

End of Frustration: Catalytic Precision Polymerization with Highly Interacting Lewis Pairs

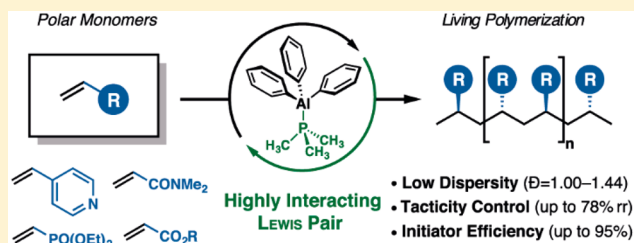
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S Supporting Information

ABSTRACT: Herein we report on the catalytic polymerization of diverse Michael-type monomers with high precision by using simple but highly active combinations of phosphorus-containing Lewis bases and organoaluminum compounds. The interacting Lewis pair catalysts enable the control of molecular weight and microstructure of the produced polymers. The reactions show a linear M_n vs consumption plot thus proving a living type polymerization. The initiation has been investigated by end-group analysis with ESI mass spectrometric analysis. With these main-group element Lewis acid base pairs, it is not only possible to polymerize sterically demanding, functionalized as well as heteroatom containing monomers but also, for the first time, to catalytically polymerize extended Michael systems, like 4-vinylpyridine.



INTRODUCTION

Since their first appearance in the 1920s polymers developed to be the most predominantly used materials in modern life.¹ The future challenges humanity is facing in the 21st century demand a new generation of those functional materials.² The application of them varies in the biomedical sector from self-healing materials to switchable polymers. To meet the requirements of a new class of functional materials, a precise control of the macromolecular structure is inevitable.³ So far polar monomers are mostly polymerized radically with common techniques invented over 100 years ago. Enormous efforts have been made to develop radical polymerizations with living character, since this is the key to specifically add functionality to materials.⁴⁻⁷ In the case of living radical polymerization, this living character is achieved at the expense of reaction rates and conversions due to the low concentration of the active species.^{8,9} However, for feasible applications, methods with a high precision of the macromolecular parameters in combination with rapid reaction rates are needed. With their impressive work in the field of single-electron-transfer living radical polymerization (SET-LRP), the research groups of Percec and Haddleton introduced a Cu(0)-based polymerization technique with remarkably enhanced reaction rates.¹⁰⁻¹⁵

Nonradical catalytic approaches to polymerize Michael-type monomers have been made by using classical metallocene¹⁶ as well as rare-earth metal catalysts,¹⁷ pathways, which suffer from very complex catalyst syntheses. Furthermore, a variety of monomers, as for example, functionalized and sterically demanding acrylates and extended Michael-type monomers like 4-vinylpyridine, were not accessible with these complexes (Figure 1).^{17,18} First pioneering attempts to use frustrated and classical Lewis pairs by Chen et al. based on highly acidic Lewis

acids showed fascinating results but failed to satisfactorily polymerize complex acrylate and acrylate-analogue structures.^{19,20}

One of the most interesting examples in this context is furfuryl methacrylate. The reactive furfuryl substituent offers the possibility to cross-link the corresponding polymer via UV irradiation²¹ or conduct post polymerization modification via [4 + 2] cycloaddition.^{22,23} This opens up the possibility to use it in clinical, adhesive, or coating applications. Its beneficial properties such as a low shrinkage volume and the low reaction heat of polymerization make its corresponding polymer an ideal candidate for substituting inferior materials like poly(methyl methacrylate).²⁴

Nevertheless, due to the high degree of chain transfer induced by the reactive pending group, classical radical polymerization leads to insoluble and gelled polymers, which has restricted an industrial application of these materials until now.²⁵ First attempts to polymerize this monomer by the frustrated combinations of the highly acidic tris-(pentafluorophenyl)aluminum and different Lewis bases (combinations, which are able to polymerize methyl methacrylate) failed.¹⁹

RESULTS AND DISCUSSION

Evaluation of the different parameters influencing the catalytic activity of the applied Lewis pairs was achieved by using literature known scales. For quantification of the Lewis acidity, we employed the well-established fluoride ion affinity index.²⁶⁻²⁸ The fluoride ion affinity is the energy released

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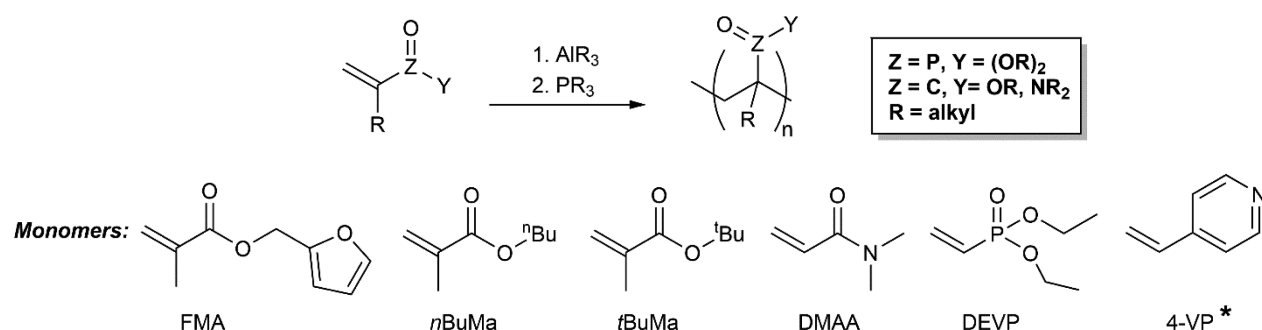
Lewis Acids: $\text{Al}(\text{CH}_3)_3$ $\text{Al}(\text{C}_2\text{H}_5)_3$ $\text{Al}(\text{C}_4\text{H}_9)_3$ $\text{Al}(\text{C}_6\text{H}_5)_3$ Lewis Bases: $\text{P}(\text{CH}_3)_3$ $\text{P}(\text{C}_2\text{H}_5)_3$ $\text{P}(\text{C}_6\text{H}_{11})_3$ 

Figure 1. Lewis acids, Lewis bases, and monomer scope of this work (* extended Michael system, see Scheme 3).

with coordination of a fluoride ion to a Lewis acid center in kJ/mol. Therefore, high values represent a strong Lewis acidic center. For comparing basicities of different phosphines, Angelici et al. supplied a sophisticated method based on the protonation energy determined by the reaction with $\text{F}_3\text{CSO}_3\text{H}$.²⁹ Since the zwitterionic propagating species of conjugate addition polymerization has a high degree of steric crowding, steric encumbrance of the initiating group has a substantial influence on the polymerization. As a scale for the steric demand, we used the Tolman angle (Θ in degrees).³⁰

Inspired by the idea that a milder reactivity of the Lewis pairs leads to a better control of the polymerization and less side reactions, we used weaker acidic Lewis acids as well as less basic phosphines with less steric encumbrance. In comparison to frustrated Lewis pairs, these highly interacting Lewis pairs (HIPs) form the expected, classical Lewis adducts as proven, e.g., by the crystal structure of triphenylaluminum and trimethylphosphine (Figure 2).

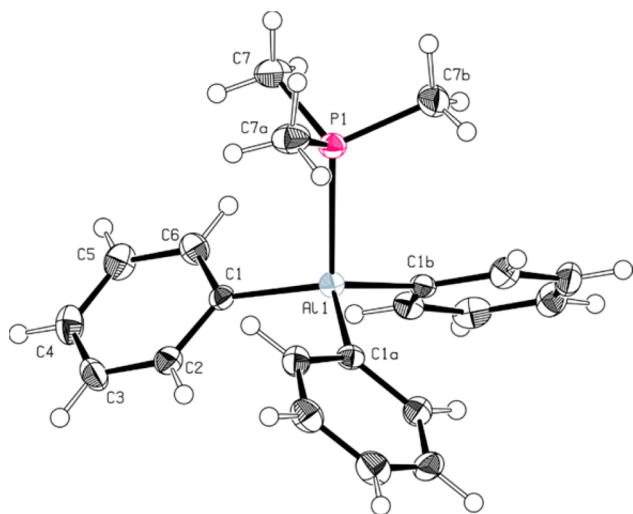


Figure 2. Solid-state structure of a triphenylaluminum-trimethylphosphine adduct from single crystal X-ray analysis.

Indeed, applying these pairs as polymerization catalysts affords a highly controlled polymerization process, which is characterized by excellent initiator efficiencies^{31,32} of the catalyst and narrow molecular weight distributions of the resulting polymers (Table 1). In a polymerization procedure conducted with the Lewis pair $\text{AlPh}_3/\text{PEt}_3$ poly(FMA), a

number-averaged molecular weight of 64 000 g/mol and a narrow dispersity of 1.16 can be obtained (run 1, Table 1). Switching to a sterically more demanding phosphine (PCy_3 , $\Theta = 170$)²⁴ causes a slightly decreased yield (85%, run 2, Table 1). The broadened dispersity of 1.38 and a higher molecular weight (121 000 g/mol) points to a hampered initiation process due to the high steric demand of the initiator.

Electron spray ionization mass spectrometry (ESI-MS) of short chain oligomers reveals phosphonium end groups, which is in accordance with a conjugate-addition initiation mechanism induced by the phosphine (Figure S8).¹⁹ As emphasized in an intensive study toward chain propagation,³³ termination reactions via intramolecular cyclization are one of the major factors for broad molecular weight distributions and a decreased living character of this polymerization type. Our reactions conducted with highly interacting Lewis pairs indicate a linear growth of the molecular weight with increasing yield, while dispersities stay narrow over the course of time (Chart 1). Additionally, we could not detect any induction period for our reactions (Figure S5).

The preliminary results imply that the choice of the Lewis pair is of crucial importance for the overall polymerization process. As a consequence of adapting the steric and electronic parameters of the Lewis pair according to the electronic and steric properties of the respective monomer, it is possible to polymerize a broad variety of acrylate monomers and their analogues. A deeper understanding of the underlying factors is inevitable for this purpose. Hence, different Lewis pairs were tested for their ability to polymerize various acrylic monomers with unique electronic and steric properties.

Starting point of our investigation was the polymerization of sterical encumbered methacrylates such as *n*-butyl- and *t*-butyl methacrylate, which are industrially well-known monomers, with a variety of applications.³⁴

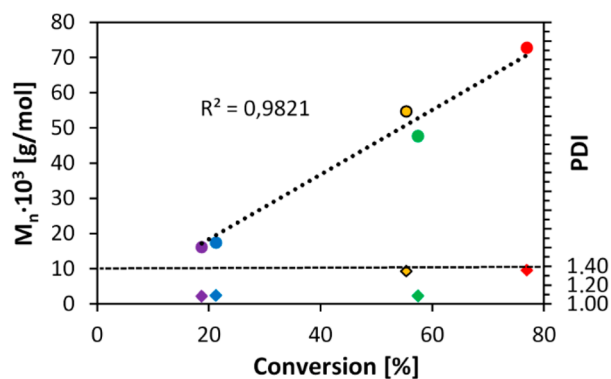
The polymerization with tris(pentafluorophenyl)aluminum as Lewis acid in combination with different Lewis bases such as carbenes or phosphines resulted in low conversions and broad polydispersities.¹⁹ We assume that the strong interaction of the electron-rich acrylate with the highly acidic aluminum compound (FIA: 552.1 kJ/mol)²⁸ leads to a deactivation of the catalyst. Therefore, we used the less acidic triphenylaluminum (FIA: 442.7 kJ/mol)³⁵ for our attempts. In fact, the use of AlPh_3 affords an extremely controlled polymerization process with a high yield (100%, run 3, Table 1). The resulting polymer shows a remarkably narrow dispersity of 1.00 and a molecular mass of 42 000 g/mol. Using $\text{P}(n\text{Hex})_3$ leads to a lower initiator efficiency (45%) of the process resulting in an

Table 1. Polymerization of Michael Monomers with Lewis Pairs^a

run	monomer [M]	Lewis acid [LA]	Lewis base [LB]	[M]/[LA]	T (°C)	yield (%) ^b	M _n (10 ³ g mol ⁻¹) ^c	<i>D</i> M _w /M _n
1	FMA	AlPh ₃	PEt ₃	100	rt	88	64	1.16
2	FMA	AlPh ₃	PCy ₃	100	rt	85	121	1.38
3	<i>n</i> BuMa	AlPh ₃	PMe ₃	100	rt	100	42	1.00
4	<i>n</i> BuMa	AlPh ₃	P <i>n</i> Hex ₃	100	rt	100	62	1.04
5	<i>t</i> BuMa	AlMe ₃	PMe ₃	200	rt	100	61	1.01
6	<i>t</i> BuMa	AlMe ₃	PEt ₃	200	rt	100	102	1.05
7	<i>t</i> BuMa	AlMe ₃	PCy ₃	200	rt	100	458	1.08
8	DMAA	AlMe ₃	PMe ₃	200	-30	100	127	1.08
9	DMAA	AlMe ₃	PMe ₃	500	-30	100	181	1.14
10	DEVP	AlPh ₃	PEt ₃	100	-30	75	55	1.33
11	DEVP	AlPh ₃	PEt ₃	100	-10	100	148	1.42
12	DEVP	AlPh ₃	P <i>n</i> Hex ₃	100	-30	93	84	1.38
13	4-VP	AlEt ₃	PMe ₃	100	rt	92	84	1.21
14	4-VP	AlEt ₃	PCy ₃	100	rt	17	46	1.20
15	4-VP	Al <i>i</i> Bu ₃	PMe ₃	100	rt	20	18	1.44

^aConditions: All polymerization reactions were conducted at rt for 60 min (90 min in the case of *n*BuMA) and a LA/LB ratio of 2; total reaction volume 2.5 mL (solvent toluene). ^bConversion and yields of the isolated polymers were determined by ¹H and ³¹P NMR spectroscopy and confirmed by gravimetric methods. ^cDetermined by GPC with multi-angle laser light scattering (MALS) or dual angle laser light scattering detection methods in H₂O/THF (9 g/L tetrabutylammonium bromide) or THF at 40 °C.

Chart 1. Linear Growth of the Mean Molecular Weight of Poly(furfurylmethacrylate) with Increasing Conversion



increased molecular weight of 62 000, whereas dispersity stays narrow at 1.04 (run 4, Table 1).

After achieving these promising results for *n*-butyl-methacrylate, we switched to the sterically even more demanding *t*-butyl-methacrylate. The *t*-butyl substituent has a higher electron-donating nature. Since catalyst deactivation proceeds presumably via a too strong coordination of the monomer to the Lewis acid, we used an even less acidic Lewis acid (AlMe₃, (FIA: 343.0 kJ/mol))^{36,37} for our polymerization attempts. As a Lewis base, a sterically unhindered phosphine should facilitate the initiation process because of the high degree of steric demand of the monomer (PMe₃, $\Theta = 117^\circ$).³⁰ These assumptions are confirmed by our results (runs 5–7, Table 1). Conducting the polymerization with the Lewis pair AlMe₃/PMe₃ leads to poly(*t*BuMA) with a number-averaged molecular weight of 61 000 g/mol (initiator efficiency of 93%) and a surprisingly narrow dispersity of 1.01 (run 5, Table 1). The reaction shows full conversion within 60 min. The influence of the steric encumbrance of the phosphine on the initiation degree can be clearly evidenced by the comparison of PMe₃, PEt₃, and PCy₃. An increase in steric hindrance (Tolman angle increasing from 117° to 132° to 170°)³⁰ leads to lower initiator efficiencies (decreasing from 95 to 56 to 12%) as well

as to slightly broadened dispersities (*D* increasing from 1.01 to 1.05 to 1.08), supposing a delayed initiation process.

Based on the zwitterionic propagating species, proposed as the active species for conjugate-addition polymerization,¹⁹ the steric demand of the catalyst pair has a high impact not only on the initiator activity of the polymerization but also on the microstructure of the produced polymers (runs 1–2, Table 2).

Table 2. Synthesis of Poly(*t*BuMA) with Enriched Tacticity^a

run	Lewis acid [LA]	Lewis base [LB]	yield (%) ^b	M _n (10 ³ g mol ⁻¹) ^c	<i>D</i> M _w /M _n	mm ^d	rr ^d
1	AlEt ₃	PEt ₃	95	66	1.11	0.00	0.61
2	AlEt ₃	PCy ₃	100	61	1.30	0.00	0.78

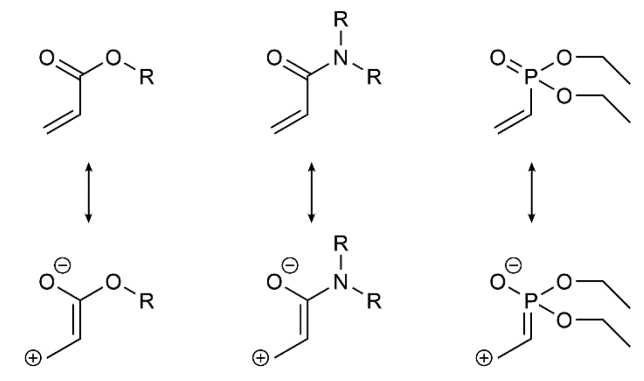
^aConditions: All polymerization reactions were conducted at room temperature for 60 min, a M/LA ratio of 50 and a LA/LB ratio of 2; total reaction volume 2.5 mL (toluene). ^bConversion and yields of the isolated polymers were determined by ¹H and ³¹P NMR spectroscopy and confirmed by gravimetric methods. ^cDetermined by GPC with MALS in THF at 40 °C. ^dDetermined by triad analysis with ¹³C NMR spectroscopy.³⁷

The influence on the tacticity of the produced polymer can be tailored by the steric demand of the Lewis base and acid. Whereas steric unhindered combinations afford a facilitated initiation process with a narrow dispersity (1.11) but a lower degree of tacticity (rr = 61%) of the resulting polymer (run 1, Table 2), switching to steric encumbered pairs gives a higher syndiotacticity of the final product (rr = 78%) combined with a broader molecular weight distribution (run 2, Table 2).

Another fascinating class of acrylic polymers are poly-(acrylamides). Due to their high polarity, they possess a broad application field,^{38–43} which varies from floating⁴³ to gelling^{39,40,44,45} agents to oil production additives.⁴² Nevertheless, their high reactivity makes a precise polymerization of the corresponding monomers challenging. According to the above-described observations, a less acidic Lewis acid is needed for a successful polymerization of the electron rich *N,N*-dimethylacrylamide (DMAA). By using a combination of AlMe₃ and PMe₃ as catalyst, polymeric material with a

molecular weight of 127 000 g/mol and a narrow dispersity of 1.08 can be obtained with quantitative conversion (run 8, Table 1). The reaction can be still conducted at a monomer to catalyst ratio of 500, which leads to a higher molecular weight (181 000 g/mol) and a slightly broadened molecular weight distribution of 1.14 (run 9, Table 1). The structural similarity of Michael monomers encouraged us to examine the catalytic activity for another monomer class, which deserved enormous attention within the last years: vinylphosphonates (Scheme 1).^{3,31,46–49}

Scheme 1. Proposed Structural Similarity of (Meth)acrylates, (Meth)acrylamides, and Vinylphosphonates



First attempts to polymerize diethylvinylphosphonate (DEVP) with main-group element catalysts containing tris-(pentafluorophenyl)alane led to unsatisfying results.¹⁹ This can be clearly attributed to the highly acidic nature of this Lewis acid. The results of our work imply that a weaker Lewis acid (AlPh_3) would lead to a controlled polymerization for diethylvinylphosphonate (runs 10–12, Table 1). Within 60 min reaction time, poly(DEVP) with a mean molecular mass of 55 000 g/mol and a molecular weight distribution of 1.33 can be obtained in a monomer to catalyst ratio of 100 (run 10, Table 1). Increasing the reaction temperature from -30 to -10 °C leads to a higher degree of side reactions, which can be deduced from an increased polydispersity of 1.42 (run 11, Table 1).

DEVP shows, in comparison to classical (meth)acrylates, a slightly broader molecular weight distribution and a lower initiator efficiency. This observation deserves special attention since it can be helpful for further catalyst design. Therefore, we

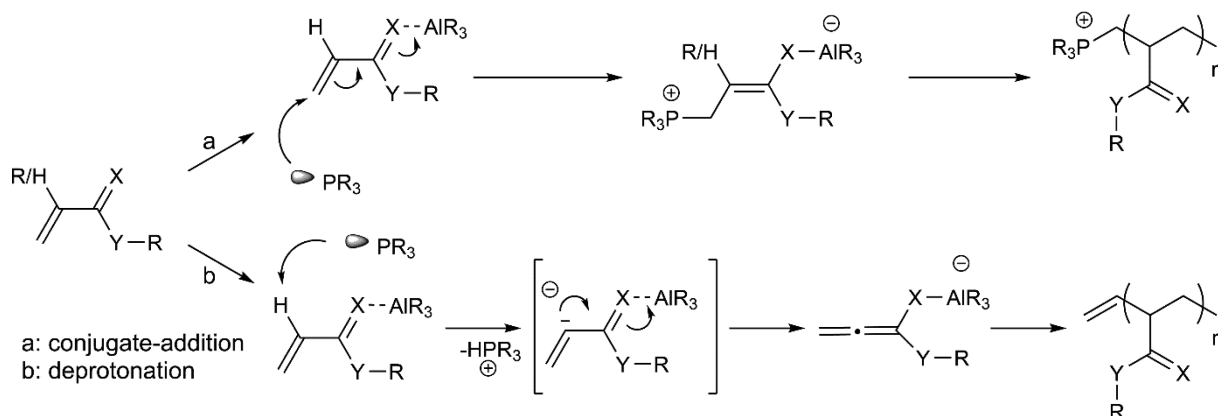
performed ESI-MS analysis of a 1:1 mixture of the catalyst and monomer. The spectrum shows two different series of masses (Figure S6). The first can be clearly attributed to the conjugate-addition mechanism. This initiation starts with the nucleophilic addition of the phosphine to the monomer (Scheme 2, conjugate-addition pathway). The second series is induced by the deprotonation of the α -carbon, which leads to an active species with cumulated double bond (Scheme 2, deprotonation pathway). Propagation yields oligomers/polymers with unsaturated chain-ends. The competing character of these two initiating pathways can be also seen by temperature variation. Increasing the temperature to -10 °C leads to a broadened molecular weight distribution (1.42) as well as to a higher molecular weight (148 000 g/mol, run 11, Table 1). Since micro-gc measurements do not show an increase of methane concentration with increasing concentration of Lewis acid (Figure S4), we can rule out that deprotonation occurs via the alkyl ligand of the Lewis acid. Methane formation presumably derives from residual water of the monomer. As a consequence, deprotonation should occur via free phosphine in solution. This assumption is reassured by the fact that a more basic phosphine (P^nHex_3 , $\text{p}K_a = 9.7$, PEt_3 , $\text{p}K_a = 8.7$)²⁹ leads to slightly broadened dispersity (1.38, run 12, Table 1) and a higher molecular weight (93 000 g/mol), resulting from an enhanced competition of the two initiation mechanisms. Suppression of one of these mechanisms significantly enhances the precision of the polymerization of α -acidic, heterofunctionalized monomers and is part of the ongoing research in our group.

According to quantum chemical calculations, the chain initiation is the rate-determining step in conjugate-addition polymerization.¹⁹

The results of our kinetic investigation imply that this process follows a bimetallic chain initiation mechanism (Figures S2 and S3), in which the active chain is transferred to a preactivated monomer molecule, whereas a reaction order of one with respect to initiator indicates that only one phosphine is involved in the initiation process. These findings are in accordance with the theoretical calculations.¹⁹

After the successful polymerization of heteroatom-containing acrylate analogues, we investigated the possibility to extend the applicability of this method even beyond the boundaries of the classical Michael structure. One prominent example for such an “extended” Michael system is 4-vinylpyridine (4-VP).^{50,51} The catalytic polymerization has not been possible up to now due to the constraint geometry of initiating group and metal center in

Scheme 2. Possible Mechanisms of the Initiation Process of the Lewis Pair-Mediated Polymerization of Polar Monomers

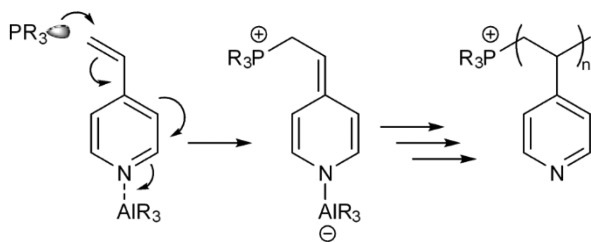


classical catalysts. Living radical polymerization techniques have been, so far, the only pathway for a controlled synthesis.^{50,52}

By applying our approach for the polymerization of 4-VP, we can show that the method is not bound to a conventional Michael system. Due to the electron-rich character of 4-VP, we used AlEt₃ as slightly acidic Lewis acid in combination with PMe₃. With this catalyst pair, poly(4-VP) with a narrow dispersity of 1.21 and a molecular weight of 84 000 g/mol (run 13, Table 1) can be obtained. 4-VP is an ideal candidate to demonstrate the importance of the appropriate choice of the Lewis pair. Whereas the Lewis couple AlEt₃/PMe₃ leads to a well-defined polymeric material in high yield (92%), switching to PCy₃ as alternative initiator dramatically decreases the yield (17%, run 14, Table 1). Using Al(*i*Bu)₃ as Lewis acid in combination with PMe₃ negatively affects the yield (20%), and an inferior material in terms of molecular weight distribution (1.44) is obtained (run 15, Table 1).

To gain a deeper understanding which initiation mechanism is involved in the polymerization of this extended Michael monomer, we again performed ESI-MS analyses of short-chain oligomers. They reveal that the phosphine is directly bound to the chain end (Figure S7). Hence, most presumably, the double-bond activation can be achieved even over several bonds, following a mechanism shown in Scheme 3.

Scheme 3. Initial Step of the Lewis Pair-Mediated Polymerization of 4-VP



CONCLUSION

In this report we presented the precision polymerization of Michael-type monomers with HIPs. In comparison to well-established rapid radical polymerization techniques like SET-LRP, this Lewis pair approach does not rely on (water-soluble) metal salt catalysts. Therefore, this method is an attractive alternative especially for unpolar methacrylates (*t*BuMA, *n*BuMA) or polar monomers, which cannot be polymerized radically (FMA, DEVP) due to chain-transfer reactions. The remarkably active combinations of simple aluminum and phosphorus compounds afford the living polymerization of a broad variety of sterically demanding and functionalized monomers with high initiator efficiencies. In addition, the applicability can be even extended beyond Michael-type structures, as evidenced by the first catalytic polymerization of the prolonged Michael system 4-VP. Another evident advantage of this system is the possibility to easily influence the key parameters of the polymer products like molecular mass or tacticity by the choice of the Lewis pair. Whereas mass spectrometric analyses clearly proof phosphine as the initiating group, our kinetic analysis suggests that the initiation step proceeds via a transfer of the zwitterionic intermediate to a preactivated monomer molecule. Furthermore, we could develop a deeper understanding about the side reactions of

this initiation, enabling new approaches for a tailor-made catalyst design.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04129.

Experimental procedures, further analytical and characterization data for polymers (PDF)

Crystallographic data (CIF)

CIF/PLATON report (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*; CRC Press: Boca Raton, FL, 2007.
- Kreimeyer, A.; Eckes, P.; Fischer, C.; Lauke, H.; Schuhmacher, P. *Angew. Chem., Int. Ed.* **2015**, *54*, 3178.
- Soller, B. S.; Salzinger, S.; Rieger, B. *Chem. Rev.* **2016**, *116*, 1993.
- Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6186.
- Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
- Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 1465.
- Chieffari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. *Macromolecules* **1998**, *31*, 5559.
- Sciannamea, V.; Jérôme, R.; Detrembleur, C. *Chem. Rev.* **2008**, *108*, 1104.
- Monteiro, M. J.; de Brouwer, H. *Macromolecules* **2001**, *34*, 349.
- Percec, V.; Guliasvili, T.; Ladislav, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156.
- Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109*, 5069.
- Anastasaki, A.; Nikolaou, V.; Nurumbetov, G.; Wilson, P.; Kempe, K.; Quinn, J. F.; Davis, T. P.; Whittaker, M. R.; Haddleton, D. M. *Chem. Rev.* **2016**, *116*, 835.
- Enayati, M.; Jezorek, R. L.; Monteiro, M. J.; Percec, V. *Polym. Chem.* **2016**, *7*, 3608.
- Gavrilov, M.; Zerk, T. J.; Bernhardt, P. V.; Percec, V.; Monteiro, M. J. *Polym. Chem.* **2016**, *7*, 933.
- Nguyen, N. H.; Rosen, B. M.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1752.
- Cameron, P. A.; Gibson, V. C.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329.
- Yasuda, H.; Ihara, E. *Macromol. Chem. Phys.* **1995**, *196*, 2417.
- Hultsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227.
- Zhang, Y.; Miyake, G. M.; John, M. G.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *J. Chem. Soc., Dalton Trans.* **2012**, *41*, 9119.

- (20) Zhang, Y.; Miyake, G. M.; Chen, E. Y. X. *Angew. Chem.* **2010**, *122*, 10356.
- (21) Celiz, A.; Smith, J.; Patel, A.; Langer, R.; Anderson, D.; Barrett, D.; Young, L.; Davies, M.; Denning, C.; Alexander, M. *Biomater. Sci.* **2014**, *2*, 1604.
- (22) Tarducci, C.; Badyal, J. P. S.; Brewer, S. A.; Willis, C. *Chem. Commun.* **2005**, 406.
- (23) Goiti, E.; Huglin, M. B.; Rego, J. M. *Eur. Polym. J.* **2004**, *40*, 219.
- (24) Kavitha, A. A.; Singha, N. K. *Macromol. Chem. Phys.* **2007**, *208*, 2569.
- (25) Davidenko, N.; Zaldívar, D.; Peniche, C.; Sastre, R.; San Román, J. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2759.
- (26) Haartz, J.; McDaniel, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 8562.
- (27) Larson, J.; McMahan, T. *J. Am. Chem. Soc.* **1985**, *107*, 766.
- (28) Müller, L. O.; Himmel, D.; Stauffer, J.; Steinfeld, G.; Slattery, J.; Santiso-Quiñones, G.; Brecht, V.; Krossing, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 7659.
- (29) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.
- (30) Müller, T. E.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533.
- (31) Salzinger, S.; Soller, B. S.; Plikhta, A.; Seemann, U. B.; Herdtweck, E.; Rieger, B. *J. Am. Chem. Soc.* **2013**, *135*, 13030.
- (32) $M_n(\text{theo})/M_n(\text{real}) \times 100\%$; $M_n(\text{theo}) = [M]/[P] \times M_{\text{monomer}}$
- (33) He, J.; Zhang, Y.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *Macromolecules* **2014**, *47*, 7765.
- (34) *Acrylates: Advances in Research and Application* Acton, Q. A., Ed.; Scholarly Editions: Atlanta, GA, 2012
- (35) Timoshkin, A. Y.; Frenking, G. *Organometallics* **2008**, *27*, 371.
- (36) Damrauer, R.; Krempp, M.; Damrauer, N. H.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 5218.
- (37) Varshney, S. K.; Gao, Z.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 1076.
- (38) Banks, M.; Ebdon, J. R.; Johnson, M. *Polymer* **1994**, *35*, 3470.
- (39) Choules, G. L.; Zimm, B. H. *Anal. Biochem.* **1965**, *13*, 336.
- (40) Vimala, K.; Sivudu, K. S.; Mohan, Y. M.; Sreedhar, B.; Raju, K. M. *Carbohydr. Polym.* **2009**, *75*, 463.
- (41) Zhang, K.; Wu, W.; Guo, K.; Chen, J.; Zhang, P. *Langmuir* **2010**, *26*, 7971.
- (42) Sparlin, D. D.; Hagen, R. *Oil World* **1984**, *199*, 137.
- (43) Shing, J. B. W.; Tubergen, K. R. U.S. Patent 6019904, February 1, 2000.
- (44) Hu, Z.; Zhang, X.; Li, Y. *Science* **1995**, *269*, 525.
- (45) Tan, J.; Gemeinhart, R. A.; Ma, M.; Saltzman, W. M. *Biomaterials* **2005**, *26*, 3663.
- (46) Salzinger, S.; Seemann, U. B.; Plikhta, A.; Rieger, B. *Macromolecules* **2011**, *44*, 5920.
- (47) Seemann, U. B.; Dengler, J. E.; Rieger, B. *Angew. Chem., Int. Ed.* **2010**, *49*, 3489.
- (48) Altenbuchner, P. T.; Soller, B. S.; Kissling, S.; Bachmann, T.; Kronast, A.; Vagin, S. I.; Rieger, B. *Macromolecules* **2014**, *47*, 7742.
- (49) Macarie, L.; Ilia, G. *Prog. Polym. Sci.* **2010**, *35*, 1078.
- (50) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 3531.
- (51) Nishide, H.; Tsuchida, E. *Makromol. Chem.* **1976**, *177*, 2295.
- (52) Convertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 4679.