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Review

Lewis pairs polymerization of polar vinyl monomers

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ABSTRACT

The globally increasing demands for polymer materials stimulate the significantly intense attention focused on the Lewis pair polymerization (LPP) of various polar vinyl monomers catalyzed by Lewis pairs (LPs) composed of Lewis acid (LA) and Lewis base (LB). According to the degree of interaction between LA and LB, LPs could be divided into classical Lewis adduct (CLA), interacting Lewis pair (ILP) and frustrated Lewis pair (FLP). Regulation of the Lewis basicity, Lewis acidity, and steric effects of these LPs has a significant impact on the polymer chain initiation, propagation and termination as well as chain transfer reaction during polymerization. Compared with other polymerization strategies, LPP has shown several unique advantages towards the polymerization of polar vinyl monomers such as high activity, control or livingness, mild conditions, and complete chemo- or regioselectivity. We will comprehensively review the recent advances achieved in the LPP of polar vinyl monomers according to the classification of the employed LPs based on different LAs, by highlighting the key polymerization results, polymerization mechanisms as well as the currently unmet challenges and the future research directions of LPP chemistry.

1. Introduction

As an emerging polymerization technique, Lewis pair polymerization (LPP) of polar vinyl monomers has attracted much attention in recent years. Different from other polymerization methods, such as anionic/cationic polymerization [1,2], radical polymerization [3], group transfer polymerization (GTP) [4,5], and coordination-insertion polymerization [6], LPP is catalyzed by frustrated Lewis pairs (FLP), interacting Lewis pairs (ILP), or classical Lewis adducts (CLA) depending on the degree of interaction between LA and LB. The first example of LPP of conjugated acrylic monomers was reported by Chen's group [7] in 2010. Since then, LPP has shown its high polymerization activity towards different types of monomers, such as polar vinyl monomers, lactones, lactide, and other cyclic monomers, exhibiting very promising prospects in the field of polymer synthesis [8–10]. Recently, Chen and co-workers [11,12] overviewed the polymerization of polar monomers catalyzed by main-group Lewis pairs, Wu and co-workers [13] published a mini review on the polymerization of lactide and cyclic esters by LPs, and we also reviewed the polymerization of acrylic monomers by LPs [14,15]. This review will focus on the recent advances that have been made in the LPP of polar vinyl monomers.

LPP of polar vinyl monomers generally adopts a bimolecular activation polymerization mechanism (as shown in Scheme 1) [16]. First, in the chain initiation step, the LB nucleophilically attacks the LA-activated monomer to generate zwitterionic intermediates. Next, in the propagation step, the zwitterionic intermediates and LA-activated monomers undergo the repetitive Michael addition reaction to produce polymer chains, which is the rate-determining step. The shuffle of the LA catalyst from its complex with the last inserted monomer unit in the growing polymer chain to an incoming monomer is relatively fast. It is noted that Lewis basicity, Lewis acidity, and steric effects of LPs significantly affect the polymerization performance of LPP. Therefore, various complexes based on Al, B, Si or rare-earth elements were utilized as LAs to combine with different LBs, such as *N*-heterocyclic carbenes (NHCs), *N*-heterocyclic olefins (NHOs) and phosphines, to achieve highly effective polymerization of polar vinyl monomers.

According to the classification of LPs based on different LAs, we divided the current advances made in LPP of polar vinyl monomers into three sections including polymerization by Al-based LPs, B-based LPs, and Rare-earth metal- or Si-based LPs and discussed chain initiation, propagation and termination as well as chain transfer during LPP in detail, followed by the Summary and Outlook section. The employed polar vinyl monomers, LA and LB were summarized in Figs. 1 and 2, respectively.

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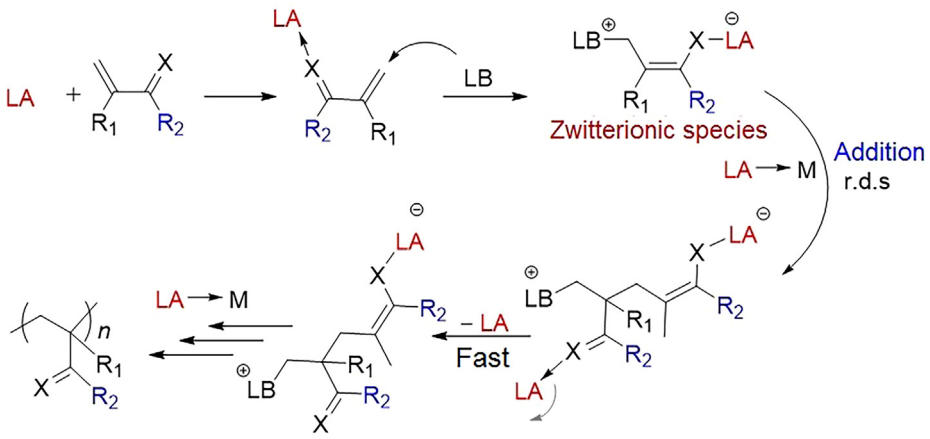


Scheme 1. (Color online) General LPP mechanism for polar vinyl monomers.

2. Al-based LPs

Al-based complexes are widely used in catalysis, such as organic synthetic methodology [17], small molecule activation [18] and polymer synthesis [19,20], due to their easy modification and low toxicity. The first example of Al-based LA ($AlEt_3$) in combination with a phosphine LB (Et_3P) in 2:1 ratio was reported for the polymerization of methyl methacrylate (MMA) in the 1960s, only showing sluggish activity [21]. In 1971, Ikeda and co-workers [22] expanded this system by using $AlEt_3$, $InEt_3$, or $ZnEt_2$ as the LAs and α,α′-dipyridal or Ph_3P as the LBs for polymerization of MMA and acrylonitrile, obtaining similarly low activity and TOF of ~2 h^{-1}. Later in 1992, $AlEt_3$ was mixed with P-based LB in 2:1 ratio for polymerization of MMA and other methacrylates as well as the block copolymerization of MMA and *t*-butyl methacrylate (^{t}BMA) [23]. Although these early examples demonstrated that both LA and LB are necessary for the polymerization, this LP polymerization strategy did not attract much attention due to their poor polymerization activity and elusive polymerization mechanism.

On the other hand, ever since Stephan and Erker disclosed the concept of "frustrated Lewis pair" in 2006, the field of FLP chemistry has received explosive interests [24,25]. However, compared with the well-established application of FLPs in small-molecule chemistry, the application of LPP in polymer synthesis is still in its infancy [17,26–30]. In 2010, Chen and co-workers [7] achieved the first example of LPP of polar vinyl monomers such as linear MMA and its cyclic analogue, α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL) by Al-based FLP or CLA. It should be noted that neither LA nor LB itself is effective for MMA polymerization in toluene (TOL), whereas they could synergistically promote the MMA polymerization. Due to the inactivity or low activity of the combinations of $AlMe_3$, $B(C_6F_5)_3$ or MeAl $(BHT)_2$ (BHT = 4-Me-2,6-^{t}Bu$_2$C$_6$H$_2$O) with phosphines, they focused on the LPP by using the strongly acidic, sterically encumbered Al $(C_6F_5)_3$ as the LA to combine with different LBs, such as phosphines (^{t}Bu$_3$P, Mes$_3$P, and Ph_3P) or NHCs (I^{t}Bu and IMes). Their studies revealed that the addition sequence of LA and LB plays an important role in affecting the polymerization activity. No polymerization occurred when MMA was added to the mixture of ^{t}Bu$_3$P with either $Al(C_6F_5)_3$·0.5TOL adduct or unsolvated $Al(C_6F_5)_3$. However, if ^{t}Bu$_3$P was added to the mixture of MMA and $Al(C_6F_5)_3$ in TOL (P/Al/MMA = 1/2/800), MMA could be quantitatively converted to PMMA with number-averaged molecular weight (M_n) of 315 kg/mol and molecular weight distribution (MWD) ($Đ$ = 1.72) within 7 min, affording a TOF value of 6,840 h^{-1}. Interestingly, the direct use of zwitterionic intermediate generated from the reaction of ^{t}Bu$_3$P with $Al(C_6F_5)_3$·MMA for MMA polymerization led to a drastically enhanced TOF value of 12,000 h^{-1}, suggesting zwitterionic intermediate was the real active species. Switching from ^{t}Bu$_3$P to Mes$_3$P, no zwitterionic active species was generated, thus no MMA polymerization was observed. It is noted that the reaction of Ph_3P with $Al(C_6F_5)_3$ generated a CLA that also achieved a high TOF value of 48,000 h^{-1} for MMA polymerization, despite the formation of polymer with bimodal MWD. On the other hand, LPs composed of NHCs were extremely active for MMA polymerization. IMes showed a high polymerization rate with TOF of 48,000 h^{-1} for polymerization in a ratio of IMes:Al:MMA = 1:2:800, producing PMMA with M_n = 26.6 kg/mol and $Đ$ = 1.77. I^{t}Bu showed relatively lower activity (TOF = 3,200 h^{-1}) and initiation efficiency (I^*), as revealed by the relatively higher molecular weight of PMMA obtained under the same conditions. *In-situ* NMR reaction indicated the formation of stable CLA from the reaction of $Al(C_6F_5)_3$ with either IMes or I^{t}Bu whereas the reaction of $Al(C_6F_5)_3$·MMA with IMes or I^{t}Bu generated corresponding zwitterionic species, respectively. Stereoregularity analyses revealed that LPP of MMA produced syndio-rich PMMAs with *rr* ranging between 72.7% and 75.8%. Furthermore, this $Al(C_6F_5)_3$ based LPs could also be utilized for the polymerization of biorenewable MBL and MMBL, which are the cyclic analogues of MMA and possess greater reactivity than MMA due to the presence of a nearly planar five-membered lactone ring. The cyclic ring in both monomers imparts significant enhancements in the properties of the resultant polymers, such as high glass-transition temperature (T_g), increased optical properties as well as resistance to solvent, heat and scratch [31]. In contrast to the incomplete monomer conversion observed for MBL polymerization by both phosphine/$Al(C_6F_5)_3$ and NHC/$Al(C_6F_5)_3$ LPs, LPP of MMBL in dichloromethane (DCM) is homogeneous and highly effective (TOF up to 48,000 h^{-1}), achieving quantitative monomer conversion within 10 min and furnishing PMMBL with M_n up to 192 kg/mol.

In 2012, Chen and co-workers [16] further expanded the scope of LPP system. A large number of LPs consisting of 11 LAs, 10 achiral and 4 chiral LBs have been investigated for LPP of 12 monomers. Both experimental data and computational studies revealed that LPP adopts a bimolecular polymerization mechanism, in which LB acts as nucleophile to attack the LA-activated monomer to form zwitterionic an enolaluminate active species in the chain initiation step, subsequent nucleophilic attack of the LA-activated monomer by the zwitterionic enolaluminate active species resulted in the propagation of polymer chain (Scheme 1). Among the investigated LPs, the combination of phosphazene superbase (^{t}Bu-P$_4$) with Al $(C_6F_5)_3$ showed the highest activity, achieving a remarkably high

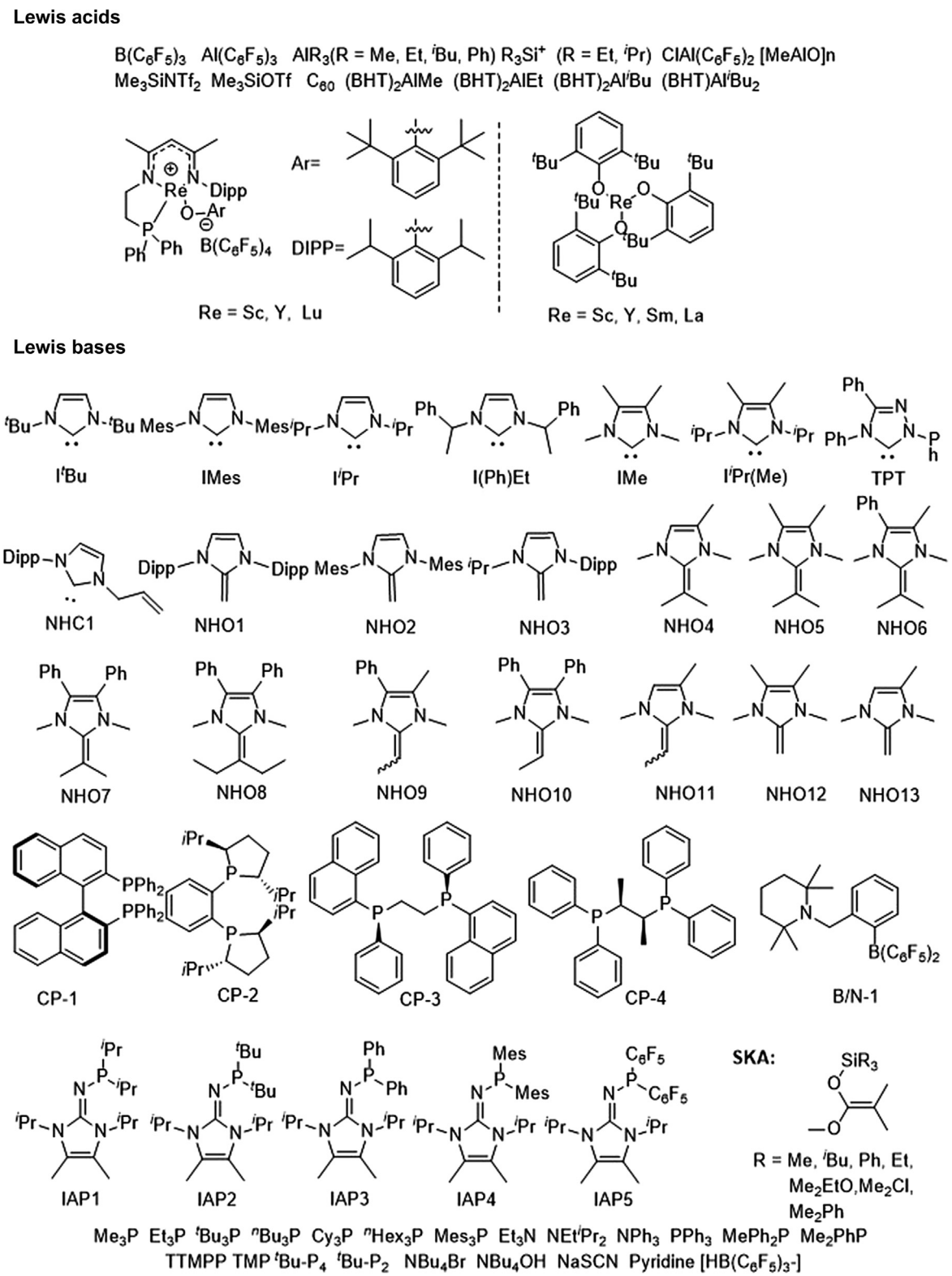


Fig. 1. LA and LB employed in LPP of polar vinyl monomers.

TOF value of 9.6×10^4 h^{-1} and producing PMMA with M_n = 212 kg/mol and $Đ$ = 1.34. Both $Al(C_6F_5)_3/^tBu_3P$ and $Al(C_6F_5)_3$/IMes LPs were ineffective for polymerization of bulky furfuryl methacrylate (FMA). $Al(C_6F_5)_3/^tBu_3P$ LP exhibited much slower polymerization rate for *N*,*N*-diphenylacrylamide (DPAA) whereas both $Al(C_6F_5)_3/^tBu_3P$ and $Al(C_6F_5)_3/I^tBu$ LPs were highly active for polymerization of *N*,*N*-dimethylacrylamide (DMAA), producing PDMAA with M_n = 293 kg/mol, $Đ$ = 1.43 and M_n = 369 kg/mol and $Đ$ = 1.28, respectively. For polymerization of diethyl vinylphosphonate (DEVP), both $Al(C_6F_5)_3/^tBu_3P$ and $Al(C_6F_5)_3$/IMes LPs exhibited comparable activity (TOF = 6 h^{-1} vs. 10 h^{-1}). As far as the cyclic esters and lactones were concerned, only incomplete monomer

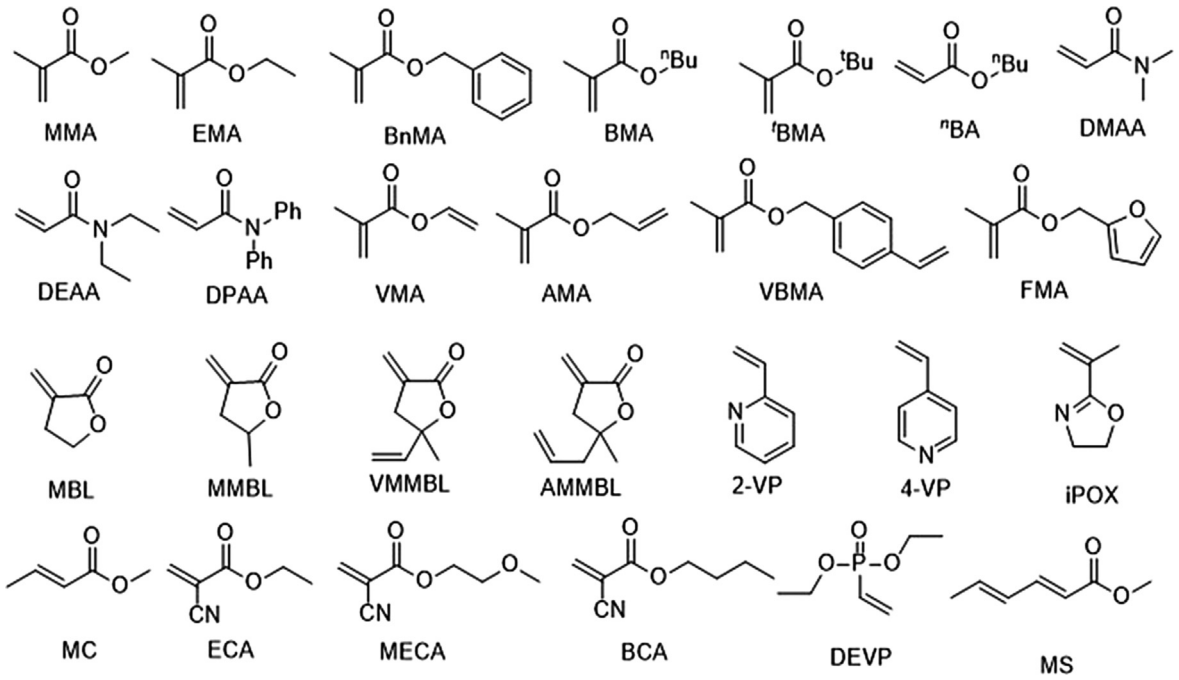
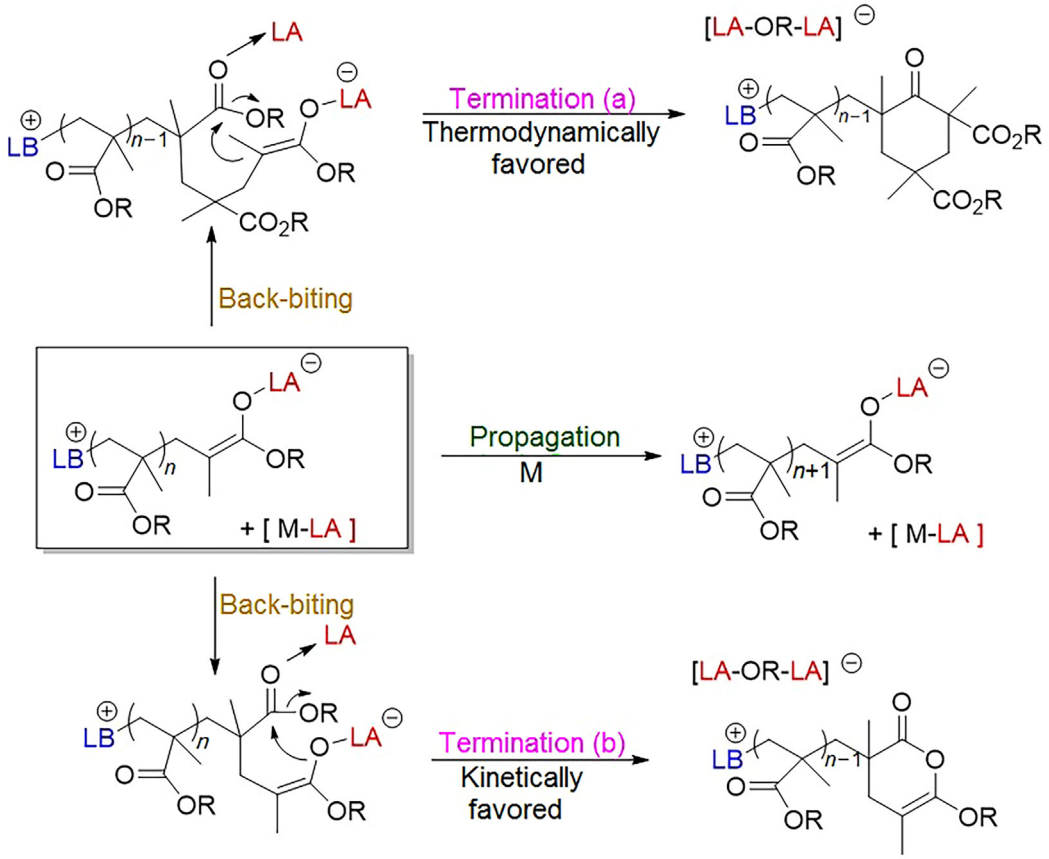


Fig. 2. Polar vinyl monomers employed in LPP.

conversion was obtained for polymerization of ε-caporalactone (ε-CL) by $Al(C_6F_5)_3/P^tBu_3$ and none of the five-membered lactones including γ-butyrolactone (γ-BL), γ-valerolactone (γ-VL) and α-angelica lactone (α-AL), was polymerized by the investigated LPs. It is worth mentioning that the combination of $Al(C_6F_5)_3$ with a variety of LBs such as $^tBu_3P$, Ph_3P, IMes, I^tBu, or TPT all showed high polymerization activity towards MMBL polymerization in DCM. Furthermore, they found such LPs could produce highly syndiotactic PMMA with *rr* ~91% at −78 °C. Up to now, there is no report on the synthesis of highly stereoregular polymers produced by LPP under mild conditions. On the other hand, tertiary amines were also examined for polymerization of MMA and MMBL. Only $NEt^iPr_2/Al(C_6F_5)_3$ LP was active for MMBL polymerization, furnishing PMMBL with M_n = 97.7 kg/mol and $Đ$ = 1.90. In 2015, Chen and co-workers [32] employed the tetramethylpiperidine (TMP) to combine with $Al(C_6F_5)_3$ to quantitatively convert 800 equiv. of MMBL into PMMBL in 0.5 min, achieving TOF values up to 96,000 h^{-1}.

In 2014, Chen and co-workers [33] reported the first example of LPP of polar vinyl monomers bearing the C=C—C=N functionality including 2-vinyl pyridine (2-VP) and 2-isopropenyl-2-oxazoline (*i*POx) by $Al(C_6F_5)_3$/NHC. In sharp contrast with the low activity for polymerization of *i*POx (TOF = 7 h^{-1}), $I^tBu/Al(C_6F_5)_3$ rapidly converts 200 equiv. of 2-VP into P(2-VP) with M_n = 80.2 kg/mol and $Đ$ = 1.60, giving a corresponding TOF of 580 h^{-1}. This polymerization was significantly accelerated by increasing the amount of the LA, suggesting the activated-monomer propagation for the FLP-mediated polymerization. Meanwhile, the M_n of the resulting polymer also indicated the increased initiation efficiency in the presence of a higher concentration of the LA. The addition of I^tBu to the (2-VP)·$Al(C_6F_5)_3$ adduct cleanly resulted in zwitterionic species, which could be structurally characterized by single-crystal X-ray diffraction analysis. Control experiment revealed that such zwitterionic species was inactive for 2-VP polymerization whereas addition of a small amount of the LA (0.2 equiv. $Al(C_6F_5)_3$) to the above-mentioned solution immediately started the polymerization and quantitatively converted monomers into polymers. All these results confirmed that an excess amount of the LA is required for LPP such that one equiv. of LA is utilized for the activation of the monomer while the other equiv. of LA is reacted with LB and monomer to generate a zwitterionic enolaluminate active species.

Later, kinetic studies revealed that the polymerization of 2-VP by $I^tBu/Al(C_6F_5)_3$ follows a zero-order dependence on monomer concentration and a first-order dependence on LA and LB concentrations, thus indicating a bimolecular, activated monomer propagation mechanism [34]. Chen and co-workers also investigated the mechanistic aspects of polymerization of polar vinyl monomers by $Al(C_6F_5)_3$/NHC FLPs through the combined experimental and theoretical studies including active propagating intermediate characterization, propagation kinetics and chain termination pathways. It is worth noting that they proposed two possible chain-termination pathways (Scheme 2): termination pathway (a) proceeded via intramolecular backbiting cyclization where the *C*-ester enolate active chain end nucleophilically attacked the activated *antepenultimate* ester group of the growing polymer chain to generate a cyclic β-ketoester-terminated polymer chain. This type of intramolecular backbiting cyclization was previously observed in the anionic polymerization of acrylates [2] and polymerization of acrylates by metallocenium catalyst [35]. Pathway (b) proceeded via nucleophilic attack of the activated adjacent ester group of the growing polymer chain by the *O*-ester enolate active chain end to generate a six-membered lactone (δ-valerolactone)-terminated polymer chain, which is consistent with what is reported by Lu and co-workers [36]. Chain-end analyses of the resulting low molecular weight polymer samples by the matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) provided evidence for these possible chain termination side reactions, but cannot differentiate between the possible cyclic β-ketoester and δ-valerolactone chain ends. Computational calculation indicated that the formation of cyclic δ-valerolactone-terminated chain ends was kinetically favored but thermodynamically disfavored, as compared to the formation of β-ketoester-terminatedw chain ends. In addition, MALDI-TOF MS of the low molecular weight PMMBL produced by IMes/Al



Scheme 2. (Color online) Proposed two possible backbiting chain termination pathways that compete with chain propagation cycles in the LPP of methacrylates by LPs. Reprinted with permission from Ref. [46]. Copyright 2014 American Chemical Society.

$(C_6F_5)_3$ showed only one major series of mass ions, similar to that obtained for polymerization of MBL by NHC alone [37], but living polymerization could not be realized by such LPs.

In 2014, Lu and co-workers [36] employed the strongly nucleophilic *N*-heterocyclic olefin (NHO) based LPs to achieve highly effective polymerization of MMA, *n*-butyl methacrylate (^{n}BMA), DMAA and DPAA. NMR reactions of NHO1-3 with equimolar amounts of $Al(C_6F_5)_3$ led to the formation of stable NHO·$Al(C_6F_5)_3$ adducts. Thus, monomers need to be premixed with $Al(C_6F_5)_3$ to achieve high polymerization activity. Among the investigated LAs, the combination of $Al(C_6F_5)_3$ with NHO quantitatively converted monomers such as MMA, ^{n}BMA and DMAA into high molecular weight polymers within 5 min for polymerization performed in an 800:2:1 monomer:LA:LB ratio. The corresponding initiation efficiencies are rather low ($I^*\% < 26$), probably due to the formation of stable NHO·$Al(C_6F_5)_3$ adducts. Attempts to synthesize block copolymer were unsuccessful: only random copolymer could be obtained when both monomers were added at the same time. Both electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS) and NMR spectroscopy revealed the formation of six-membered lactone chain ends, which was generated from the nucleophilic backbiting of the polymeric anion to the carboxyl carbon of the adjacent unit (Scheme 2).

Much attention has been focused on the chemo- or regioselectivity polymerization of monomers containing two polymerizable functionalities, such as divinyl polar monomers with a conjugated acrylic moiety and an unconjugated double bond, since it provides convenient access to the functional polymers having wide applications [38–40]. However, it generally could not be achieved by radical [41–43], anionic polymerization [44], or group transfer polymerization [45], due to the occurrence of crosslinking reactions in the late-stage of these polymerizations. In 2014, Lu and co-workers [46] reported the highly regioselective polymerization of several unsymmetrical divinyl polar monomers including 4-vinyl-benzyl methacrylate (VBMA), vinyl methacrylate (VMA), and ally methacrylate (AMA) by $Al(C_6F_5)_3$-based LPs under mild conditions. In addition to the higher reactivity of the vinyl group conjugated with the carbonyl than that of the unconjugated vinyl group, only the conjugated vinyl group could be activated by LA during LPP, thus leading to the completely chemoselective polymerization of the conjugated vinyl groups and leaving the pendant C=C bonds unreacted. It should be noted that LPP of all these unsymmetrical divinyl polar monomers produced high molecular weight polymers, implying low initiation efficiencies (25%–45%).

In 2018, Lu and co-workers [47] developed a strategy for the synthesis of block copolymers PMMA-*b*-PLA via polymerization of MMA by $Al(C_6F_5)_3$/NHC LP, followed by the "thio-ene" click reaction to generate "PMMA-OH" as macroinitiators for the ring-opening polymerization of lactide catalyzed by 1,5-diazabicyclo [4.3.0]non-5-ene (DBU). Moreover, brush copolymers P(MMA-*co*-VMA)-*g*-PLA were prepared in a similar tandem manner through random copolymerization of MMA and VMA by $Al(C_6F_5)_3$/NHO LP, "thio-ene" click reaction and organocatalytic ring-opening polymerization of lactide.

Chen and co-workers [48] reported the chemoselective LPP of renewable multivinyl-functionalized γ-butyrolactones, including γ-vinyl-γ-methyl-α-methylene-γ-butyrolactone (VMMBL) and γ-allyl-γ-methyl-α-methylene-γ-butyrolactone (AMMBL), by using NHC as the LB and $Al(C_6F_5)_3$ as the LA. This system could quantitatively and chemoselectively polymerize the conjugated

α-methylene double bond of multivinyl monomers to high molecular weight polymers with M_n ranging between 116 and 122 kg/mol and broad MWD ($Đ$ > 2.90), without participation of the γ-vinyl or γ-allyl double bonds.

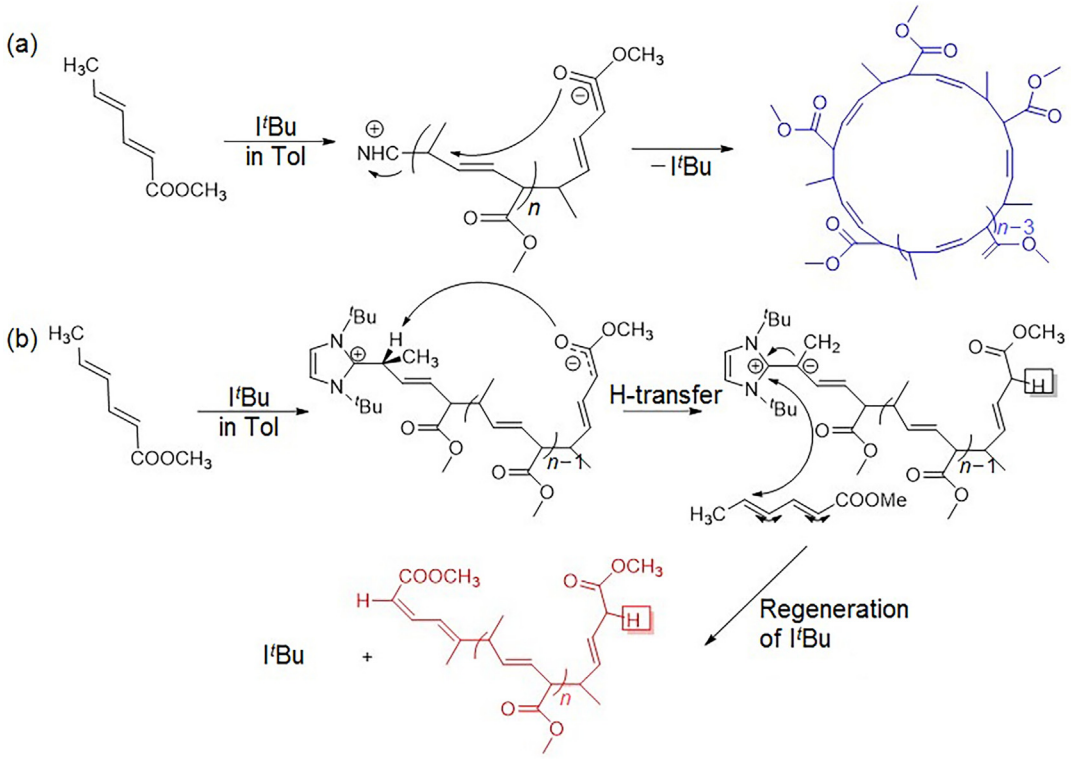
In 2017, Takasu and co-workers [49] reported the LPP of biorenewable monomers (*E*,*E*)-methyl sorbate (MS) by I^{t}Bu/(BHT)$_2$AlMe, producing functionalized PMS with cyclic structure via 1,4-addition in THF or TOL at −20 °C. They proposed that during the LPP of MS, the α-terminal imidazolinium group acted as counter cation neighboring at the propagating anion chain end, in which the cyclic propagating chain preferred the ring-closing rather than H-transfer after reaching full monomer consumption (Scheme 3). The resulting PMS had a 1,4-trans structure, and 86% of threo diastereoselectivity with M_n up to 23.0 kg/mol and narrow MWD. However, both 1,4-addition and 1,2-addition were observed in the I^{t}Bu-mediated anionic polymerization in DMF, furnishing PMS with M_n of 3.5 kg/mol and relatively broader MWD ($Đ$ = 2.1). In the presence of bulky LA (BHT)$_2$AlMe, the combination of I^{t}Bu and (BHT)$_2$AlMe could synergistically not only accelerate the consumption of MS but also inhibit the proton transfer reaction, thus affording relatively controlled MS polymerization.

As revealed by the above overview, the practical application of LPP was still hampered by the low initiation efficiencies and chain-termination side reactions, as evidenced by the much higher observed M_n than the calculated M_n, broad MWD of the resulting polymers, and the inability to produce well-defined block copolymers via sequential copolymerization [34,36]. Recently, we employed E(C$_6$F$_5$)$_3$ (E = B, Al) to combine with silyl ketene acetals (SKAs) to achieve living and controlled polymerization of MMBL, which proceeded via a GTP mechanism [50,51].

In 2016, by using the well-established fluoride ion affinity (FIA) as an index for the Lewis acidity of LA [52–54] and Tolman angle (Θ in degrees) as a measure scale for the steric demand of LB [55], Rieger and co-workers [56] employed less acidic organoaluminum compounds as the LA and less basic phosphines with less steric encumbrance as the LB to construct highly ILP to precisely polymerize the Michael-type monomers into polymers with the predicted M_n, narrow MWD, thus affording up to 95% initiation efficiencies. They proposed that the steric hindrance and electron cloud density of the monomer should match with the employed LPs, which could be confirmed by the controlled polymerization of ^{t}BMA with high electron-donating ability and steric hindrance by LPs composed of less acidic AlMe$_3$ and sterically unhindered PMe$_3$. Based on this, different polar vinyl monomers were polymerized with high precision, furnishing polymers with controlled M_n and microstructure. However, no chain-extension experiment and block copolymerization have been performed to further confirm the living characteristic of this ILP system.

In 2017, our group [19] reported that the combination of Al(C$_6$F$_5$)$_3$ with NHO could cooperatively promote the living ring-opening (co)-polymerization of lactones, affording linear (co) polyesters with medium to high molecular weight (M_w up to 855 kg/mol) and narrow MWD ($Đ$ as low as 1.02). Since then, our interest has continued to focus on the development of living polymerization system for polar vinyl monomers.

In 2018, we reported the first living polymerization of conjugated polar alkenes by a non-interacting, authentic FLP system [57]. It turned out that for living polymerization, it is essentially important to strike the fine balance between the sufficient LA acidity needed for monomer activation and the lowest possible LA acidity to suppress the LA-activated side reaction, as well as the fine balance between the sufficient LP steric hindrance to minimize the LA–LB interaction and the reduced LB steric hindrance to ensure effective initiation of the reaction. Among the investigated LAs, (BHT)$_2$AlMe possessing suitable acidity and steric hindrance was combined with the strongly nucleophilic NHO bearing exocyclic methyl (NHO4-NHO7) to accomplish the rapid and living polymerization of alkyl methacrylates. The living characters of this LPP could be unequivocally verified by five lines of evidence including: (1) the predictable polymer M_n (up to 351 kg/mol) and



Scheme 3. (Color online) Proposed (a) ring-closing mechanism to Cyclic PMS, and (b) termination pathway via proton transfer and an enamine intermediate to form a linear PMS.

low $Đ$ (1.05–1.09); (2) high to quantitative initiation efficiencies (I^*% ~100); (3) a linear increase of polymer M_n vs. monomer conversion and the monomer-to-initiator ratio; (4) successful multiple chain extensions; and (5) synthesis of well-defined di- and triblock copolymers, as shown in Scheme 4. The MALDI-TOF MS analysis of the low molecular weight PMMA sample produced by $(BHT)_2AlMe$/NHO4 LP also confirmed the formation of living polymer chain without the occurrence of cyclic backbiting chain ends.

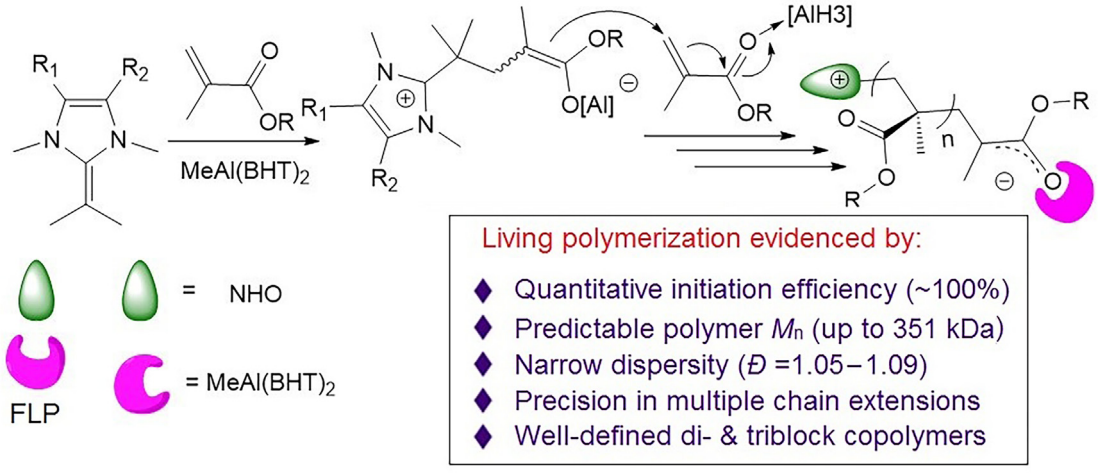
Nonetheless, polymerization of DMAA by above-mentioned highly effective LPP system only produced PDMAA with a bimodal MWD, indicating the coexistence of different active species [57]. Using Gutmann-Beckett method as an index for the Lewis acidity of different LAs, we found $AlPh_3{\cdot}Et_2O$ is the right LA with suitable acidity and steric hindrance to be combined with NHO7 to synergistically promote living polymerization of DMAA and *N*,*N*-diethylacrylamide (DEAA) [58]. Even 3,200 equiv. of DMAA could be quantitatively converted into polymers within 1 min, affording PDMAA with M_n = 447 kg/mol and $Đ$ = 1.13. The livingness of this LPP system was also verified by the successful chain extensions, synthesis of well-defined block polymer as well as the chain-end analyses by MALDI-TOF MS spectroscopy.

As mentioned above, chemoselective polymerization of polar divinyl monomers has been received substantial attention since they provide convenient access to various advanced functionalized materials with wide applications through post-functionalization [38–40]. LPP could be employed as a powerful strategy to accomplish this goal since it could selectively polymerize the conjugated C=C double bonds of these unsymmetrically polar divinyl monomers according to the mechanism of LPP. Recently, Lu's group and our group [59,60] independently reported the chemoselective and living/controlled polymerization of polar divinyl monomers by using NHO-based classical and frustrated LPs. By controlling the monomers addition time, well-defined block copolymers of MMA and divinyl monomers as well as copolymers of different divinyl monomers could be prepared through the sequential addition of monomer method. Furthermore, we found CLAs consisting of NHO9-NHO11 and $(BHT)_2AlMe$ showed comparable polymerization activity and chemoselectivity towards the polymerization with that obtained by FLPs composed of NHO4-NHO7 and $(BHT)_2$-AlMe. It should be noted that the backbiting side reaction was determined by LA rather than NHO. Moreover, the Claisen-rearrangement reaction also could lead to the deactivation of AMA polymerization, in addition to backbiting reaction.

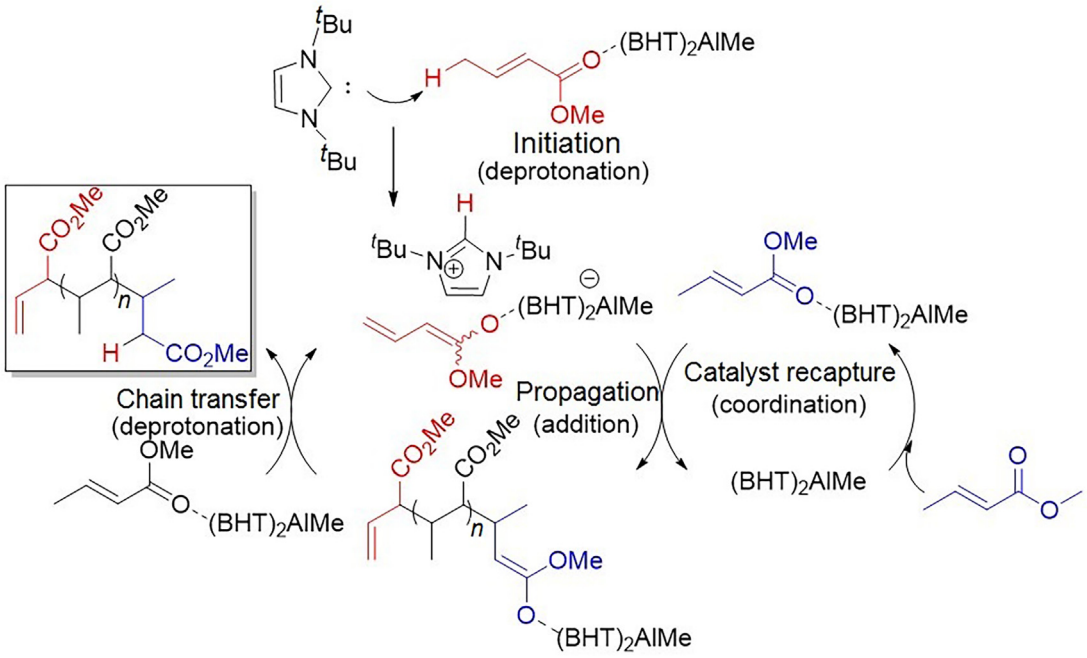
On the other hand, Hong and co-workers [61] also reported that the combination of NHCs including I(Ph)Et, I^{t}Bu, and I^{i}Pr with $(BHT)_2AlMe$ could shut down the intramolecular backbiting termination during polymerization of MMA, achieving high polymerization activity up to 3000 h^{-1} TOF and furnishing polymers with high molecular weight (M_n up to 130 kg/mol) and narrow MWD.

In 2018, Chen and co-workers employed $(BHT)_2AlMe$ as the LA to combine with NHO, ^{t}BuOK, or NHC to polymerize methyl crotonate (MC), a renewable monomer derived from poly(3-hydroxybutyrate) [62], into PMC with M_n up to 161 kg/mol under ambient temperature and solvent-free conditions [63]. Without LA, a single addition product was generated from the reaction of MC with TPT or IMes via a proton transfer reaction, while a dimerization product was obtained from the reaction of MC with I^{t}Bu or NHO7. The addition of LA to the reaction would initiate the polymerization of MC. Among the investigated LAs, $(BHT)_2AlMe$ was more active and achieved near quantitative monomer conversion for all ratios. Two different initiation mechanisms were proposed on the basis of MALDI-TOF MS and NMR spectroscopy (Scheme 5). The basic pathway was preferred when I^{t}Bu acted as LB whereas the nucleophilic initiation pathway was preferred when NHO7 or TPT was used. Chain transfer reaction was observed in all cases as revealed by high initiation efficiency (I^*% > 100). Tacticity measurement revealed that all the synthesized PMC had an approximately 70% disyndiotacticity.

Considering the high activity, control and livingness feature of LPP, we envisioned the LPP should enable us to synthesize ultra-high molecular weight (UHMW) polymer. In 2018, we synthesized a series of strong organophosphorus superbase, imidazolin-2-ylidenamino substituted phosphines (IAPs), and employed them to combine with different organoaluminum LAs for polymerization of MMA at room temperature [64]. Among the examined LPs, (BHT)Al^iBu_2/IAP3 exhibited the best polymerization performance, achieving near quantitative monomer conversion at high polymerization rate for all polymerizations with MMA to IAP3 ratio ranging from 400 to 20,000 and furnishing PMMA with medium to UHMW (M_n up to 1,927 kg/mol) and narrow MWD ($Đ$ < 1.10). Meanwhile, this LP (Fig. 3) also achieved precise chain extension and well-defined block copolymerization. In order to synthesize UHMW polymer, a polymerization system must meet the following three criteria: (1) the system should have extraordinarily high polymerization activity. (2) The generated active species should exclusively initiate the polymerization. (3) The system should have long lifetime polymerization performance and no interference with other side reactions such as chain-termination. Fortunately, our LP system met with all the above-mentioned requirements. First, as an organophosphorus superbase, the combination of IAP3 with $(BHT)Al^iBu_2$ could achieve high to quantitative monomer conversion for polymerization with $[MMA]_0/[IAP3]_0/[(BHT)Al^iBu_2]_0$ ratio



Scheme 4. (Color online) Structures of NHOs that form true FLP systems with $MeAl(BHT)_2$ for the living LPP of methacrylates.



Scheme 5. (Color online) Proposed mechanism for MC polymerization by $(BHT)_2AlMe/I^tBu$, involving basic initiation as well as bimetallic chain propagation and transfer (Not including unimolecular chain transfer). Reprinted with permission from Ref. [63]. Copyright 2018 American Chemical Society.

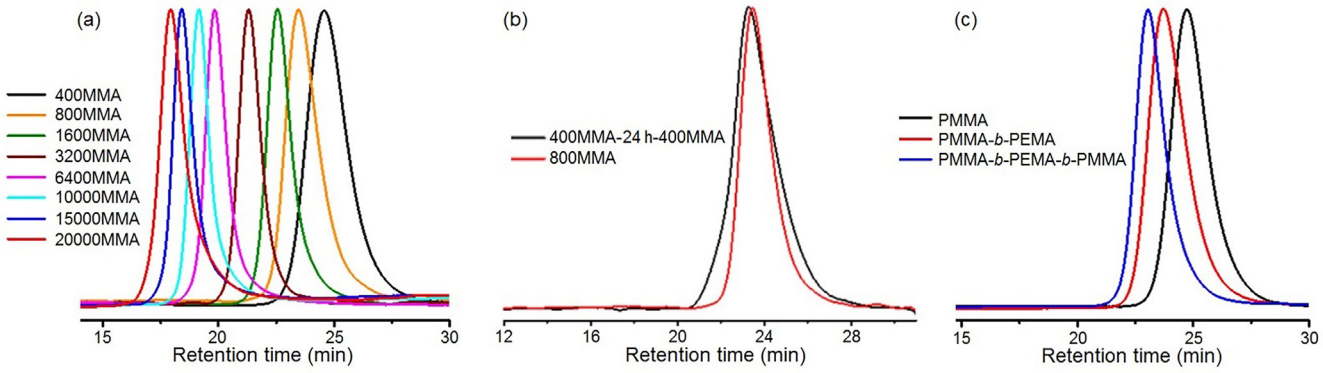


Fig. 3. (Color online) GPC traces of (a) PMMA produced by IAP3/(BHT)Al^{i}Bu$_2$ LP at various $[MMA]_0/[IAP3]_0/[(BHT)Al^iBu_2]_0$ ratio at RT. Conditions: $[MMA]_0/[IAP3]_0/[(BHT)Al^iBu_2]_0$ = 400:1:2, 800:1:2, 1,600:1:2, 3,200:1:2, 6,400:1:2, 10,000:1:2, 15,000:1:2, 20,000:1:2, $[MMA]_0$ = 0.936 M. (b) GPC traces of PMMA produced from the IAP3/(BHT)Al^{i}Bu$_2$-catalyzed polymerization of MMA in a ratio of $[MMA]_0/[IAP3]_0/[(BHT)Al^iBu_2]_0$ = 800:1:2 (red) and from IAP3/(BHT)Al*i*Bu$_2$-catalyzed chain extension experiments of two batch of 400 equiv. of MMA after the polymerization of the first batch of MMA reach full monomer conversion and kept at RT for 24 h (black) and (c) homopolymer (black), diblock copolymer (red), and ABA triblock copolymer (blue) produced from the sequential block copolymerization of MMA and EMA by IAP3/(BHT)Al^{i}Bu$_2$ in TOL at RT: polymerizing MMA first, $[MMA]_0$ = 0.936 mol/L. Reprinted with permission from Ref. [64]. Copyright 2018 John Wiley and Sons.

ranging from 400:1:2 to 20,000:1:2. Second, IAP3 itself was completely ineffective whereas (BHT)Al^{i}Bu$_2$ only exhibited negligible effect for polymerization in up to 24 h. Moreover, stoichiometric NMR reaction of MMA/IAP3/(BHT)Al^{i}Bu$_2$ cleanly generated zwitterion species without any side reaction; Third, the living polymerization system was immortal and could reinitiate the desired living polymerization after 400 equiv. of MMA was fully consumed and the resulting system was held in the absence of free MMA at RT for 24 h by the sequential addition of another batch (400 equiv.) of MMA, producing PMMA with M_n = 96.1 kg/mol and Đ = 1.18, which is similar with that (M_n = 92.8 kg/mol, $Đ$ = 1.10) obtained from polymerization in an 800:1:2 $[MMA]_0/[IAP3]_0/[(BHT)Al^iBu_2$-·$MMA]_0$ ratio (Fig. 3).

Furthermore, Al-based LPs were also employed for preparation of acrylic monomers [65] and lactones [66] containing polymer brushes in material chemistry.

3. B-based LPs

Compared with Al-containing LA, LPs based on the B-containing LA generally exhibit lower polymerization activity or higher I^* (because of chain transfer), thus receiving less attention. Only several papers have been reported.

For example, Chen and co-workers [7] disclosed that the reaction of $^tBu_3P$ with $B(C_6F_5)_3$·MMA produced zwitterionic phosphonium enolborate $^tBu_3PCH_2C(Me)$ = C-(OMe)O$B(C_6F_5)_3$, but it was inactive towards polymerization of MMA, with or without an additional equiv. of $B(C_6F_5)_3$. In contrast, its enolaluminate analogue $^tBu_3PCH_2C(Me)$ = C-(OMe)O$Al(C_6F_5)_3$ rapidly polymerizes MMA into polymers even without additional amount of $Al(C_6F_5)_3$.

In 2014, Xu and Chen [67] developed seven phosphorus (**P**) and borane (**B**) intra- or intermolecular LPs with different degree of "frustration" (from FLPs to ILPs to CLAs) for polymerization of the

renewable acrylic monomer MMBL. Kinetic studies revealed that the polymerization activity follows the order $Mes_3P/B(C_6F_5)_3$ (0 h^{-1}) = **P/B-1** (0 h^{-1}) < **P/B-2** (96 h^{-1}) < **P/B-3** (382 h^{-1}) < **P/B-4** (1,174 h^{-1}) < **P/B-5** (5,652 h^{-1}) < **P/B-6** (24,000 h^{-1}) (Scheme 6), displaying an apparent inverse relationship between the polymerization activity and the degree of LP "frustration". Neither intermolecular $Mes_3P/B(C_6F_5)_3$ nor intramolecular FLP **P/B-1** were active for polymerization of MMBL, whereas the intermolecular CLA $Ph_3P{\cdot}B(C_6F_5)_3$**P/B-6** exhibited the highest activity. In the presence of monomer or donor solvent, Ph_3P and $B(C_6F_5)_3$ can be released from **P/B-6**, thus resulting in chain initiation and propagation. Furthermore, varying the substitution on the **P** and **B** sites led to the formation of CLAs with different degree of adduct strength, which exhibited different activity towards MMBL polymerization. On the basis of these results, they proposed that to achieve high polymerization activity, it is important to strike a fine balance between **B** site acidity, **P** site basicity, steric crowding around **P** and the strength of the **P-B** association in solution.

In 2015, Chen and co-workers [68] reported the polymerization of acrylic monomers including MMA, MMBL and AMA by NHC/$B(C_6F_5)_3$ LPs. For MMA polymerization, I^iPr was the most active and effective LB among the investigated LBs and its combination with $B(C_6F_5)_3$ exhibited high polymerization activity, achieving TOF value up to 2,722 h^{-1}. It should be noted that chain transfer reaction occurred in MMA polymerization by $I^iPr/B(C_6F_5)_3$ and $IMe/B(C_6F_5)_3$ LPs, thus producing PMMA with M_n lower than the calculated M_n based on the [MMA]/[NHC] ratio. On the other hand, these NHC/$B(C_6F_5)_3$ LPs were highly effective for polymerization of MMBL, achieving TOF values up to 48,000 h^{-1} while they also showed chemoselectivity towards the polymerization of conjugated vinyl groups in divinyl acrylic monomer AMA, leaving the unconjugated C=C double bonds unreacted.

Chen and co-workers [63] also found that the combination of $B(C_6F_5)_3$ with TPT, NHO7 or I^tBu are all effective for polymerization of renewable monomer MC, but furnishing PMC with bimodal distribution and low initiation efficiency (I^*% < 50). In sharp contrast, replacing $B(C_6F_5)_3$ with $(BHT)_2AlMe$ led to a significantly enhanced activity towards polymerization of MC.

Besides phosphines and NHCs, amines could also serve as the LBs for polymerization of MMBL [32]. Different from the generation of CLAs from the reaction of $Al(C_6F_5)_3$ with Et_3N or TMP, the reaction of $B(C_6F_5)_3$ with TMP afforded FLP. Whereas due to disproportionation reaction, the reaction of $B(C_6F_5)_3$ with Et_3N yielded equimolar amounts of ammonium hydridoborate and iminium zwitterion. Among the investigated amine/$B(C_6F_5)_3$ LPs, $B(C_6F_5)_3$/TMP exhibited the highest polymerization activity, achieving a TOF value up to 96,000 h^{-1} and producing PMMBL with M_n higher than that obtained by $Al(C_6F_5)_3$/TMP LPs and bimodal distribution.

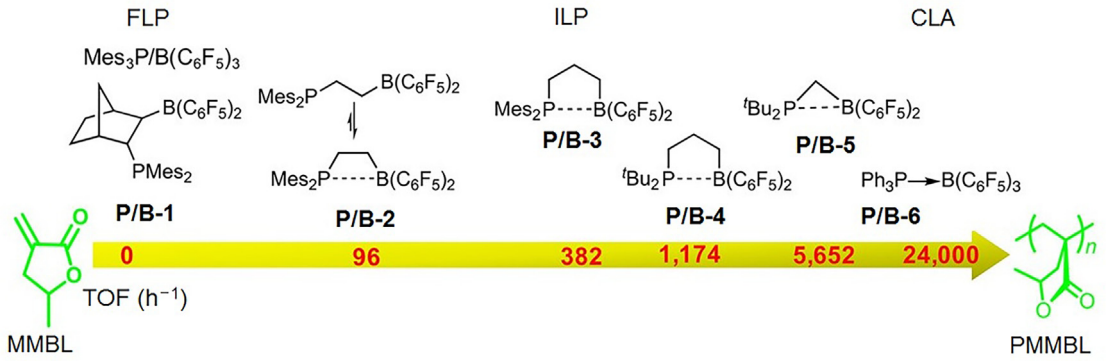
In 2018, we found the reaction of SKA with $B(C_6F_5)_3$ generated FLP, which could be utilized to catalyze the living GTP of MMBL and MBL, producing well-defined PMMBL and PMBL as well as block copolymers through sequential monomer addition method [51]. Kinetic studies revealed the polymerization follows a first-order dependence on MMBL concentration, first-order dependence on SKA concentration and second-order on $B(C_6F_5)_3$ concentration, indicating a bimolecular, activated monomer propagation mechanism, which is different from what we observed for the $Al(C_6F_5)_3$ catalyzed GTP [50].

More recently, Sebastián and co-workers [69] employed a hydrogenated FLP $[TMPH^+][HB(C_6F_5)_3^-]$ to achieve the first example of living/controlled polymerization of cyanoacrylates, including *n*-butyl cyanoacrylate (BCA), ethyl ayanoacrylate (ECA) and *β*-methoxyethyl cyanoacrylate (MECA) in THF. NBu_4Br, NBu_4OH, or NaSCN itself did not show any control on the polymerization of BCA. Their combination with $B(C_6F_5)_3$ yielded CLAs that did not promote the reaction. Although TMP/$B(C_6F_5)_3$ FLP showed certain control on polymerization, the produced polymers had M_n higher than expected and broad MWD. In contrast, the employment of a hydrogenated FLP $[TMPH^+][HB(C_6F_5)_3^-]$ can achieve a living/controlled polymerization of cyanoacrylates, affording PBCA with M_n up to 98.9 kg/mol and $Đ$ = 1.02–1.11. Its living characteristic can also be verified by the successful chain extension experiments and synthesis of well-defined block copolymers.

4. Rare-earth metal- or Si-based LPs

In 2017, Taton and co-workers [70] reported a Si/P based LPs composed of *N*-(trimethylsilyl)bis(trifluoromethane sulfonyl)imide (Me_3SiNTf_2) as the LA and a phosphine such as tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), $^nBu_3P$ or $^tBu_3P$ as the LB for polymerization of MMA. Among the LPs investigated, TTMPP/Me_3SiNTf_2 exhibited the highest activity, producing PMMA with M_n ranging between 7.5 and 31.0 kg/mol and narrow $Đ$ (<1.08). Only the LP with a 1:2 TTMPP/Me_3SiNTf_2 ratio can polymerize the MMA, suggesting a dual reaction mechanism. Mechanistic studies revealed that the conjugated addition of the phosphine onto Me_3SiNTf_2-activated MMA formed a α-phosphonium SKA ion pair rather than zwitterionic-type intermediate LA-stabilized enolate (vide supra) as observed in the Al-based LP system [16]. The propagation step proceeded via the attack of an incoming Me_3SiNTf_2-activated MMA by α-phosphonium SKA along with the concomitant release of Me_3SiNTf_2. These SKA-type growing chain ends are very similar to those observed for GTP of MMA [5].

Recently, Xu and co-workers [71,72] developed unique, rare-earth metal-based LPs. They consist of rare-earth metal such as Sc, Y, or Lu and the ancillary ligand of phosphorus-tethered



Scheme 6. (Color online) Polymerization activity trend observed for MMBL polymerization by inter- and intramolecular P/B-based FLPs, interacting FLPs and CLAs. Reprinted with permission from Ref. [11]. Copyright 2018 American Chemical Society.

β-diketiminate, for polymerization of MMA, MBL, and MMBL at room temperature. It is noted that all catalysts can not completely convert MMA into polymers in up to 24 h even at a low monomer-catalyst ratio (50:1). In sharp contrast, MMBL can be rapidly and quantitatively converted to polymers with M_n ranging between 2.78 and 3.54 kg/mol and $Đ$ = 1.44–1.60. Mechanistic investigations revealed that the LPP was initiated by the nine-membered addition intermediate resulting from the intramolecular 1,4-addition of rare-earth metal complexes to the monomer. Later in 2018, they reported the polymerization of conjugated polar alkenes, such as MMA, ^{t}BuMA, DMAA, and FMA as well as divinyl monomers AMA, VMA, and VBMA, by LPs consisting of homoleptic rare-earth aryloxides (Ln = Sc, Y, Sm, and La) as the LA and phosphines or NHCs as the LBs [73,74]. Among the investigated monomers, polymerization of MMA was relatively controlled over the M_n and MWD in spite of low I^*. Moreover, the polymerization activity was increased with an increase in the ionic radii of the rare-earth metals (La > Sm > Y > Sc).

5. Summary and outlook

Since Chen group introduced the concept of FLP to the polymer synthesis in 2010, the development of LPP has achieved significant progresses in polymerization of polar vinyl monomers. Thanks to the binary, independent but synergy and cooperativity between LA and LB catalytic sites, the polymerization performance of LPs could be tailored by regulating the acidity of LA and basicity of LB as well as the steric hindrance of both LA and LB. Highly effective LPP and even living/controlled polymerization of diverse polar vinyl monomers have been achieved through this manner, not only producing polymers with predicted molecular weight and narrow MWD, thus affording high to quantitative initiation efficiencies, but also achieving some polymers what are difficult to be accomplished by other polymerization methods, such as the synthesis of UHMW PMMA at room temperature, high molecular weight PMC and so on. Compared with other polymerization strategy such as GTP, radial polymerization, coordination-insertion, LPP has shown several unique properties towards the polymerization of polar vinyl monomers such as the catalysts are easier to synthesize, raw materials are cheaper and more environmentally friendly as well as high activity, control or livingness, mild conditions, and complete chemo- or regioselectivity.

Although LPP is a powerful synthetic strategy for polymer synthesis, there are still some challenges that have not been overcome yet. Future research directions in the field of LPP chemistry are specified in the following five aspects: (1) taking full advantage of the existing living/controlled LPP systems for preparation of the functionalized polymers, such as thermoplastic elastomers, hybrid polymers, self-assembled polymers, and so on; (2) precise polymerization of other monomers into polymers with the desirable molecular weight and narrow MWD; (3) expanding the monomer scope of LPP to such as α-olefins, allenes, and dienes as well as other renewable monomers; (4) designing and developing new type of LPP systems with strong tolerance, excellent recyclability, and green chemistry characteristics; (5) synthesizing highly stereoregular polymers by stereoselective LPP system under mild conditions.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Yuetao Zhang designed, instructed and polished the manuscript. Wuchao Zhao collected the literatures and wrote the initial draft. Jianghua He and Yuetao Zhang reviewed and finalized the manuscript.

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