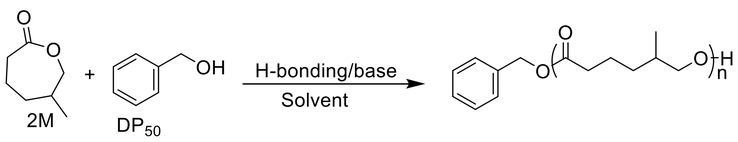
Co-Polymerization with TOSUO and εCL



% Conv. TOSUO	% Conv. CL	Time (min)	Rate Constant TOSUO	Rate Constant CL	PDI
99	95	30	0.1556	0.0989	1.09

Reaction Conditions: TOSUO (0.500 mmol), εCL (0.500 mmol), Benzyl alcohol (0.020 mmol), Benzoic acid (0.100 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC

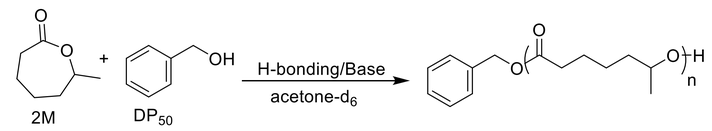
5-MeCL ROP



H-Bonding	Mol %	Base	Mol %	Solvent	% Conv.	Time (min)	Rate Constant	PDI
CyTU	5	MTBD	5	C_6D_6	91	7180	0.0003	1.18
BisTU	2.5	MTBD	5	C_6D_6	88	1450	0.0015	1.21
TCC	5	MTBD	5	C_6D_6	95	691	0.0054	1.34
TrisU	1.66	MTBD	1.66	C_6D_6	98	180	0.0205	1.13
TrisU	1.66	MTBD	1.66	Acetone-d_6	97	111	0.0344	1.13

Reaction Conditions: 5-MeCL (0.936 mmol), Benzyl alcohol (0.0187 mmol), Benzoic acid (0.0936 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.

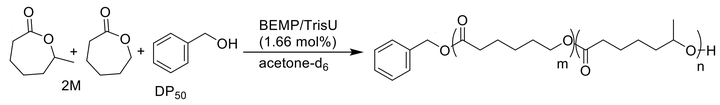
6-MeCL ROP



H-Bonding	Mol %	Base	Mol %	% Conv.	Solvent	Time (hrs)	Rate Constant	PDI
TrisU	10	BEMP	10	96	Acetone-d_6	70	0.0009	2.22
-	-	TBD	5	78	Acetone-d_6	267	0.0001	1.47

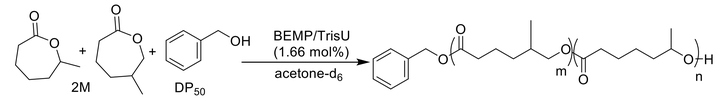
Reaction Conditions: 6-MeCL (0.936 mmol), Benzyl alcohol (0.0187 mmol), Benzoic acid (0.0936 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.

Co-Polymerizations with 6-MeCL



% Conv. εCL	% Conv. 6-MeCL	Time (hrs)	Rate Constant εCL	Rate Constant 6-MeCL
100	31	70	0.0158	0.0003

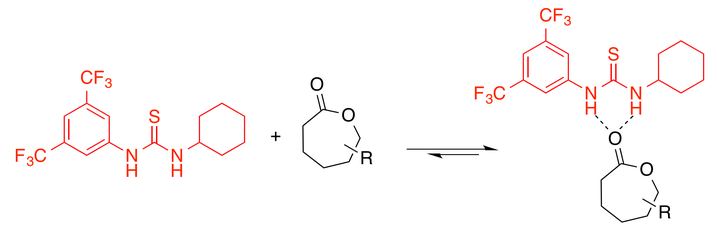
Reaction Conditions: 6-MeCL (0.500 mmol), εCL (0.500) Benzyl alcohol (0.020 mmol), Benzoic acid (0.100 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.



% Conv. 5-MeCL	% Conv. 6-MeCL	Time (hrs)	Rate Constant 5-MeCL	Rate Constant 6-MeCL
100	26	122	0.0016	0.0002

Reaction Conditions: 6-MeCL (0.500 mmol), 5-MeCL (0.500), Benzyl alcohol (0.020 mmol), Benzoic acid (0.100 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.

Binding Studies



H-Bonding	Monomer	Solvent	Keq
CyTU	TOSUO	C_6D_6	14.1
CyTU	5-MeCL	C_6D_6	14.8
CyTU	6-MeCL	C_6D_6	18.9

Reaction Conditions: Monomer (0.024 mmol), CyTU (0.024 mmol). Monomer conversion determined via 1H NMR. Mw/Mn determined via GPC.

Acknowledgments

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