Commercial Organic Lewis-pair Catalysts for Efficient Ring-Opening Polymerization of 1,2-Butylene oxide

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Entry	LA/LB	BO/LA/LB/- OH	Temp. (°C)	Time (h)	Conv. (%)	TOF (h ⁻¹)
1 ^a	Et ₃ B /TBPBr	500/1/1/0	20	6	97.4	81
2 ^b	TPBX /PPNCl	500/1/0.5/0	0	11	75.0	34
3°	Et ₃ B/P2	250/2/1/1	0	2	94.3	125
4 ^d	Et ₃ B /NHO 3	1500/4/1/5	80	72	13.0	2.7
5	Et ₃ B /DBU	1500/4/1/5	80	72	7.0	1.5

Table S1 Ring-opening polymerization of BO catalyzed by different Lewis acids /Lewis bases

^aThis work. ^bRef. 34. ^c Ref. 35. ^d Ref. 30



Fig. S2. ¹H NMR spectrum of PBO produced by Et₃B/TBPBr (Table 1, entry 2) in CDCl₃.



Fig. S3. ¹³C NMR spectrum of PBO produced by Et₃B/TBPBr (Table 1, entry 2) in CDCl₃.









Fig. S8. ¹H NMR spectrum of PBO produced by Et₃B/TBPBr (Table 1, entry 12) in CDCl₃.



Fig. S9. ¹H NMR spectrum of PPO produced by Et₃B/TBPBr (Table 2, entry 1) in CDCl₃.



Fig. S10. ¹H NMR spectrum of PBO produced by Et₃B/TBPBr (Table 2, entry 2) in CDCl₃.



Fig. S11. ¹H NMR spectrum of POO produced by Et₃B/TBPBr (Table 2, entry 3) in CDCl₃.



Fig. S12. ¹H NMR spectrum of PAGE produced by Et₃B/TBPBr (Table 2, entry 4) in CDCl₃.







Fig. S14. ¹H NMR spectrum of PBO by Et₃B/TBABr/PEtOH (entry 1, Table 3) in CDCl₃.



Fig. S15. ¹H NMR spectrum of PBO by Et₃B/DBU/PEtOH (entry 2, Table 3) in CDCl₃.



Fig. S16. ¹H NMR spectrum of PBO by Et₃B/MTBD/PEtOH (entry 3, Table 3) in CDCl₃



Fig. S17. ¹H NMR spectrum of PBO by Et₃B/TBPBr/PEtOH (entry 4, Table 3) in CDCl₃.



Fig. S18. The corresponding GPC traces of PBOs (BO/PEtOH = 50/1, 40/1, 30/1, 20/1).



Fig. S19. ¹H NMR spectrum of PBO by Et₃B/TBPBr/1,4-PMeOH (entry 8, Table 3) in CDCl₃.



Fig. S20. ¹H NMR spectrum of PBO Et₃B/TBPBr/1,3,5-PMeOH (entry 9, Table 3) in CDCl₃.



Fig. S21. ¹H NMR spectrum of the isolated polyurethane.

Entry	Time (h)	Conv.	$M_{ m n,GPC}{}^{ m b}$	D^{b}
1	0.17	_	_	_
2	0.33	-	-	_
3	0.67	5.8	_	_
4	1	10.9	0.24	1.01
5	2	18.6	0.72	1.07
6	4	31.1	1.3	1.06
7	6	48.1	2	1.05
8	8	61.3	2.5	1.04

Table S2 BO conversion vs time data obtained from polymerization of using Et_3B /TBPBr at molar ratio of BO/PEtOH = 50/1

^aConv. (%) was the conversion of the epoxides, which was determined by ¹H NMR spectroscopy. ^bDetermined by GPC in THF with polystyrene standard (kg mol⁻¹).



Fig. S22. The corresponding GPC traces of PBO with different molar mass synthesized with PEtOH as the initiator and Et₃B/TBPBr as the catalyst.

Entry	Time (h)	Conv. ^a	$M_{ m n,GPC}{}^{ m b}$	D^{b}
1	0.17	12	3.5	1.06
2	1	35.5	11.9	1.09
3	2	51	13.4	1.1
4	4	61.5	18.8	1.1
5	6	67.6	23.0	1.07
6	8	75.2	25.5	1.1

Table S3 BO conversion vs time data obtained from polymerization of using Et_3B /TBPBr at molar ratio of BO/TBPBr = 500/1

^aConv. (%) was the conversion of the epoxides, which was determined by ¹H NMR spectroscopy. ^bDetermined by GPC in THF with polystyrene standard (kg mol⁻¹).



Fig. S23. The corresponding GPC traces of PBO with different molar mass synthesized with Et₃B/TBPBr as the catalyst.



Fig. S24. *In situ* FTIR study: three-dimensional stack plots for the ROP of BO at the molar ratios of BO/Et₃B/TBPBr/PEtOH = (a) 500/3/1/10 (-20 °C); (b) 500/3/1/0 (-20 °C). Traces of different linkages and species for the ROP of BO at the molar ratios of BO/Et₃B/TBPBr/PEtOH = (c) 500/3/1/10 (-20 °C); (d) 500/3/1/0 (-20 °C).



Fig. S25 Reaction time *vs.* conversion (¹H NMR) for BO polymerization at -20°C using organobase/Et₃B catalyst systems. Base/Et₃B/PEtOH/BO = 10: 1: 3: 500 (molar ratio).