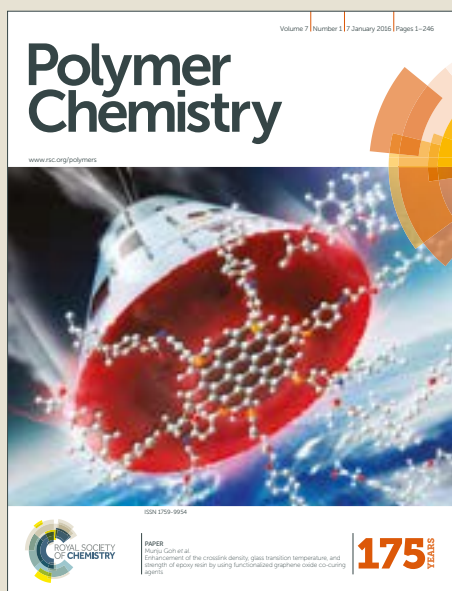


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ARTICLE

Fully alternating and regioselective ring-opening copolymerization of phthalic anhydride with epoxides using highly active metal-free Lewis pairs as a Catalyst

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Recent work has been directed to the design of metal-free Lewis pair catalysts for ring-opening alternating copolymerization (ROAP) reactions to enhance both activity and selectivity. While the simplest type of organic bases/Lewis bases (for example: PPN⁺Cl⁻, DMAP, DBU and TBD) are able to copolymerize anhydride-epoxide in a non-living and non-quantitative manner, the introduction of Lewis acids radically changes this behaviour. In this study, various Lewis acids namely B(C₂H₅)₃, Al(CH₃)₃, Et₂Zn and ⁿBu₂Mg in combination with various Lewis bases PPN⁺Cl⁻, DMAP, DBU and TBD were tested as Lewis pair catalysts for anhydride-epoxide ring-opening copolymerization (ROCOP) studies. Based on the observed results, the B(C₂H₅)₃/PPNCl pair stood out as the most active and effective Lewis pair for the perfectly alternating and regioselective controlled ROCOP of various epoxides (cyclohexene oxide, CHO; *tert*-butyl glycidyl ether, tBGE and 2-benzyloxirane, BO) with phthalic anhydride (PA). Medium to high molecular weight linear poly(anhydride-co-epoxide)s (*M_n* up to 57.5 kg mol⁻¹) are achieved, and most of them exhibit narrow molecular weight distributions (*M_w*/*M_n* as low as 1.07). However, in the presence of strong Lewis acids (Al(CH₃)₃, Et₂Zn and ⁿBu₂Mg) and neutral Lewis bases (DMAP/DBU/TBD) this broad applicability is offset by a lack of control over the polymerizations, including side reactions as a consequence of strong acidity/alkalinity. Hence, the ideally suitable acidity/alkalinity and matched size of the Lewis pair are considered crucial for the effective copolymerization of PA and epoxides. In addition, from P(PA-*alt*-tBGE) copolymers hydroxyl-functionalized poly(ester-*alt*-glycerol)'s were successfully synthesized by deprotection of the *t*-butyl groups.

Introduction

The most commercially successful aliphatic polyester today namely polylactide (PLA), is made from starch-rich crops such as corn and has found use in biomedical devices, packaging materials and a variety of commodity consumer products.¹ Unfortunately, regular PLA shows modest glass transition temperature (*T_g* = 50–60 °C).^{1b} Hence it is a poor alternative to glassy petroleum based polymers such as polystyrene, (*T_g* = 100 °C). Therefore an alternative synthetic route for amorphous, high-*T_g* aliphatic/aromatic polyester is the alternating copolymerization of epoxides and cyclic anhydrides as seen from the recent literature.^{2,3a–3f} The most common route to produce these aliphatic/aromatic polyesters is the ring-opening copolymerization (ROCOP) of cyclic anhydrides with epoxides, which is gaining increasing attention both in academia and in the industry.² The respective polymers have been extensively used as fibers, plastics, films for engineering,

packaging, biomedical materials, and so on.¹ Over the last decade, the design of single-site metal catalysts for the efficient ROCOP of cyclic anhydrides and various epoxides to obtain these poly(anhydride-*alt*-epoxide)s has made significant improvement.² The copolymerization of epoxides and anhydrides was originally reported from 1960s,^{4a} suffer from harsh conditions, low reactivity, low molecular weight, and/or ether formation.⁴ The first remarkable breakthrough in this reaction was not noted until the use of a 2-cyano- β -diketiminato Zn catalyst was reported by Coates and co-workers in 2007.^{2a} After this discovery, increasing attention has been paid to this pathway in the recent years, other successful single-site catalysts have also been reported in this context as highly efficient mediators of ROCOP using a variety of cyclic anhydrides and epoxides.^{2b–2k,3a–3f} In all these organometallic complexes, the chain enchainment occurs by prior coordination of the epoxides to the growing metal complex before their insertion at the chain ends. The complexity of the ligands with and as an integral part of these complexes that are generally synthesized through multistep synthesis is the another common feature of these very active catalysts. Moreover, the polymers afforded from these transition-metal complexes are colored due to metal residues and often toxic, and post-polymerization metal exclusion step is always necessary.

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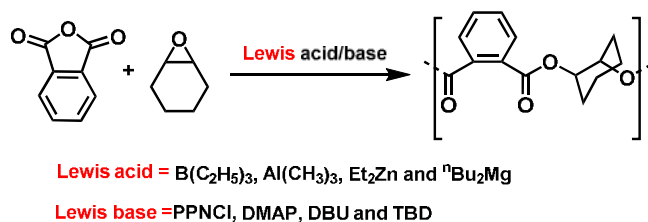
The main challenge in ring-opening copolymerization (ROCOP) is to establish a powerful polymerization technique, using simple metal-free approach that combines the ability to produce fully alternating poly(anhydride-*alt*-epoxide)s with low dispersities and controllable macromolecular characteristics. There are not many such reports for synthesizing oxygenated copolymers with controlled M_n , MWD's and with rigorously alternating microstructures by using this convenient and less expensive approach.^{4i-j,5,6b,7,12,13,15} Hence, recent work has been directed to the design of simple single-site metal-free catalysts, which has strong cooperative effects between Lewis acids and organocatalytic nucleophiles/Lewis bases for ROCOP of cyclic anhydrides with epoxides to enhance both activity and selectivity.⁶ However, recent organocatalytic systems showed less degree of control with low M_n values and broad molecular weight distributions (M_w/M_n) for alternating copolymerization of epoxides with cyclic anhydrides.⁴ⁱ In this context, very recently Zhao and coworkers demonstrated a highly active organocatalysts for the ring-opening alternating copolymerization (ROAP) of phthalic anhydride and epoxides by using simple phosphazene base (*t*-BuP₁).⁵ This phosphazene catalysed ROAP proceeded in a living and highly selective manner, with full conversion of PA, leading to tailor-made alternating polyesters in the presence of monohydroxyl benzyl alcohol. Moreover, metal-free Lewis pair initiators, especially B(C₂H₅)₃/NBu₄Cl (PPNCl) and B(C₂H₅)₃/DTMeAB (DBU) were recently explored for CO₂ or COS/epoxide copolymerization studies.^{6b,7} In 2016, Gnanou, Feng, and co-workers reported an elegant study and achieved highest activity and excellent selectivity for the copolymerization of CO₂ and propylene oxide (PO) or cyclohexane oxide (CHO) using B(C₂H₅)₃/NBu₄Cl (PPNCl)-based active systems.⁶ In 2017, Zhang, Darensbourg and co-workers successfully demonstrated a highly active B(C₂H₅)₃/DTMeAB (DBU) based catalyst for the fully alternating and perfectly regioselective COS/PO copolymerization to provide well-defined poly(monothiocarbonate)s.⁷ They proposed that, the cooperative effects of the Lewis acid and the Lewis base/nucleophile, together with the steric effects of the Lewis pair are the deciding factors for these effective metal-free catalysts. Inspired by the work of Gnanou group and Darensbourg group and in view of the promising properties of this class of simple Lewis pairs, the activity of various Lewis bases, including PPNCl, DMAP, DBU and TBD with Lewis pair of B(C₂H₅)₃, Al(CH₃)₃, Et₂Zn and ⁿBu₂Mg for ROCOP of phthalic anhydride (PA) and various epoxides (cyclohexene oxide, CHO; *tert*-butyl glycidyl ether, tBGE and 2-benzyloxirane, BO) were investigated. While the defining structural prerequisites of B(C₂H₅)₃ and various Lewis bases for efficient CO₂ or COS/epoxide copolymerization studies have been illustrated,⁶ the behaviour of these Lewis pairs (LPs) towards cyclic anhydrides with epoxides copolymerization studies are scarcely reported. Very recently Zhang group published on ROCOP epoxides with anhydrides using similar metal-free organoboranes and quaternary onium salts as Lewis acid-base pairs.¹² These LP afforded perfectly alternating copolymers with M_n 's from 1 to 20 kg/mol and molecular

weight distributions ranging from 1.12 to 1.37, which are relatively lower than our results. But the copolymers regioselectivity was competitive with our results. In particular, they achieved high M_n (20 kg/mol) in a 1/1/100/350 [B(C₂H₅)₃/PPh₄Br/PA/PO] LP to monomers feed at 80 °C, 0.3h under neat condition. Also Recently simple low-toxic zinc alkyls (or aryls) and amines as Lewis pairs were used as effective catalysts for ROCOP of epoxides with anhydrides by Wang group.¹³ The obtained copolymers $M_{n,GPC}$ values (3 to 17.9 kg/mol) and molecular weight distribution values (M_w/M_n = 1.11 to 1.28) would be lower than our results. However, they achieved high M_n (17.9 kg/mol) in a 1/2/400/500 [LA/LB/PA/CHO] LP to monomers feed at 110 °C, 3h under neat condition. In contrast, the epoxides, tBGE and BO used in the present work (with the hope to increase the reactivity and molecular weights) are an interesting alternative monomers that are distinct from other oxiranes, such as propylene oxide or cyclohexene oxide, by its electron-withdrawing pendant group. This pendant group increases the epoxide acidity and leads to enhanced ring-opening through insertion of the nucleophiles on epoxide. Indeed, the monosubstituted epoxides such as tBGE and BO are scarcely involved in the studies on alternating copolymerization.^{8,5b}

We have recently reported ROCOP of *tert*-butyl glycidyl ether (tBGE) with maleic anhydride (MA) or *L*-Lactide (*L*-LA) utilizing single-site group 4 complexes as Lewis acidic catalysts.⁹ However, because of their hindered steric coordination environments these catalytic systems displayed low activity and significant amounts of ether linkages were observed. In the present work, simple less steric B(C₂H₅)₃ (TEB) was used as Lewis acid to activate the epoxide and anhydride monomers and various Lewis bases, including PPNCl, DMAP, DBU and TBD for nucleophilic attack of the B(C₂H₅)₃-activated monomer to enhance the rate-determining ring-opening steps. This contribution also reports that with respect to the other systems studied (eg. Al(CH₃)₃, Et₂Zn and ⁿBu₂Mg as LA and PPNCl, DMAP, DBU and TBD as LB), B(C₂H₅)₃/PPNCl-based LPs promote the nearly controlled ring-opening alternating copolymerization (ROAP) of phthalic anhydride (PA) with various epoxides (cyclohexene oxide, CHO; *tert*-butyl glycidyl ether, tBGE and 2-benzyloxirane, BO) to produce medium to high molecular weight (M_n = 21 to 57 kgmol⁻¹) fully alternating tailor-made polyesters with narrow molecular weight distributions (M_w/M_n = 1.07 to 1.28). Finally this contribution demonstrates that the choice of Lewis acid is decisive for the monomer reactivity.

Results and discussion

To study the effect of Lewis pair on catalytic performance, we decided to vary both the Lewis acid (LA) and Lewis base (LB) (Scheme 1). The alternating copolymerizations were carried out in toluene at elevated temperatures using a variety of LPs/epoxides/PA ratios summarized in Tables 1 and 2.



Scheme 1. Fully alternating copolymerization of PA with CHO by Lewis pairs.

Since respectively CHO is less prone to the formation of cyclic ester byproducts and also well reactive substrate for anhydride copolymerization, we chose to first study the copolymerization of this epoxide with PA. We initially probed the Lewis pair polymerization (LPP) approach by examining the cooperative effects of various LBs on the B(C₂H₅)₃/Al(CH₃)₃/Et₂Zn or ⁿBu₂Mg-based LPs for the CHO-PA copolymerization in a fixed 200/200/1/2 CHO/PA/LB/LA ratio (Table 1). Based on the results of this initial screening, the B(C₂H₅)₃/PPNCI pair stood out as the most active and effective LP for the anionic copolymerization of PA with CHO. ¹H NMR spectra (Figure 1 and Figures S1, S3 and S6 in ESI) indicates that clean formation of completely alternating structures of CHO-PA copolymers, P(PA-*alt*-CHO), with no traces of aliphatic ethers (absence of signals at 3.60 – 3.45 ppm for CHOCHO diads). All samples displayed chemical shifts in the 4–6 ppm range indicative of hydrogens bound to the carbons α to the ester group, from the epoxide units. (Figure 1). The ¹³C NMR spectra of synthesized polyesters exhibited good regioselectivity (methine versus methylene attack), for unsymmetrical epoxides (tBGE and BO). For example, for P(PA-*alt*-BO) and P(PA-*alt*-tBGE) in ¹³C NMR two main peaks for carbonyl carbon signals were observed, which can be attributed as head-to-tail (HT) junctions, whereas for symmetrical epoxide (CHO) the resulting P(PA-*alt*-CHO), one single peak for carbonyl carbon was observed (Figures S5 and S8 in ESI). In addition, methine carbon region also for P(PA-*alt*-BO) and P(PA-*alt*-tBGE) only one signal was observed and no additional signals were found (Figure 2), which indicated that the respective polyesters have good regioselectivity. The ¹H and ¹³C NMR spectra of all other polyester synthesized in this work may be found in the Supporting Information (Figure S1–S17). In contrast to B(C₂H₅)₃, different trend of Lewis acid activation was observed by the addition of other LAs (Al(CH₃)₃ or Et₂Zn or ⁿBu₂Mg) to the PPNCI-based nucleophile or Lewis base towards CHO-PA copolymerization, such that the activity of LAs in the order of B(C₂H₅)₃ >>> ⁿBu₂Mg > Al(CH₃)₃ > Et₂Zn was found. Beyond the screening of different Lewis acids, three other Lewis bases screened for CHO-PA copolymerization are DMAP, DBU and TBD respectively. In combination with a range of Lewis acids these neutral LB's suffered from sluggishness and overall low activity was observed than those obtained from the action of PPNCI. In agreement with previous studies into Lewis acid

activated processes, the greater catalytic activity of B(C₂H₅)₃ over ⁿBu₂Mg, Et₂Zn and Al(CH₃)₃ may be explained by its mild Lewis acidic nature.⁶ The activation of PA and epoxides provided by this mild Lewis acid is strong enough to allow the addition of both monomers by growing chain-end and mild enough not to foster the homopolymerization of epoxides and the subsequent formation of ether units (see Figure 3 for its mild activation of PA and tBGE). In contrast, the greater activity of PPNCI over DMAP, DBU and TBD may be explained by its cationic character that results from faster dissociation of Cl⁻ anion. The activity of the LBs with B(C₂H₅)₃ in the order of PPNCI >>> DMAP > DBU > TBD was observed. In combination with B(C₂H₅)₃ and PPNCI for CHO-PA copolymerization, after 6 h (Table 1, entry 3), almost quantitative monomer consumption had occurred, while at the same time the *M_n* remained high (*M_{n,exp}* = 21.3 kg mol⁻¹) and the MWD was good (*M_w*/*M_n* = 1.07) than in the case of other Lewis acids. The catalytic performance of B(C₂H₅)₃/PPNCI-based LP compares well, whether in terms of activity or as a well-controlled process, to other well defined organometallic complexes based on Cr^{10a,10b}, Co²⁵ and Al^{10c} reported to initiate the ROCOP of PA and CHO (see Table 3). However, all of these complexes synthesis required tedious procedures for their synthesis which may not be commercially feasible. In fact, the polymers obtained by B(C₂H₅)₃/PPNCI-based LP shown bimodal molecular weight distributions measured by GPC, which is very likely due to background polymerization initiated by PPNCI itself.⁴¹ Indeed, from the recent reports⁴¹ and from our control experiment studies we noticed that PPNCI alone able to give alternating low *M_n* copolymer from PA and CHO. Hence, in addition to the high *M_n* shoulder, low molecular weight tailing being observed in GPC analysis (Figure S18–S25, in ESI).² However, the observed number-average molar mass (*M_{n,exp}*) of 21.3/8.0 kg mol⁻¹ (Table 2, entry 4 and Figure S18 in ESI), is still lower than theoretical value calculated from the feed ratio of monomers and initiator (*M_{n,calc}*). This is may be due to the presence of trace quantities of protic species in the system, acting as transfer agent and converting the excess turnover monomers into small oligomers (eg. chain lengths around 5–7 monomer units).² Hence, no transesterification products were seen in the high molecular weight region of the MALDI-ToF-MS analysis.

Table 1. PA/CHO copolymerization catalyzed by various simple Lewis acids and Lewis bases.^a

entry	LA	Nu	$[LA]_0/[Nu]_0/[PA]_0/[CHO]_0$	Conv ^c (%)	time (h)	$M_{n,calc}^d$ ($kg\ mol^{-1}$)	$M_{n,exp}^e$ ($kg\ mol^{-1}$)	M_w/M_n^e	Ester: ether (%)	T_g^f
1	Et ₃ B	PPNCl	1/1/200/200	91	10	49.3	16.7 (64%)/3.8 (36%) ^g	1.14/1.12	97:3	88.4
2 ^b	Et ₃ B	PPNCl	1/1/200/200	85	12	49.3	13.5 (73%)/3.4 (27%) ^g	1.23/1.18	95:5	66.8
3	Et ₃ B	PPNCl	2/1/200/200	>99	6	49.3	21.3 (59%)/8.0 (41%) ^g	1.07/1.1	100:0	98.8
4 ^b	Et ₃ B	PPNCl	2/1/200/200	91	10	49.3	17.1(77%)/5.5 (23%) ^g	1.04/1.1	94:6	-
5	-	PPNCl	0/1/200/200	86	10	49.3	8.8	1.21	91:9	33.4
6	Et ₃ B	PPNCl	2/1/100/100	>99	4	24.6	8.2 (58%)/6.7 (42%) ^g	1.15/1.12	100:0	78.3
7	Et ₃ B	DMAP	2/1/200/200	79	8	49.4	13.6 (56%)/4.8 (44%) ^g	1.18/1.23	94:6	61.5
8	Et ₃ B	DMAP	2/1/100/100	75	5	24.7	6.7 (58%)/3.7 (42%) ^g	1.17/1.21	95:5	53.7
9	-	DMAP	0/1/200/200	57	5	49.4	5.3	1.21	88:12	20.2
10	Et ₃ B	TBD	2/1/200/200	88	12	49.4	10.5 (55%)/3.6 (45%) ^g	1.34/1.25	86:14	-
11	-	TBD	0/1/200/200	51	12	49.4	4.1	1.33	72:28	-
12	Al(CH ₃) ₃	PPNCl	1/1/200/200	90	12	49.3	4.4	1.21	81:19	27.1
13	Al(CH ₃) ₃	PPNCl	2/1/200/200	94	9	49.3	6.8	1.34	85:15	31.1
14	Al(CH ₃) ₃	DMAP	2/1/200/200	85	12	49.4	5.2	1.32	81:19	-
15	Al(CH ₃) ₃	TBD	2/1/200/200	71	12	49.4	4.8	1.28	77:23	-
16	Et ₂ Zn	PPNCl	1/1/200/200	93	12	49.3	4.1	1.34	70:30	-
17	Et ₂ Zn	PPNCl	2/1/200/200	95	10	49.3	5.2	1.37	76:24	41.2
18	Et ₂ Zn	DMAP	2/1/200/200	81	12	49.4	4.5	1.33	79:21	-
19	Et ₂ Zn	TBD	2/1/200/200	77	12	49.4	4.2	1.37	71:29	-
20	ⁿ Bu ₂ Mg	PPNCl	2/1/200/200	81	12	49.3	4.4	1.27	72:28	54.2
21	ⁿ Bu ₂ Mg	DMAP	2/1/200/200	71	12	49.4	3.6	1.32	74:26	-
22	ⁿ Bu ₂ Mg	TBD	2/1/200/200	70	12	49.4	3.3	1.35	71:29	-

^aEach reaction was performed in 2.5 mL of dry toluene, $[PA]_0/[CHO]_0/[LA]_0/[Nu]_0 = 200/200/2/1$, at 100 °C, Unless otherwise noted. ^bReaction temp at 80 °C. ^cmonomer conversion as determined by ¹H NMR spectroscopy. ^d $M_n^{[calc]}$ calculated using $\{[PA]_0/[Nu]_0 \times (\% \text{ conversion of PA}) \times (\text{mol wt of MA})\} + \{[CHO]_0/[Nu]_0 \times (\% \text{ conversion of CHO}) \times (\text{mol wt of CHO})\} + \text{molecular weight of end group}$. $M_{PA} = 148.12\ g\ mol^{-1}$, $M_{CHO} = 98.15\ g\ mol^{-1}$, $M_{Nu} = (Cl, 35.5; DMAP, 122.17; TBD, 139.2; DBU, 152.2)\ g\ mol^{-1}$. ^e $M_n^{(GPC)}$ measured by GPC at 27 °C in THF relative to polystyrene standards. ^f T_g values were detected by DSC measurement. ^gBimodal distribution (number in parentheses denotes the percentage of each population calculated by GPC peak areas).

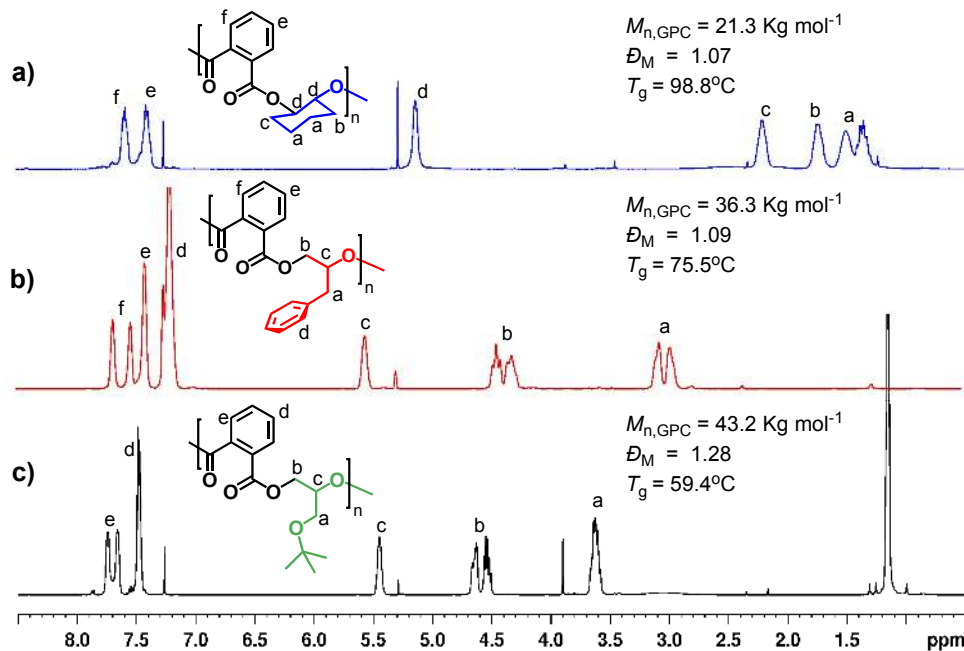


Figure 1. ^1H NMR spectra (400 MHz, CDCl_3) of copolymers obtained by $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ -based Catalyst, entry 4 (a) entry 14 (b) and entry 8 (c) from Table 2.

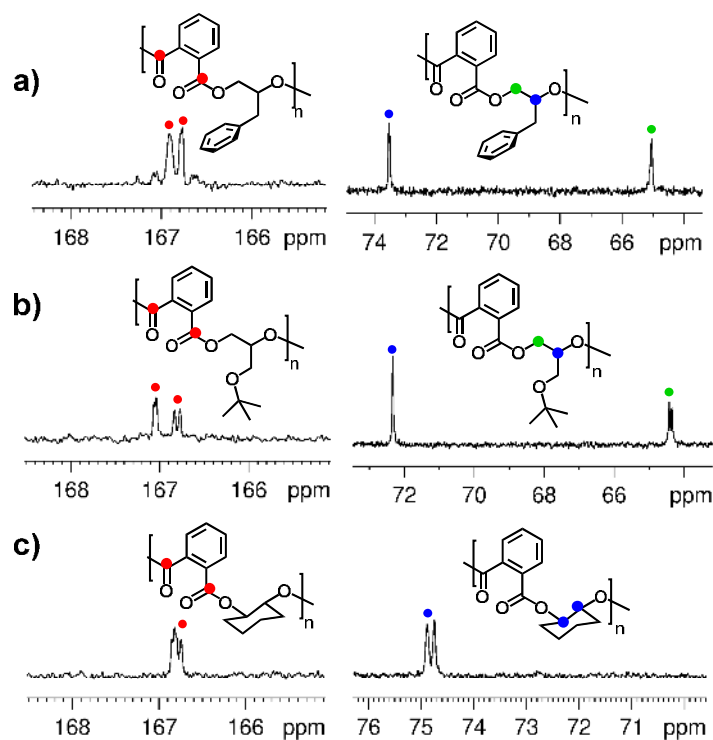


Figure 2. Quantitative ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298K) spectra showing the carbonyl carbon (red dot), methine carbon (blue dot) and methylene carbon (green dot) regions of copolymers obtained by copolymerization of PA with various epoxides by $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ -based Catalyst, entry 4 (c) entry 8 (b) and entry 14 (a) from Table 2.

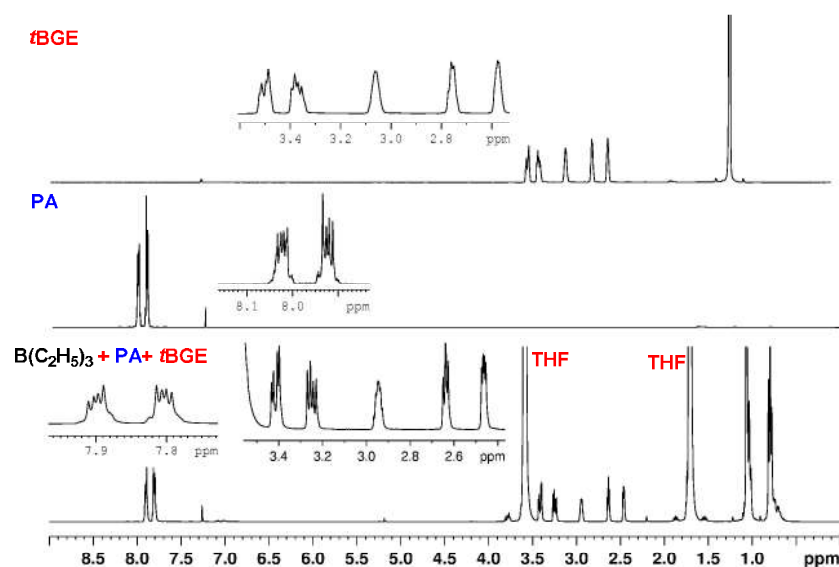
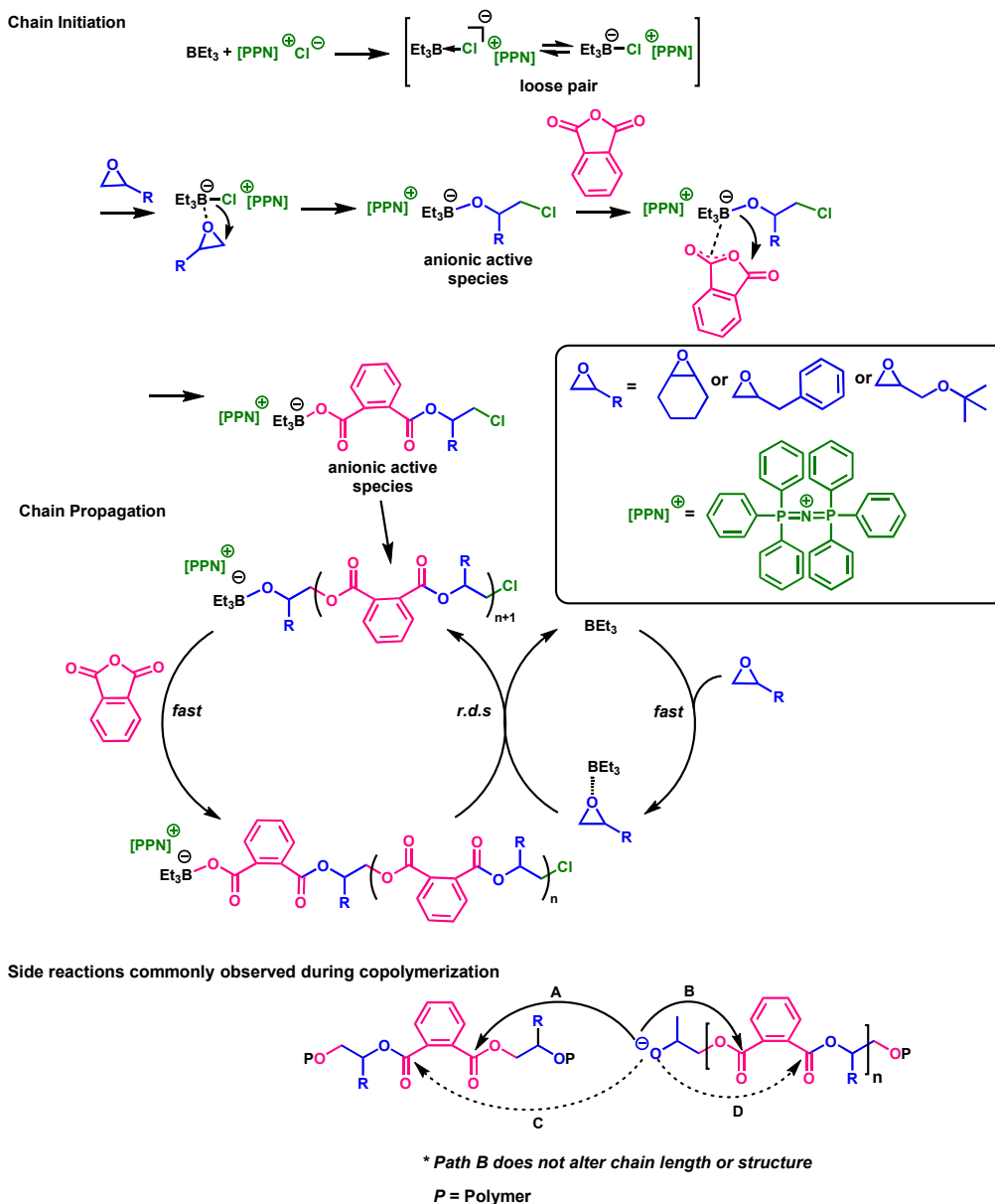


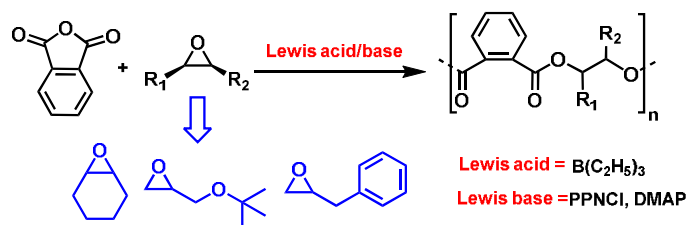
Figure 3. Activation of PA and tBGE with $B(C_2H_5)_3$.

Attempts to eliminate these chain transfer agents from the anhydrides by repeated careful sublimation did not result in a significant improvement of the molecular weight. This observation is well consistent with previous reports.^{2c,2d,2i} Further, MALDI-ToF-MS analysis of a crude low molecular weight samples showed two major distribution of linear poly(anhydride-co-epoxide)s chains, endcapped with Lewis base/Nucleophile groups (Figures 4&5 and Figure S27-S30, in ESI), which further supports this bimodal molecular weight distributions and also no measurable polyether linkages formed. The MALDI-ToF clearly shows one main distribution pattern (A) of perfectly alternating polyesters including one additional ether unit with PPNCl as initiator and TEB as activator. A second distribution (B) of less intensity can also be seen from the PPNCl alone as the initiating system (Figures 4&5 and Figures S27-S30, in ESI). In both distributions the mass differences between the peaks represent precisely the molar mass of PA and epoxide monomer, explaining the expected alternating structure and underpinning the incorporation of either Cl^- or *N*-Heterocyclic Nucleophiles (DMAP/TBD/DBU) at the chain ends during the initiating step. However, similar to previous works^{2s,2z,13} some of the ionization peaks were observed without Na^+ or K^+ adducts in the MALDI-ToF spectrum (Figures 4, 5 and S29 in ESI). In an effort to gain more insight into the rate determining ring-opening step for these reactions, *in situ* NMR reactions between the Lewis pair and monomers were carried out to investigate the synergistic effects of PPNCl and TEB. Indeed, the synergistic effect of TEB/LB pair was recently observed in the CO_2/PO or COS/PO copolymerization reactions.⁶ In this work too, the activation of tBGE and PA by TEB was clearly observed from the 1H NMR

spectra (Figure 3). The proton chemical shifts of the neat tBGE (3.5, 3.38, and 3.08 ppm) were significantly upfield shifted to 3.4, 3.22, and 2.92 ppm, respectively (Figure 3). However, the proton chemical shifts of the neat PA (7.93 and 8.03 ppm) were fairly upfield shifted to 7.89 and 7.8 ppm, suggesting that PA activation by TEB was somewhat lower than tBGE activation. Even though TEB showing the electron-withdrawing effect, the upfield shift is due to the strong interaction between monomers and THF molecules and partial transfer of electrons from THF to activated monomers. Further the activation of tBGE in the presence of different Lewis pairs was characterized by 1H NMR spectroscopy. Concomitantly, the chemical shifts of the H^a and H^b protons of the neat tBGE (2.75 and 2.57 ppm) were significantly upfield shifted with all series of Lewis pairs respectively (Figure S31 in ESI). This observation is indicative of tBGE activation by the Lewis pair. During the monomers activation the role of the LB or nucleophile is to labilize the boron-nucleophile bond of either the initiator or growing polymer chain towards heterolytic bond cleavage. As depicted in Scheme 2 and Figure S32, in Supporting Information, first by mixing $B(C_2H_5)_3$ and PPN^+Cl^- it will give the ate complex.^{4h} Thus the resulting borate serves as active initiator for polymerization. The excess of $B(C_2H_5)_3$ which is not engaged in the ate complex formation serves to activate the epoxide. In the present work 2 equiv of LA with respect to LB needed for achieving high monomers conversion and high M_n 's. Such that, $B(C_2H_5)_3$ and the other Lewis acids used in the present work have a double role: first to form an ate complex upon mixing with a Lewis base, and second to activate the epoxide when used in excess.



Scheme 2. Proposed cooperative mechanism for anionic copolymerization of epoxides and PA catalyzed by $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ -based LP.



Scheme 3. Fully alternating copolymerization of PA with various epoxides by Lewis pairs.

Table 2. PA and various epoxides copolymerization catalyzed by various simple Lewis acids and Lewis bases.^a

entry	[Et ₃ B] ₀ /[Nu] ₀ /[PA] ₀ /[Ep] ₀	Nu	Ep	con v ^b (%)	time (h)	M _{n,calc} ^c (kg mol ⁻¹)	M _{n,exp} ^d (kg mol ⁻¹)	M _w /M _n ^d	Ester : ether (%)	T _g ^e
1	0.5/1/200/200	PPNCl	CHO	44	6	49.3	8.4(88%)/2.1 (12%) ^g	1.21/1.18	88:12	-
2	1/1/200/200	PPNCl	CHO	71	6	49.3	11.3(79%)/2.5 (21%) ^g	1.25/1.22	95:5	-
3	1.5/1/200/200	PPNCl	CHO	84	6	49.3	16.3(61%)/4.2 (39%) ^g	1.15/1.21	94:6	-
4	2/1/200/200	PPNCl	CHO	>99	6	49.3	21.3(59%)/8.0 (41%) ^g	1.07/1.1	100:0	98.8
5	2/1/400/400	PPNCl	CHO	97	12	98.5	46.1(83%)/11.9 (17%) ^g	1.24/1.24	95:5	-
6	2/1/600/600	PPNCl	CHO	95	18	147.8	57.5(81%)/13.2 (19%) ^g	1.24/1.33	93:7	-
7	2/1/800/800	PPNCl	CHO	95	24	197.0	51.0(81%)/12.3 (19%) ^g	1.1/1.4	93:7	-
8	2/1/200/200	PPNCl	<i>t</i> BGE	>99	8	55.7	43.2(89%)/12.4 (11%) ^g	1.28/1.1	100:0	59.4
9	2/1/100/100	PPNCl	<i>t</i> BGE	>99	5	27.8	18.5(76%)/7.1 (24%) ^g	1.22/1.19	100:0	-
10	0/1/200/200	PPNCl	<i>t</i> BGE	91	8	55.7	12.2	1.27	94:6	20.1
11	2/1/200/200	DMAP	<i>t</i> BGE	94	12	55.8	21.4(55%)/9.4 (45%) ^g	1.31/1.29	96:4	41.9
12	2/1/100/100	DMAP	<i>t</i> BGE	96	6	27.9	13.7(61%)/5.4 (39%) ^g	1.29/1.27	95:5	-
13	0/1/200/200	DMAP	<i>t</i> BGE	83	12	55.8	8.3	1.38	77:23	18.5
14	2/1/200/200	PPNCl	BO	>99	8	56.5	36.3(41%)/13.0 (59%) ^g	1.09/1.15	100:0	75.5
15	2/1/100/100	PPNCl	BO	>99	5	28.3	19.5(49%)/7.1 (51%) ^g	1.07/1.12	100:0	-
16	0/1/200/200	PPNCl	BO	90	8	56.5	10.3	1.33	81:19	26.7
17	2/1/200/200	DMAP	BO	94	12	56.5	17.1(69%)/5.4 (31%) ^g	1.38/1.35	92:8	55.8
18	2/1/100/100	DMAP	BO	96	6	28.3	8.4(59%)/3.2 (41%) ^g	1.33/1.31	95:5	-
19	0/1/200/200	DMAP	BO	88	12	56.5	9.2	1.27	81:19	23.8

^aEach reaction was performed in 2.5 mL of dry toluene, [PA]₀ / [Ep]₀ / [LA]₀ / [Nu]₀ = 200/200/2/1, at 100 °C, Unless otherwise noted. ^bmonomer conversion as determined by ¹H NMR spectroscopy. ^cM_n^(calcd) calculated using {[PA]₀/[Nu]₀ × (% conversion of PA) × (mol wt of MA)} + {[Ep]₀/[Nu]₀ × (% conversion of Ep) × (mol wt of Ep)] + molecular weight of end group. M_{pA} = 148.12 g mol⁻¹, M_{Nu} = (Cl, 35.5 and DMAP, 122.17) g mol⁻¹. ^dM_n^(GPC) measured by GPC at 27 °C in THF relative to polystyrene standards. ^eT_g values were detected by DSC measurement. ^gBimodal distribution (number in parentheses denotes the percentage of each population calculated by GPC peak areas).

Further, the activation of epoxide by the B(C₂H₅)₃ which subsequently increases the positive character on the methylene carbon, the attacking site for all nucleophiles or LB's. The ring-opened epoxide acts as the chain initiating species for reacting with PA. From Figure 6, in general the rate of alkoxide anion reacting with an anhydride monomer (K₁₂) is much faster than a carboxylate anion ring-opening an epoxide (K₂₁), hence the latter process is rate-determining. The reaction between alkoxide anion and anhydride is very fast

and there is no chance for anhydride homopolymerization to occur (K₂₂). It is important to note that as seen from recent literature⁷ here also the copolymerization of PA and epoxides catalyzed by this Lewis pair exhibits an induction period of around 2 h, suggesting the formation of such initiating species is rate determining (Scheme 2 and Figure S32 and S33 in ESI). Furthermore, the following conditions should be fulfilled for successive alternating copolymerization: as shown in Figure 6 (i) the addition of PA to the growing alkoxide chain-end (k₁₂)

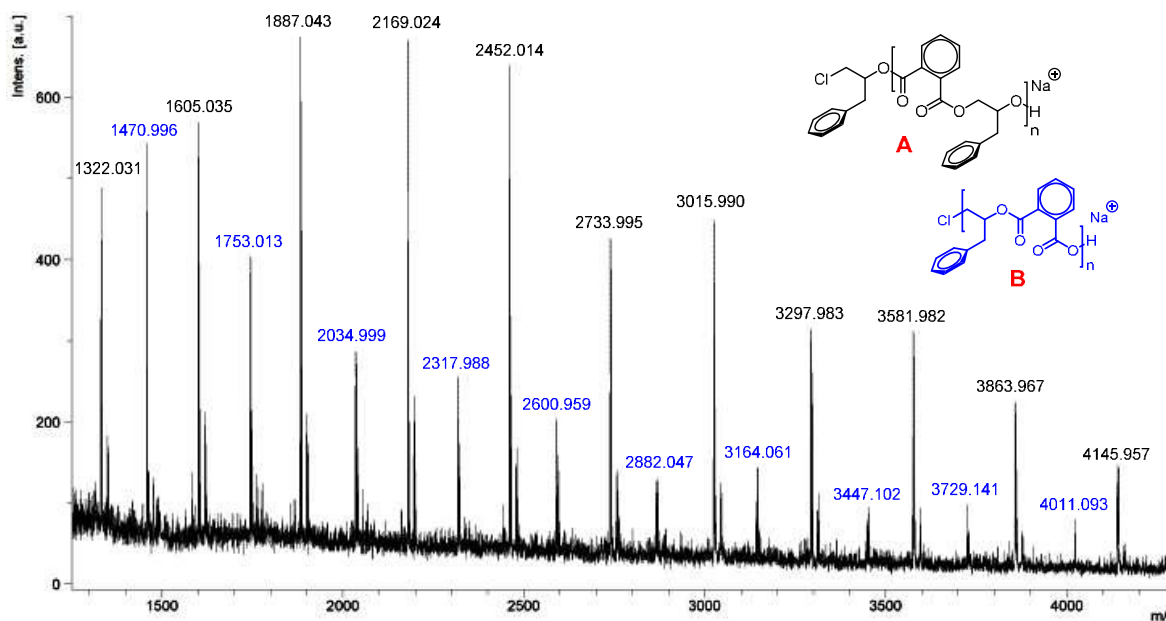


Figure 4. MALDI-TOF MS spectrum of the low-molecular-weight P(PA-*alt*-BO) polyester synthesized by the catalysis of TEB/PPNCl-based LP. The two (A and B) series shows $m/z = [35.45 (\text{Cl}) + 134.18 (\text{BO}) + (282.3 \times n) (\text{PA} + \text{BO}) + 22.99 (\text{Na}^+) + 1.01 (\text{H}^+)]$ ($n = 4\text{--}14$) for A; $m/z = [35.45 (\text{Cl}) + (282.3 \times n) (\text{PA} + \text{BO}) + 1.01 (\text{H}^+)]$ ($n = 5\text{--}14$) for B.

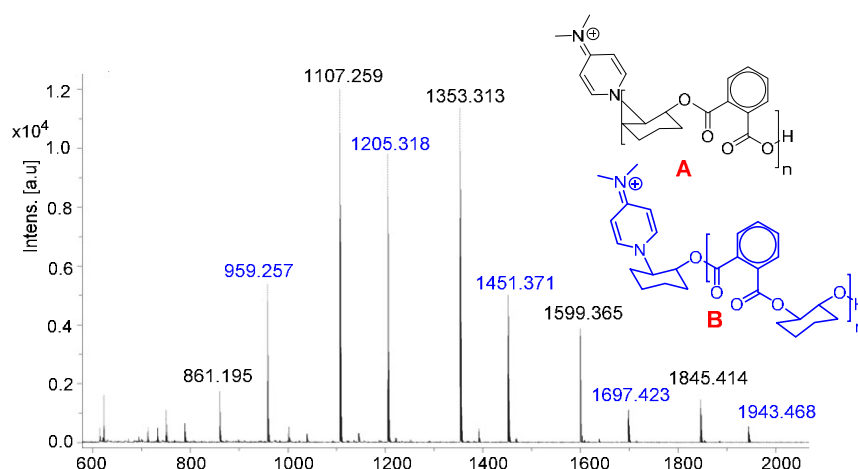


Figure 5. MALDI-TOF MS spectrum of the short P(PA-*alt*-CHO) precursor synthesized by the catalysis of TEB/DMAP-based LP. The two (A and B) series shows $m/z = [122.17 (\text{DMAP}) + (246.27 \times n) (\text{PA} + \text{CHO}) + 1.01 (\text{H}^+)]$ ($n = 3\text{--}7$) for A; $m/z = [122.17 (\text{DMAP}) + 98.15 (\text{CHO}) + (246.27 \times n) (\text{PA} + \text{CHO}) + 1.01 (\text{H}^+)]$ ($n = 3\text{--}7$) for B.

was much higher than the reactivity of epoxide homopolymerization (k_{11}) due to the coordination of the ester functionality to a PPN⁺ cation or TEB by increasing the positive polarization on the carbonyl carbon the attacking site for the growing anion, thus preventing the formation of ether units; (ii) because of the activation of epoxide by TEB, the ester chain ends could ring-open it (K_{21}) affording perfectly alternating copolymers. However, during the activation, the growing anions may undergo back-biting reactions, affording perfectly linear vs cyclic selectivity (Figure S32, in ESI).

For comparison (Scheme 1 and Table 1), ⁿBu₂Mg, Et₂Zn and Al(CH₃)₃ were also investigated with various LB's (PPNCl, DMAP, DBU and TBD) for PA/CHO copolymerization reaction. From the observed results it is clear that ⁿBu₂Mg/PPNCl-based LP gave the better selectivity (Figure S16 and Figure S26 in ESI), followed by the Al(CH₃)₃/PPNCl and Et₂Zn/PPNCl (Figure S13, S15 and Figure S25 in ESI). In the case of ⁿBu₂Mg /PPNCl system the copolymers were obtained with high alternating sequences confirmed from the ¹H NMR spectrum (Figure S16 in ESI), but the overall activity was significantly lower than that

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of the nonmetallic systems tried (Figure S26 in ESI). The molar masses measured by GPC shown relatively low molecular weight material with a broad molecular weight distributions (MWDs) and low thermal properties (81% conversion, $M_n = 4.4 \text{ kg mol}^{-1}$, PDI = 1.27, entry 20 Table 1). It is probable that the excess turnover monomers were converted into cyclic oligomers as a result of intramolecular transesterification.² In the case of $\text{Et}_2\text{Zn}/\text{PPNCl}$ and $\text{Al}(\text{CH}_3)_3/\text{PPNCl}$ the copolymer's molecular weight, yield and selectivity decreased greatly ($\text{Et}_2\text{Zn}/\text{PPNCl}$: 95% conversion, $M_n = 5.2 \text{ kg mol}^{-1}$, PDI = 1.37, entry 17 Table 1; $\text{Al}(\text{CH}_3)_3/\text{PPNCl}$: 94% conversion, $M_n = 6.8 \text{ kg mol}^{-1}$, PDI = 1.34, entry 13 Table 1). Investigation of the ^1H NMR spectra reveals the occurrence of the undesirable side reaction of epoxide homopolymerization in addition to alternating sequence (Figures S13, S15 and S16, in ESI). Further, the samples of low DPs exhibited unimodal distribution with lower M_n 's. The MWDs are broadened indicative of slow deactivation of the active species and intramolecular transesterification reactions (Figure S25 and Figure S26, in ESI).⁹ This can be attributed by strong coordination of PPNCl to this highly Lewis acidic Et_2Zn or $\text{Al}(\text{CH}_3)_3$ decreases the acidity at the active site and leads to dissociation of the growing polymer chain, thus leading to increased probability of back-biting.

It is noteworthy that no interesting polymers were observed upon replacing PPNCl with other neutral organic bases under the same conditions employed in Table 1. In the case of DMAP as initiator with TEB the copolymers were obtained with high molecular weight, but the overall activity was significantly lower than that of our $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ system. Thus, from the observed results, it should be noted that the growing anions (anionic tetrahedral boron moieties) stabilized by the bulky cation (PPN^+), that is, an intermolecular cation as shown in Scheme 2, favours a higher propagation rate and crucial as for good performance towards the copolymerization of PA and epoxides in this study. In contrast, in the case of $\text{B}(\text{C}_2\text{H}_5)_3/\text{DMAP}$ or DBU or TBD based systems the anionic active species (zwitter ionic) stabilized by the cation, that is, an intramolecular cation as shown in Scheme S32, in the Supporting Information, involving in propagation cycles at a slow level and exhibited less activity for the copolymerization of PA and epoxides.⁷ This can be attributed to strong binding of DMAP/DBU/TBD to the boron center than oxygen anions in the chain-end, *i.e.* either alkoxide or carboxylate in epoxide-anhydride copolymerization. However, because of the weaker basicity,⁷ DMAP was more effective than DBU/TBD, when combined with TEB for catalysing the PA and epoxides copolymerization. In brief, as observed from previous reports,⁷ it appears that the activation will be restricted by fundamental aspects like optimum acidity/alkalinity and matched size of the Lewis pair are necessary for effective copolymerization of PA and epoxides.

Importantly, control experiments demonstrated that TEB alone could not induce any polymerization under the same conditions (100 °C, 6 h). Although PPNCl alone lead to

reasonable monomers conversion. Since the observed molecular weight decreased greatly, the excess turnover monomers were converted into cyclic esters (Table 1, entry 5). Thus, when both components are combined result in high activity because of bifunctional action, most probably involving Lewis pair dissociation and monomers activation by the Lewis acid (Scheme 2), which facilitates nucleophilic ring-opening of incoming monomers by either initiators (LB's) or anionic end of growing polymer chain (Scheme 2 and Scheme S32 in ESI). Such that, in both mechanisms (anionic copolymerization, Scheme 2 or zwitterionic copolymerization, Scheme S32) LB's behave as a nucleophile rather than base. The effect of temperature on the CHO-PA copolymerization reaction was also investigated, and the results are summarized in Table 1. The decrease of temperature from 100 to 80 °C considerable decrease of monomers conversion and molecular weight was observed (Table 1 entry 2 and 4). However, at 100 °C reaction temperature shown to have huge adverse effects on copolymer selectivity.

Table 3. $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ -based Catalyst Compared with Active Cr, Co and Al Catalysts.

Cat.	[Cat.] ₀ /[Cocat.] ₀ /[PA] ₀ /[CHO] ₀	temp °C	time h	M_n (kDa)	M_w/M_n
$\text{B}(\text{C}_2\text{H}_5)_3$ (This work)	2/1/200/200	100	6	21.3	1.07
Co (refer 10c)	1/1/500/500	100	1	19.1	1.10
Al (refer 10d)	1/2/250/250	25	50	6.1	1.24
Cr (refer 10b)	1/1/200/200	100	24	17.0	1.12
Cr (refer 10a)	1/1/250/250	110	1	15.0	1.20

Next as shown in Scheme 3, the best performing LP's from the above studies for example, $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ and $\text{B}(\text{C}_2\text{H}_5)_3/\text{DMAP}$ systems were examined for copolymerization of PA/*t*BGE and PA/BO under the same experimental conditions (see Table 2). For example, perfectly alternating and nearly controlled polyesters were obtained for PA and *t*BGE copolymerisation using PPNCl as nucleophile accompanied by TEB at 100 °C (Table 2, entry 8, 14). As expected, the polymer molecular weight seemed to be related to the reactivity of the epoxides.^{2g} The polymers obtained from PA and *t*BGE copolymerization reactions showed quite high M_n values (Table 2 entry 8, *t*BGE + PA: 99% conversion, $M_n = 43.2 \text{ kg mol}^{-1}$, PDI = 1.28), near to theoretical values. In comparison, PA with BO- and CHO-based copolymers generally exhibited lower molecular weights than predicted (Table 2 entry 14, BO + PA: 99% conversion, $M_n = 36.3 \text{ kg mol}^{-1}$, PDI = 1.09; Table 2 entry 4, CHO + PA: 99% conversion, $M_n = 21.3 \text{ kg mol}^{-1}$, PDI = 1.07). The high M_n values for P(PA-*alt*-*t*BGE) copolymers explained by polymer propagation via chain-end transesterification rather

than normal propagation.¹⁶ This is due to transesterification of active secondary alkoxide, which is formed after insertion of a *t*BGE, with the chain end of another chain, resulting in the formation of a linear polymers. This observation was well investigated recently by Duchateau and coworkers by using branched ϵ -decalactone (eDL) as monomer.¹⁶ They investigated efficiently the effect of sterichindrance at the α -methylene groups of both the growing chain and the (macro)lactones towards polymerization rate.

¹H NMR and MALDI-TOF MS spectra indicate that an alternating copolymer of P(PA-*alt*-*t*BGE) and P(PA-*alt*-BO), are formed without traces of aliphatic ethers (Figure 4 and Figure S27-S30 in ESI). The polymers characterized by GPC exhibited narrow molecular weight distributions ($M_w/M_n = 1.07$ to 1.38) and the M_n values ($M_{n,exp}$) are lower than theoretical value calculated from the feed ratio of monomers and initiator ($M_{n,calc}$) and bimodal distributions were observed (Figure S18-S25, in ESI). As shown in Table 2, a stepwise increase of the B(C₂H₅)₃/PPNCl molar ratio from 0.5 to 2.0 equiv was shown to result in a considerable increase of monomers conversion and molecular weights. Further, from our control experiments, PPNCl or DMAP alone able to give good monomer's conversion, but the M_n and MWDS are not well controlled (see Table 2). Runs 4 – 7 (Table 2) summarized ROCOP results of PA and CHO by B(C₂H₅)₃/PPNCl system, achieved quantitative monomer conversion for all ratios examined, and produced copolymers with very low M_w/M_n values of 1.07 – 1.24 for [PA]+[CHO]/[LP] = 200 – 800 (Figure S18-S21, in ESI). However, with increasing monomers to LP ratio from 600 to 800, the copolymer M_n was decreased from 57 to 51 kg/mol (Table 2, run 6 and 7). This can be attributed by the faster dissociation of the chain end from the active center than the monomer insertion at high monomers to LP ratio leads to low M_n 's. Next, the cleavage of the *t*-butyl group in P(PA-*alt*-*t*BGE) copolymer was carried out by the reaction under TFA¹¹ and achieved quantitative deprotection, confirmed from ¹H, ¹³C NMR spectrum and GPC data (Figure S34-S36, in ESI). Deprotection was monitored by comparison of the intensity of the decreasing *tert*-butyl signal. It was observed that all *tert*-butyl groups were removed (>94%) in the region from $\delta = 1.3$ -1.0 ppm after 8h. After deprotection significant shift in the epoxide methylene proton signals were observed (Figure S34 in ESI). Prolonged reaction times led to polymer degradation. However, precisely defined conditions are required to obtain fully deprotected poly(ester-*alt*-glycerol). In addition, the kinetic studies by using TEB and PPNCl as Lewis pair for the ROAC of PA and *t*BGE ($[tBGE]_0/[PA]_0/[TEB]_0/[PPNCl]_0 = 200/200/2/1$ at 100 °C in dry toluene) showed that the M_n 's against PA conversion was in a linear correlation with a narrow molecular weight distribution (M_w/M_n values varied a little from 1.19 to 1.28) (Figure S37 in ESI), suggesting a controlled behaviour of the copolymerization system.

Next, thermal properties of the various polyesters synthesized from the monomers listed in Scheme 3 was

determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC curves obtained from the second scan were depicted in Figure S38-S44, in ESI. The glass transition temperature (T_g) values showing in a range from 18 to 98 °C, depending on the monomers. As anticipated, the T_g is sensitive to chemical structure, there is expected to be a difference in T_g values for synthesized various polyesters. Such that, the T_g increases with an increase in the rigidity of the main chain, following the order: Poly(PA-*alt*-CHO), 98.8 °C > Poly(PA-*alt*-BO), 75.5 °C > Poly(PA-*alt*-*t*BGE), 59.4 °C. Thus, Poly(PA-*alt*-CHO) with the most rigid main chain exhibits the highest T_g of 98.8 °C, while Poly(PA-*alt*-*t*BGE) with the flexible main chain (relatively) displays the lowest T_g of 51.7 °C. TGA and derivative thermogravimetry (DTG) curves of the synthesized polyesters were provided in Figure S45-S49, in ESI. The polymers synthesized using Al(CH₃)₃, Et₂Zn and ⁿBu₂Mg as catalysts showed low thermal stability ($T_d = \sim 155$ °C, T_d defined by the temperature of 5% weight loss in the TGA curve) with a two-step degradation profile. On the other hand, fully alternating copolymers exhibited high thermal stability showing one-step degradation profiles with high T_d 's ranging from 270 to 300 °C (T_d , temperature at which 95% of copolymer mass loss occurred) and high maximum degradation temperatures (T_{max} , measured by the derivative TGA curves) ranging from 360 to 390 °C (Figure S45-S47, in ESI). Two-step degradation profile can be attributed to the stepwise quantitative thermal degradation process *i.e.* in nearly alternating polymer the first stage of weight loss approximately between 150 and 255 °C indicates the thermal cleavage of the poly ether block followed by the second step around 255 and 320 °C indicates the thermal cleavage of the main alternating copolymer block. This observation is similar to previous reports.^{9,14}

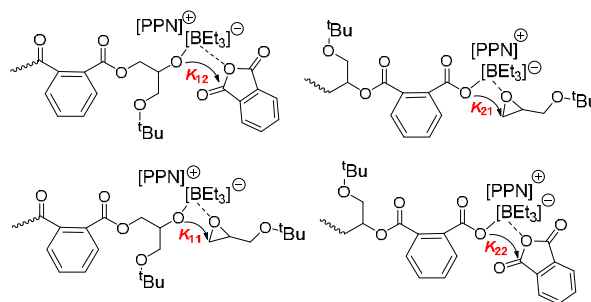


Figure 6. Kinetic parameters for the PA and *t*BGE copolymerization catalyzed by TEB/PPNCl-based LP.

Conclusions

Metal-free Lewis pair approach presented in this study is versatile, of broad applicability and very convenient to employ

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for the synthesis of perfectly alternating copolymers from the copolymerization of PA with epoxides. We examined various Lewis acids (Et_3B , $\text{Al}(\text{CH}_3)_3$, Et_2Zn and ${}^n\text{Bu}_2\text{Mg}$) and Lewis bases/nucleophiles (PPNCl, DMAP, DBU and TBD) for the copolymerization of epoxides with phthalic anhydride. Based on the observed results, the $\text{B}(\text{C}_2\text{H}_5)_3/\text{PPNCl}$ pair stood out as the most active and effective LP for the anionic copolymerization of PA with CHO. In combination with $\text{B}(\text{C}_2\text{H}_5)_3$ and PPNCl for copolymerization, the poly(anhydride-co-epoxide)s synthesized with M_n values up to 57.5 kg mol^{-1} with a M_w/M_n of 1.2 within 18h. Of all Lewis bases/nucleophiles tested, PPN^+Cl^- exhibited the highest activity, and only 1 equiv was sufficient to reach the optimum activity. In contrast, *N*-heterocyclic Lewis bases (DMAP/DBU/TBD) were less effective nucleophiles. Further from Poly(PA-*alt*-tBGE) copolymers hydroxyl-functionalized poly(ester-co-glycerol)'s were successfully synthesized by deprotection of the *t*-butyl groups. The powerful cooperative effects of simple Lewis acids and Lewis bases/nucleophiles for monomer selective catalysis in ROCOP reactions is very attractive by virtue of its simplicity and potential flexibility, suggesting a much greater potential to still explore.

Conflicts of interest

There are no conflicts to declare

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TOC:

Cooperative metal-free Lewis pairs effectively catalysed controlled ring-opening copolymerization of phthalic anhydride (PA) with epoxides was reported here.

