Supporting Information

An Investigation of the Organoborane/Lewis Base Pairs on the Copolymerization of Propylene Oxide with Succinic Anhydride

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Table of Contents

Table S1. pKa values of LBs from the Literature S2

Table S2. SA/PO copolymerization catalyzed by various LBs with TEB..... S2

Table S3. SA/PO copolymerization catalyzed by TEB/*t*-BuP$_1$ pair at different temperature..... S2

Figure S1. Selected GPC curves of poly(propylene succinate)s..... S3

Figure S2. GPC curve of the poly(propylene succinate) of enrty 6 in Table 2. ..... S3

Table 1. pKa values of LBs from the Literature [1].

LB	pKa, MeCN	pKa, THF	pKa, DMSO	pKa, H_2O	pKa, cal
TEA	18.7	12.5	9.0	10.7	10.62
TEEA					9.03
MTBD	25.4	17.9		13.0	14.37
DBU	24.3	16.8	13.9	11.9	13.28
t-BuP_1	26.9		15.7		
t-BuP_2	33.5		21.5		

pKa, cals were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02(©1994-2019 ACD/Labs), pK_a values of *t*-BuP_1 and *t*-BuP_2 are collected from "R. Schwesinger, et al., Liebigs Ann. 1996, 1055".

Table 2. SA/PO copolymerization catalyzed by various LBs with TEB. [1]

Entry	LB	PO:SA:TEB:LB	Time (h)	SA Conv. (%) [2]	Ester (%) [2]	TOF(h^{-1}) [3]	M_n(kg/mol) [4]	$Đ$ [4]
1	TEA	400:100:4:1	3	50	87	17	4.1	1.18
2	TEEA	400:100:4:1	3	72	92	24	3.5	1.13
4	*t*-BuP_1	400:100:4:1	1.5	89	95	59	5.0	1.15
6	*t*-BuP_2	400:100:4:1	1.5	56	81	37	1.7	1.14
8	DBU	400:100:4:1	3	>99	37	33	8.2	1.16
10	MTBD	400:100:4:1	3	67	92	22	4.5	1.14

[1] Reactions were run at 60 °C in neat PO (4 mmol). [2] SA conversion and Ester was determined by ^{1}H NMR spectroscopy of crude reaction mixture. [3] TOF = turnover of frequency, (Mol SA consumed)/(mol LB h). [4] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

Table 3. SA/PO copolymerization catalyzed by TEB/*t*-BuP_1 pair at different temperature. [1]

Entry	[PO]:[SA]: [TE]B: [*t*-BuP_1]	Temp. (°C)	Time (h)	SA Conv. (%) [2]	Ester (%) [2]	TOF (h^{-1}) [3]	M_n (kg/mol) [4]	$Đ$ [4]
1	400:100:4:1	60	1.5	89	95	59	5.0	1.15
2	400:100:4:1	45	5	52	82	10	1.1	1.35
3	400:100:4:1	30	24	85	76	4	2.3	1.33
4	400:100:4:1	0	24	13	6	<1	-	-
5	400:100:1:1	80	3	>99	>99	33	2.9	1.29
6	400:100:1:1	45	5	69	>99	14	5.8	1.11
7	400:100:1:1	30	16	83	>99	5	7.7	1.14
8	400:100:1:1	0	48	31	93	0.6	5.2	1.11

[1] Reactions were run in neat PO. [2] SA conversion and Ester was determined by ^{1}H NMR spectroscopy of crude reaction mixture. [3] TOF = turnover of frequency, (Mol SA consumed)/(mol LB h). [4] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

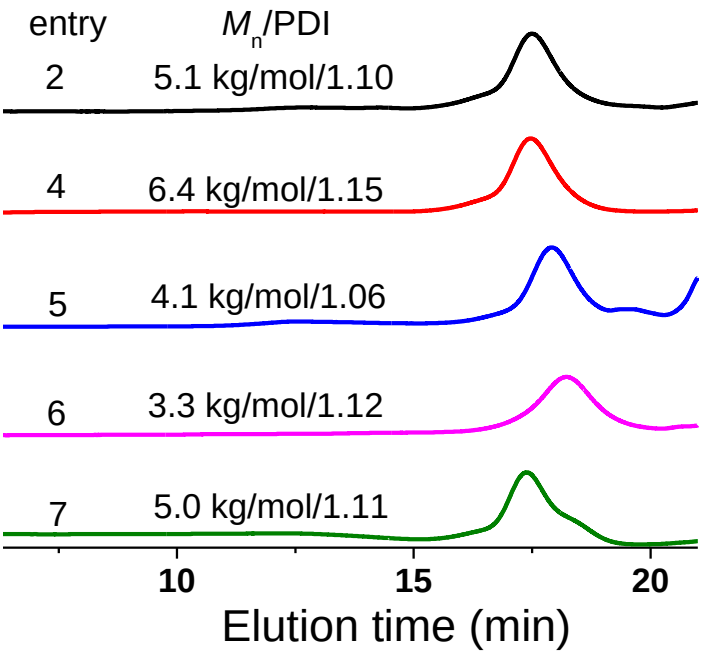

Figure 1. Selected GPC curves of poly(propylene succinate)s.(entries 2, 4–7 in Table 1).

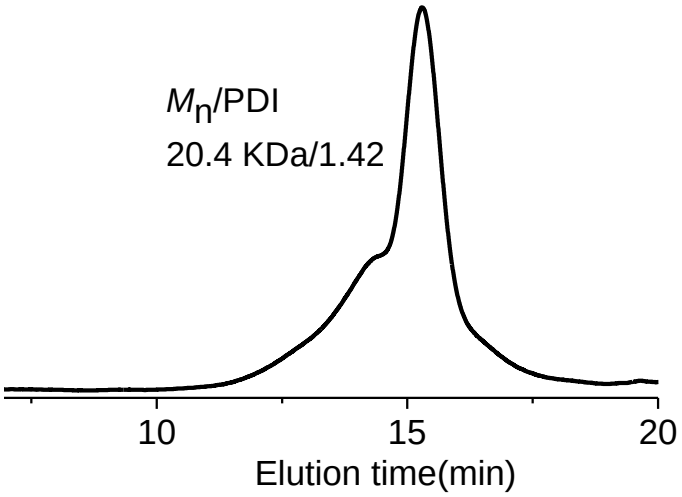

Figure 2. GPC curve of the poly(propylene succinate) of enrty 6 in Table 2.

Reference:

1. Lin, B.; Waymouth, R.M. Organic Ring-Opening Polymerization Catalysts: Reactivity Control by Balancing Acidity. *Macromolecules* **2018**, *51*, 2932–2938. doi:10.1021/acs.macromol.8b00540.