Synthesis of Pyridine- and 2-Oxazoline-Functionalized Vinyl Polymers by Alane-Based Frustrated Lewis Pairs

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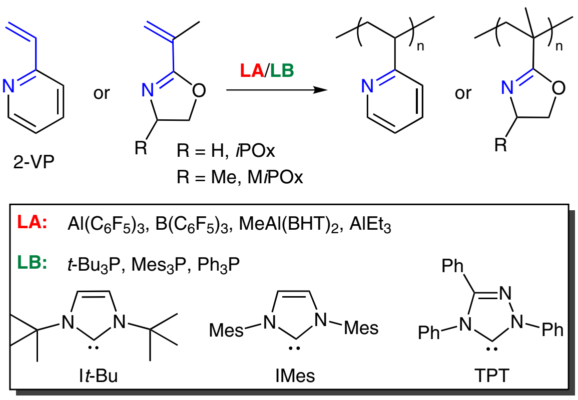
Abstract: Reported herein is the first example of polymerization of polar vinyl monomers bearing the C=C–C=N functionality by Frustrated Lewis pairs (FLPs). In particular, FLPs based on $Al(C_6F_5)_3$ and N-heterocyclic carbenes rapidly convert 2-vinyl pyridine and 2-isopropenyl-2-oxazoline into medium to high molecular weight, N-functionalized vinyl polymers. Activated monomer-alane adduct **1** and initiated zwitterionic intermediate **2** have been isolated and structurally characterized, providing strong evidence for the proposed bimolecular, activated monomer polymerization mechanism.

Key words: frustrated Lewis pairs, polymers, pyridines, nitrogen, monomers, polymerization

Much of the emerging ‘frustrated Lewis pair’ (FLP) chemistry[1] has focused on small molecules, on their activation, on stoichiometric or catalytic transformations, and on new reactivity or novel reaction development.[2] A new direction has been to veer toward polymerization catalysis mediated by Lewis pairs (LPs), either FLPs or classical Lewis pairs (CLPs), for the synthesis of macromolecules as useful polymeric materials.[3] In this type of polymerization, the Lewis acid (LA) and Lewis base (LB) of a LP work cooperatively to activate the monomer substrate and participate in chain initiation or chain propagation and termination/transfer events. We recently reported the chain-growth addition polymerization of conjugated polar alkenes, such as linear and cyclic acrylic monomers, particularly methacrylates, acrylamides, and biorenewable α-methylene-γ-butyrolactones, by bulky, strongly Lewis acidic $Al(C_6F_5)_3$-based FLPs.[4] Bourissou et al. recently communicated the ring-opening (co)polymerization of heterocyclic monomers such as lactide and lactones by $Zn(C_6F_5)_2$-based LPs.[5] Erker et al. described the radical polymerization of styrene mediated by the persistent FLP-NO aminoxyl radical derived from N,N-cycloaddition of a cyclohexylene-bridged intramolecular P→B FLP to nitric oxide.[6] We have reported the addition polymerization of biorenewable α-methylene-γ-butyrolactones by borane $B(C_6F_5)_2$-based intramolecular, interacting FLPs and $B(C_6F_5)_3$-based CLPs.[7] Herein we communicate the first example of polymerization of 2-vinyl pyridine (2-VP) and 2-isopropenyl-2-oxazoline (*i*POx) by $Al(C_6F_5)_3$-based FLPs into medium to high molecular weight, pyridine- and 2-oxazoline-functionalized vinyl polymers.

As a dual-functional monomer (M), *i*POx has been extensively investigated through cationic ring-opening polymerization of the oxazoline moiety to yield polymers exhibiting a variety of application in biomedicine and life sciences.[8] On the other hand, vinyl addition (co)polymerization of *i*POx by free radical,[9] anionic,[10] and metal-mediated coordination[11] polymerization methods leads to the formation of a vinyl polymer, poly(2-isopropenyl-2-oxazoline) (P*i*POx), with the pendant 2-oxazoline ring being connected to a vinyl polymer backbone, which provides a versatile venue for post-polymerization functionalization. Like *i*POx, 2-VP also contains a C=C–C=N functionality, which could be polymerized through a conjugated addition across the C=C double bond and the imine C=N bond. Indeed, controlled polymerization of 2-VP has been achieved.[11,12] However, to date there has been no report on the polymerization of 2-VP and *i*POx by FLPs. Accordingly, we disclose herein our results on the polymerization of 2-VP, *i*POx, and 4-methyl-2-isopropenyl-2-oxazoline (M*i*POx) by FLPs and CLPs consisting of LAs [including $Al(C_6F_5)_3$, $B(C_6F_5)_3$, $MeAl(BHT)_2$ (BHT = 4-Me-2,6-t-$Bu_2C_6H_3O$)[13] and $AlEt_3$] and LBs [including phosphines t-Bu_3P, Mes_3P (Mes = 2,4,6-$Me_3C_6H_2$) and Ph_3P], and N-heterocyclic carbene (NHC) bases [including 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*-Bu), 1,3-di(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), and 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-trizazol-5-ylidene (TPT)] (Scheme 1). The fundamental difference between the previous work and the current work is that the previously re-



Scheme 1 N-Functionalized monomers as well as LAs and LBs, which construct FLPs or CLPs, employed in the current study

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ported FLP polymerization occurs through the conjugate addition across the C=C–C=O functionality, while the present work utilizes FLPs to promote conjugate addition across the C=C–C=N functionality.

Control runs for the polymerization of 2-VP and *i*POx by all the individual LAs and LBs listed in Scheme 1 in toluene, CH_2Cl_2, or DMF, with a [M]/[LA] or [M]/[LB] ratio of 200 at room temperature (ca. 25 °C) inside an inert glovebox, afforded no monomer conversion after up to 24 hours. Furthermore, in contrast to the polymerization of conjugated polar vinyl monomers bearing the C=C–C=O functionality, FLPs based on a combination of $Al(C_6F_5)_3$ (2 equiv) and a phosphine (t-Bu_3P, Mes_3P, or Ph_3P) are inactive for polymerization of 2-VP and *i*POx bearing the C=C–C=N functionality, regardless of the mixing sequence, highlighting the large difference in the reactivity of these two classes of conjugated polar alkenes towards FLPs or CLPs. The inability of phosphine nucleophiles to initiate this polymerization is due to their inability to perform the formal Michael addition reaction between a phosphine such as t-Bu_3P and a monomer–LA adduct such as (2-VP)·$Al(C_6F_5)_3$, as shown by NMR experiments. On the other hand, FLPs based on an $Al(C_6F_5)_3$ (two equivalents)–NHC combination were found to be very effective for such polymerizations, the results of which are summarized in Table 1. A typical polymerization procedure involved premixing of the LA with monomer, followed by addition of the LB solution to start the polymerization, but the monomer can also be added last.[14]

Polymerization of 2-VP (200 equivalents) by $2Al(C_6F_5)_3$/I*t*-Bu (or 0.5 mol% FLP loading) in toluene was rapid at room temperature, achieving 96% monomer conversation in 20 minutes (run 1), which corresponds to a turn-over frequency (TOF) of 580 h^{-1}. The resulting polymer, P(2-VP), exhibited a M_n of 8.02×10^4 g/mol and a molecular weight distribution of Đ = 1.60. The calculated initiator efficiency [$I^* = M_n$ (calcd)/M_n (exptl), where M_n (calcd) = MW(M) × [M]/[FLP] × conversion (%) + MW (chain-end groups)] was only 26%. This polymerization was significantly accelerated by increasing the amount of the LA added, indicative of the activated-monomer propagation for the FLP-mediated polymerization. Thus, the TOF was increased to 790 h^{-1} (run 2), 1050 h^{-1} (run 3), and 1490 h^{-1} (run 4), when the amount of the LA was increased to three, four, and five equivalents, respectively. The M_n of the resulting polymer was actually decreased, attributed to the increased initiator efficiency in the presence of a higher concentration of the LA (e.g.,

Table 1 Selected Results of Polymerization of 2-VP and *i*POx by $Al(C_6F_5)_3$/Base FLPs[a]

Run	M	LA	LB	[LA]/[LB]	[M]/[LB]	Time (min)	Conversion (%)[b]	M_n (kg/mol)[c]	Đ (M_w/M_n)[c]
1	2-VP	$Al(C_6F_5)_3$	I*t*-Bu	2:1	200	20	96.3	80.2[d]	1.60
2	2-VP	$Al(C_6F_5)_3$	I*t*-Bu	3:1	200	15	98.6	49.2[d]	1.67
3	2-VP	$Al(C_6F_5)_3$	I*t*-Bu	4:1	200	11	95.9	44.3[d]	1.70
4	2-VP	$Al(C_6F_5)_3$	I*t*-Bu	5:1	200	8	99.2	38.4	1.59
5	2-VP	$Al(C_6F_5)_3$	I*t*-Bu	2:1	1200	1440	100	315	2.04
6	2-VP	$Al(C_6F_5)_3$	IMes	2:1	200	1440	100	10.3	4.71
7	2-VP	$MeAl(BHT)_2$	I*t*-Bu	2:1	200	1440	100	48.9	5.39
8	2-VP	$AlEt_3$	I*t*-Bu	2:1	200	1440	0	–	–
9	2-VP	$B(C_6F_5)_3$	I*t*-Bu	2:1	200	1440	0	–	–
10	2-VP	M·$Al(C_6F_5)_3$	I*t*-Bu	2:1	200	25	98.5	74.5	1.55
11	2-VP	M·$Al(C_6F_5)_3$	I*t*-Bu	3:1	200	15	96.4	54.8[d]	1.60
12	2-VP	M·$Al(C_6F_5)_3$	I*t*-Bu	4:1	200	11	94.8	49.4[d]	1.58
13	2-VP	M·$Al(C_6F_5)_3$	I*t*-Bu	5:1	200	10	97.4	45.3[d]	1.59
14	*i*POx	M·$Al(C_6F_5)_3$	I*t*-Bu	2:1	200	1440	81.4	73.7	2.98
15	*i*POx	M·$Al(C_6F_5)_3$	IMes	2:1	200	1440	>99	15.0	2.90
16	*i*POx	M·$Al(C_6F_5)_3$	IMes	2:1	400	1440	>99	14.9	3.24
17	*i*POx	$B(C_6F_5)_3$	IMes	2:1	200	1440	0	–	–

[a] Reaction conditions: reactions were carried out at ambient temperature (ca. 25 °C) in toluene with 5 mL of the total solution volume. The alane LA was used as an adduct of toluene, $(toluene)_{0.5}$·$Al(C_6F_5)_3$, or the monomer, M·$Al(C_6F_5)_3$.

[b] Monomer conversion measured by ^1H NMR spectroscopy with an internal standard.

[c] Number-average molecular weight (M_n) and molecular weight distribution (Đ) determined by GPC in DMF relative to PMMA standards.

[d] A minor (0.1–0.7%) high MW shoulder peak was present.

I^* = 55%, run 4). On the other hand, employing a high [M]/[FLP] ratio of 1200 afforded a high molecular-weight polymer with $M_n = 3.15 \times 10^5$ g/mol and Đ = 2.04 (run 5). Replacing I*t*-Bu with IMes yielded a much less active system (run 6 vs. run 1), now requiring 24 hours to achieve quantitative monomer conversion, whereas TPT was completely inactive. Substituting the strong Lewis acid $Al(C_6F_5)_3$ with $MeAl(BHT)_2$ also resulted in a much less active polymerization system (run 7 vs. run 1). More drastically, replacing $Al(C_6F_5)_3$ with $B(C_6F_5)_3$ or $AlEt_3$ led to a completely inactive polymerization system (runs 8 and 9). Polymerizations employing the preformed monomer-LA adduct, $(2\text{-VP})\cdot Al(C_6F_5)_3$, afforded the results similar to those by the toluene adduct, $(toluene)_{0.5}\cdot Al(C_6F_5)_3$ (runs 10–13 vs. runs 1–14). Also noteworthy is that, when carried out in CH_2Cl_2 or DMF, the above polymerizations were much less effective or completely shut down, attributable to rapid deactivation of $Al(C_6F_5)_3$ in CH_2Cl_2[15] or impeding of the monomer activation by virtue of strong coordination of DMF to $Al(C_6F_5)_3$.

The $Al(C_6F_5)_3$/I*t*-Bu FLP is also active for polymerization of *i*POx, but the polymerization activity was much lower than that for the polymerization of 2-VP, with a low TOF of ca. 7 h^{-1} (run 14). The polymer produced had a medium high molecular weight of $M_n = 7.37 \times 10^4$ g/mol and a relatively broad molecular weight distribution of Đ = 2.98. Replacing I*t*-Bu with IMes enabled quantitative monomer conversion for the polymerization of either 200 or 400 equivalents of *i*POx (runs 15 and 16). As in the case of the polymerization of 2-VP, the use of $B(C_6F_5)_3$, in place of $Al(C_6F_5)_3$, yielded a completely inactive system (run 17). Interestingly, all the FLPs investigated herein failed to polymerize M*i*POx. This sharp contrast in reactivity between *i*POx and M*i*POx towards FLPs can be attributed to the steric hindrance at the nitrogen atoms and the electronic richness of M*i*POx relative to *i*POx, thus rendering M*i*POx more resistant toward nucleophile attack.

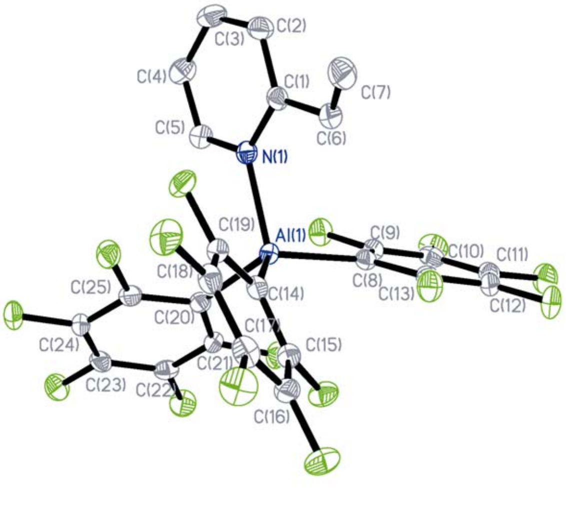


Figure 1 X-ray structure of $(2\text{-VP})\cdot Al(C_6F_5)_3$ (**1**). Hydrogen atoms have been omitted for clarity and ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.9873(11), Al(1)–C(14) 1.9894(13), Al(1)–C(8) 1.9971(13), Al(1)–C(20) 2.0010(13), N(1)–C(1) 1.3656(17), N(1)–Al(1)–C(14) 110.62(5)°, N(1)–Al(1)–C(8) 103.36(5)°, C(14)–Al(1)–C(8) 113.91(6)°, N(1)–Al(1)–C(20) 105.96(5)°, C(14)–Al(1)–C(20) 107.99(5)°, C(8)–Al(1)–C(20) 114.63(6)°.

To probe a possible chain initiation and propagation mechanism, we preformed the alane monomer adduct, $(2\text{-VP})\cdot Al(C_6F_5)_3$ (**1**), and structurally characterized it by single-crystal X-ray diffraction analysis. The structure features strong activation of 2-VP by the LA $Al(C_6F_5)_3$ through N-coordination of the monomer to the Al center of the LA [Al–N = 1.987(1) Å, Figure 1].[16] Next, addition of the base I*t*-Bu to adduct **1** cleanly formed a zwitterionic species, imidazolium pyridylaluminate I*t*-$BuCH_2CH{=}(C_5H_4N)Al(C_6F_5)_3$ (**2**), which has also been structurally characterized by single-crystal X-ray diffraction analysis (Figure 2).[17] As a consequence of conjugate addition of I*t*-Bu to adduct **1**, now a double bond is formed between C(5) and C(6) in **2** with a bond length of 1.359(4) Å, whereas a single bond is formed between C(6) and N(3) on the pyridyl ring with a bond length of 1.425(3) Å [which is comparable to a double-bond-like distance of N(1)–C(1) = 1.366(2) Å in adduct **1**].

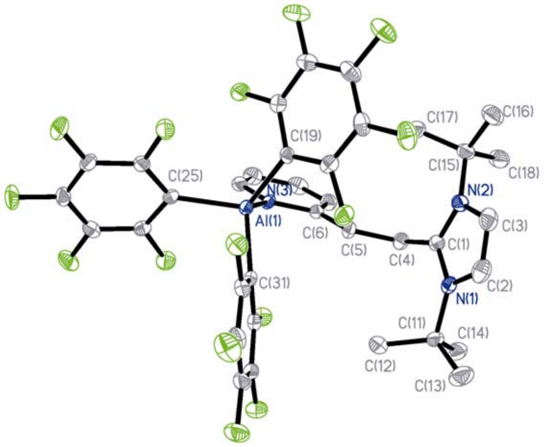
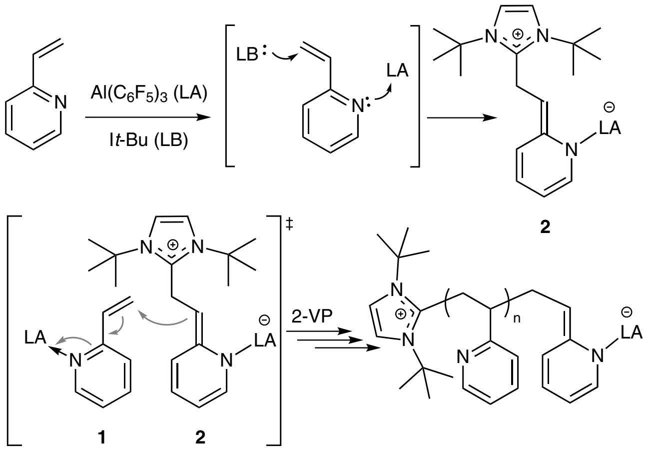


Figure 2 X-ray structure of zwitterionic intermediate $\mathbf{2}\cdot CH_2Cl_2$ derived from the activation of 2-VP by the $Al(C_6F_5)_3$/I*t*-Bu FLP. Hydrogen atoms and CH_2Cl_2 have been omitted for clarity and ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Al(1)–N(3) 1.906(2), Al(1)–C(31) 2.011(3), Al(1)–C(19) 2.010(3), Al(1)–C(25) 2.027(3), C(6)–C(5) 1.359(4), C(5)–C(4) 1.521(4), C(4)–C(1) 1.500(4), N(3)–C(6) 1.425(3), N(3)–Al(1)–C(31) 114.85(11)°, N(3)–Al(1)–C(19) 105.02(11)°, C(31)–Al(1)–C(19) 113.21(11)°, N(3)–Al(1)–C(25) 109.59(11)°, C(31)–Al(1)–C(25) 100.09(11)°, C(19)–Al(1)–C(25) 114.36(11)°.

To test whether zwitterionic species **2** itself is active for the polymerization of 2-VP, we added an excess amount of the monomer 2-VP (200 equivalents) to a solution of **2**, but we observed no polymer formation after up to 24 hours. On the other hand, addition of a small amount of the LA $Al(C_6F_5)_3$ (0.2 equivalents) to the abovementioned solution immediately started the polymerization and completely converted the monomer into polymer. Switching to the IMes base, the $Al(C_6F_5)_3$/IMes-based zwitterionic intermediate, IMes-$CH_2CH{=}(C_5H_4N)Al(C_6F_5)_3$ (**3**), was generated in the same fashion, which was found to behave similarly to zwitterion **2** in the above mechanistic probing reaction sequences. Overall, these results showed that an excess amount of the LA is required, in addition to the zwitterionic intermediate, to generate an effective polymerization, which is consistent with the bimolecular, activated monomer propagation mechanism previously proposed for the conjugate-addition polymerization by LPs.[4] In this specific case, a propagating step is proposed to involve nucleophilic attack of the activated monomer (i.e., adduct **1**) by zwitterion **2** and its homologues; the LA attached to the antepenultimate monomer unit after each addition step is recaptured by the incoming monomer, and the repeated conjugate addition in such a propagating cycle produces the high molecular-weight polymer (Scheme 2).



Scheme 2 Proposed bimolecular, activated monomer propagation mechanism for the polymerization of 2-VP by the $Al(C_6F_5)_3$-based FLP

In summary, FLPs based on $Al(C_6F_5)_3$ and NHCs have been found to effectively polymerize 2-VP and *i*POx to medium to high molecular-weight, N-functionalized vinyl polymers, representing the first example of Lewis pair polymerization of conjugated polar vinyl monomers carrying the C=C–C=N functionality. Preliminary mechanistic efforts have isolated and structurally characterized the activated monomer-LA adduct **1** and the initiated zwitterionic intermediate **2**, and the results obtained to date point to a bimolecular, activated monomer polymerization mechanism.

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Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

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(16) Selected crystallographic data for **1**: $C_{25}H_7AlF_{15}N$, monoclinic, space group P2(1)/*c*, a = 10.6644(4) Å, b = 14.0645(5) Å, *c* = 16.5182(6) Å, β = 107.349(2)°, *V* = 2364.84(15) Å^3, *Z* = 4, D_{calcd} = 1.779 Mg/m^3, GOF = 1.051, R_1 = 0.0243 [I >2σ(I)], w*R*2 = 0.0659. CCDC 972837 contains the supplementary crystallographic data for this structure.

(17) Selected crystallographic data for **2**·CH_2Cl_2: $C_{37}H_{29}AlCl_2F_{15}N_3$, monoclinic, space group P2(1)/*c*, a = 11.6507(7) Å, b = 16.8033(10) Å, c = 19.1096(12) Å, β = 94.747(3)°, *V* = 3728.3 (4) Å^3, *Z* = 4, D_{calcd} = 1.601 Mg/m^3, GOF = 1.060, R_1 = 0.0512 [I >2σ(I)], w*R*2 = 0.1482. CCDC 972835 contains the supplementary crystallographic data for this structure.