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Ultra-High-Molecular-Weight Polymers Produced by the “Immortal” Phosphine-Based Catalyst System

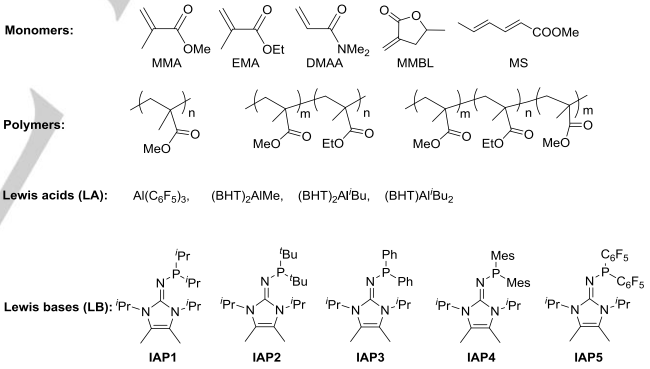
Yun Bai, Jianghua He, and Yuetao Zhang*

Abstract: A strong organophosphorus superbase, *N*-(diphenylphosphanyl)-1,3-diisopropyl-4,5-dimethyl-1,3-dihydro-2*H*-imidazol-2-imine (**IAP3**) was combined with a sterically encumbered but modestly acidic Lewis acid (LA), (4-Me-2,6-^{t}Bu$_2$-C$_6$H$_2$O)Al^{i}Bu$_2$ ((BHT)Al^{i}Bu$_2$), to synergistically promote the frustrated Lewis pair (FLP)-catalyzed living polymerization of methyl methacrylate (MMA), achieving ultrahigh molecular weight (UHMW) poly(methyl methacrylate) (PMMA) with M_n up to 1927 kg/mol and narrow molecular weight distribution (MWD) at room temperature (RT). This FLP catalyst system exhibits exceptionally long lifetime polymerization performance even in the absence of free MMA, which could reinitiate the desired living polymerization after the resulting system was held at RT for 24 h.

There have been continuing efforts in the development of living polymerization systems to produce polymers with controlled molecular weight (*MW*) and narrow MWD since properties of polymeric materials are closely related to their *MW* and MWD.[1-4] However, it remains as a challenging task to synthesize UHMW polymers,[5] especially PMMA with M_n >10^6 g/mol, only a handful of examples have been achieved under harsh reaction conditions so far, such as PMMA with M_n up to 3.6 × 10^6 g/mol prepared through free radical polymerization under high pressure of 500 MPa and ~ 60 ºC.[6-7] On the other hand, the synthesis of UHMW PMMA by anionic polymerization was restricted by difficulty in obtaining ultra-purified MMA and solvents and the requirement of low temperature.[8-9] There is no report on the production of UHMW PMMA with M_n >10^6 g/mol and narrow MWD under mild condition up to date. Therefore, it is a great impetus to research efforts to develop new catalyst system to overcome these limitations.

As a newly emerging polymerization technique, Lewis pair polymerization (LPP) has demonstrated extraordinary activity towards various monomers and exhibits very promising prospect in the polymer synthesis in recent years,[10] since the well-established application of FLP in small-molecule chemistry.[11] Despite the development of a wide range of effective LP systems, the application of LPP was still hampered by both low initiation efficiencies and chain-termination side reactions.[12-13] Until recently, by choosing appropriate combination of Lewis base (LB) and LA with matching acidity and steric hindrance,[14] the first example of authentic FLP catalyst system has been developed to successfully remove these restriction barriers and achieve living (co)polymerization of MMA and benzyl methacrylate, producing PMMA with M_n up to 351 kg/mol.

As a strong nucleophile superior than many organobases such as alkylphosphines and *N*-heterocyclic carbenes,[15] organophosphorus(III) superbase, imidazolin-2-ylidenamino substituted phosphines (**IAPs**) are capable of capturing CO$_2$ and SO$_2$ molecules to form stable phosphine-based adducts[16-18] and activating extremely inert greenhouse gas sulfur hexafluoride.[19] Although strong donor ability and easily adapted steric hindrance of IAPs should enpower them to be a very promising LB candidate for FLP system, no report on the employment of IAPs for LPP yet. Herein five sterically hindered IAPs with the same imidazolin framework but varied substituents on the N atom (*N*-diisopropylphosphanyl, **IAP1**; *N*-di-*tert*-butylphosphanyl, **IAP2**; *N*-diphenylphosphanyl, **IAP3**; *N*-dimesitylphosphanyl, **IAP4**; *N*-(bis(6,6,6,6,6-pentafluoro-6λ8-hexa-1,3,4-triyn-1-yl))phosphanyl, **IAP5**, Scheme 1) were synthesized and employed to combine with a series of organoaluminum LAs to achieve an “immortal” FLP catalyst system for living polymerization of MMA at RT, producing PMMA with medium to UHMW (up to 1927 kg/mol), narrow MWD (*Đ* as low as 1.06) and high to quantitative initiation efficiencies. To the best of our knowledge, this is for the first time UHMW PMMA with M_n >10^6 g/mol and narrow MWD was achieved in polymer synthesis under mild conditions so far.



Scheme 1. Structures of Lewis acids, Lewis bases, monomers, and resulting (co)polymers investigated in this study.

When combined with a strong acidic Al(C$_6$F$_5$)$_3$, IAP-based LPs exhibited extraordinary highly effective catalytic activity for polymerization in an 800:1:2 MMA/IAP/Al(C$_6$F$_5$)$_3$ ratio, achieving quantitative monomer conversion by **IAP1** to **IAP4**-based LPs in 30 s (runs 1-4) but only 41% MMA conversion by **IAP5**- based LP in 24 h (run 5) probably due to the lower nucleophilicity of **IAP5** resulting from the presence of electron-withdrawing pentafluorophenyl substituent. Since **IAP3** exhibited the highest initiation efficiency *I**% of 92 among the investigated IAPs, it was employed for the following polymerization. MALDI-TOF MS spectrum indicated the exclusive presence of a cyclic chain end derived from backbiting cyclization side reactions in the low-MW PMMA produced by **IAP3**/Al(C$_6$F$_5$)$_3$ LP

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Supporting information containing experimental details, NMR spectra and further tabular data (PDF, 41 pages) is available on the WWW under http://

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Table 1. Results of polymerization by IAP-based LPs[a]

Run	LB	LA	M	M/LB/LA	Time	Conv.[b] (%)	M_n[c] (kg/mol)	MWD[c]	I^*[d] (%)
1	**IAP1**	Al(C$_6$F$_5$)$_3$	MMA	800:1:2	30 s	100	100	1.17	80
2	**IAP2**	Al(C$_6$F$_5$)$_3$	MMA	800:1:2	30 s	100	154	1.21	52
3	**IAP3**	Al(C$_6$F$_5$)$_3$	MMA	800:1:2	30 s	100	86.9	1.11	92
4	**IAP4**	Al(C$_6$F$_5$)$_3$	MMA	800:1:2	30 s	100	99.2	1.14	81
5	**IAP5**	Al(C$_6$F$_5$)$_3$	MMA	800:1:2	24 h	41	392	1.35	8
6	**IAP3**	(BHT)$_2$AlMe	MMA	800:1:2	10 min	100	88.3	1.19	91
7	**IAP3**	(BHT)$_2$Al^{i}Bu	MMA	800:1:2	340 min	100	72.0	1.13	112
8	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	400:1:2	40 s	100	54.0	1.06	75
9	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	800:1:2	2 min	100	92.8	1.10	86
10	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	1600:1:2	10 min	100	153	1.06	105
11	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	3200:1:2	30 min	100	297	1.07	108
12	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	6400:1:2	135 min	100	656	1.09	98
13	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	10000:1:2	11 h	100	1029	1.08	97
14	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	15000:1:2	21 h	100	1568	1.08	96
15	**IAP3**	(BHT)Al^{i}Bu$_2$·MMA	MMA	20000:1:2	48 h	89	1927	1.10	92
16	**IAP3**	(BHT)Al^{i}Bu$_2$·EMA	EMA	400:1:2	2 min	100	49.7	1.16	90
17[e]	**IAP3**	(BHT)$_2$Al^{i}Bu	MMBL	800:1:2	340 min	100	85.6	1.12	105
18	**IAP3**	(BHT)Al^{i}Bu$_2$	DMAA	800:1:2	5 min	100	833 44.4	1.64 1.39	
19	**IAP3**	(BHT)Al^{i}Bu$_2$	MS	400:1:2	24 h	16	n.d	n.d	n.d

[a] Conditions: carried out at RT in toluene using procedure A; for a 800MMA/1LB/2LA ratio, [M] = [MMA]$_0$ = 0.936 M and [LA]$_0$ = 2[LB]$_0$ = 2.34 mM. n.d. = not determine. [b] Monomer conversions measured by ^{1}H NMR. [c] M_n and $Đ$ determined by GPC relative to PMMA standards in DMF. [d] Initiator efficiency (I^*)% = M_n(calcd)/M_n(exptl) × 100, where M_n(calcd) = [MW(MMA)]([MMA]$_0$/[I]$_0$) (conversion) +MW of chain-end groups.[e] performed in CH$_2$Cl$_2$.

(Figure S36 and S37), which revealed that polymerization catalyzed by **IAP3**/Al(C$_6$F$_5$)$_3$ LP is not a living process.

Previously, we have demonstrated that both the acidity and steric hindrance of LA play significantly important role in the reactivity of polymerization. Therefore, a series of organoaluminum LAs with descending acidity (Al(C$_6$F$_5$)$_3$ (100%) > (BHT)$_2$AlMe (86%) ≈ (BHT)$_2$Al^{i}Bu (85%) > (BHT)Al^{i}Bu$_2$ (74%), Table S1) on a relative scale[20] were examined for MMA polymerization in an 800:1:2 MMA/**IAP3**/LA ratio. It turned out that LP composed of bulky (BHT)$_2$AlMe with lower acidity relative to Al(C$_6$F$_5$)$_3$ fully converted MMA to PMMA with M_n = 88.3 kg/mol, $Đ$ = 1.19 and I^*% = 91 in 10 min (run 6). However, MALDI-TOF MS spectrum indicated that the final product still contained a cyclic chain end (Figure S38 and S39). Using (BHT)$_2$Al^{i}Bu with similar acidity but larger steric hindrance to that of (BHT)$_2$AlMe, we could successfully suppress backbiting cyclization (Figure S40 and S41) at the expense of polymerization activity (run 7). Excitingly, switching to a (BHT)Al^{i}Bu$_2$·MMA adduct with lower acidity but reduced steric hindrance led to the significantly enhanced polymerization activity, producing PMMA with M_n = 92.8 kg/mol, $Đ$ = 1.10, thus furnishing I^*% = 86 (run 9). Moreover, chain-end analyses revealed that the produced polymer is a linear, living chain, capped with **IAP3**/H chain ends, and showed no evidence for the formation of cyclic backbiting chain end (Figure 1). These results further highlight the importance of considering both electronic and steric factors when matching LA with LB for generating a suitable LP that can promote living polymerization. The living feature of the polymerization could be confirmed by the linearly (R^2 = 0.9996, Figure S35) increased M_n values of PMMA with an increase in [MMA]$_0$/[**IAP3**]$_0$/[(BHT)Al^{i}Bu$_2$·MMA]$_0$ ratio from 400:1:2 to 20000:1:2 (runs 8-15), while $Đ$ values remained narrow (from 1.06 to 1.10) (Figure 2a). Worth noting that UHMW PMMA with M_n up to 1927 kg/mol were achieved by FLP for the first time (runs 13-15). The livingness and robustness also enable successful chain-extension experiments performed with the sequential addtion of three batches (1000/1000/1000 equiv) of MMA (Figure 2b, Table S5) and the synthesis of well-defined diblock copolymer PMMA-*b*-PEMA and triblock copolymer PMMA-*b*-PEMA-*b*-PMMA (runs 2 and 3, Table S6; Figure 2c) by using EMA as co-monomer. Next, we investigated the effectiveness of **IAP3**-based LPs for polymerization of the other monomers and found that it also exhibited well control on polymerization of both EMA (run 16) and renewable monomer, γ-methyl-α-methylene-γ-butyrolactone (MMBL) (run 17). Polymerization of *N*,*N*-dimethylacrylamide (DMAA) produced polymers with a bimodal MWD, indicating the coexistence of different active species (run 18) whereas only 16% monomer conversion was obtained for polymerization of methyl sorbate (MS) in 24 h (run 19).

To gain further insight into the above-described polymerization behavior, we systematically investigated polymerization by **IAP3**/(BHT)Al^{i}Bu$_2$ LP system. It is generally accepted that a catalyst system should meet the following requirements to synthesize UHMW polymers: First, extraordinarily effective polymerization activity. Second, exclusive active species to initiate polymerization. Third, long lifetime polymerization performance and no interference with other side reactions such as chain-termination. As an organophosphorus superbase, the combination of **IAP3** with (BHT)Al^{i}Bu$_2$ could achieve high to quantitative monomer conversion for polymerization with [MMA]$_0$/[**IAP3**]$_0$/[(BHT)Al^{i}Bu$_2$]$_0$ ratio ranging from 400:1:2 to 20000:1:2. Different from NHO alone could initiate polymerization of MMA,[14] **IAP3** itself is completely ineffective whereas (BHT)Al^{i}Bu$_2$ only exhibits negligible effect for polymerization in up to 24 h (Table S2). We performed a series of stoichiometric reactions at RT and observed the formation of classic Lewis adduct for reaction of **IAP3** and Al(C$_6$F$_5$)$_3$ (Figure S16-S18) and the exclusive generation of noninteracting, true FLP for reaction of **IAP3** with (BHT)$_2$AlMe, (BHT)$_2$Al^{i}Bu or (BHT)Al^{i}Bu$_2$, respectively (Figure S19-S24). As revealed by ^{1}H and ^{31}P NMR spectroscopy, reaction of **IAP3** and (BHT)Al^{i}Bu$_2$·MMA immediately and exclusively yielded a clean zwitterionic species **IAP3**-CH$_2$C(Me)=C(OMe)OAl(BHT)^{i}Bu$_2$, which possessed analogous structure with that of **IAP2**-CH$_2$C(Me)=C(OMe)OAl(C$_6$F$_5$)$_3$ (Figure 3) generated from the reaction of **IAP2** and Al(C$_6$F$_5$)$_3$·MMA adduct (Scheme S1, Figure S30-S33). Above results indicated that such zwitterionic species is the exclusive active species for polymerization and there is no unwanted reaction resulting from the other active species. Comparative studies performed with different activation procedures (check supporting information for details of procedures A and B) afforded the exactly same PMMA as revealed by their completely overlapped GPC traces (Figure 4, Table S3), which further confirmed the uniqueness of zwitterionic species. In addition to meet the requirement of no occurrence of side reaction (vide supra), **IAP3**/[(BHT)Al^{i}Bu$_2$ FLP system exhibited exceptionally longlife catalytic performance, which is significantly important for synthesis of UHMW polymer. The living polymerization system is "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, $Đ$ = 1.18 (run 2, Table S4), which is similar with that (M_n = 92.8 kg/mol, $Đ$ = 1.10, run 8) obained for polymerization in an 800:1:2 [MMA]$_0$/[**IAP3**]$_0$/[(BHT)Al^{i}Bu$_2$·MMA]$_0$ ratio (Figure S34). As discussed above, **IAP3**/(BHT)Al^{i}Bu$_2$ FLP system meets all requirements for synthesis of UHMW polymers and thus accomplishing the goal.

In summary, the first example of UHMW PMMA with M_n = 1927 kg/mol and small $Đ$ = 1.10 was produced from the noninteracting, authentic **IAP3**/(BHT)Al^{i}Bu$_2$ FLP-promoted living polymerization of MMA at RT. Systematic investigation revealed that the combination of extraordinarily effective polymerization activity, exclusive zwitterionic active species and immortal polymerization process without observance of side reaction or chain termination enabled **IAP3**/(BHT)Al^{i}Bu$_2$ FLP system to accurately control over polymerization of MMA and achieve UHMW PMMA in the end. These findings not only provide significantly important foundation to synthesis of UHMW polymer in the future, but also enable us to synthesize advanced polymers such as thermoplastic elastomer or self-assembling polymers by this highly effective and "immortal" catalyst system. Relevant research work is in progress.

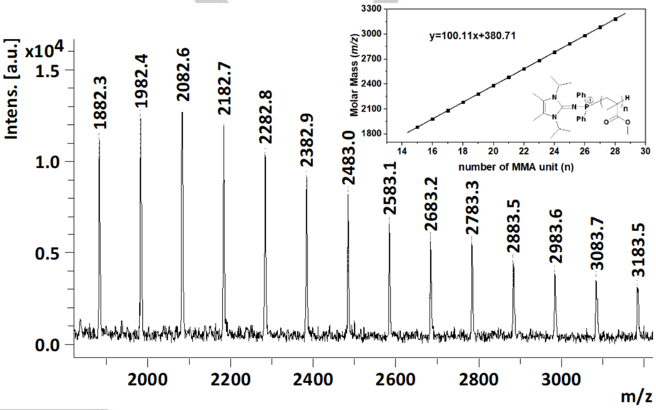

Figure 1. MALDI-TOF MS spectrum of the low-MW PMMA sample produced by **IAP3**/(BHT)Al^{i}Bu$_2$ LP in toluene at RT. Inset: Plot of *m*/*z* values vs the number of MMA repeat units (*n*).

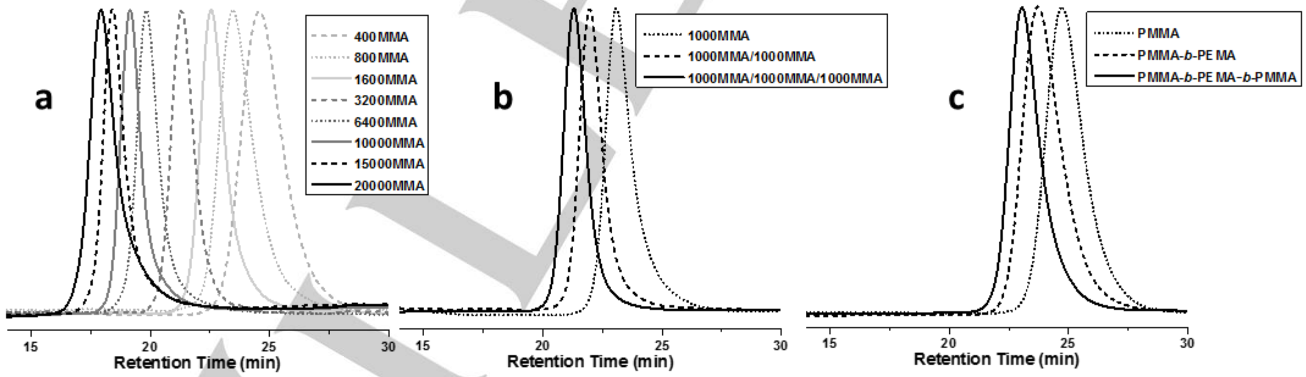

Figure 2. GPC traces of (a) PMMA produced by **IAP3**/(BHT)Al^{i}Bu$_2$ LP at various [MMA]$_0$/[**IAP3**]$_0$/[(BHT)Al^{i}Bu$_2$]$_0$ ratio at RT. Conditions: [MMA]$_0$/[**IAP3**]$_0$/[(BHT)Al^{i}Bu$_2$]$_0$ = 400:1:2, 800:1:2, 1600:1:2, 3200:1:2, 6400:1:2, 10000:1:2, 15000:1:2, 20000:1:2, [MMA]$_0$ = 0.936 M and (b) PMMA samples obtained from chain extension experiments in toluene at RT, [MMA]$_0$ = 0.47 M and (c) homopolymer, diblock and triblock copolymer produced from the sequential block copolymerization of MMA and EMA by **IAP3**/(BHT)Al^{i}Bu$_2$ in toluene at RT: polymerizing MMA first, [MMA]$_0$ = 0.936 M.

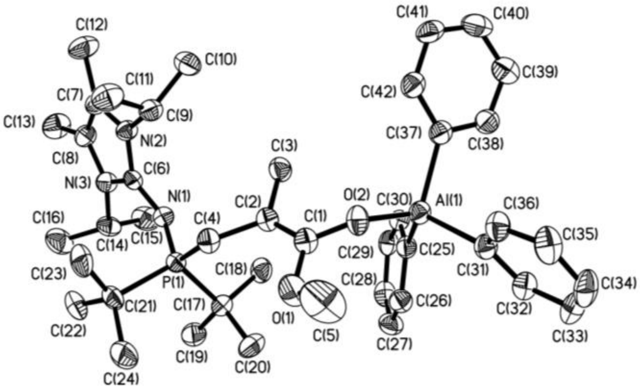

Figure 3. X-ray crystal structure of **IAP2**-CH$_2$C(Me)=C(OMe)OAl(C$_6$F$_5$)$_3$. Hydrogen and Fluorine atoms are omitted for clarity and ellipsoids drawn at 50% probability.

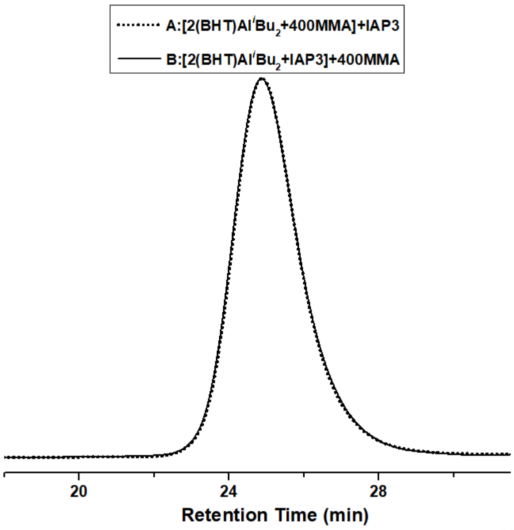

Figure 4. GPC traces of PMMA obtained from the polymerization performed using different activation procedures

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Keywords: frustrated Lewis Pair • living polymerization • organoaluminum • organophosphorus superbase • ultrahigh molecular weight polymer

[1] a) N. Hadjichristidis, A. Hirao, Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications, Springer, **2015**; b) D. Baskaran, *Prog. Polym. Sci.* **2003**, *28*, 521-581.

[2] a) K. Matyjaszewski, eds. "Cationic Polymerization of Heterocyclics." *Cationic Polymerizations*. CRC Press, **1996**. 451-568; b) A. Kanazawa, S. Kanaoka, S. Aoshima, *Chem. Lett.* **2010**, *39*, 1232-1237; c) Y. Kwon, R. Faust, *Adv. Polym. Sci*. **2004**, *167*, 107-136.

[3] a) O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. Rajanbabu, *J. Am. Chem. Soc.* **1983**, *105*, 5706-5708; b) O. W. Webster, *J. Polym. Sci. Part A: Polym. Chem*. **2000**, *38*, 2855-2860; c) M.R. Kalourkoti, O. W. Webster, C. S. Patrikios, Group Transfer Polymerization Encyclopedia of Polymer Science and Technology; John Wiley & Sons, Inc., **2013**, Vol. 99, pp 1-17. DOI: 10.1002/0471440264.pst603.

[4] a) K. Matyjaszewski, eds. Controlled/Living Radical Polymerization: Progress in ATRP, ACS Symposium Series; American Chemical Society: Washington, DC, **2009**; b) A. Anastasaki, V. Nikolaou, G. Nurumbetov, P. Wilson, K. Kempe, J. F. Quinn, T. P. Davis, M. R. Whittaker, D. M. Haddleton, *Chem. Rev*. **2016**, *116*, 835-877; c) M. Ouchi, M. Sawamoto, *Macromolecules* **2017**, *50*, 2603-2614.

[5] a) V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro, S. Sahoo, *J. Am. Chem. Soc,* **2006**, *128*, 14156-14165; b) B. Mao, L. Gan, Y. Gan, *Polymer* **2006**, *47*, 3017-3020; c) R. W. Simms, M. F. Cunningham, *Macromolecules* **2007**, *40*, 860-866; d) L. Mueller, W. Jakubowski, K. Matyjaszewski, J. Pietraskik, P. Kwiatkowski, W. Chaladaj, J. Jurczak, *Eur. Polym. J.* **2011**, *47*, 730-734; e) E. Read, A. Guinaudeau, D. J. Wilson, A. Cadix, F. Violleau, M. Destarac, *Polym. Chem.* **2014**, *5*, 2202-2207; f) N. P. Truong, M. V. Dussert, M. R. Whittaker, J. F. Quinn, T. P. Davis, *Polym. Chem.* **2015**, *6*, 3865-3874; g) Z, Huang, J. Chen, L. Z. Zhang, Z. Cheng, X. Zhu, *Polymer* **2016**, *8*, 59; h) Z. Liu, Y. Lv, Z. An, *Angew. Chem. Int. Ed.* **2017**, *56*, 13852-13856; i) R. N. Carmean, T. E. Becker, M. B. Sims, B. S. Sumerlin, *Chem* **2017**, *2*, 93-101.

[6] J. Rzayev, J. Penelle, *Angew. Chem. Int. Ed.* **2004**, *43*, 1691-1694; *Angew. Chem.* **2004**, *116*, 1723-1726.

[7] T. Arita, Y. Kayama, K. Ohno, Y. Tsujii, T. Fukuda, *Polymer* **2008**, *49*, 2426-2429.

[8] S. K. Varshney, J. P. Hautekeer, R. Fayt, R. Jérôme, Ph. Teyssié, *Macromolecules* **1990**, *23*, 2618-2622.

[9] J.P. Hautekeer, S. K. Varshney, R. Fayt, C. Jacobs, R. Jérôme, Ph. Teyssié, *Macromolecules* **1990**, *23*, 3893-3898

[10] a) E. Y.-X. Chen, *Top. Curr. Chem*. **2013**, *334*, 239-260; b) E. Piedra-Arroni, A. Amgoune, D. Bourissou, *Dalton Trans*. **2013**, *42*, 9024-9029; c) Y. Zhang, G. M. Miyake, E. Y.-X. Chen, *Angew. Chem. Int. Ed.* **2010**, *49,* 10158-10162; *Angew. Chem.* **2010**, *122*, 10356-10360; d) Y. Zhang, G. M. Miyake, M. G. John, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *Dalton Trans.* **2012***, 41,* 9119-9134; e) T. Xu, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2014***, 136,* 1774-1777; f) J. He, Y. Zhang, E. Y.-X. Chen, *Synlett.* **2014***, 25,* 1534-1538; g) Y. Jia, W. Ren, S. Liu, T. Xu, Y. Wang, X. Lu, *ACS Macro Lett.* **2014***, 3,* 896-899; h) J. Chen, E. Y.-X. Chen, *Isr. J. Chem*. **2015**, *55*, 216-225; i) P. Xu, X. Xu, *ACS Catal.* **2018**, *8*, 198-202; j) E. Piedra-Arroni, C. Ladaviere, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc*. **2013**, *135*, 13306-13309; k) J. Zhu, E. Y.-X. Chen, *J. Am. Chem. Soc*. **2015**, *137*, 12506-12509; l) X. Li, B. Wang, H. Ji, Y. Li, *Catal. Sci. Technol.* **2016**, *6*, 7763-7772; m) Q. Wang, W. Zhao, J. He, Y. Zhang, E. Y.-X. Chen, *Macromolecules* **2017**, *50*, 123-136; n) H. Zhang, Y. Nie, X. Zhi, H. Du, J. Yang, *Chem. Commun.* **2017**, *53*, 5155-5158; o) H. Ji, B. Wang, L. Pan, Y. Li, *Green Chem.* **2018**, *20*, 641-648; p) J. Yang, H. Wu, Y. Li, X. Zhang, D. Darensbourg, *Angew. Chem. Int. Ed*. **2017**, 56, 5774-5779; *Angew. Chem.* **2017***, 129,* 5868-5873; q) C. Zhang, H. Wu, Y. Li, J. Yang, X. Zhang, *Nat. Commun.* **2018**, *9*, 2137; r) M. G. Knaus, M. M. Giuman, A. Pöthig, B. Rieger, *J. Am. Chem. Soc.* **2016**, *138*, 7776-7781; s) W. Ottou, E. Conde-Mendizabal, A. Pascual, A.-L Wirotius, D. Bourichon,; J. Vignolle, F. Robert, Y. Landais, J.-M. Sotiropoulos, K. Miqueu, *Macromolecules* **2017**, *50*, 762-774; t) P. Xu, Y. Yao, X. Xu, *Chem. Eur. J.* **2017**, *23*, 1263-1267; u) M. Wang, F. Nudelman, R. R. Matthes,; M. P. Shaver, *J. Am. Chem. Soc.* **2017**, *139*, 14232-14236; v) Y. Hosoi, A. Takasu, S. Matsuoka, M. Hayashi, *J. Am. Chem. Soc.* **2017**, *139*, 15005-15012.

[11] Selected some reviews and recent examples on activation of small molecules by FLPs: a) D. W. Stephan, *Science* **2016**, *354*, aaf7229; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441;

10.1002/anie.201811946

Angew. Chem. **2015**, *127*, 6498-6541; c) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306-316; d) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032; e) W. Meng, X. Feng, H. Du, *Acc. Chem. Res.* **2018**, *51*, 191-201; f) C. Tang, Q. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. Song, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2017**, *56*, 16588-16592; *Angew. Chem.* **2017**, *129*,16815-16819; g) A. Simonneau, R. Turrel, L. Vendier, M. Etienne, *Angew. Chem. Int. Ed.* **2017**, *56*, 12268-12272; *Angew. Chem.* **2017**, *129*, 12436-12440; h) L. Liu, L. Cao, Y. Shao, D. W. Stephan, *J. Am. Chem. Soc.* **2017**, *139*, 10062-10071; i) Z. Jian, G. Kehr, C. G. Daniliuc, B. Wibbeling, T. Wiegand, M. Siedow, H. Eckert, M. Bursch, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2017**, *139*, 6474-6483; j) M. Trunk, J. F. Teichert, A. Thomas, *J. Am. Chem. Soc.* **2017**, *139*, 3615-3618; k) Z. Mo, T. Szilvasi, Y. Zhou, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 3699-3702; *Angew. Chem*. **2017**, *129*, 3753-3756; l) O. J. Metters, S. J. K. Forrest, H. A. Sparkes, I. Manners, D. F. Wass, *J. Am. Chem. Soc.* **2016**, *138*, 1994-2003.

[12] J. He, Y. Zhang, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *Macromolecules* **2014**, *47*, 7765-7774.

[13] Y. Jia, Y. Wang, W. Ren, T. Xu, J. Wang, X. Lu, *Macromolecules* **2014**, *47*, 1966-1972.

[14] Q. Wang, W. Zhao, S. Zhang, J. He, Y. Zhang, E. Y.-X. Chen, *ACS Catal.* **2018**, *8*, 3571-3578.

[15] M. A. Wünsche, P. Mehlmann, T. Witteler, F. Buß, P. Rathmann, F. Dielmann, *Angew. Chem. Int. Ed.* **2015**, *54*, 11857-11860; *Angew. Chem.* **2015**, *127*, 12024-12027.

[16] F. Buß, P. Mehlmann, C. Mück-Lichtenfeld, K. Bergander, F. Dielmann, *J .Am. Chem. Soc.* **2016**, *138*, 1840-1843.

[17] P. Mehlmann, C. Mück-Lichtenfeld, T. T. Y. Tan, F. Dielmann, *Chem. Eur. J.* **2017**, *23*, 5929-5933.

[18] F. Buß, P. Rotering, C. Mück-Lichtenfeld, F. Dielmann, *Dalton Trans.* **2018**, *47*, 10420-10424.

[19] F. Buß, C. Mück-Lichtenfeld, P. Mehlmann, F. Dielmann, *Angew. Chem. Int. Ed .***2018**, *57*, 4951-4955; *Angew. Chem.* **2018**, *130*, 5045-5049.

[20] a) M. A. Breckett, D. S. Brassinton, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530-533; b) Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818-1827.

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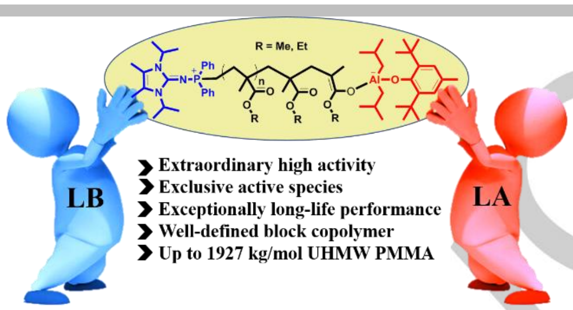
Layout 1:

COMMUNICATION

An "immortal" FLP system composed of organophosporus superbase and organoaluminum promoted the living polymerization of methyl methacrylate, achieving polymers with medium to ultrahigh molecular weight (M_n up to 1927 kg/mol) and narrow molecular weight distribution.



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Ultra-High-Molecular-Weight Polymers Produced by the "Immortal" Phosphine-Based Catalyst System