

Probing Site Cooperativity of Frustrated Phosphine/Borane Lewis Pairs by a Polymerization Study

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S Supporting Information

ABSTRACT: The first highly active phosphine (P)/borane (B) Lewis pair polymerization is promoted unexpectedly by P–B adducts. The P and B site cooperativity is essential for achieving effective polymerization, as shown by this study examining the reactivity of a library of P/B Lewis pairs toward polymerization of a renewable acrylic monomer.

The chemistry of “frustrated Lewis pairs” (FLPs) has attracted an explosive level of interest since the FLP concept was uncovered through the seminal works of Stephan and Erker.¹ In essence, an FLP can be described as a nonclassical Lewis pair comprising a bulky Lewis acid {LA, e.g., the most commonly used $B(C_6F_5)_3$ } and a bulky Lewis base (LB, e.g., the most commonly used P^tBu_3 and $PMes_3$, Mes = 2,4,6- $Me_3C_6H_2$) that are sterically precluded from forming stable classical LA–LB adducts (CLAs). FLPs can also result from electronic frustration due to weak LA–LB bonds. Such FLPs exhibit the unquenched, orthogonal LA and LB reactivity that can promote unusual reactions, or reactions that were previously known to be possible only by transition-metal complexes, and display FLP-induced or enhanced reactivity in the activation of small molecules, catalyzing the rapidly growing interest in FLP chemistry.² Herein we report a study that probes the site cooperativity of P/B LPs through investigations into the reactivity of such LPs toward polymerization of the renewable γ -methyl- α -methylene- γ -butyrolactone (γ -MMBL).³ This study has led to the first highly active polymerization by P/B LPs and also yielded fundamental insights into why an apparent inverse relationship between the polymerization activity and the degree of LP “frustration” was exhibited, with the most frustrated LP (FLP) being the least active (inactive), the less frustrated LPs (interacting FLP) being more active, and the least-frustrated LP (CLA) being the most active (Figure 1).

Lewis pair polymerization,⁴ which utilizes a CLA or FLP so that the LA and LB work cooperatively to activate the monomer substrate and participate in chain initiation as well as chain propagation and termination/transfer events, has attracted recent interest in the addition polymerization of conjugated polar alkenes such as linear and cyclic acrylic monomers by bulky aluminum LA $Al(C_6F_5)_3$ -based FLPs,⁵ the ring-opening (co)-polymerization of heterocyclic monomers such as lactide and lactones by $Zn(C_6F_5)_2$ -based LPs,⁶ and the radical polymerization of styrene mediated by the persistent FLP–NO aminoxyl radical derived from N,N -cycloaddition of a cyclohexylene-

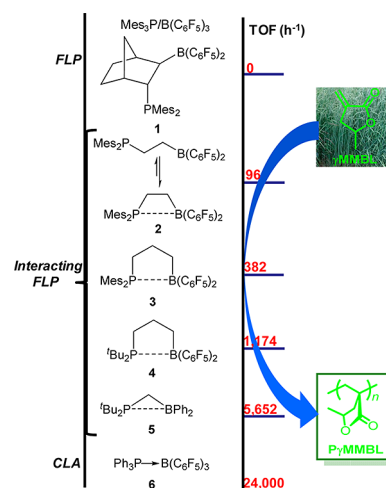


Figure 1. Increasing TOF on going from FLPs to interacting FLPs to CLAs in γ -MMBL polymerization (CH_2Cl_2 , rt).

bridged intramolecular P···B FLP to nitric oxide.⁷ We reported earlier that a bulky LA/LB pair comprising $Al(C_6F_5)_3$ and 2,6-di-*tert*-butyl pyridine works cooperatively to activate and break C–H bonds,⁸ and that $Al(C_6F_5)_3$ -based FLPs with bulky phosphine and *N*-heterocyclic carbene (NHC) bases rapidly polymerize acrylics, including methyl methacrylate (MMA) and biorenewable α -methylene- γ -butyrolactone (MBL) and γ -MMBL to high molecular weight (MW) polymers.⁵ This polymerization was proposed to proceed via zwitterionic phosphonium or imidazolium enolaluminate propagating species, which have been structurally characterized.^{4,5} Interestingly, the FLPs comprising the borane congener $B(C_6F_5)_3$ and the bulky NHC or phosphine LBs are *inactive* for such polymerization. Intrigued by this finding and motivated by the challenge to “turn on” the polymerization activity of the more useful and user-friendly borane-based LPs [$Al(C_6F_5)_3$ is shock- and air/moisture-sensitive⁹], we hypothesized that P/B LPs with varying degrees of “frustration” regulated by steric, electronic, and spatial controls in both inter- and intramolecular LPs should impart their cooperativity in such polymerization so that an active polymerization system by P/B LPs could be discovered. Gratifyingly, this study indeed led to a highly active polymerization system, but surprisingly, we observed an increasing

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Table 1. Selected Results of γ -MMBL Polymerization by Intramolecular P \cdots B LPs 1–5 and CLA 6^a

run no.	P \cdots B pairs	[M]/[P \cdots B]	time (min)	conv. ^b (%)	M_n^c (kg/mol)	PDI ^c (M_w/M_n)	I^*^d (%)
1	1	200	1440	0	—	—	—
2	2	200	160	100	37.0	1.97	61
3	3	200	75	100	128	1.26	18
4	4	200	19	100	67.0	1.21	33
5	5	200	15	83	39.0	1.94	48
6	5	800	120	75	117	2.09	57
7	6	200	1	100	41.0 ^e	1.18 ^e	55
8	6	800	2	100	102 ^f	1.34 ^f	88
9	4/2ArO \bullet	200	19	100	64.0	1.33	35
10	4/5ArO \bullet	200	19	100	53.0	1.53	42

^aCarried out inside an inert glovebox ($\sim 25^\circ\text{C}$). Conditions: 2.0 mL of CH_2Cl_2 , 0.50 mL (4.68 mmol) of γ -MMBL. ArO \bullet = galvinoxyl free radical inhibitor. $[\gamma\text{-MMBL}]/[\text{base}] = 200$. ^bConv. = % monomer conversions measured by ^1H NMR spectroscopy. ^cNumber-average molecular weight (M_n) and polydispersity index (PDI) measured by gel permeation chromatography (GPC) analyses in DMF relative to PMMA standards. ^d $I^* = M_n(\text{calcd})/M_n(\text{exptl})$, where $M_n(\text{calcd}) = \text{MW}(\text{M}) \times [\text{M}]/[\text{I}] \times \text{conversion} (\%) + \text{MW}(\text{chain-end groups})$. ^eBimodal distribution: $M_n = 41.0$ kg/mol, PDI = 1.18 (86%); $M_n = 3.00$ kg/mol, PDI = 1.05 (14%). ^fTrimodal distribution: $M_n = 1060$ kg/mol, PDI = 1.06 (2%); $M_n = 102$ kg/mol, PDI = 1.34 (55%); $M_n = 2.00$ kg/mol, PDI = 1.26 (43%).

turnover frequency (TOF) on going from FLPs to interacting FLPs to CLAs in γ -MMBL polymerization (Figure 1).

Under our current standard conditions ($\sim 25^\circ\text{C}$, 2.0 mL of CH_2Cl_2 , 0.50 mL or 4.68 mmol of γ -MMBL, 200 equiv relative to the LP, or 0.5 mol % LP loading), all γ -MMBL polymerization control runs with the LB PMes_3 alone, or the LAs $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{HB}(\text{C}_6\text{F}_5)_2$ alone, or the FLPs comprising the above LB/LAs in a 1:1 or 1:2 ratio, yielded no monomer conversion up to 24 h.¹⁰ Next, we examined the reactivity of five intramolecular FLPs toward polymerization of γ -MMBL and yielded intriguing results that were summarized in Table 1. Specifically, noninteracting vicinal FLP 1¹¹ exhibited no polymerization activity up to 24 h (run 1), as anticipated; however, Erker's interacting vicinal FLP 2¹² showed good polymerization activity, achieving 100% monomer conversion in 160 min and producing γ -MMBL with $M_n = 3.70 \times 10^4$ g/mol and polydispersity ($\text{PDI} = M_w/M_n$) = 1.97 (run 2). The resulting initiator efficiency (I^*) was calculated to be 61%. Moving to more interacting, three-carbon-linked intramolecular FLP 3,¹³ we observed an even more rapid polymerization; thus, this FLP consumed all of the monomer in 75 min, affording γ -MMBL also with a much higher M_n of 1.28×10^5 g/mol (thus a much lower I^* of only 18%) and a lower PDI of 1.26 (run 3). Substituting the Mes group in FLP 3 with the more basic ^tBu group in intramolecular FLP 4¹⁴ further enhanced the rate of polymerization by about 4-fold (run 4 vs 3). Preorganized intramolecular FLP ^tBu₂PCH₂BPh₂ (5)¹⁵ with a one-carbon linkage showed even higher activity (run 5) such that the FLP loading can be lowered from 0.5 to 0.125 mol % (run 6); these two runs gave I^* values of 48% and 57%, respectively. The ability of the interacting FLPs to control the resulting polymer MW was demonstrated by a study that monitored the γ -MMBL polymerization through analyzing the quenched polymer MW at each monomer conversion point up to quantitative conversion (Tables S2–S5, Figure S38). Most intriguingly, CLA 6, an isolable and structurally characterized LB–LA adduct,^{16,17} exhibited the highest activity within the current LP series, achieving 100% conversion in only 1 min with a 0.5 mol % LP loading (run 7) or 2 min with a 0.125 mol % LP loading (run 8).

To more precisely rank the initial rates of the γ -MMBL polymerization, we calculated the maximum TOF value for each of the above LPs from the steepest slope of the conversion vs time plot under the same polymerization conditions (Figure 2). This kinetic analysis clearly shows that the polymerization

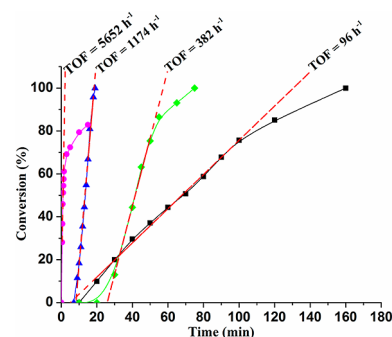


Figure 2. Conversion–time plots and determination of the catalytic activity (maximum TOF) of intramolecular FLP 5 (●), 4 (▲), 3 (◆), and 2 (■) for the polymerization of γ -MMBL.

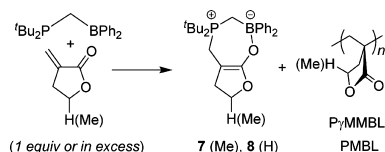
activity follows the order 6 ($24\,000\text{ h}^{-1}$) > 5 (5652 h^{-1}) > 4 (1174 h^{-1}) > 3 (382 h^{-1}) > 2 (96 h^{-1}) \gg 1, $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ (0 h^{-1}), displaying an apparent inverse relationship between the polymerization activity and the degree of LP “frustration”: the more frustrated LP has a lower polymerization activity, with the FLP being the least active (or inactive), the CLA being the most active, and the interacting FLP being somewhere in between.

Regarding a possible polymerization mechanism by the current P/B LPs, we have previously shown that the polymerization of acrylic monomers by the alane-based LPs proceeds in a bimolecular propagation mechanism via zwitterionic active species derived from cooperative activation of the monomer by the LB and LA sites of the LP, in which the LB becomes the cationic initiating chain end while the LA attaches to the anionic growing chain end.^{4,5} The possibility that the observed polymerization activity could be due to some radical species present in the LPs as a result of the possible single electron transfer was ruled out: (a) by the observations that the $\text{PMes}_3/\text{Al}(\text{C}_6\text{F}_5)_3$ pair, which was shown to form the radical cation–anion pair,^{2b} is actually inactive for this polymerization, while other alane-based FLPs without electron transfer are highly active, and (b) by the structural characterization of the active intermediates and the mechanistic understanding of this polymerization.^{4,5} As the polymerization by intramolecular P/B FLPs has not previously been investigated, we first tested the possibility of radically initiated polymerization. At the outset, it is taken under consideration that the $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ pair (which forms a violet solution, ascribed to π -stacking of electron-rich and

-poor arene rings¹⁸) is inactive for the current polymerization.¹⁹ Nevertheless, 2 equiv (relative to the LP) of the potent free radical scavenger (inhibitor) galvinoxyl was added to the γ MMBL polymerization by FLP 4. No reduction of the polymerization activity was observed, and the resulting polymer MW characteristics and the I^* value were also rather similar (run 9 vs 4). Even the addition of 5 equiv of galvinoxyl did not alter the activity, although there was some modulation on the polymer MW (run 10). Furthermore, vinyl acetate, which can be readily polymerized by a radical process but not by the conjugate-addition mechanism, was not polymerized by the current LPs. In short, this evidence ruled out the possibility of radical species being responsible for the observed polymerization activity by the current P/B LPs.

Next, we examined the reaction of the two representative intramolecular FLPs of the series, ^tBu₂PCH₂BPh₂ (5) and Mes₂P(CH₂)₂B(C₆F₅)₂ (3), with γ MMBL in a stoichiometric ratio and in excess. Mixing initiator FLP 5 with 1 equiv of γ MMBL in CD₂Cl₂ at rt resulted in immediate formation of a cycloaddition intermediate, zwitterionic phosphonium enolborate 7²⁰ (Scheme 1), and the polymer P γ MMBL, plus an

Scheme 1. Formation of Intermediates 7 and 8 through Cycloaddition of the FLP to γ MMBL and MBL

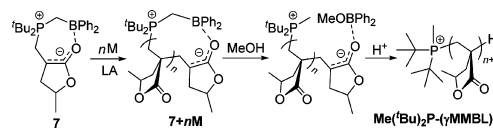


appreciable amount of unreacted FLP 5. After all the monomer was consumed, at which time the mixture contained 40% 5, 27% 7, and 33% P γ MMBL, another 5 equiv of γ MMBL were added to the reaction mixture, after which more initiator was consumed and the amount of the polymer gradually increased as the added monomer continued to be converted (Figure S1). Interestingly, once all the initiator was consumed the polymerization stopped, although a substantial amount of intermediate 7 and some monomer were still present. The remaining 7 after the above 1:6 ratio reaction was isolated in 35% yield from the reaction mixture by separation from the polymer followed by crystallization.¹⁰ The same 1:1 ratio reaction with MBL yielded similar observations but with much less polymer formation and thus led to the higher-yield isolation (68%) of MBL-based intermediate 8 (Scheme 1).¹⁰ These results indicate that 7 itself cannot polymerize γ MMBL directly, requiring the presence of the FLP as the LA to activate the monomer. This scenario was confirmed by the following two experiments. First, an independent polymerization by 7 yielded no monomer conversion, but the polymerization took place as 5 was added and the rate of polymerization was proportional to the amount of 5 added. Second, the addition of 10 mol % (relative to 7) of the strong LA B(C₆F₅)₃ to the reaction mixture containing 7 and γ MMBL (200 equiv) brought about rapid polymerization that converted all of the monomer in only 3 min. A similar rate enhancement by B(C₆F₅)₃ was also seen for all the polymerizations by the current interacting LPs, except for the noninteracting intermolecular FLP PMes₃/B(C₆F₅)₃ and intramolecular FLP 1, which were still inactive upon addition of another equivalent of B(C₆F₅)₃.²¹ In contrast, the 1:1 ratio reaction of FLP 3 and γ MMBL afforded no such cycloaddition intermediate, while all of the monomer, including another 8

equiv that were added, was converted to the polymer, with a substantial amount of the initiator 3 still unconsumed. Overall, the above results are consistent with those obtained from the batch polymerization runs by 5, which did not achieve quantitative monomer conversion and gave an I^* value below 60% (runs 5 and 6), and runs by 3, which, on the other hand, achieved 100% monomer conversion but gave a low I^* value of only 18% (run 3). These key differences between the above two FLPs can be explained by a scenario in which initiation is rate-limiting and the intermediate is consumed as soon as it is generated for the polymerization by 3, whereas the cycloaddition intermediate is the resting state in the case of FLP 5.

To provide additional evidence to support the zwitterionic polymerization via intermediate 7, we analyzed low MW oligomers produced by FLP 5 with a [γ MMBL]/[5] ratio of 20 by MALDI-TOF MS. A plot of m/z values of the major mass series vs the number of γ MMBL repeat units (n) yielded a straight line with a slope of 112.04 and an intercept of 161.38 (Figures S11–S12). The slope corresponds to the mass of the γ MMBL monomer, whereas the intercept is the sum of the masses of H⁺ (from the matrix acid) and end groups, which correspond to a formula of C₉H₂₁P. Hence, this analysis suggests that the polymer has a structural formula of Me(^tBu)₂P⁺–(γ MMBL) _{n} –H. This end group was corroborated by NMR data at δ 1.24 (^tBu) and 0.92 (Me) in ¹H NMR (Figure S15) and δ 60.9 in ³¹P NMR. The oligomerization using a lower [γ MMBL]/[5] ratio of 6 gave the same result (Figures S13–S14). The initiation chain end, Me(^tBu)₂P⁺–, was proposed to originate from initiator 5, where the borane moiety in polymer 7+nM produced from repeated conjugate addition of 7, and its homologs to the monomer activated by the LA (either externally added or FLP 5 itself) was cleaved during the quenching with CH₃OH, while the termination chain end was derived from protonation of the enolate (Scheme 2). This mode of bond cleavage was confirmed

Scheme 2. A Possible Pathway for Formation of Me(^tBu)₂P–(γ MMBL) _{n}



with the model reaction between FLP 5 and CH₃OH, which shows cleavage of the C–B bond and clean formation of the corresponding phosphine and borane products: ^tBu₂PCH₂BPh₂ + CH₃OH → ^tBu₂PMe + Ph₂BOMe.^{10,22}

A key fundamental question unaddressed so far is what accounts for the observed apparent inverse relationship between the activity of the polymerization by the P/B LPs and the degree of “frustration” in such LPs (*cf.*, Figure 1). To this end, we designed three sets of experiments to test a hypothesis that it is the LB and LA site cooperativity that determines the relative polymerization activity of such LPs, regardless of the degree of frustration. *First*, the effect of the P site basicity was manifested by a C₆F₅-substituted derivative of FLP 5, (C₆F₅)₂PCH(Me)B(C₆F₅)₂ (9),²³ which became inactive for the polymerization up to 24 h; this was reaffirmed by the observed 4-fold rate enhancement by substituting the Mes group in FLP 3 with the more basic ^tBu group in FLP 4 (*vide supra*) and by the observed lack of activity by the Ph derivative, Ph₂P(CH₂)₃B(C₆F₅)₂ (10). This effect can also be seen within the intermolecular FLPs: under the current conditions, the PMes₃/B(C₆F₅)₃ pair yielded

no monomer conversion up to 24 h; while the $P^tBu_3/B(C_6F_5)_3$ pair also yielded no polymer formation for up to 2 h, it became active with a longer reaction time (Table S1). *Second*, the effect of the B site acidity was readily revealed by moving from the CLA $Ph_3P \cdot B(C_6F_5)_3$ (**6**), which is highly active, to $Ph_3P \cdot BPh_3$ (**11**), which is inactive. *Third*, the effect of the LB \rightarrow LA adduct strength was evidenced by the observed relative polymerization activity of CLAs: $Ph_3P \cdot B(C_6F_5)_3$ (**6**, $24\,000\ h^{-1}$), $MePh_2P \cdot B(C_6F_5)_3$ (**12**, $6000\ h^{-1}$), $Me_2PhP \cdot B(C_6F_5)_3$ (**13**, $800\ h^{-1}$), and $Me_3P \cdot B(C_6F_5)_3$ (**14**, $0\ h^{-1}$). The decreased activity with an increase in the adduct strength (Figure S39) can be understood with an equilibrium established in solution between the adduct and the free P and B sites, analogous to that proposed by Stephan in the case of lutidine $\cdot B(C_6F_5)_3$ for H_2 cleavage.²⁴ The dissociation, or lack thereof, of the adducts in the presence of the monomer μ MMBL solution was investigated using DMSO and acetone as the surrogate. Thus, dissolving adduct **6** in DMSO- d_6 or acetone- d_6 ($S-d_6$) readily generated the free Ph_3P and $(S-d_6) \cdot B(C_6F_5)_3$ (Figures S42–43), while the strong adduct **14** remained intact in such solvents. The use of water to determine such dissociation generated two interesting structures: $Ph_3P \cdot H_2O \cdot B(C_6F_5)_3$ (**15**), derived from classical adduct **6**, and $[Mes_3PH]^+[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ (**16**), derived from the FLP $PMes_3/B(C_6F_5)_3$.¹⁰

In conclusion, we have discovered the first highly active Lewis pair polymerization by P/B LPs. Initial attempts to generate an active polymerization system by focusing on P/B FLPs such as $PMes_3/B(C_6F_5)_3$ were futile because, although they have essentially quantitative “free” LB and LA sites for catalysis, the extremely high steric demand of the P site renders such FLPs inactive for this polymerization. On the other hand, the interacting, tethered intramolecular FLPs (**2–5**) exhibit good to high polymerization activity, due to the relieved steric stress on the P site. Finally, P–B CLAs, which form stable adducts in the solid state, can have very high polymerization activity (e.g., **6**), being “frustrated” in solution (prone to dissociation), or no activity (e.g., **14**), being “non-frustrated” in solution (no dissociation). Hence, the most active system is brought about by a good compromise between B site acidity, P site basicity, steric crowding around P, and the strength of the P–B association in solution. This study further highlights the importance of the cooperativity of the P and B sites of LPs, regulated by steric, electronic, and spatial controls, for achieving high polymerization activity.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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📄 Notes

The authors declare no competing financial interest.

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(19) Under highly concentrated (0.2 mL μ MMBL in 0.5 mL CH_2Cl_2) and high FLP loading (2.0 mol%) conditions, some polymerization activity can be observed, but addition of galvinoxyl (2 or 5 equiv) completely shut down the activity attributed to radical species.

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(21) In the presence of 1 equiv of $B(C_6F_5)_3$, all interacting FLPs converted 800 equiv of μ MMBL quantitatively to P_μ MMBL in a short time period: **2** (3 min), **3** (4 min), **4** (7 min), and **5** (14 min).

(22) Direct reaction of intermediate **7** with MeOH gave the same C–B cleavage product for the B site (Ph_2BOMe), but for the P site, H^+ was connected with the CH_2 (bridging) and α -enolate carbons.

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