Supporting Information

Ureate anion-catalyzed ring-opening polymerization (ROP) of CO_2-derived lactones: rapid catalysis through pK_a matching

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Materials and Methods

All air and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an MBraun glovebox containing a nitrogen atmosphere. All polymerizations were carried out in a nitrogen-filled glovebox (MBraun) unless otherwise specified. All glassware was oven-dried overnight at 130 ^{o}C before use.

Solvents and reagents were purchased from MilliporeSigma, STREM, Oakwood Chemicals, Matheson, and Airgas and were used without further purification unless otherwise noted. Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories and dried over anhydrous CaH_2 and distilled under a nitrogen atmosphere before use.

Ureas were synthesized according to a procedure developed by Waymouth and group.[1] EVP and EtVP were synthesized according to procedure developed by Tonks and group.[2]

Size exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) using a Thermo Separation Products AS1000 system equipped with a Waters 515 Pump connected in series with two Agilent PLgel MIXED-C columns and fitted with a Waters 2410 refractive index detector at 25 °C and a flow rate of 1 mL/min. Determination of molar masses and dispersities was made by calibration against polystyrene standards.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR were recorded on Bruker Avance III HD 400 MHz spectrometer. ^{1}H NMR spectra of all polymeric reaction mixtures were run with a relaxation delay of 10 seconds unless otherwise noted. Chemical shifts are reported with respect to tetramethylsilane (TMS).

Matrix-assisted laser desorption/ionization spectra were obtained using an Applied Biosysytems Sciex 5800 MALDI TOF/TOF system equipped with an Nd:YAG laser. MALDI data was processed using Sierra Analytics' Polymerix software.

A Sciex X500R quadrupole time-of-flight (qtof) mass spectrometer was used for accurate mass measurement of EHA.

Synthesis and purification of DEtP – Modified procedure for obtaining high purity DEtP

DEtP was synthesized using a modified literature procedure. **EVP** (60 g, 394 mmol), THF (60 mL) and 10 wt% Pd/C were added into a 300 mL Parr reactor with a magnetic stirring bar. The reactor was then pressurized with hydrogen gas to 500 psi and heated at 60 °C for 2 h until all the **EVP** is consumed. The reactor was placed in an ice bath and cooled to 20 °C, and then depressurized. The resulting solution was filtered through approximately 10 g silica gel. After removal of the solvent, the obtained mixture was purified by and vacuum distillation. The obtained **DEtP** was a colorless liquid with an isolated yield of approximately 80% in high purity according to ^{1}H NMR spectroscopy. To obtain "polymerization purity" **DEtP**, the isolated **DEtP** was stirred over CaH_2 overnight and then vacuum distilled. This process was repeated for a total of three times, after which it was stored under 3 Å molecular sieves for 3 days in a nitrogen glovebox before use.

Safety note: Avoid fully drying the Pd/C on the silica because of the fire risk.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.20-4.13 (m, 1H), 2.39-2.27 (m, 1H), 2.08-1.37 (m, 8H), 0.98-0.91 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm) 175.79, 173.93, 82.60, 79.34, 42.14, 39.73, 29.18, 28.32, 26.28, 24.90, 23.89, 22.92, 11.63, 11.09, 9.61, 9.27.

Synthesis of KBHT:

KBHT was synthesized using a modified literature procedure.[3] Inside a glovebox, 1 equiv BHT (1 g, 4.5 mmol) was added to a round bottom flask along with 1 equiv. KHMDS (0.89 g, 4.5 mmol). 10 mL THF was then added to the flask and stirred at room temperature for 6 h, resulting in the formation of a white precipitate. The white precipitate (KBHT) was isolated via vacuum filtration and washed with 20 mL pentane three times before residual solvent was removed under vacuum.

^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm): 6.17 (s, 2H), 1.73 (s, 3H),1.02 (s, 18H); **^{13}C NMR** (101 MHz, d_6-DMSO, δ, ppm) 168.27, 135.90, 124.05, 110.42, 35.05, 30.83, 21.99.

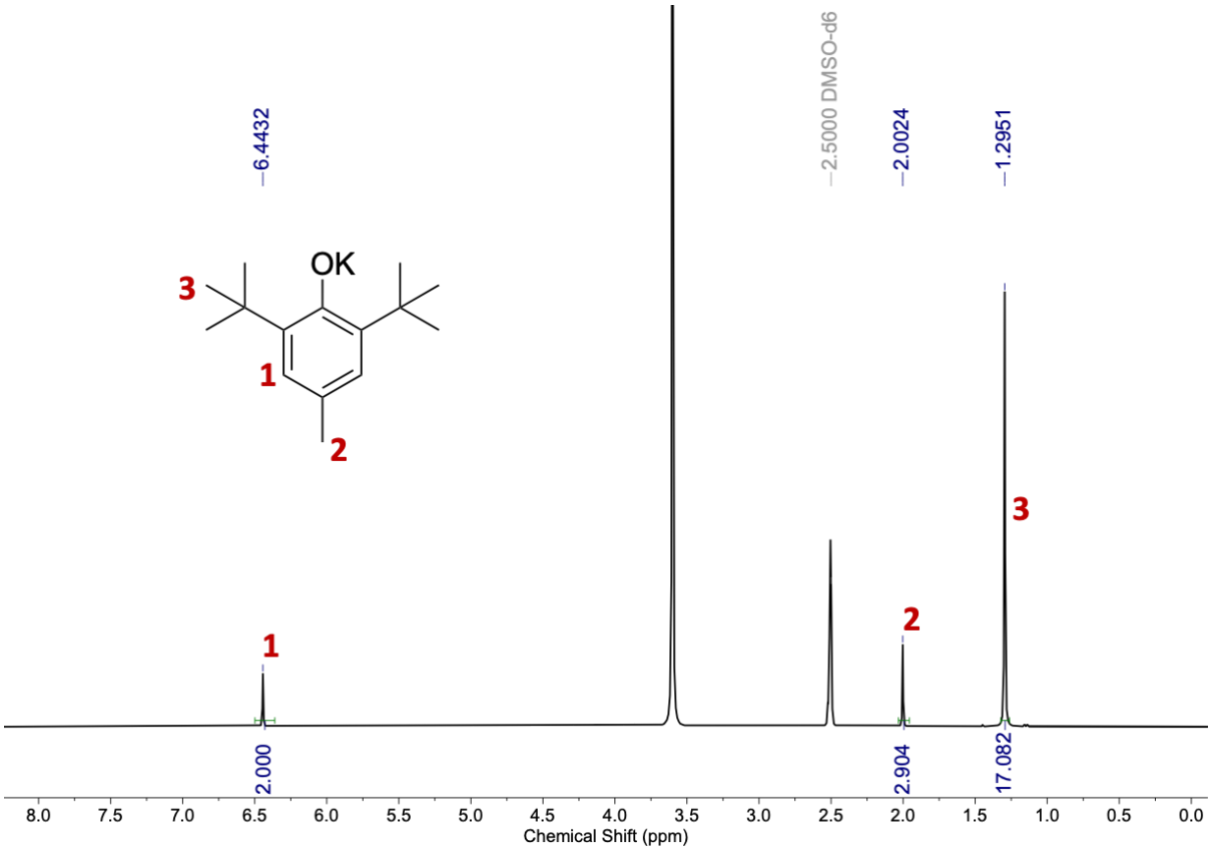


Figure S1. ^{1}H NMR spectrum of KBHT in d_6-DMSO

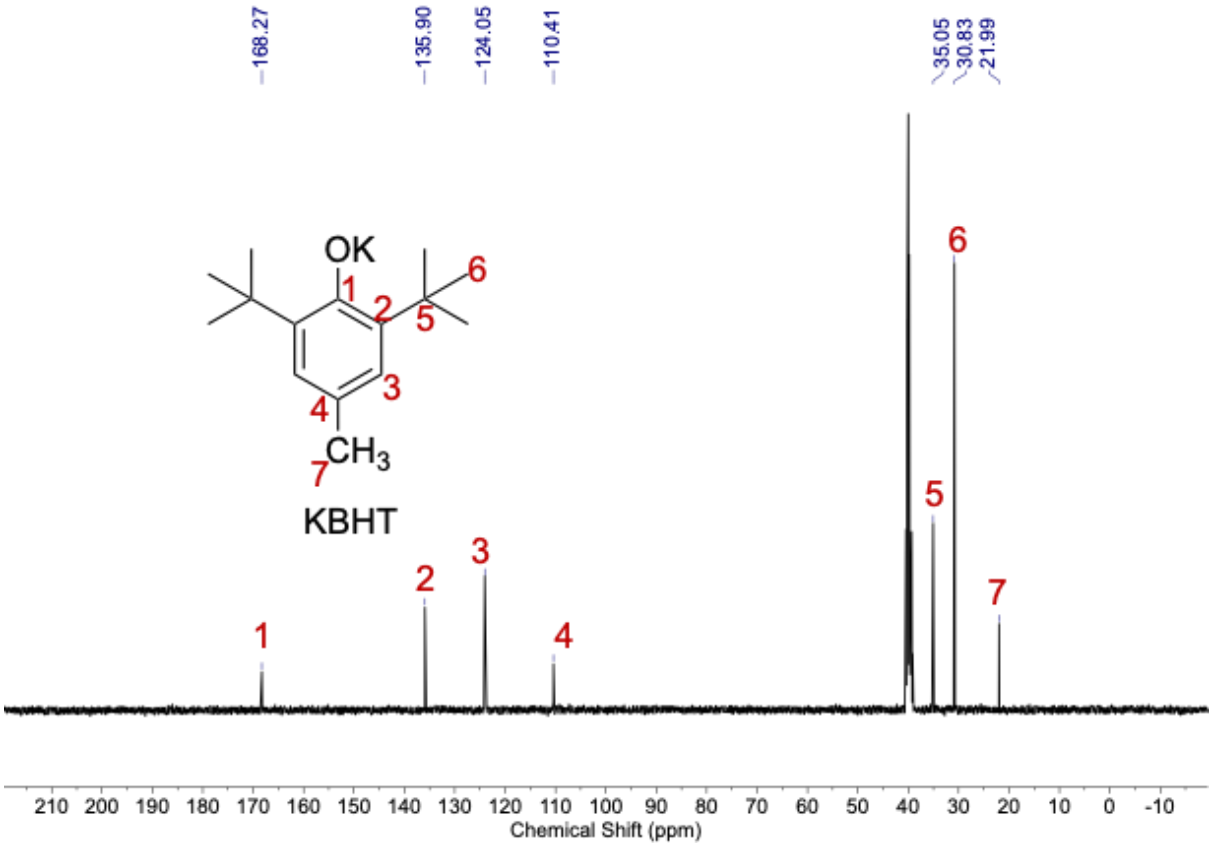


Figure S2. ^{13}C NMR spectrum of KBHT in d_6-DMSO

Synthesis of $KO^{(CF3)t}Bu$:
Inside a glovebox, 1 equiv of (1 g, 7.8 mmol) of 2-Trifluoromethyl-2-propanol was added to a round bottom flask.1 equiv (1.55 g, 7.8 mmol) of KHMDS was then added. 20 mL THF was then added to the reaction mixture and stirred overnight. The solvent was then evaporated under vacuum and white solid was washed with 0 mL pentane three times before residual solvent was removed under vacuum.

^{1}H NMR (400 MHz d_6-DMSO, δ, ppm): 1.06 (s, 3H) **^{13}C NMR** (101 MHz, d_6-DMSO, δ, ppm): 130.67, 70.25, 25.39 **^{19}F NMR** (376 MHz, d_6-DMSO, δ, ppm): 81.68.

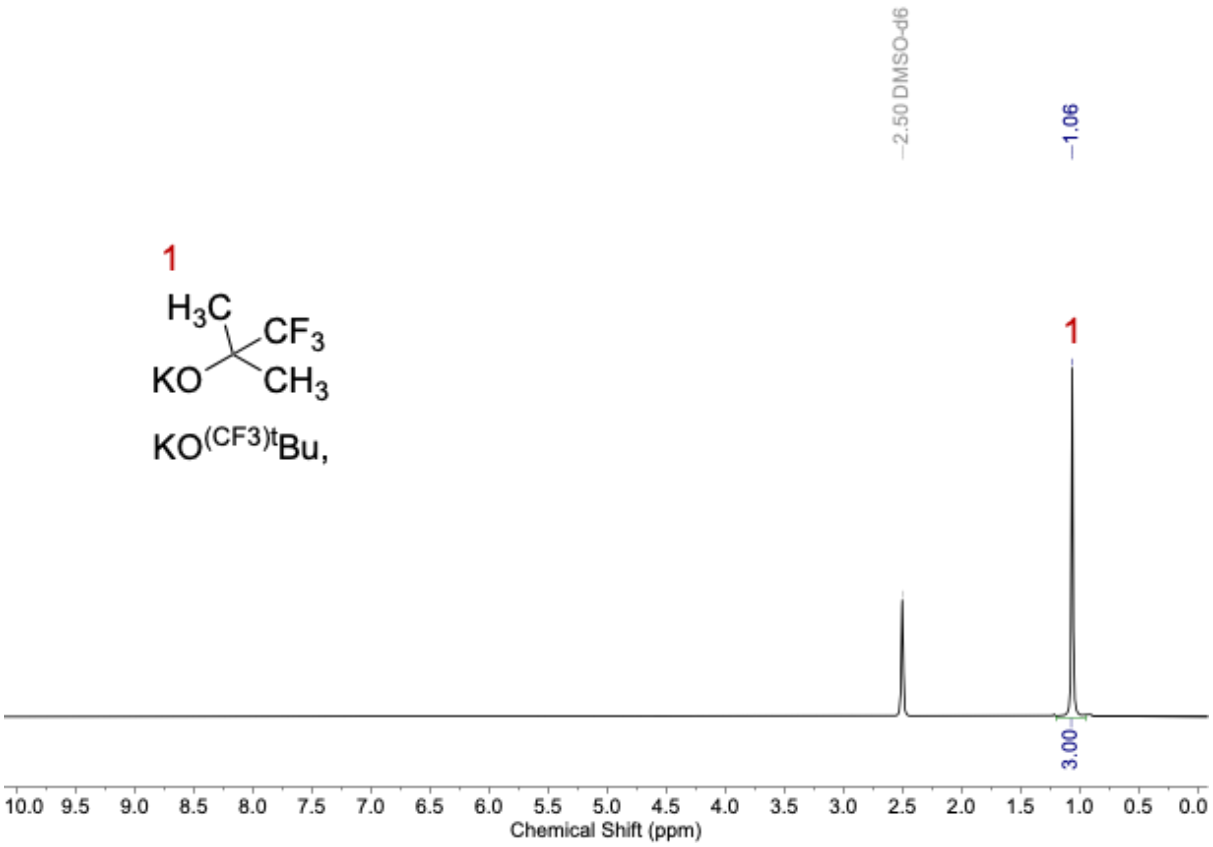


Figure S3. ^{1}H NMR spectrum of $KO^{(CF3)t}Bu$ in d_6-DMSO

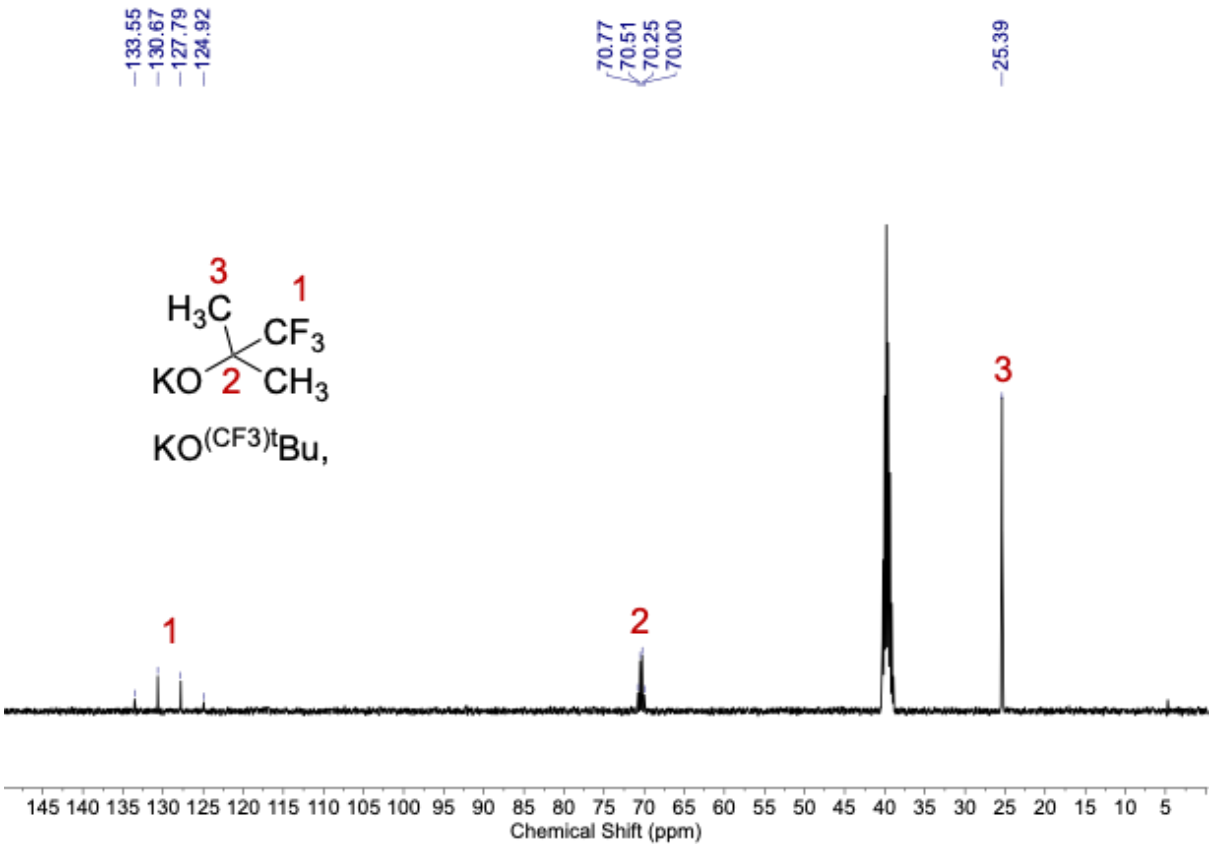


Figure S4. ^{13}C NMR spectrum of $KO^{(CF3)t}Bu$ in d_6-DMSO

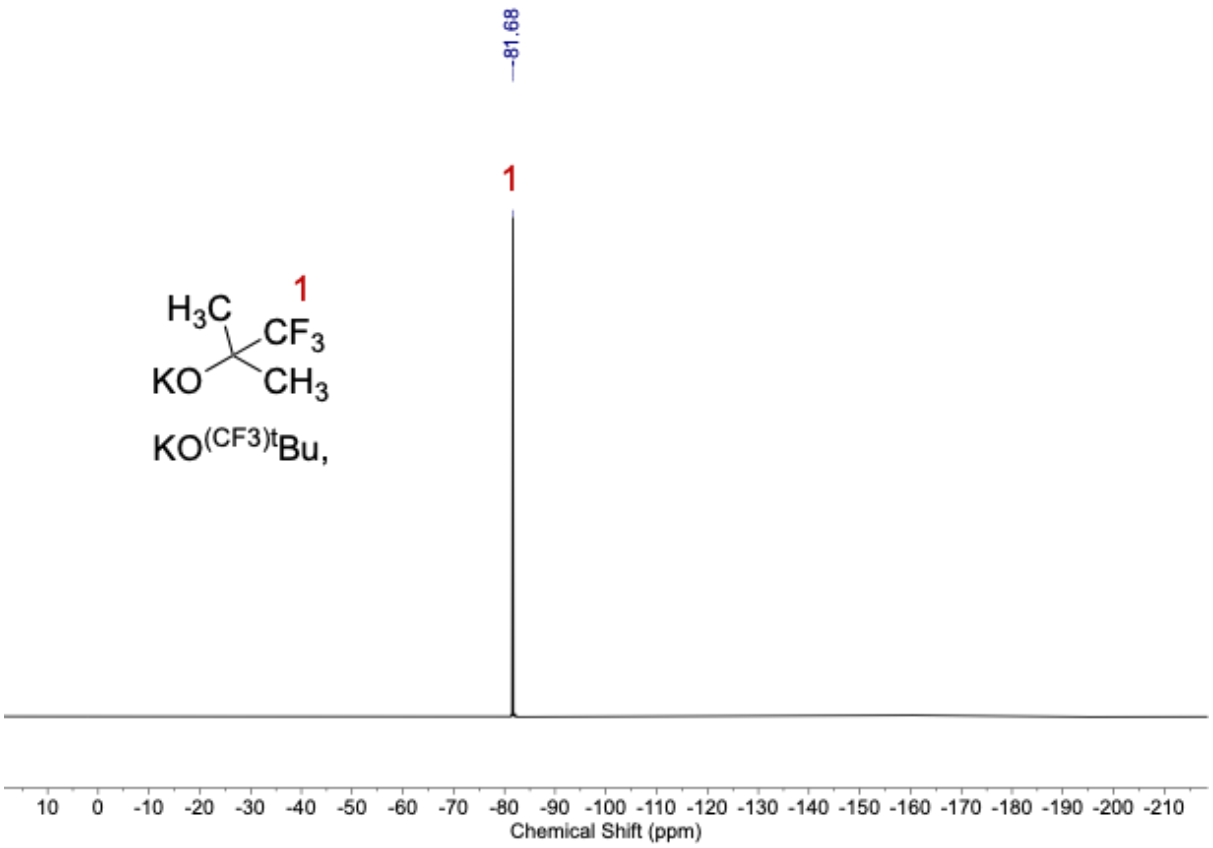
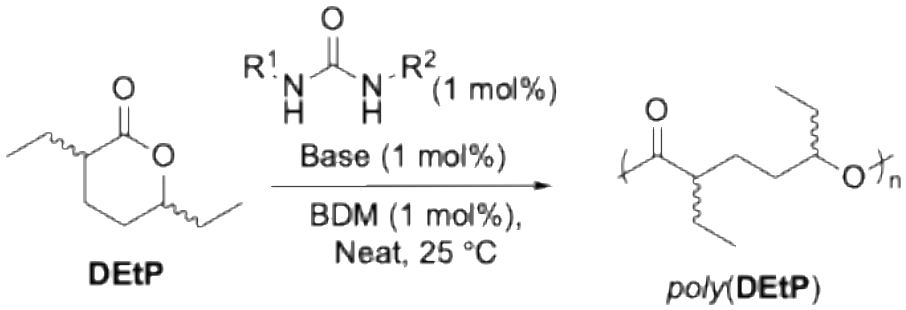


Figure S5. ^{19}F NMR spectrum of $KO^{(CF3)t}Bu$ in d_6-DMSO

General polymerization condition:



0.016 mmol urea (0.01 equiv.) and 0.016 mmol base (0.01 equiv.) were added to a 4 mL vial equipped with a teflon-coated rare earth extra power stir bar. In another vial, a 0.016 mmol,1,4-benzenedimethanol (BDM, 0.01 equiv.) and 1.6 mmol **DEtP** (1 equiv.) were mixed until all the initiator is dissolved. The **DEtP**/BDM solution was then added to the reaction vial. Aliquots of the reactions were taken and immediately quenched by excess benzoic acid in $CDCl_3$ and were then removed from the glovebox for analysis by ^{1}H NMR spectroscopy.

Data analysis for measuring rates:

For the kinetics of polymerization of **DEtP**, aliquots were taken and quenched with benzoic acid in $CDCl_3$ at varying time intervals (time intervals vary significantly, as there is a huge variation in the rate depending upon the pK_a of Urea and p$K_{a\text{-}H}$ of base). It was important to collect sufficient data points until at least 30 % conversion to analyze the rate of reaction. Conversion at a specific time was calculated from the relative integrals in the ^{1}H NMR spectrum of the resonances assigned to **DEtP** (4.22 ppm, 1H) and *poly*(**DEtP**) (4.79 ppm,1H). Monomer concentration was plotted vs. time and the slope of the linear regime in the plot of $ln\{([\mathbf{DEtP}]_o - [\mathbf{DEtP}]_{eq}) / ([\mathbf{DEtP}]_t - [\mathbf{DEtP}]_{eq})\}$ vs time is reported as the k_{obs} for each urea and base combination.

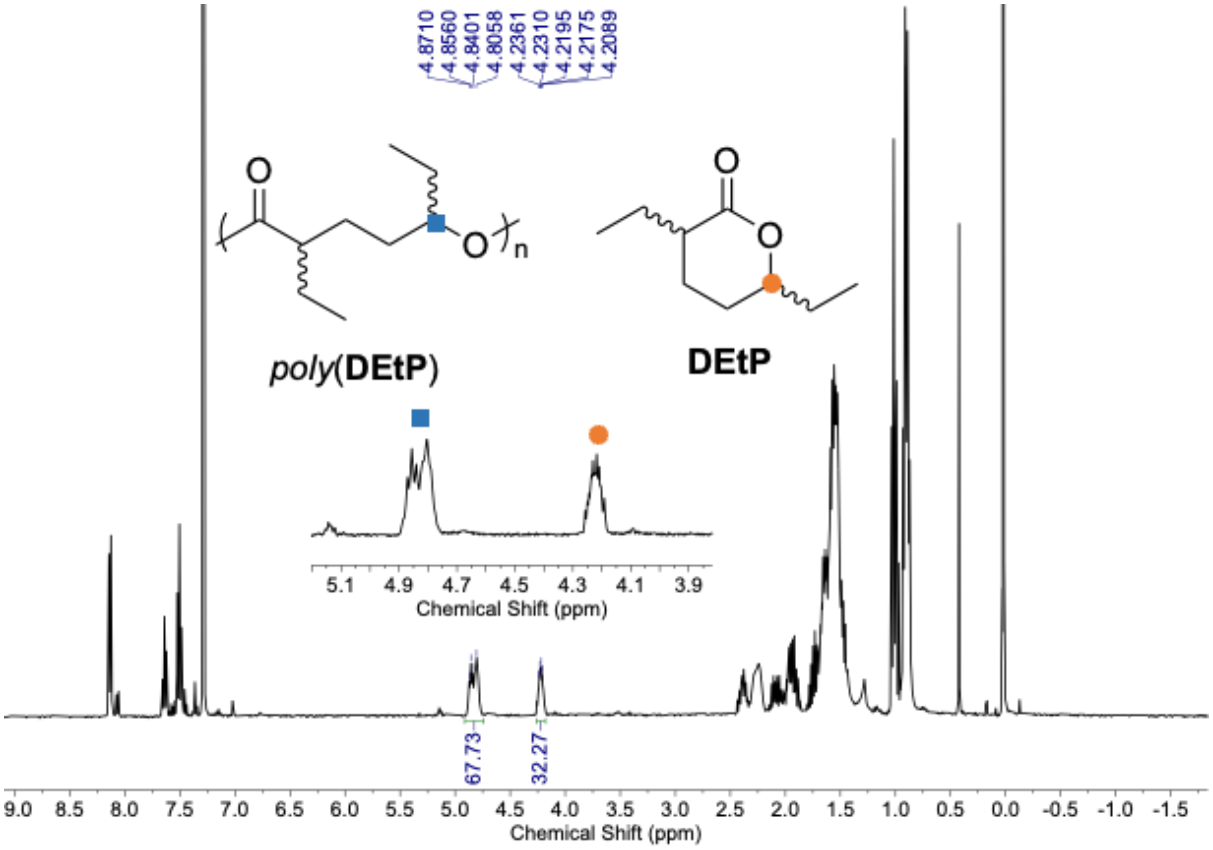
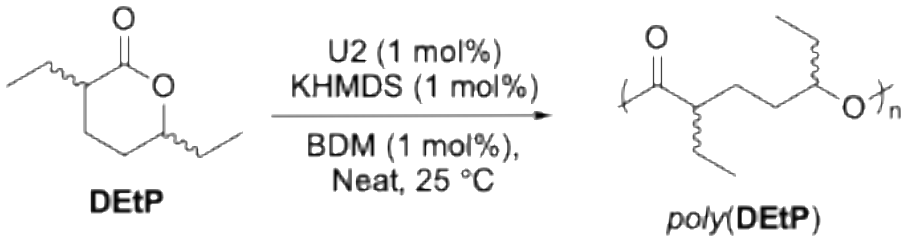


Figure S6. Example ^{1}H NMR spectrum of reaction mixture containing **DEtP** and *poly*(**DEtP**) in $CDCl_3$

Table S1. Data table for polymerization of **DEtP** with U2 and KHMDS.



Time (s)	Conv. (%)	$M_{n\ Theo}$ (kDa)	$M_{n\ SEC}$ (kDa)	$Đ$
20	5	0.7	-	-
30	11	1.7	1.5	1.2
40	18	2.8	3.5	1.1
50	22	3.4	4.4	1.1
60	29	4.5	5.2	1.1
90	44	6.8	10.1	1.1
120	58	9.1	11.5	1.1
180	62	9.7	11.9	1.1

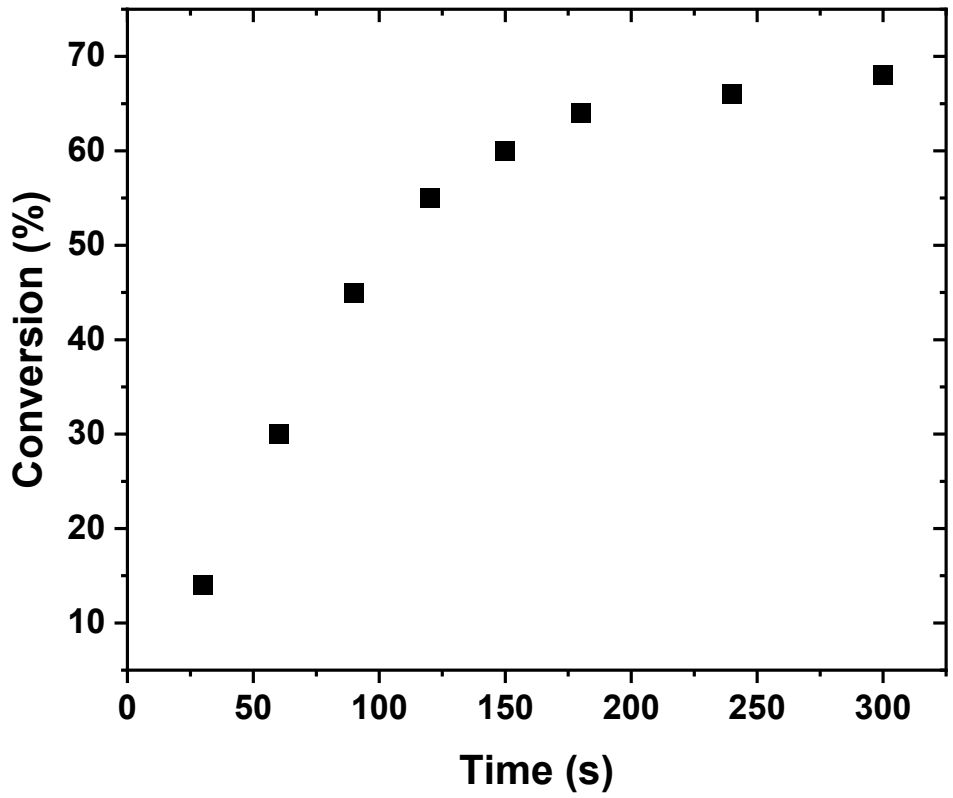


Figure S7. Conversion vs time plot for the polymerization of **DEtP**

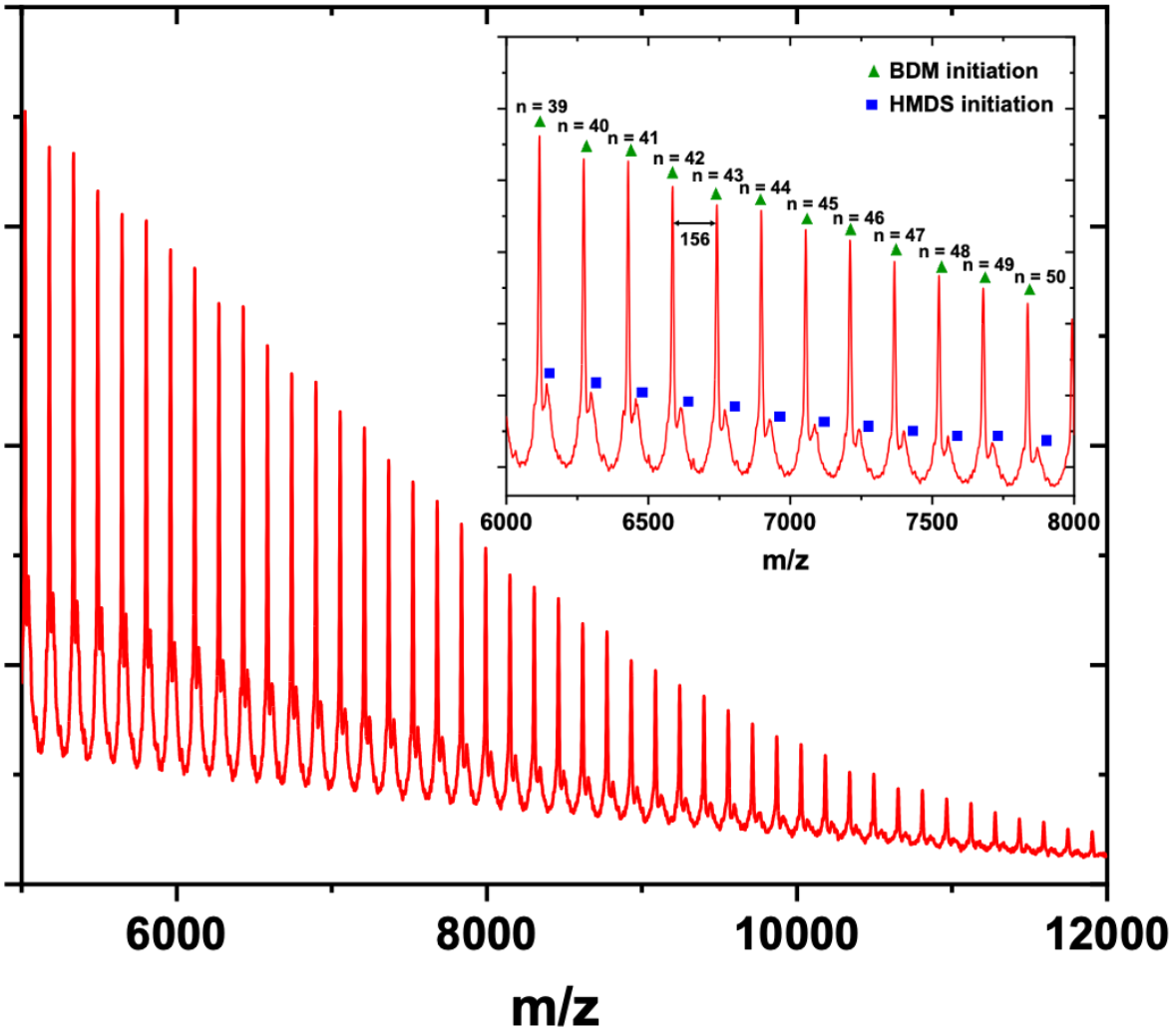
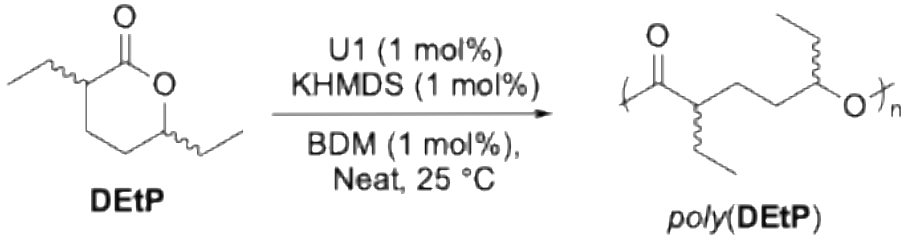


Figure S8. Full MALDI-TOF spectrum *poly*(**DEtP**)

Table S2. Conversion vs time for the polymerization of **DEtP** by U1 and KHMDS



Time (s)	Conversion
30	3
40	5
50	15
60	21
90	43
120	69
180	72
300	77

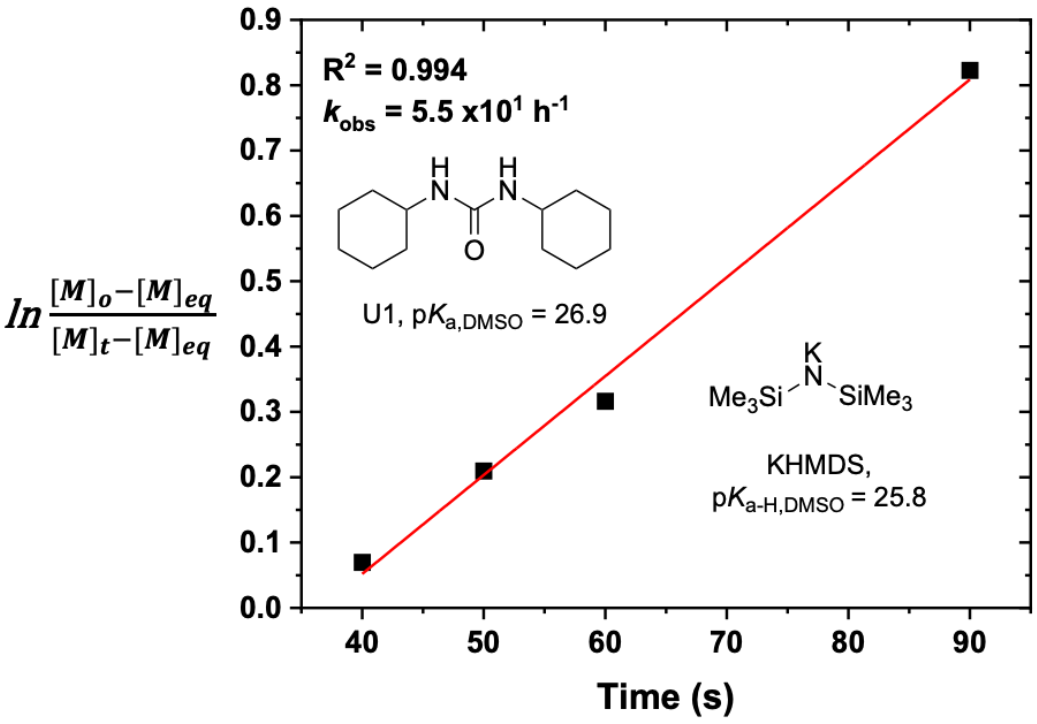
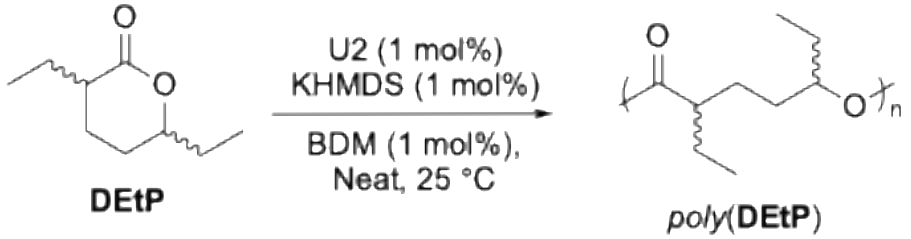


Figure S9. Kinetic plot for the polymerization of **DEtP** by U1 and KHMDS

Table S3. Conversion vs time for the polymerization of **DEtP** by U2 and KHMDS



Time (s)	Conversion (%)
15	5
30	10
45	18
60	26
90	38
150	54
180	63
240	67
270	71
300	72
600	74

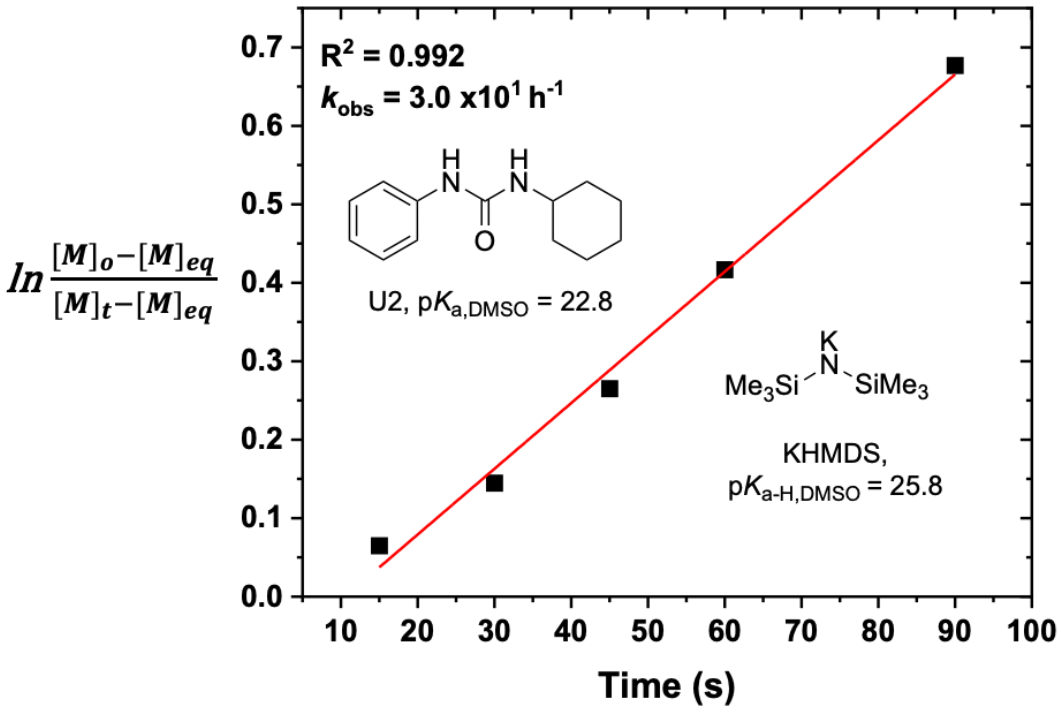
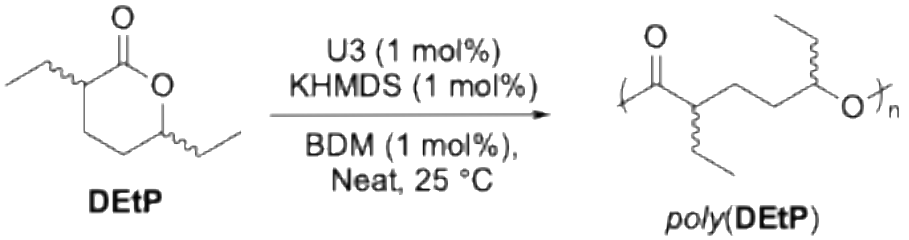


Figure S10. Kinetic plot for the polymerization of **DEtP** by U2 and KHMDS

Table S4. Conversion vs time for the polymerization of **DEtP** by U3 and KHMDS



Time (s)	Conversion (%)
30	1
60	2
120	8
180	13
300	21
360	27
420	31
540	37
600	41
900	60
1200	60

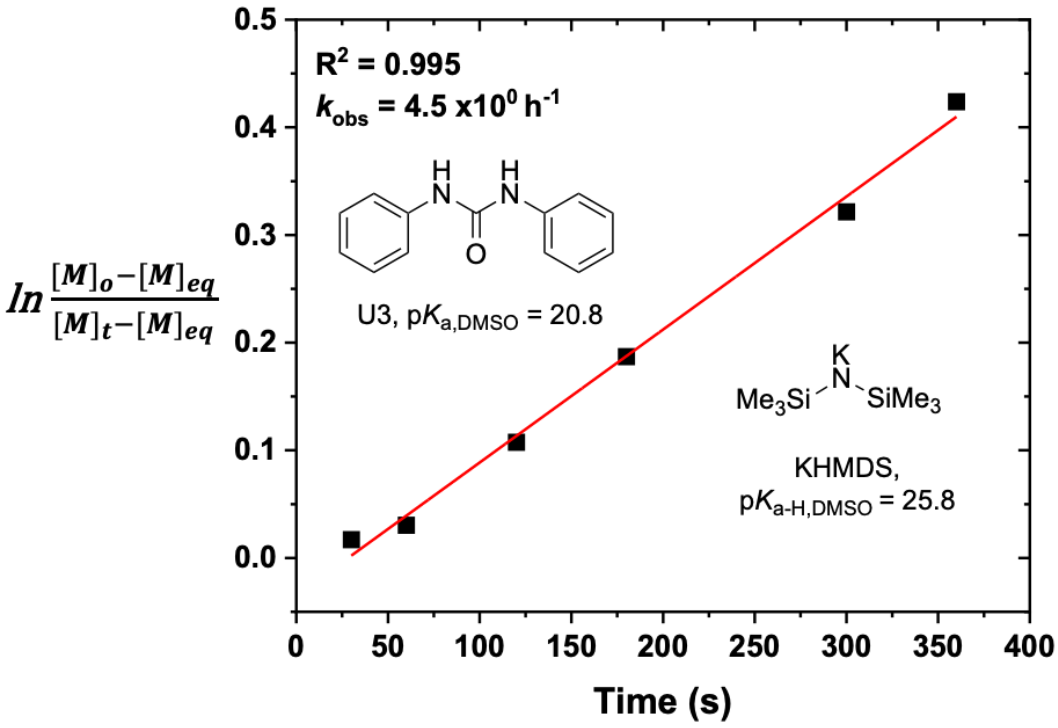
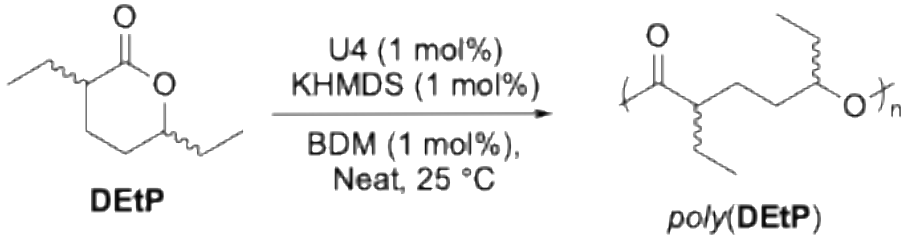


Figure S11. Kinetic plot for the polymerization of **DEtP** by U3 and KHMDS

Table S5. Conversion vs time for the polymerization of **DEtP** by U4 and KHMDS



Time (h)	Conversion (%)
2	11
4	16
6	22
8	27
21.5	60

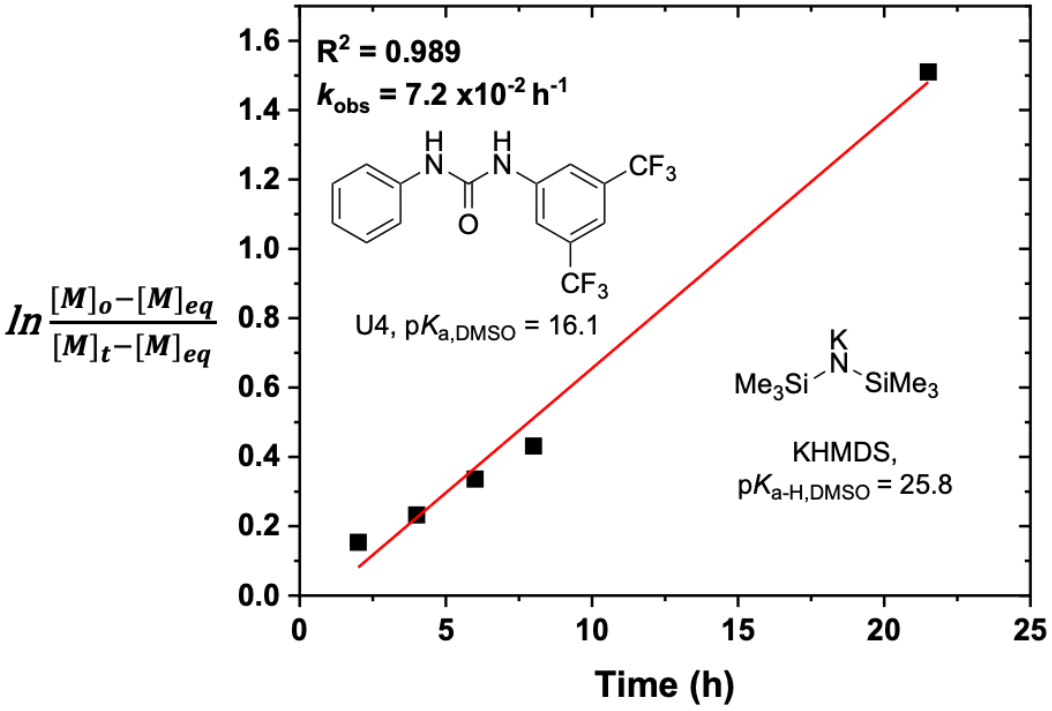
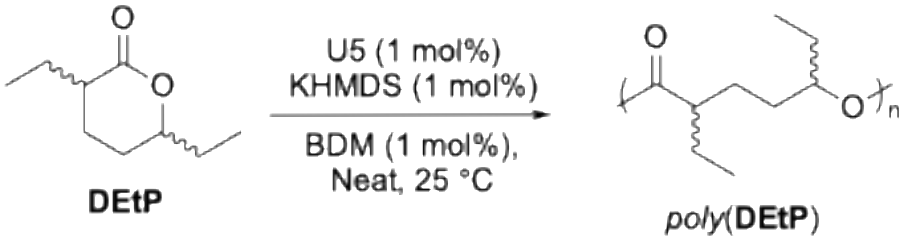


Figure S12. Kinetic plot for the polymerization of **DEtP** by U4 and KHMDS

Table S6. Conversion vs time for the polymerization of **DEtP** by U5 and KHMDS



Time (h)	Conversion (%)
8	7
20	11
27	13
43	23
71.5	31
95	43

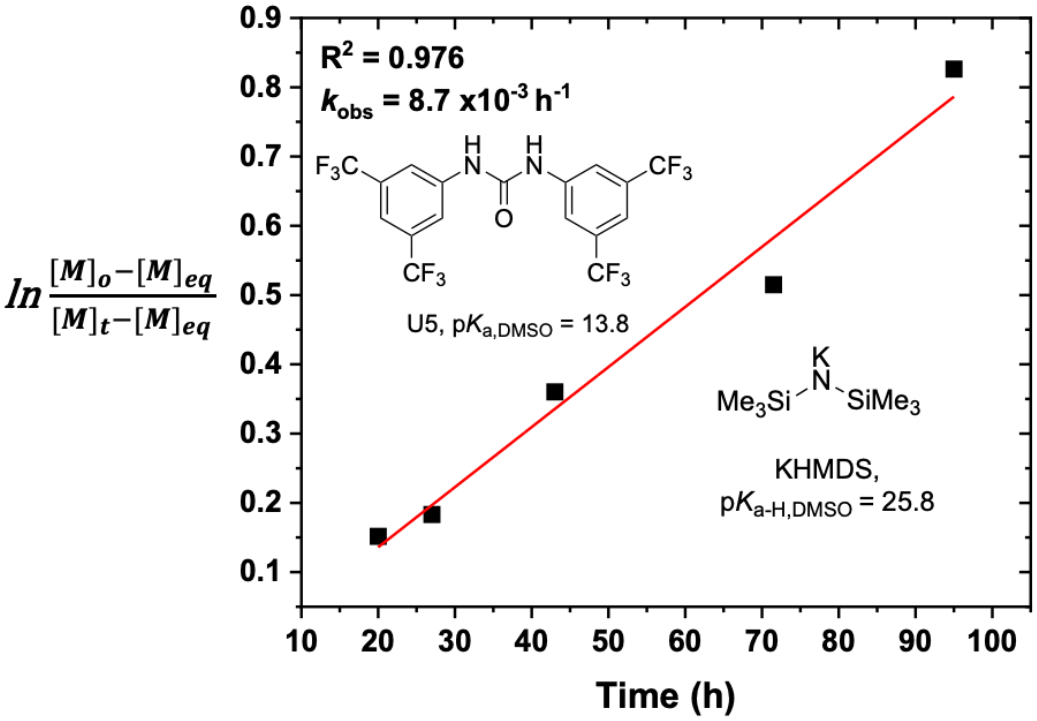
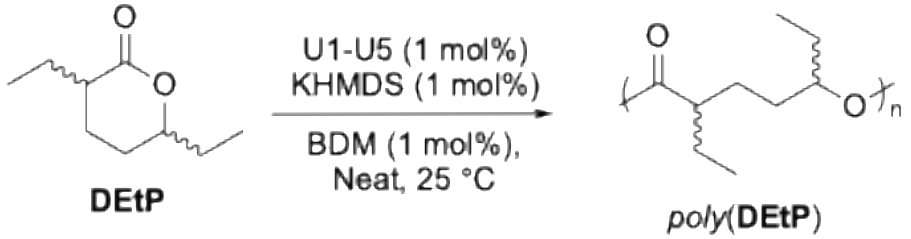


Figure S13. Kinetic plot for the polymerization of **DEtP** by U5 and KHMDS

Table S7. Data table for polymerization of **DEtP** by KHMDS and Ureas



Entry	Catalyst	Conv. %	Time	k_{obs} h^{-1}	$M_{n,\ Theo}$ kDa	$M_{n,\ SEC}$ kDa	$Đ$
1	U1	77	5 min	5.5×10^{1}	12.0	9.5	1.31
2	U2	74	10 min	3.0×10^{1}	11.5	12.5	1.24
3	U3	60	20 min	4.5×10^{0}	9.4	9.1	1.21
4	U4	60	22 h	7.2×10^{-2}	9.4	9.4	1.25
5	U5	43	95 h	8.7×10^{-3}	6.7	8.7	1.43

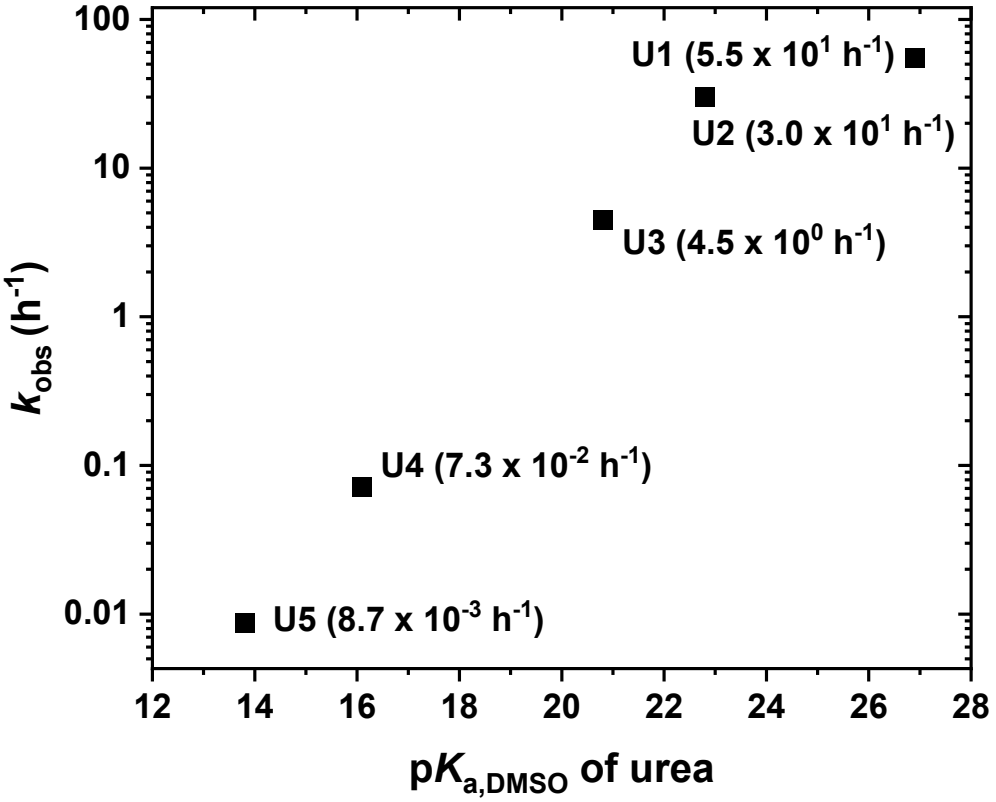
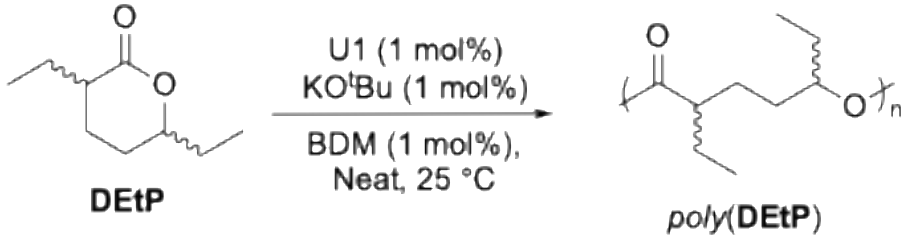


Figure S14. Plot of k_{obs} vs pK_a of urea catalysts for **DEtP** polymerizations with KHMDS as the base

Table S8: Conversion vs time for the polymerization of **DEtP** by U1 and KO^{t}Bu



Time (s)	Conversion (%)
20	2
30	6
40	10
50	18
60	29
90	52
120	66
360	73

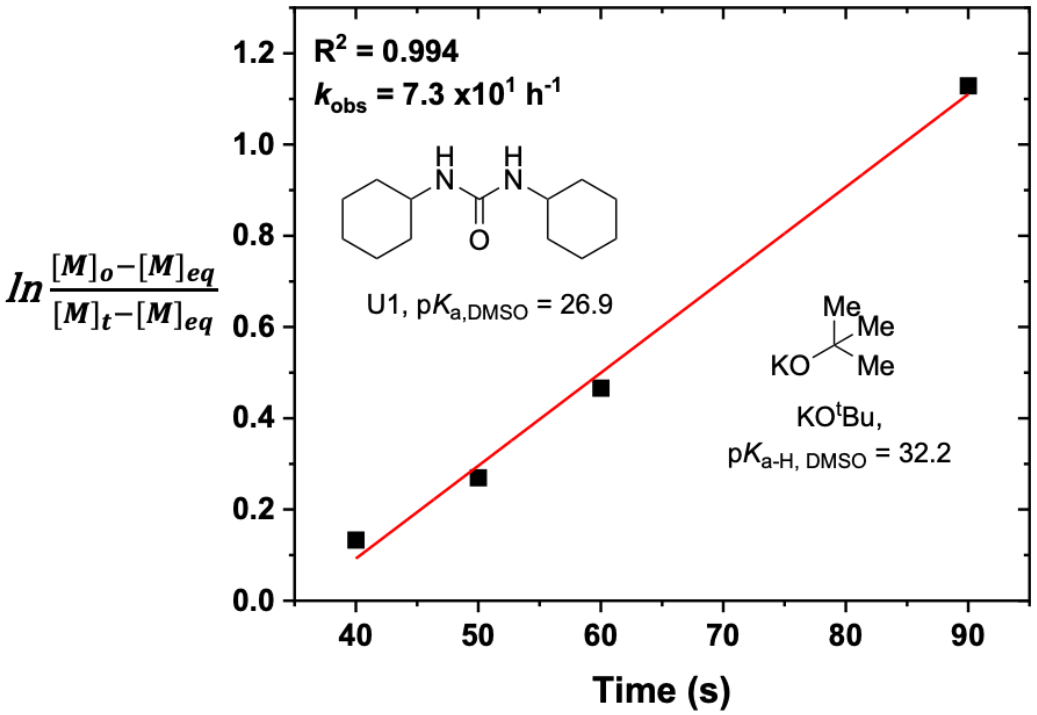
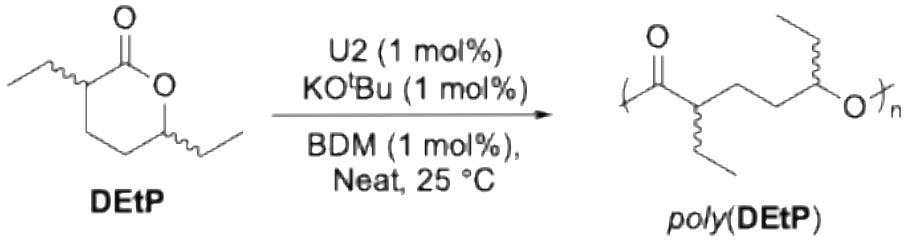


Figure S15. Kinetic plot for the polymerization of **DEtP** by U1 and KO^{t}Bu

Table S9. Conversion vs time for the polymerization of **DEtP** by U2 and KO^{t}Bu



Time (s)	Conversion (%)
10	1
20	5
30	11
40	17
50	24
60	34
90	48
120	56
360	64

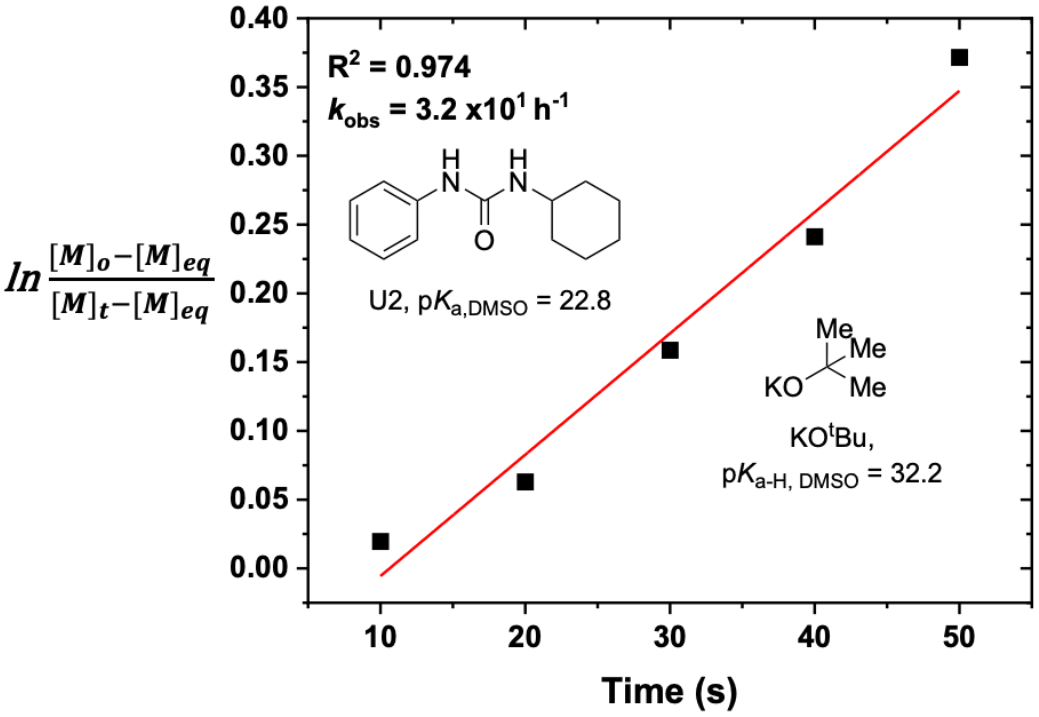
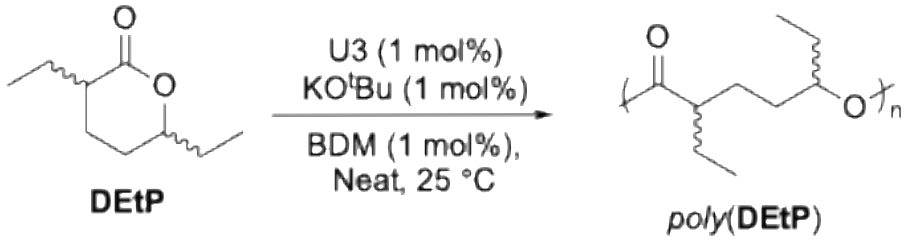


Figure S16. Kinetic plot for the polymerization of **DEtP** by U2 and KO^{t}Bu

Table S10. Conversion vs time for the polymerization of **DEtP** by U3 and KO^{t}Bu



Time (s)	Conversion (%)
30	1
60	4
90	5
120	9
150	11
180	15
300	27
420	37
600	43

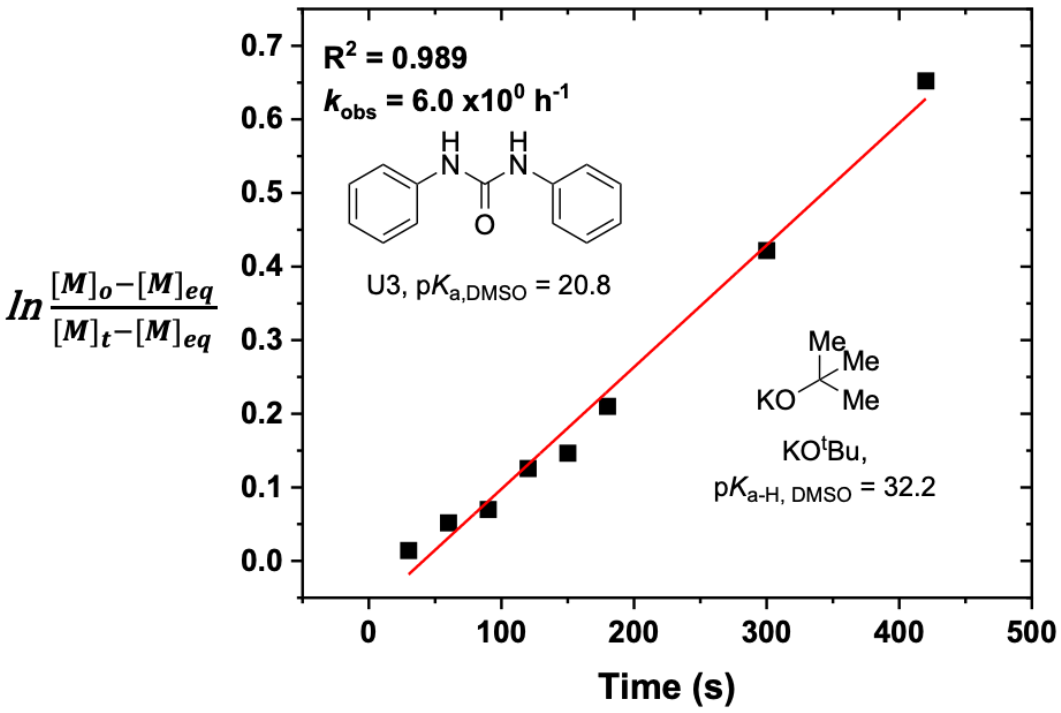
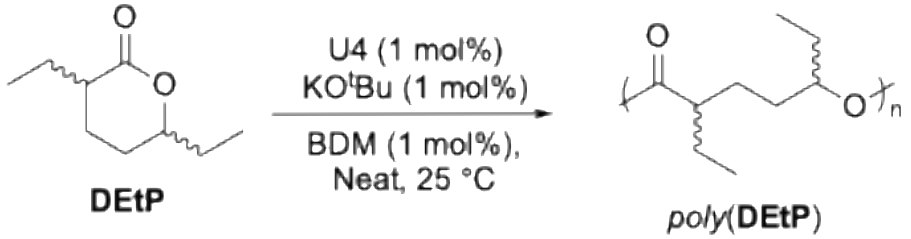


Figure S17. Kinetic plot for the polymerization of **DEtP** by U3 and KO^{t}Bu

Table S11. Conversion vs time for the polymerization of **DEtP** by U4 and KO^{t}Bu



Time (h)	Conversion (%)
0.25	7
1	12
2	19
3	26
5	34
6	38

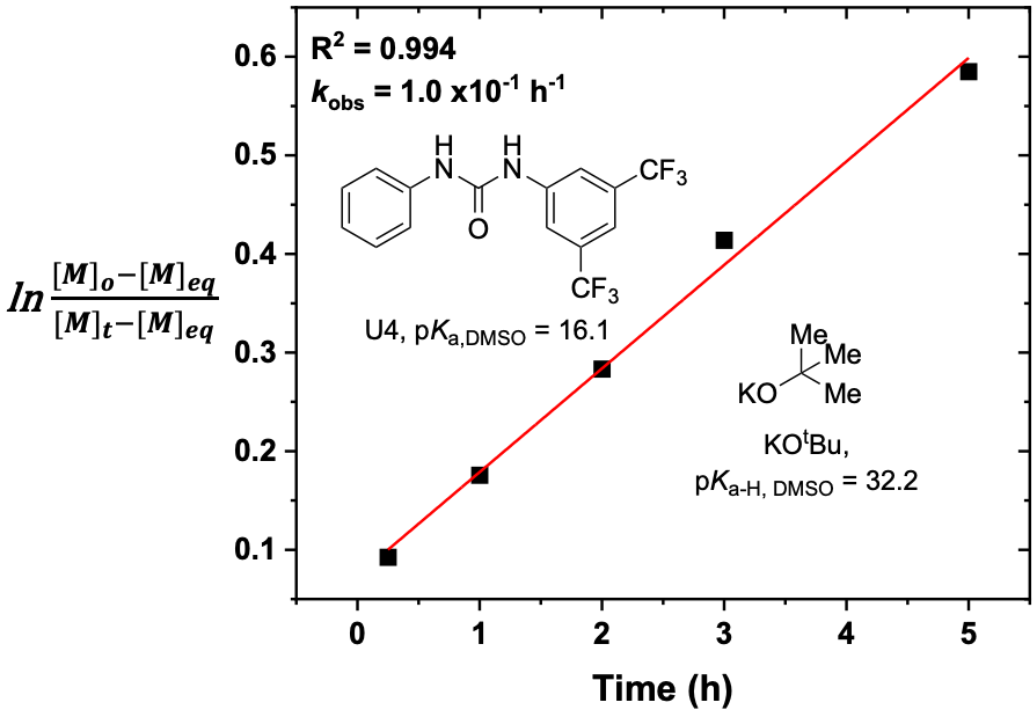
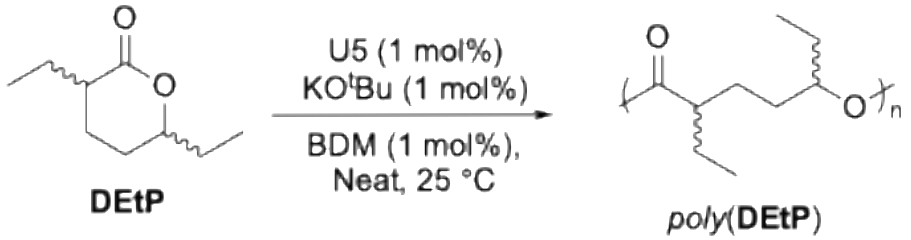


Figure S18. Kinetic plot for the polymerization of **DEtP** by U4 and KO^{t}Bu

Table S12. Conversion vs time for the polymerization of **DEtP** by U5 and KO^{t}Bu



Time (h)	Conversion (%)
6	12
22	25
27.5	27
54	40
100	56

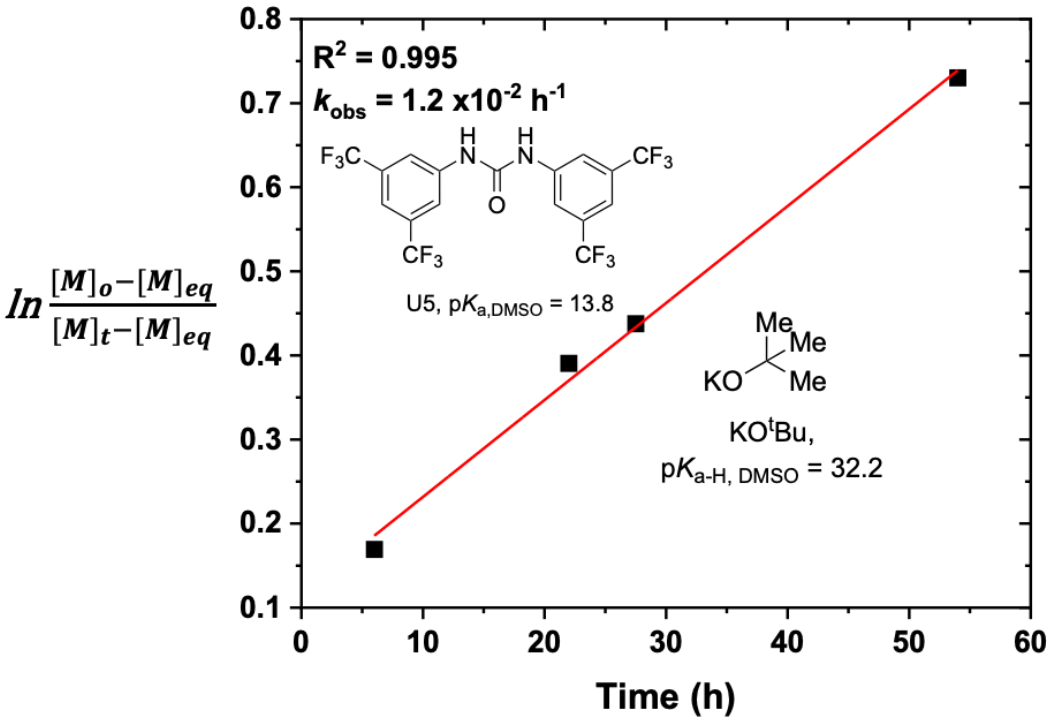
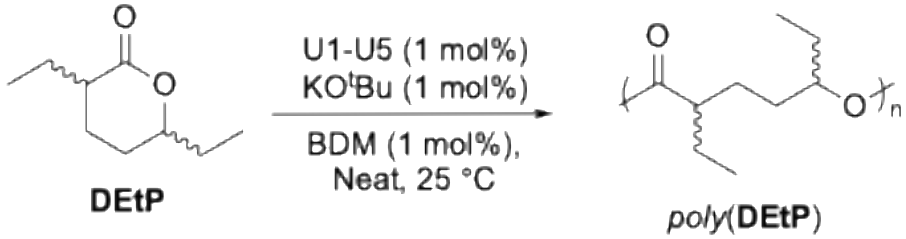


Figure S19. Kinetic plot for the polymerization of **DEtP** by U5 and KO^{t}Bu

Table S13. Data table for polymerization of **DEtP** by KO^{t}Bu and Ureas



Entry	Catalyst	Conv. %	Time	k_{obs} h^{-1}	$M_{n,\,Theo}$ kDa	$M_{n,\,SEC}$ kDa	$Đ$
1	U1	73	3 min	7.3×10^{1}	12.0	10.5	1.21
2	U2	64	10 min	3.2×10^{1}	9.9	9.8	1.28
3	U3	43	10 min	6.0×10^{0}	6.7	6.1	1.23
4	U4	38	6 h	1.0×10^{-1}	6.1	5.4	1.28
5	U5	58	100 h	1.2×10^{-2}	9.0	7.2	1.25

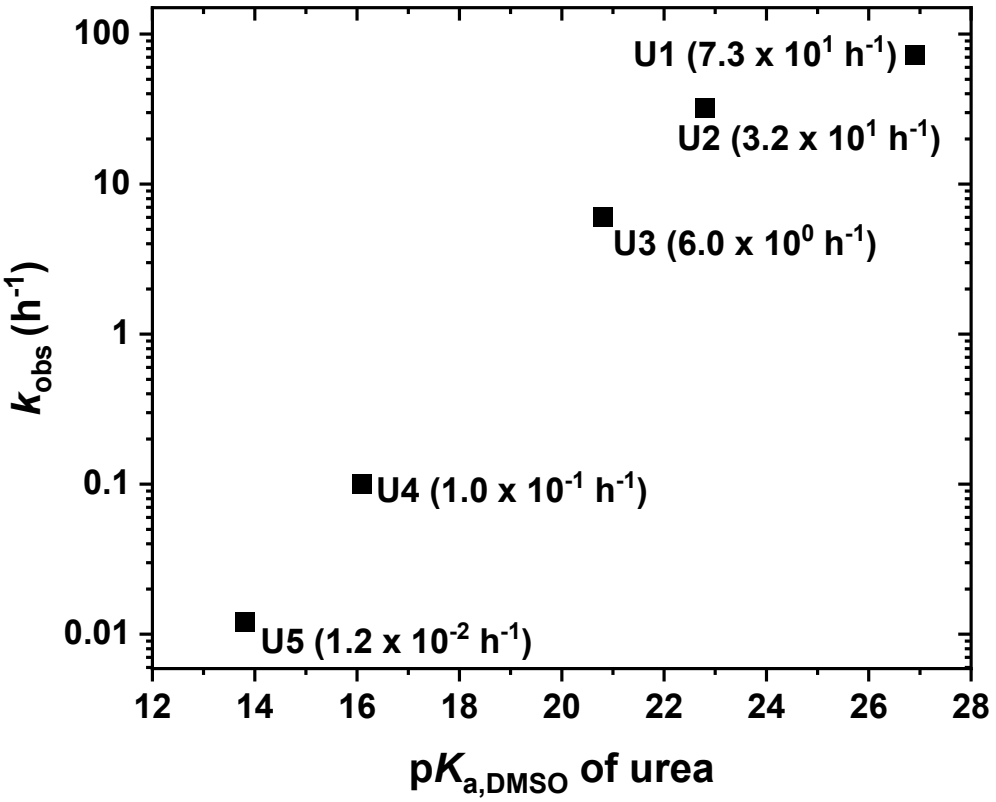
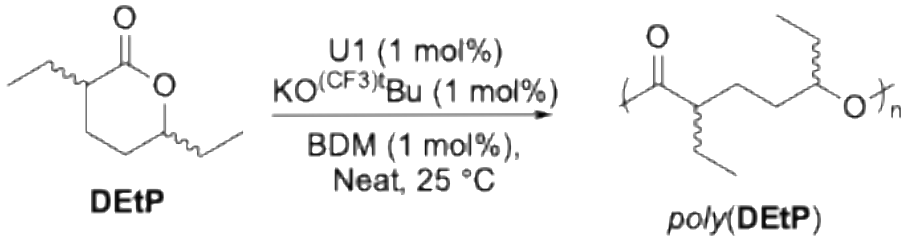


Figure S20. Plot of kobs vs pK_a of urea catalysts for **DEtP** polymerizations with KO^{t}Bu as the base

Table S14. Conversion vs time for the polymerization of **DEtP** by U1 and KO$^{(CF3)t}$Bu



Time (h)	Conversion (%)
2	8
4.5	12
6	14
22	33

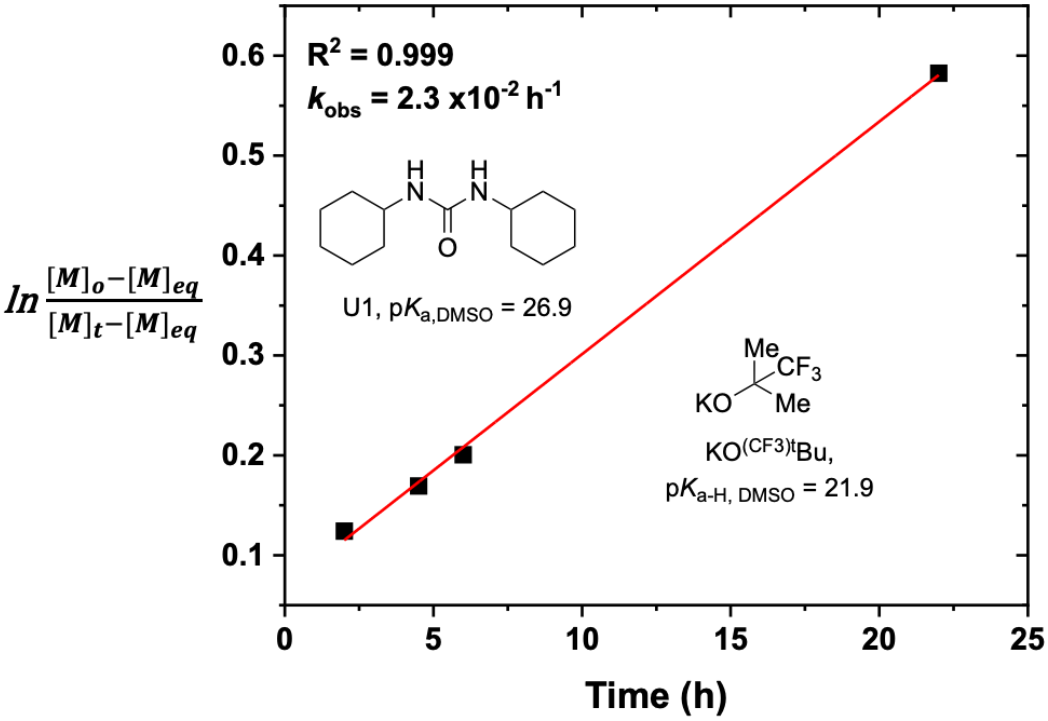
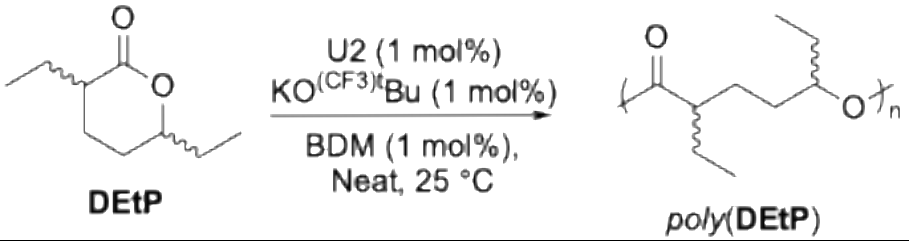


Figure S21. Kinetic plot for the polymerization of **DEtP** by U1 and KO$^{(CF3)t}$Bu

Table S15. Conversion vs time for the polymerization of **DEtP** by U2 and KO$^{(CF3)t}$Bu



Time (h)	Conversion (%)
4	22
19	38
26	47
44.5	65
70	65

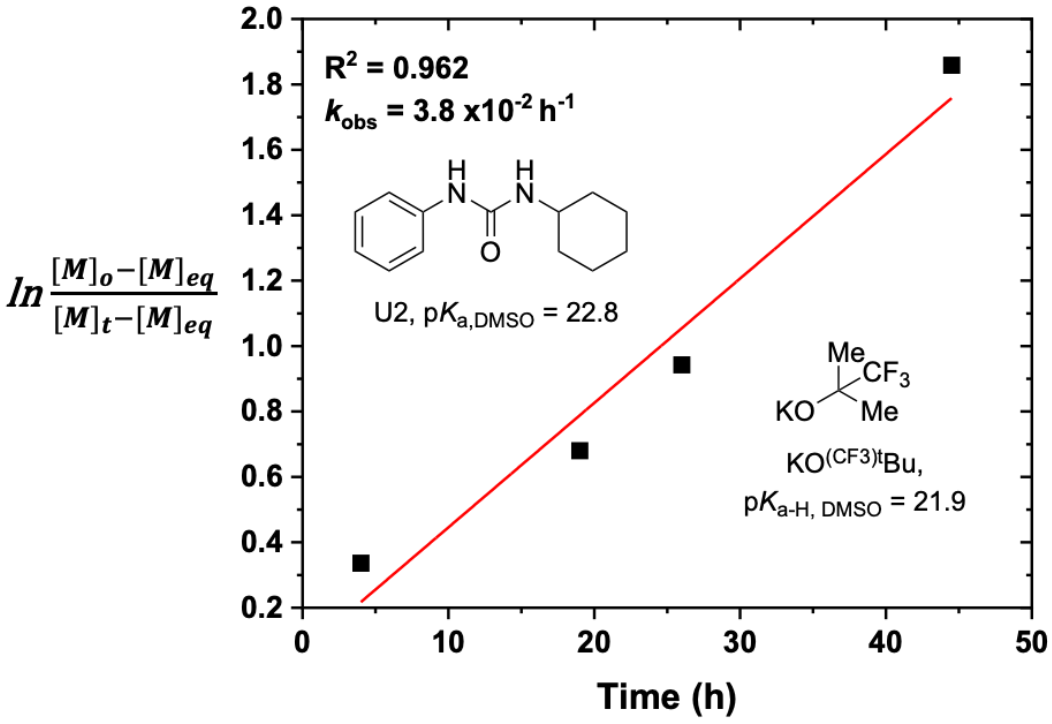
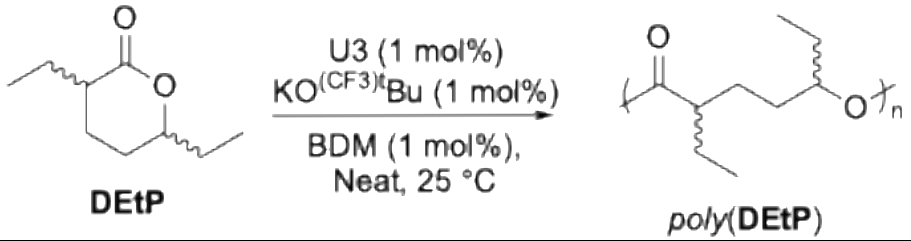


Figure S22. Kinetic plot for the polymerization of **DEtP** by U2 and KO$^{(CF3)t}$Bu

Table S16. Conversion vs time for the polymerization of **DEtP** by U3 and KO$^{(CF3)t}$Bu



Time (h)	Conv. (%)
2	5
4	9
6	12
8	15
22.5	31
52	49

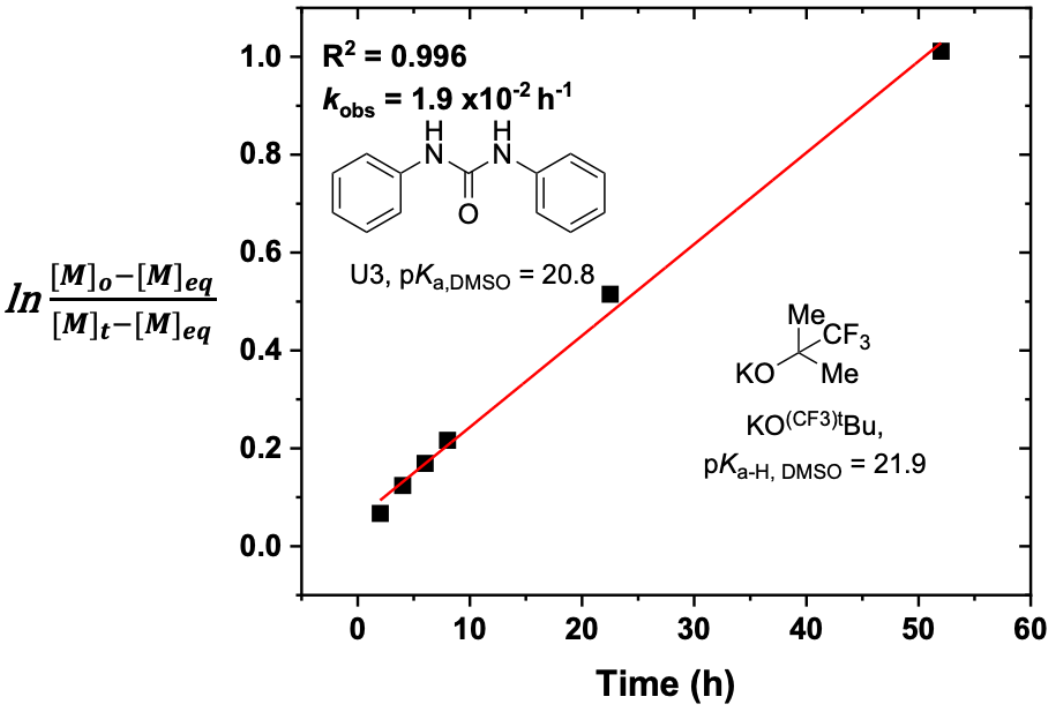
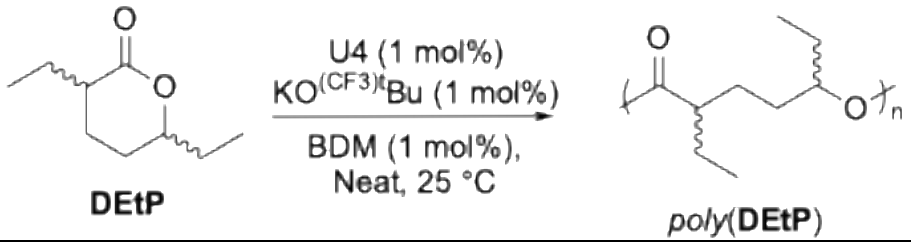


Figure S23. Kinetic plot for the polymerization of **DEtP** by U3 and KO$^{(CF3)t}$Bu

Table S17. Conversion vs time for the polymerization of **DEtP** by U4 and KO$^{(CF3)t}$Bu



Time (h)	Conversion (%)
23	13
48	24
72	34
120	46

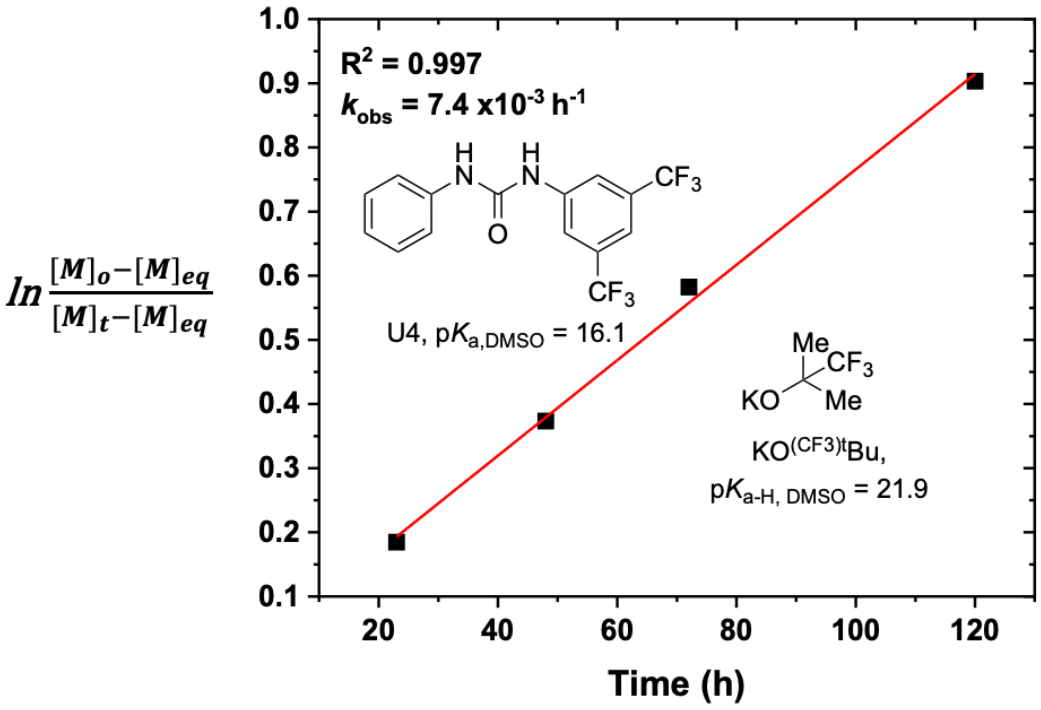
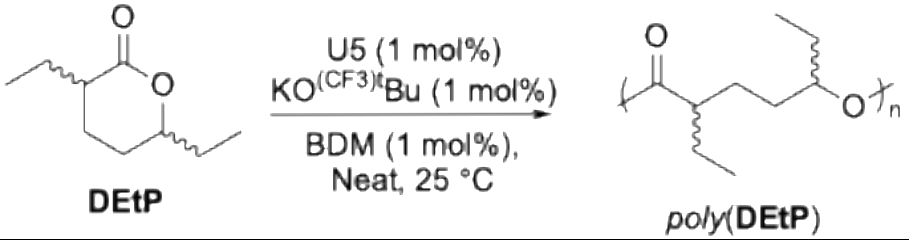


Figure S24. Kinetic plot for the polymerization of **DEtP** by U4 and KO$^{(CF3)t}$Bu

Table S18. Conversion vs time for the polymerization of **DEtP** by U5 and KO$^{(CF3)t}$Bu



Time (h)	Conversion (%)
23	8
48	14
72	20
120	29

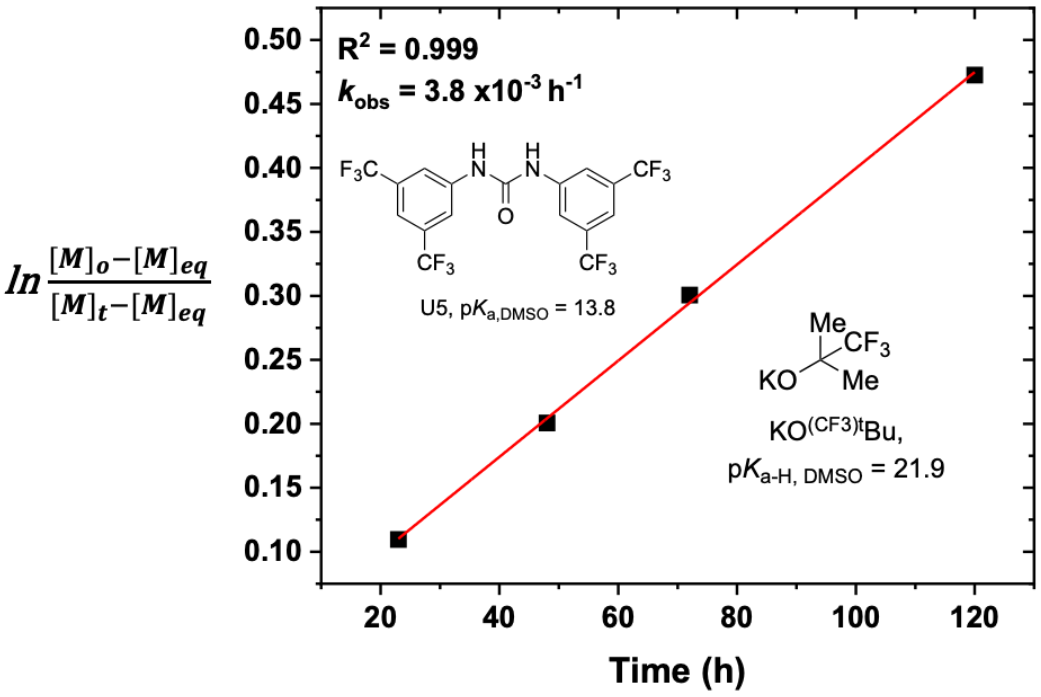
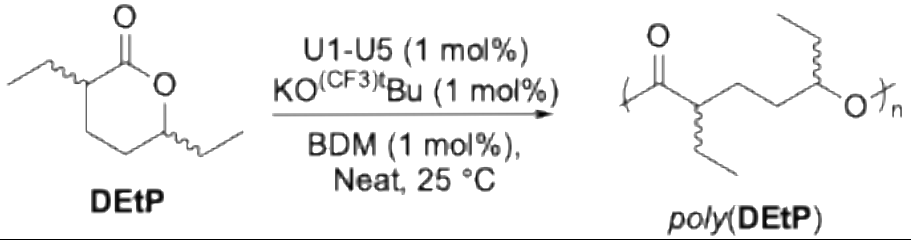


Figure S25. Kinetic plot for the polymerization of **DEtP** by U5 and KO$^{(CF3)t}$Bu

Table S19. Data table for polymerization of **DEtP** by KO$^{(CF3)t}$Bu and Ureas



Entry	Catalyst	Conv. %	Time	k_{obs} h^{-1}	$M_{n,\ Theo}$ kDa	$M_{n,\ SEC}$ kDa	$Đ$
1	U1	33	22 h	2.3×10^{-2}	5.2	10.8	1.14
2	U2	65	45 h	3.8×10^{-2}	10.1	7.7	1.11
3	U3	49	52 h	1.9×10^{-2}	7.6	9.2	1.17
4	U4	46	120 h	7.4×10^{-3}	7.2	10.7	1.13
5	U5	29	120 h	3.8×10^{-3}	4.5	8.6	1.14

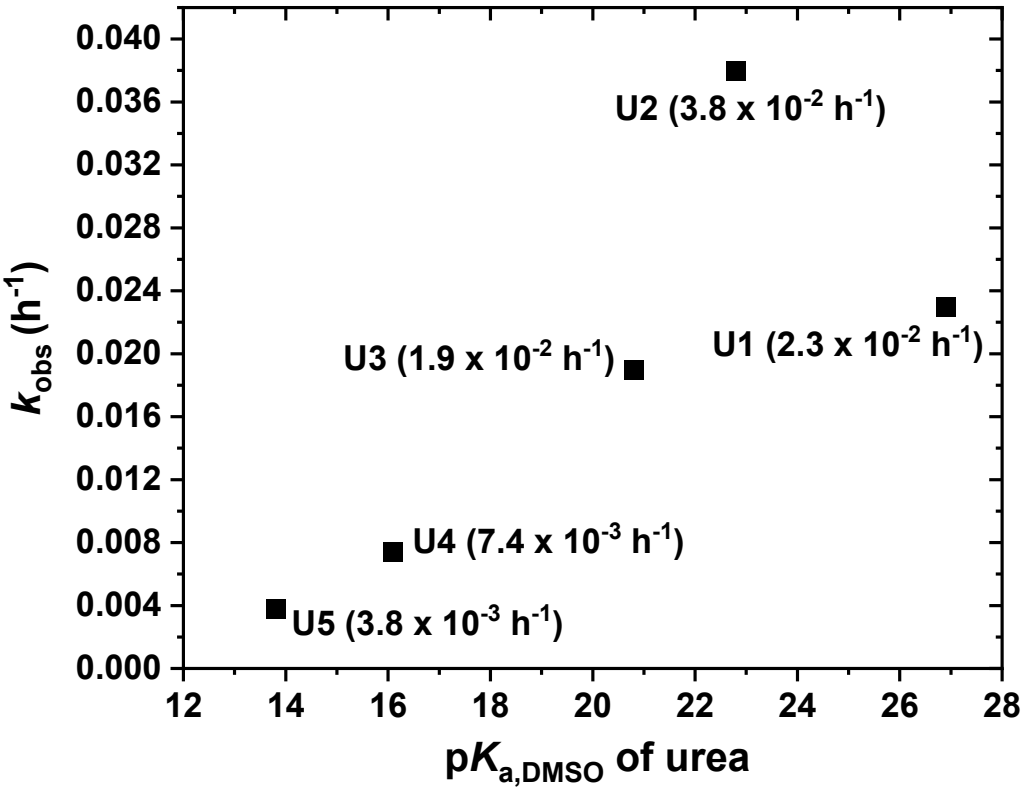
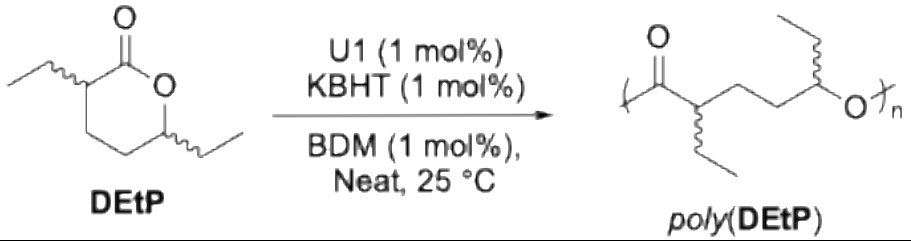


Figure S26. Plot of k_{obs} vs pK_a of urea catalysts for **DEtP** polymerizations with KO$^{(CF3)t}$Bu as the base

Table S20. Conversion vs time for the polymerization of **DEtP** by U1 and KBHT



Time (h)	Conversion (%)
6	5
23	12
49	17
72	20
100	22

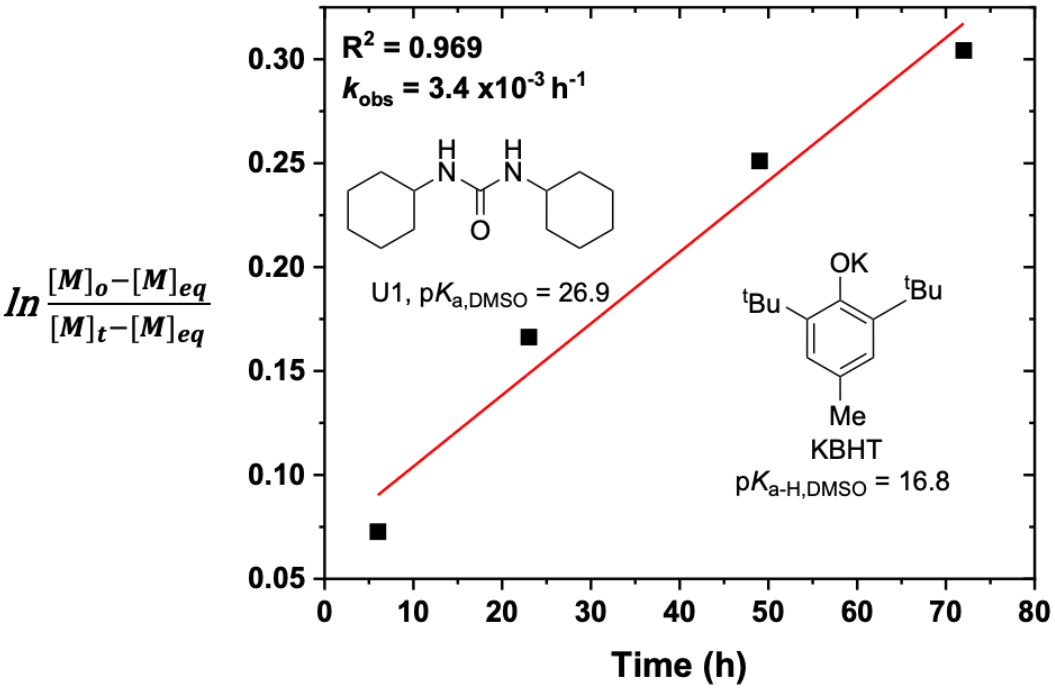
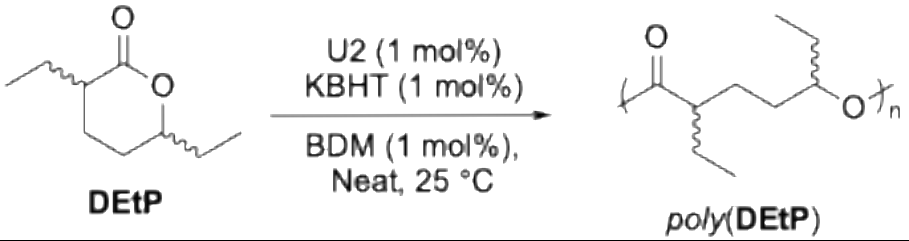


Figure S27. Kinetic plot for the polymerization of **DEtP** by U1 and KBHT

Table S21. Conversion vs time for the polymerization of **DEtP** by U2 and KBHT



Time (h)	Conversion (%)
24	9
48	14
72	17
96	20
120	22

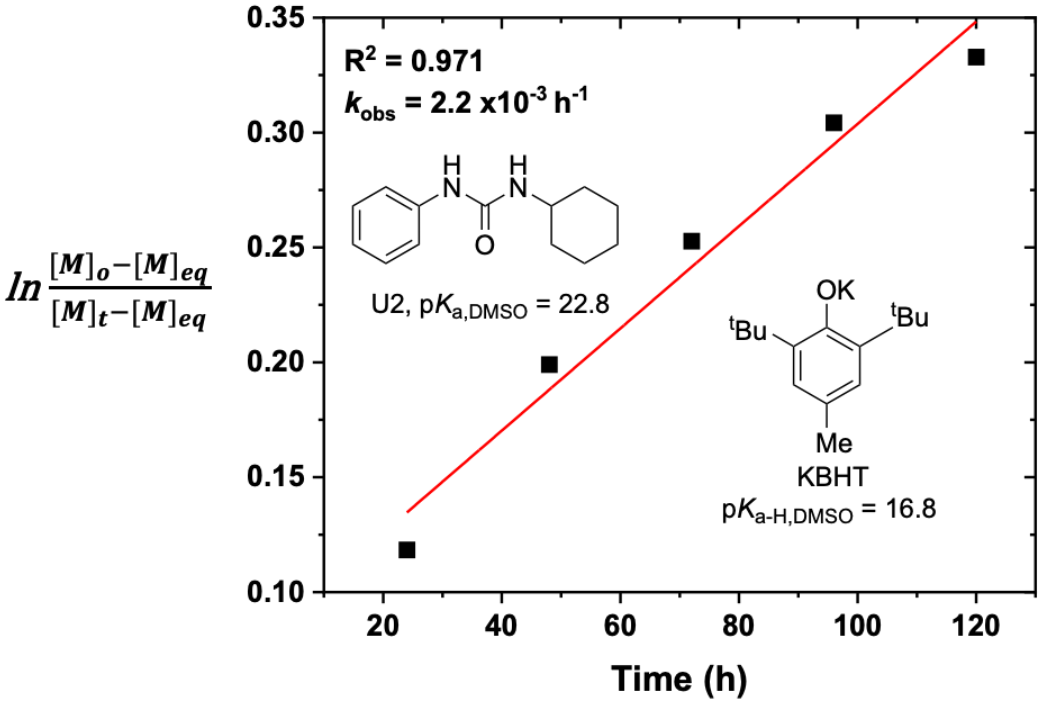
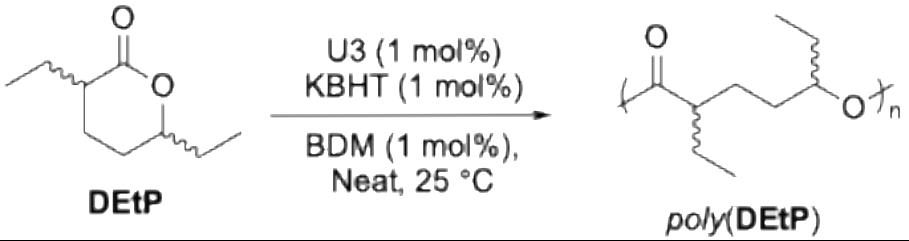


Figure S28. Kinetic plot for the polymerization of **DEtP** by U2 and KBHT

Table S22. Conversion vs time for the polymerization of **DEtP** by U3 and KBHT



Time (h)	Conversion (%)
24	6
48	11
72	15
96	18
120	21

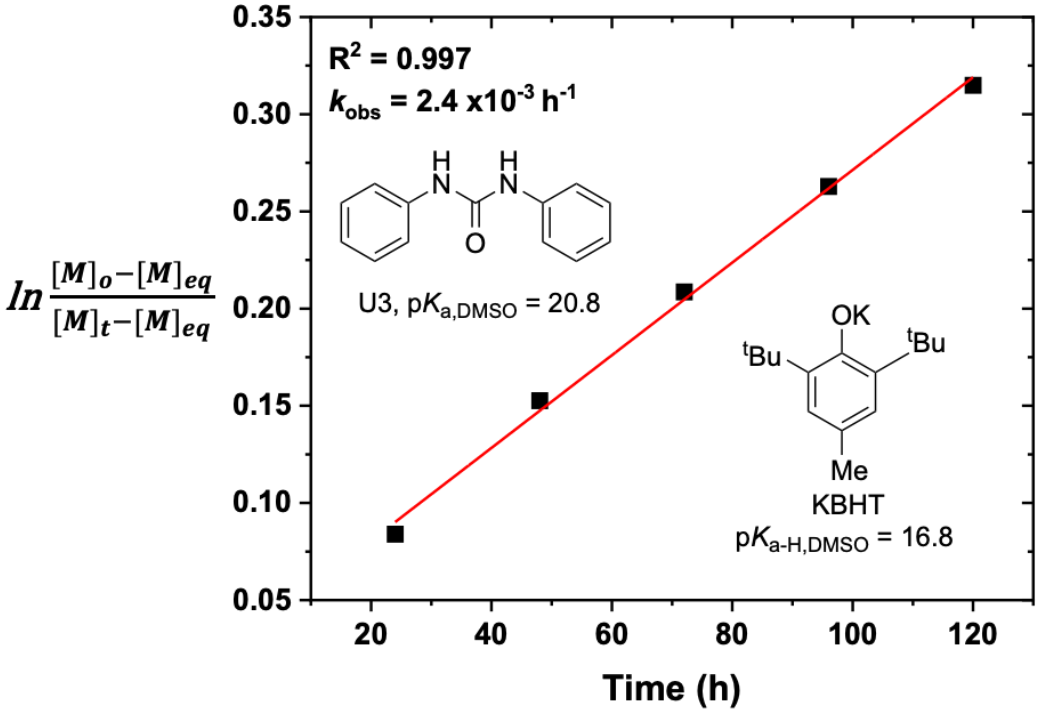
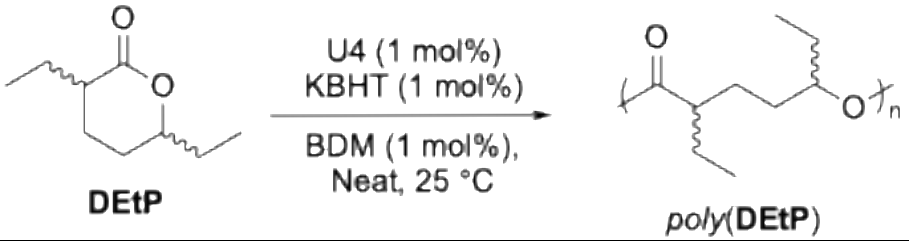


Figure S29. Kinetic plot for the polymerization of **DEtP** by U3 and KBHT

Table S23. Conversion vs time for the polymerization of **DEtP** by U4 and KBHT



Time (h)	Conversion (%)
24	11
48	17
72	24
96	28
120	33

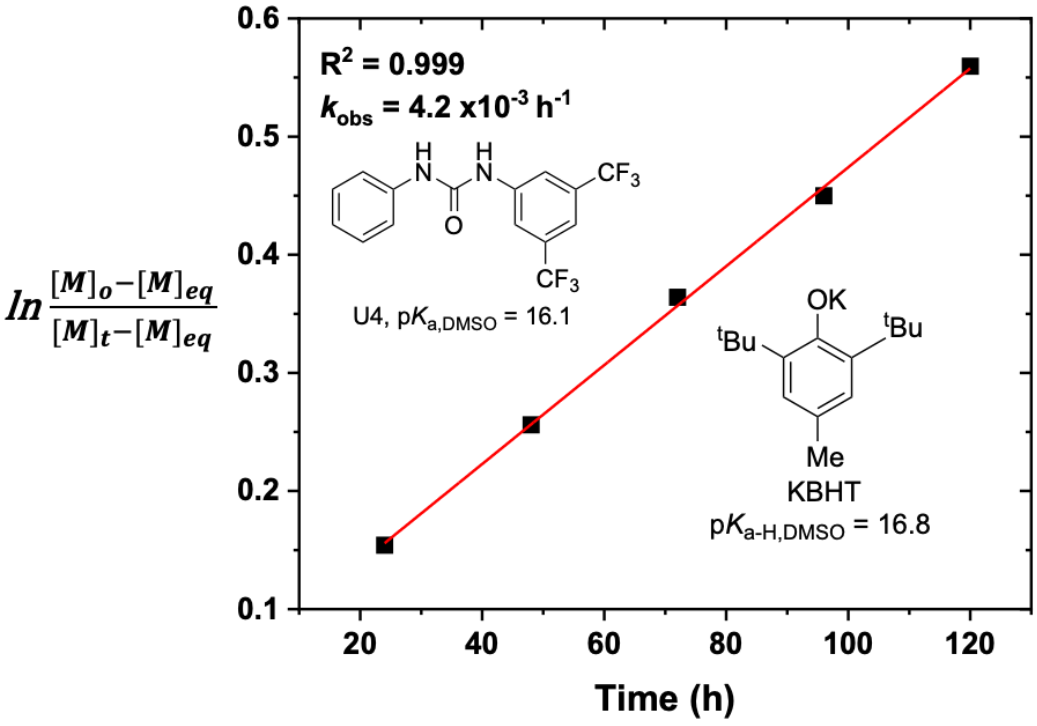
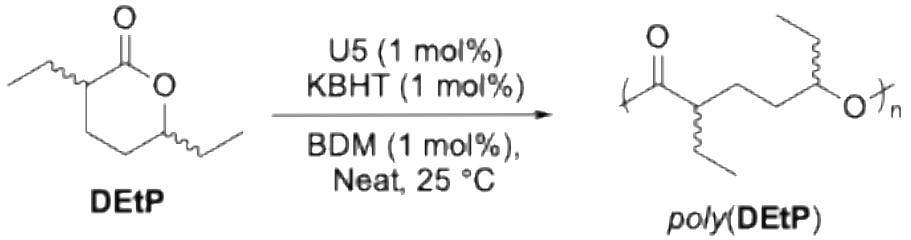


Figure S30. Kinetic plot for the polymerization of **DEtP** by U4 and KBHT

Table S24. Conversion vs time for the polymerization of **DEtP** by U5 and KBHT



Time (h)	Conversion (%)
20	11
35	13
67.5	19
144	26

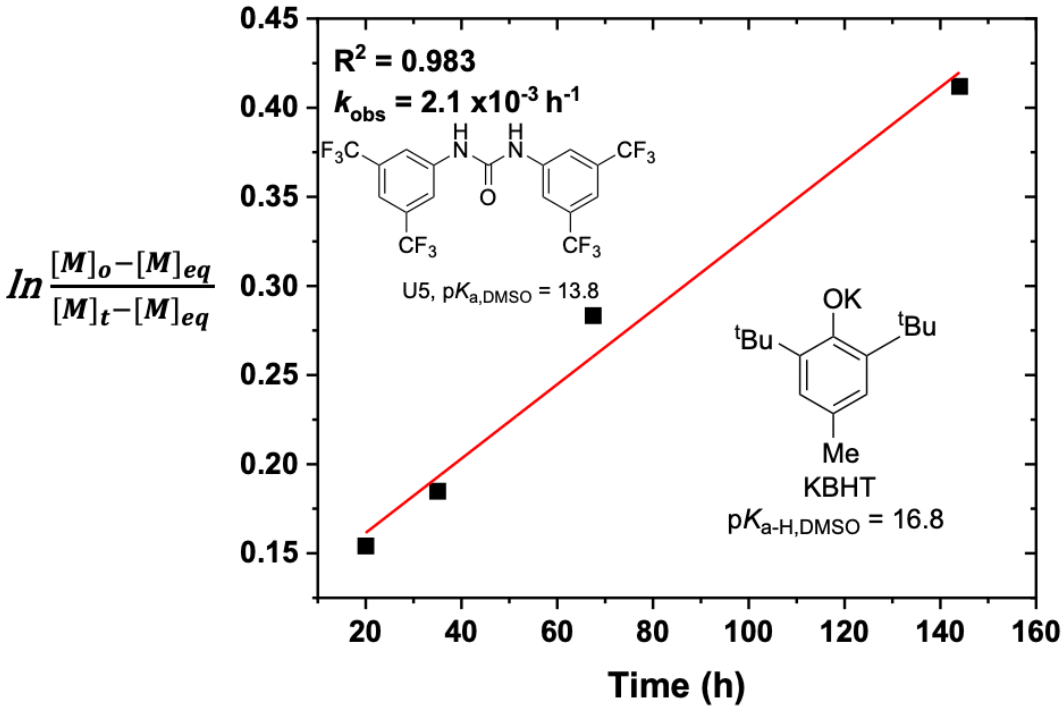
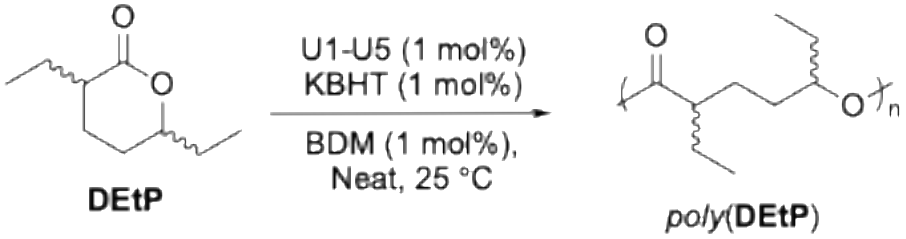


Figure S31. Kinetic plot for the polymerization of DEtP by U5 and KBHT

Table S25. Data table for polymerization of DEtP by KBHT and Ureas



Entry	Catalyst	Conv. %	Time	k_{obs} h^{-1}	$M_{n,\ Theo}$ kDa	$M_{n,\ SEC}$ kDa	$Đ$
1	U1	22	100 h	3.4×10^{-3}	3.4	8.8	1.14
2	U2	22	120 h	2.2×10^{-3}	3.4	4.2	1.14
3	U3	21	120 h	2.4×10^{-3}	3.3	4.4	1.15
4	U4	33	120 h	4.2×10^{-3}	5.2	5.8	1.14
5	U5	26	144 h	2.1×10^{-3}	4.1	7.3	1.19

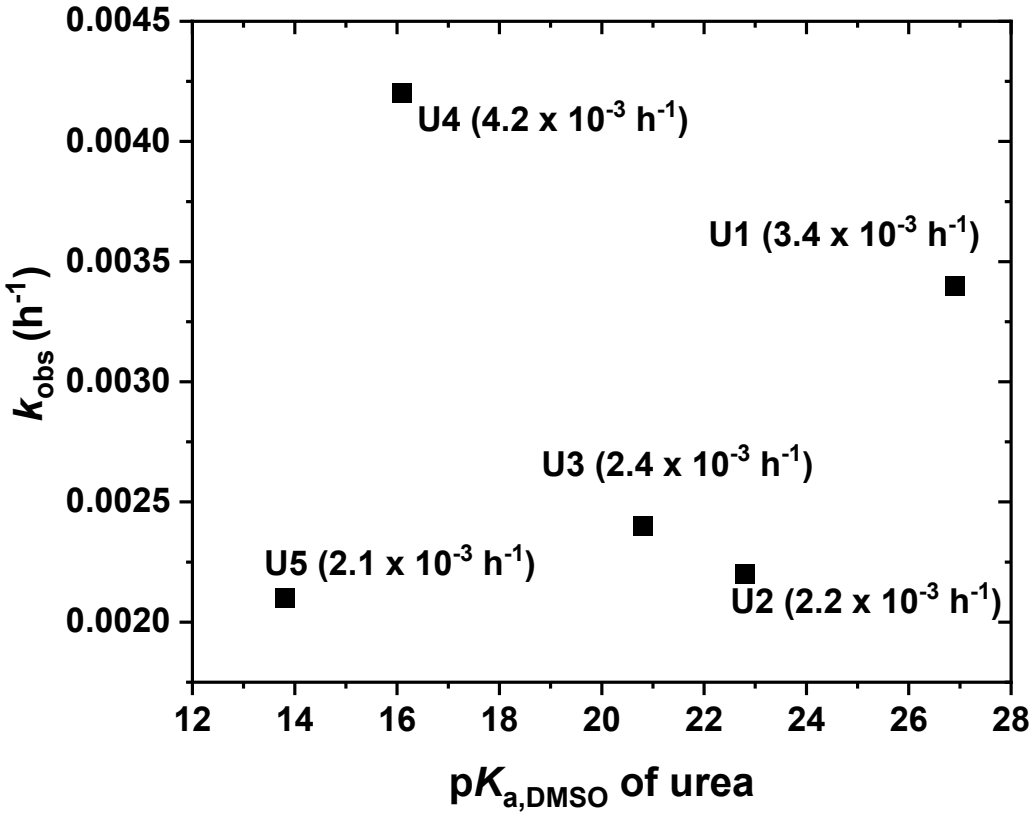


Figure S32. Plot of k_{obs} vs pK_a of urea catalysts for **DEtP** polymerizations with KBHT as the base

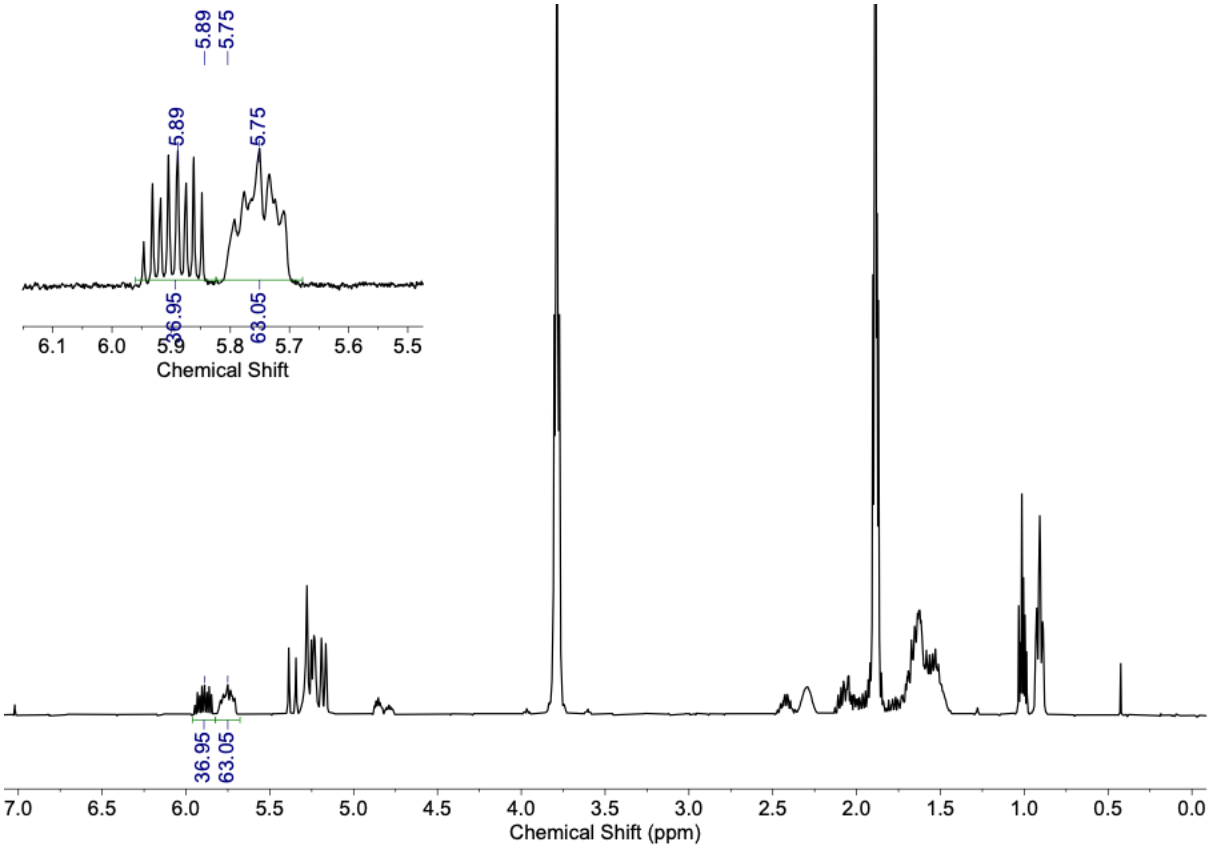


Figure S33. Example ^{1}H NMR spectrum of reaction mixture containing **EtVP** and *poly*(**EtVP**) in $CDCl_3$

Impurity Study:
Electrospray ionization mass spectrometry (ESI-MS) performed on unpurified DEtP samples demonstrated differential ionization behavior: EHA was detected exclusively in negative ion mode, whereas DEtP was observed only in positive ion mode.
The concentration of EHA in DEtP samples was estimated by generating a calibration curve. Standard solutions of EHA at known concentrations were prepared in MeOH, and the intensity of the EHA $[M-H]^-$ peak (m/z 157.12) was measured for each standard. A linear regression curve was plotted from these data points, ensuring the intercept set to zero during the fitting process.

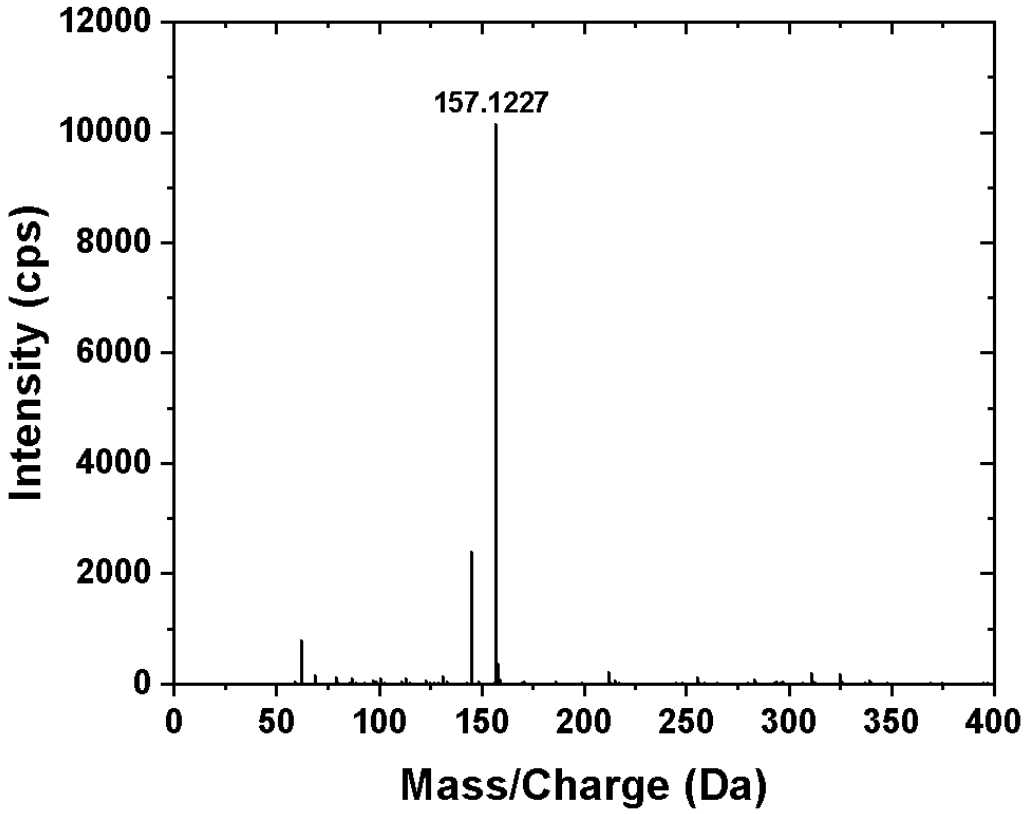


Figure S34. ESI-MS Spectrum (Negative ion mode) of EHA at 7.2 µM concentration

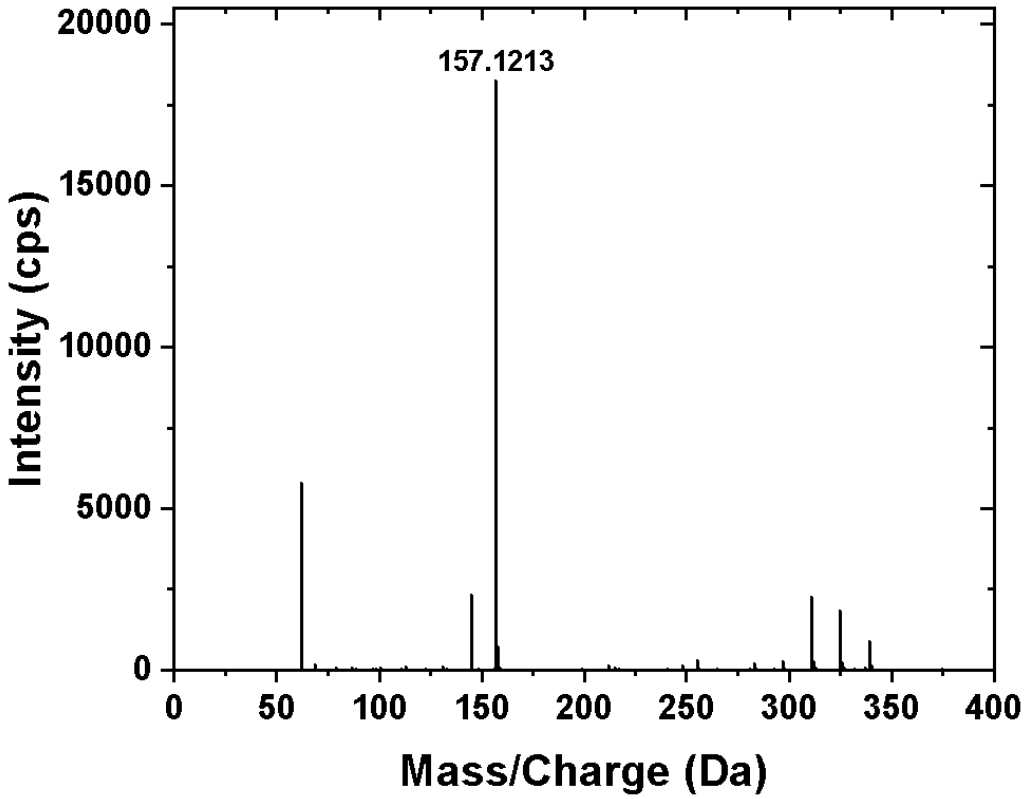


Figure S35. ESI-MS Spectrum (Negative ion mode) of EHA at 14.4 μM concentration

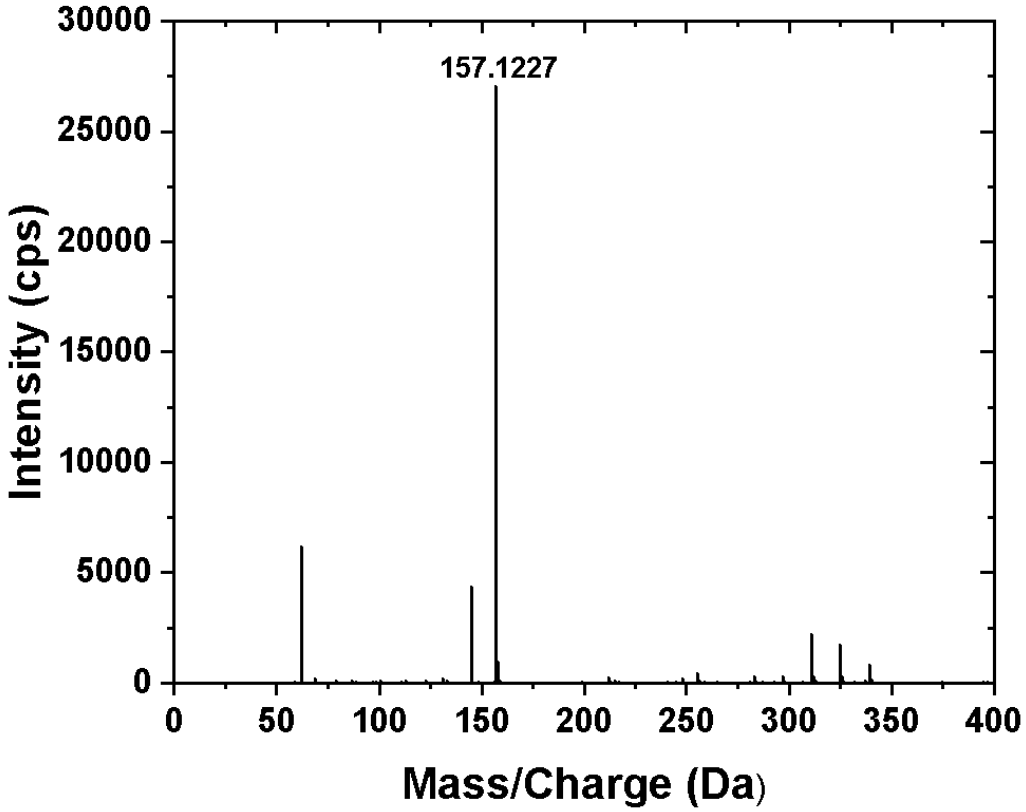


Figure S36. ESI-MS Spectrum (Negative ion mode) of EHA at 21.5 μM concentration

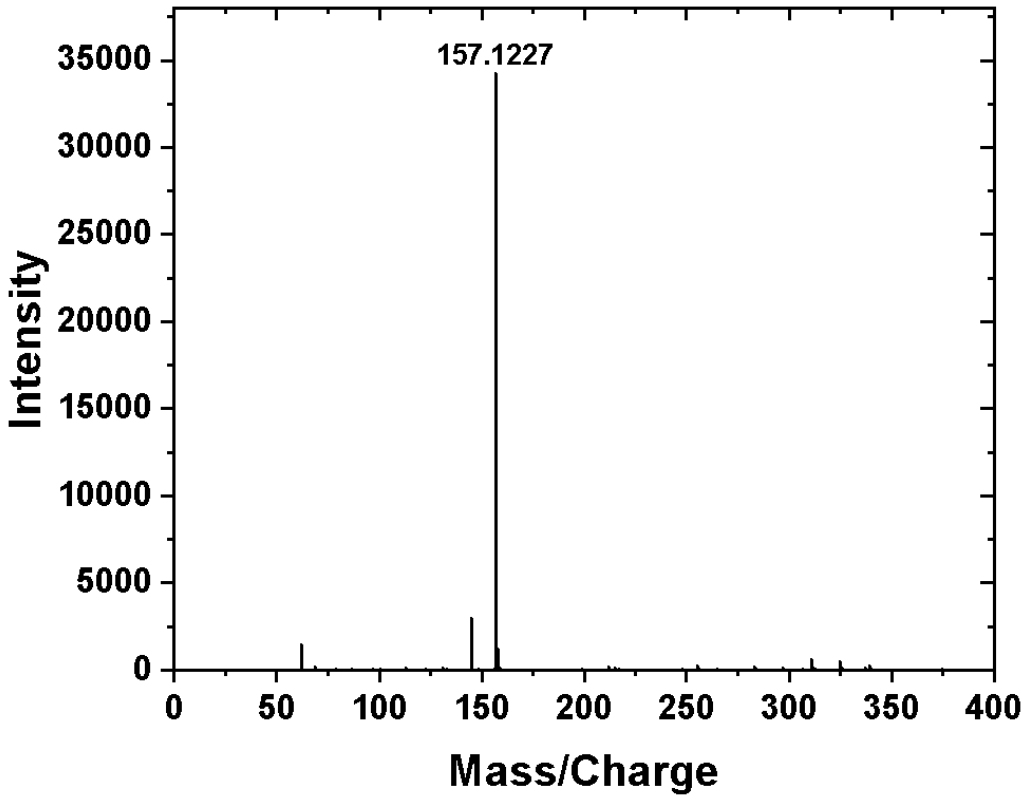


Figure S37. ESI-MS Spectrum (Negative ion mode) of EHA at 28.6 μM concentration

Table S26. Ionization intensity for different concentrations of EHA in ESI-MS (Negative ion mode)

Entry	Concentration (μM)	Ionization Intensity (cps)
1	7.2	10134
2	14.4	18234
3	21.5	27057
4	28.6	34255

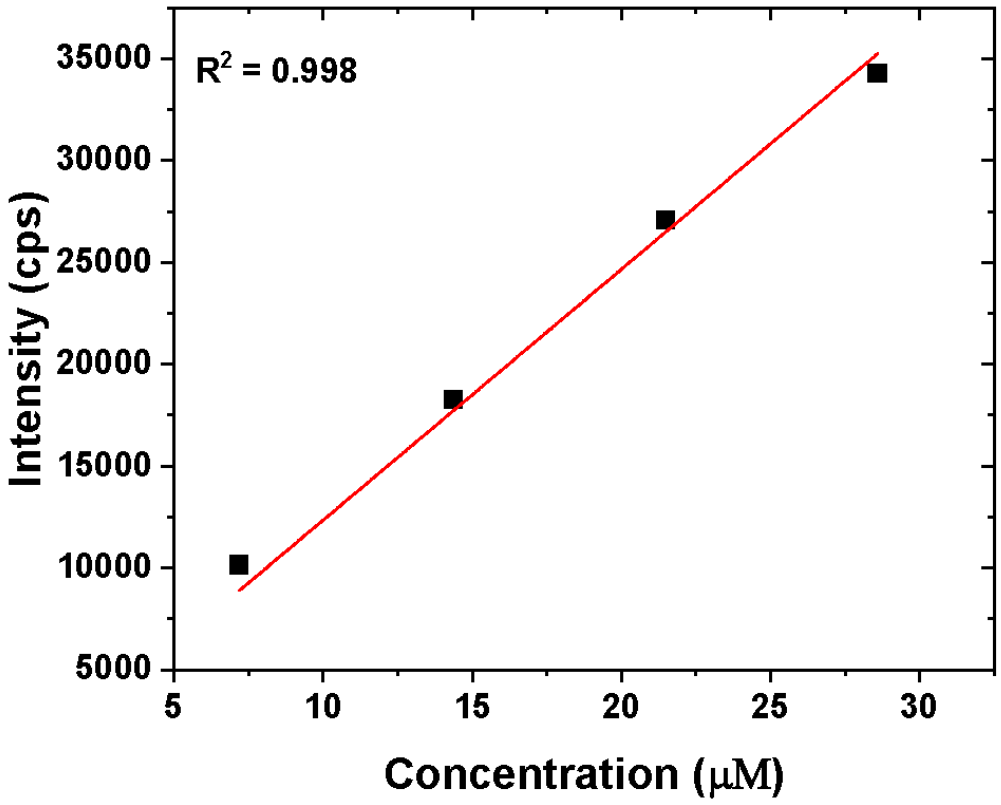
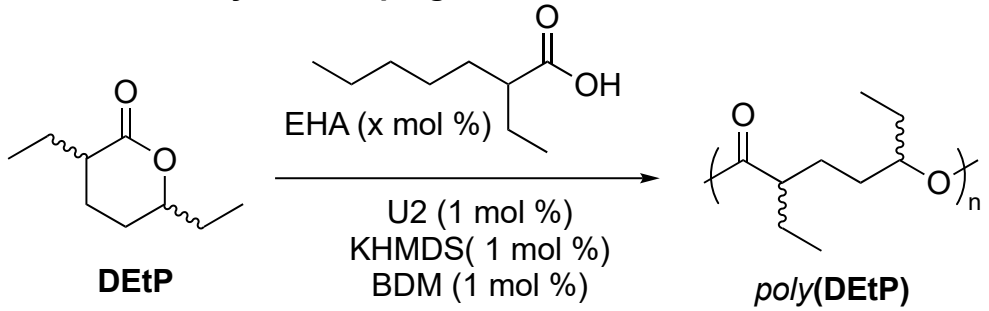


Figure S38. Calibration curve: EHA concentration vs $[M-H]^-$ ion Intensity.

Table S27. Quantification of EHA in DEtP after successive distillations using ESI-MS

Entry	Distillation Number	Ionization Intensity (cps)	Concentration (μM)	mol % of EHA (%)
1	No distillation	7411	6.0	4.1
2	One distillation	387	0.3	0.2
3	Two distillations	0	0	0
4	Three distillations	0	0	0

DEtP ROP kinetic study after Doping with EHA



DEtP *poly***(DEtP)**

0.016 mmol U2 (0.01 equiv.) and 0.016 mmol KHMDS (0.01 equiv.) were added to a 4 mL vial equipped with a teflon-coated rare earth extra power stir bar. In another vial, 0.016 mmol,1,4-benzenedimethanol (0.01 equiv.), 2-ethylheptanoic acid (X mol%) and 1.6 mmol **DEtP** (1 equiv.) were mixed until all the initiator is dissolved. The **DEtP**/BDM/EHA solution was then added to the reaction vial. Aliquots of the reactions were removed and immediately quenched by excess benzoic acid in $CDCl_3$ and were then removed from the glovebox for analysis by ^1H NMR spectroscopy.

Table S28. Conversion vs time for **DEtP** polymerization with 0 mol% **EHA** doping

Time (s)	Conversion (%)
15	5
30	10
45	18
60	26
90	38
150	54
180	63
240	67

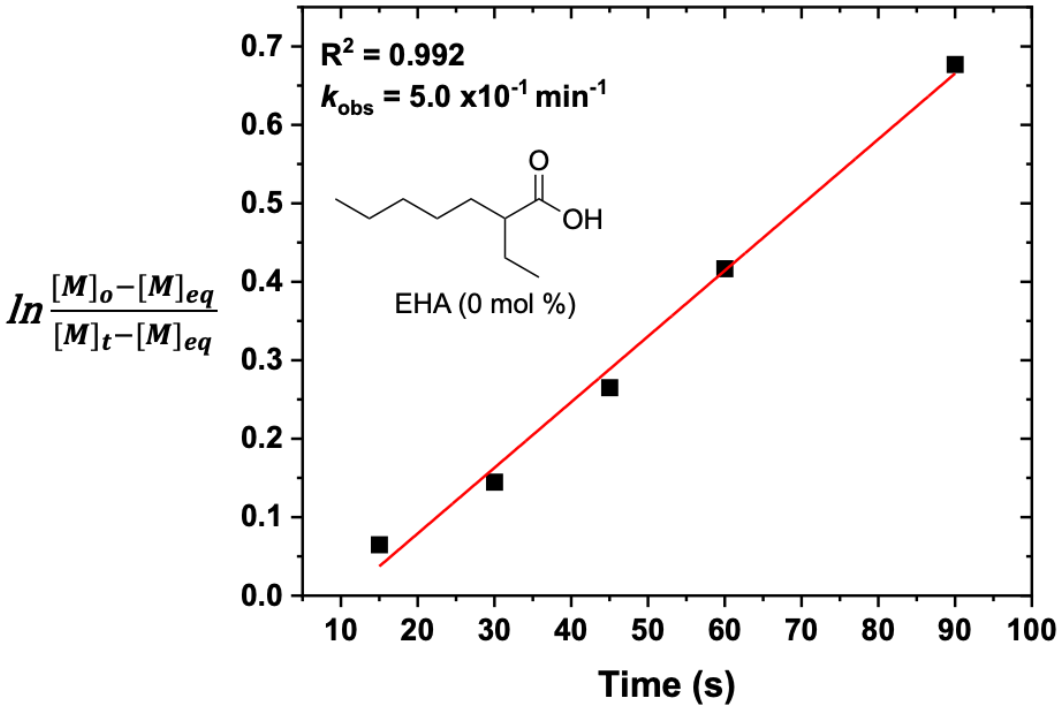
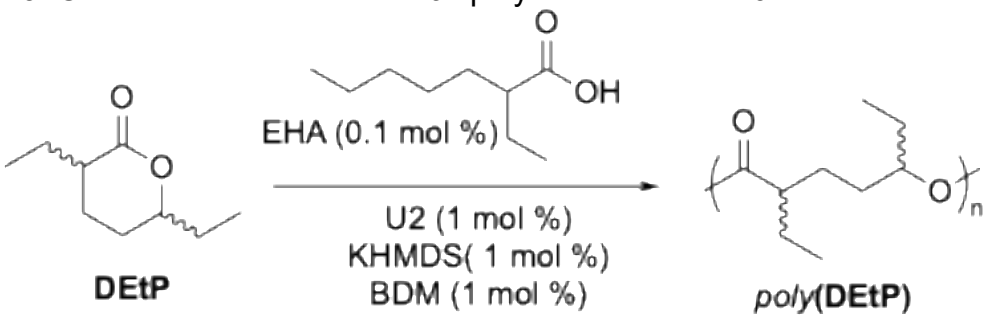


Figure S39. Kinetic Plot for **DEtP** polymerization with 0 mol% **EHA** doping

Table S29. Conversion vs time for **DEtP** polymerization with 0.1 mol% **EHA** doping



Time (s)	Conversion (%)
30	2
60	3
90	4
120	9
150	12
180	16
210	20
240	28
300	33
360	41
420	45

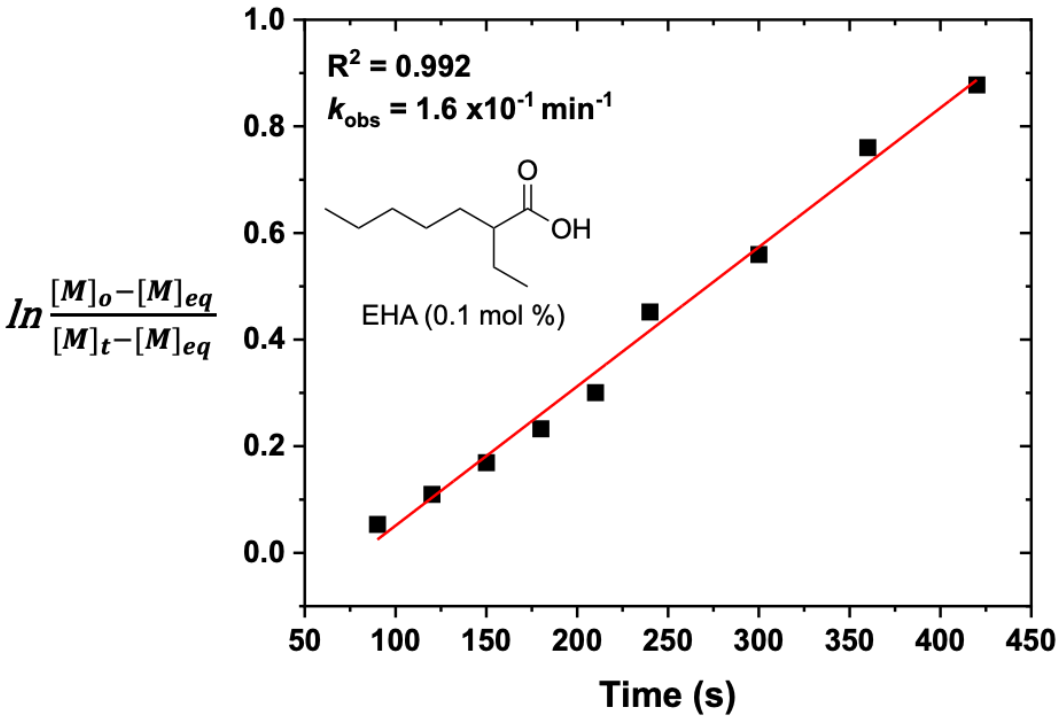
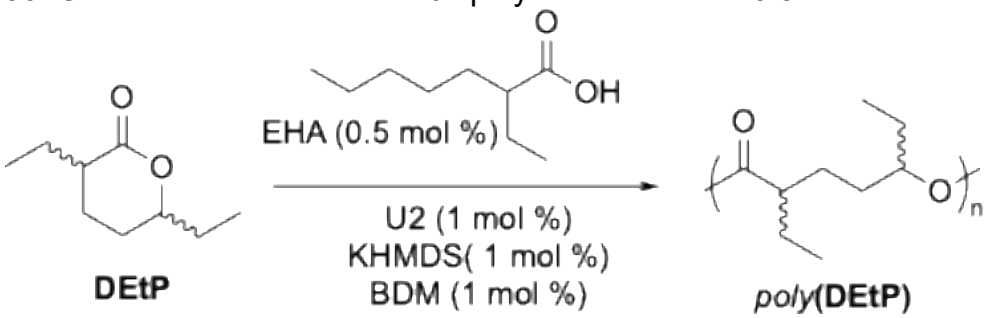


Figure S40. Kinetic Plot for **DEtP** polymerization with 0.1 mol% **EHA** doping

Table S30. Conversion vs time for **DEtP** polymerization with 0.5 mol% **EHA** doping



Time (min)	Conversion (%)
1	3
2	7
3	15
4	19
5	27
10	43
15	55
30	63

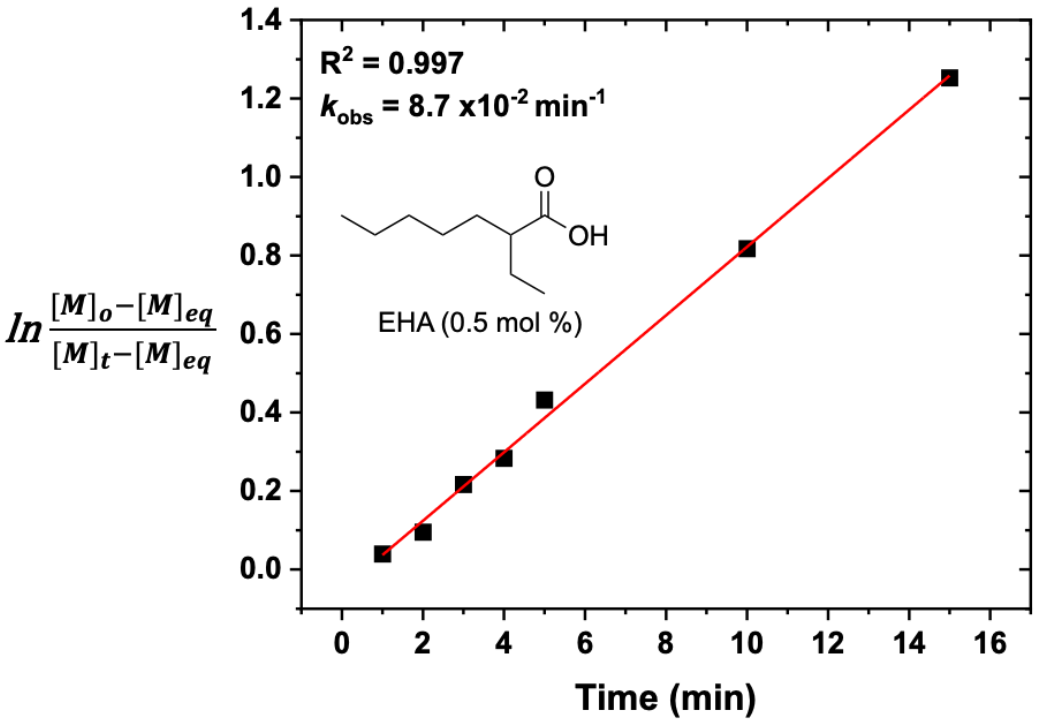
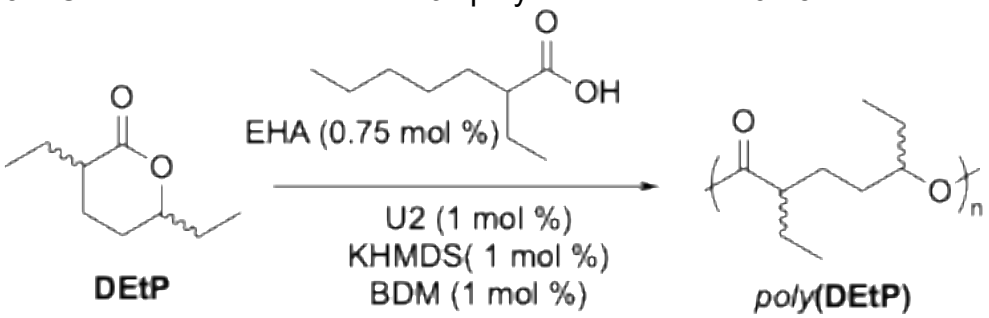


Figure S41. Kinetic Plot for **DEtP** polymerization with 0.5 mol% **EHA** doping

Table S31. Conversion vs time for **DEtP** polymerization with 0.75 mol% **EHA** doping



Time (h)	Conversion (%)
8	3
22.5	4
52	10
72	12

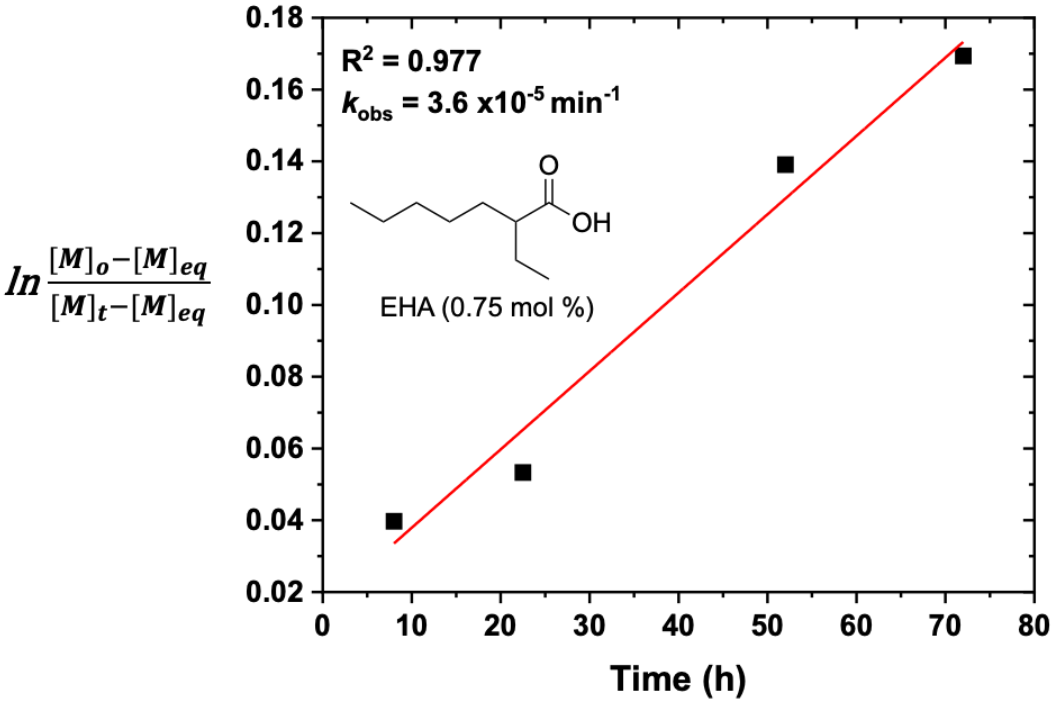
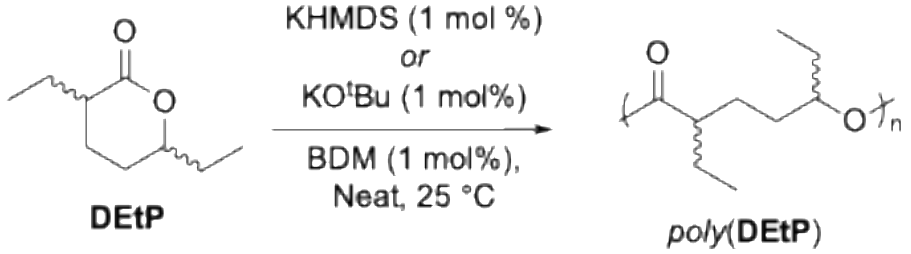


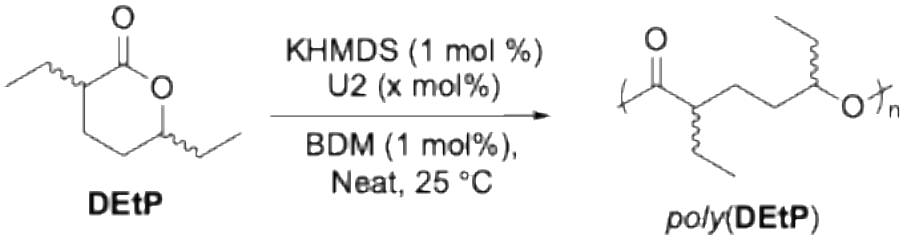
Figure S42. Kinetic Plot for **DEtP** polymerization with 0.75 mol% **EHA** doping

Table S32. Polymerization of **DEtP** with KHMDS and KO^{t}Bu in the absence of urea



Entry	Base	Conv %	Time	$M_{n,\ Theo}$ kDa	$M_{n,\ SEC}$ kDa	$Đ$
1	KHMDS	76	2 min	11.8	10.7	1.36
2	KO^{t}Bu	69	1 min	10.7		

Table S33. Dispersity vs time for **DEtP** polymerization with KHMDS (with and without urea U2)



Entry	*Time*	$Đ$ KHMDS+U2[a]	$Đ$ KHMDS[b]
1	1 min	1.21	1.38
2	10 min	1.24	1.38
3	30 min	1.26	1.43
4	6.5 h	1.33	1.43
5	24 h	1.36	1.47

[a] Urea (1 mol %), [b] Urea (0 mol%)

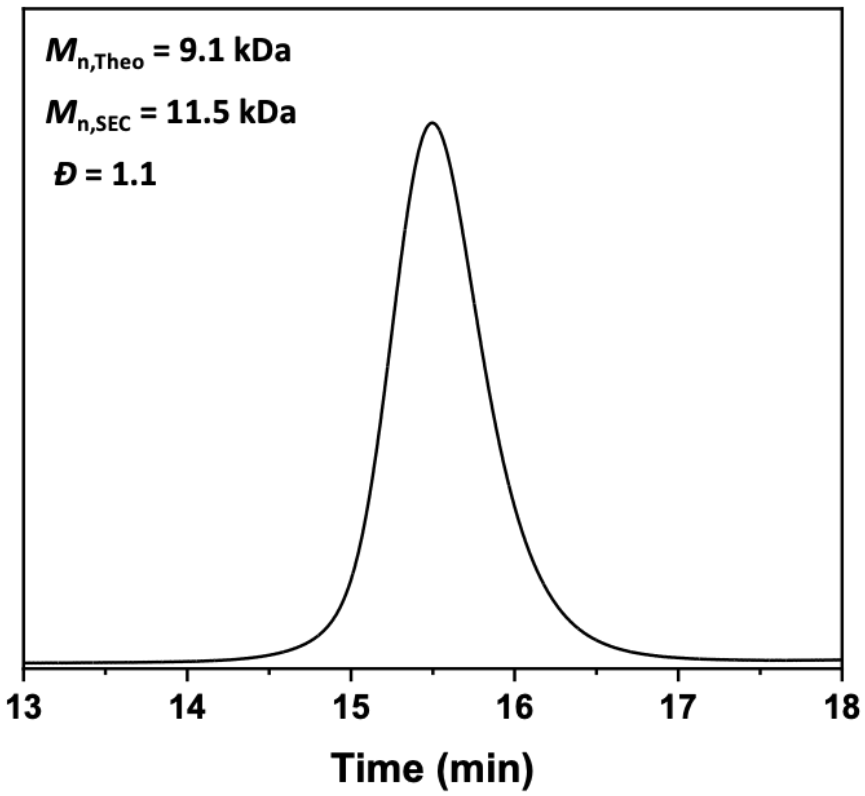


Figure S43. SEC trace (RI) of *poly*(**DEtP**) polymerized using U2/KHMDS(1 mol%) and BDM (1 mol%) at 120 s

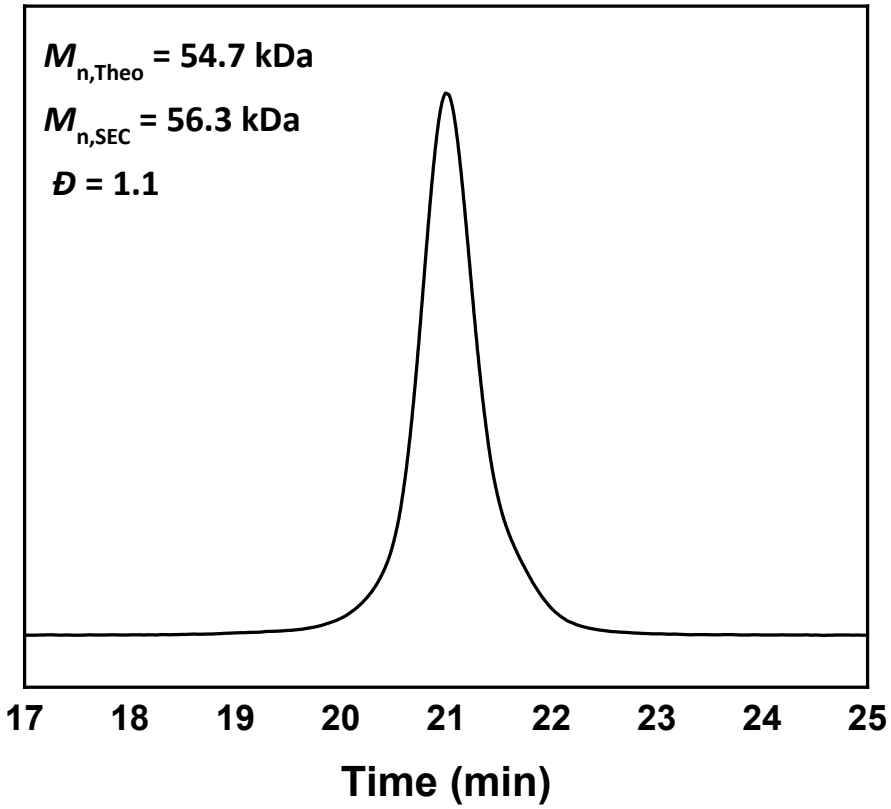


Figure S44. SEC tr ace (MALS) of *poly*(**DEtP**) polymerized using U2/KHMDS(1 mol%)and BDM (0.2 mol %) at 30 min.

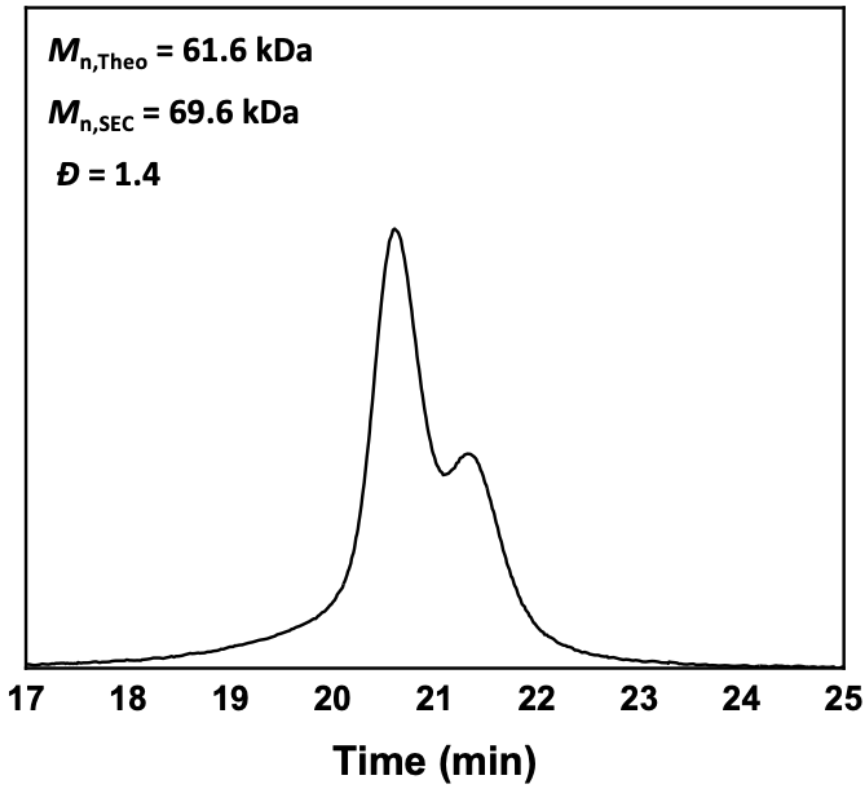


Figure S45. SEC trace (MALS) of *poly*(**EtVP**) polymerized using U2/KHMDS(1 mol%)and BDM (0.13 mol %) at 30 min.

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