

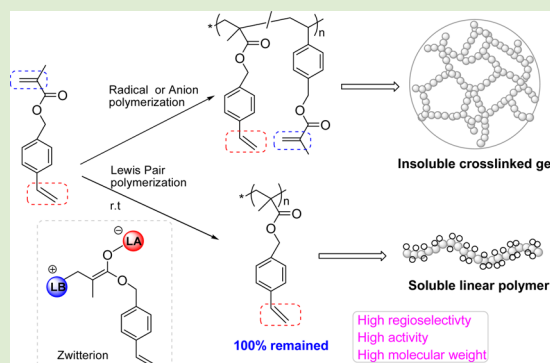
# Controlled Divinyl Monomer Polymerization Mediated by Lewis Pairs: A Powerful Synthetic Strategy for Functional Polymers

Yin-Bao Jia, Wei-Min Ren, Si-Jie Liu, Tieqi Xu, Yan-Bo Wang, and Xiao-Bing Lu\*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian, 116024, China

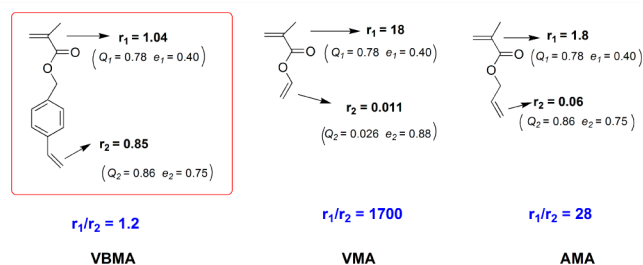
**S** Supporting Information

**ABSTRACT:** Lewis pair cooperation provides a facile approach for polymerizing dissymmetric divinyl polar monomers such as 4-vinylbenzyl methacrylate in excellent regioselectivity and high reactivity at mild conditions, affording soluble polymers bearing pendant active vinyl groups with high molecular weight (up to  $6.4 \times 10^5$  g/mol) and narrow polydispersity ( $PDI < 1.5$ ). ESI-TOF MS study demonstrated that the polymerization process only concerned the methacrylic double bond and selectively remained the pendant allylic or styrene C=C bond.



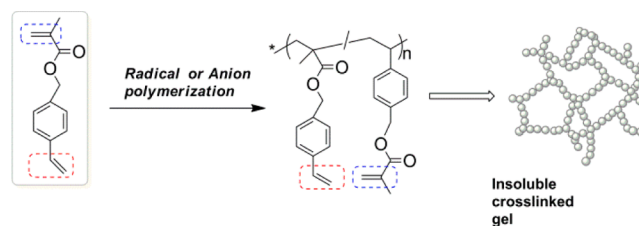
Polymers bearing pendant active vinyl groups on the backbone have many applications in material chemistry, for example, preparing the cross-linked,<sup>1–7</sup> hyperbranched,<sup>8–10</sup> and functionalized polymers.<sup>11–20</sup> Nevertheless, it is a challenging task for chemists to keep one reactive vinyl group in each repeat unit of a polymer. Selective polymerization of one vinyl group of divinyl monomers such as allyl methacrylate (AMA) is seemed to be a practical and straightforward method. With respect to the reactivity discrepancy of the two vinyl groups, anion polymerization<sup>21–23</sup> and radical polymerization<sup>24–29</sup> are two much-studied methods. Unfortunately, the reactivity difference between two types of C=C bonds could not safeguard that the polymerization only occurred in one kind of vinyl group in the whole reaction process. In the early stage, polymerization predominantly took place in the methacrylic C=C double bond due to its relatively higher reactivity. However, as reaction proceed, the polymerization readily occurred in the pendant C=C bond and, thus, formed the cross-linking network until the reaction mixture turned to gelation at last.<sup>26</sup> Especially for the monomer 4-vinylbenzyl methacrylate (VBMA), in which the methacrylate C=C double bond ( $r_1 = 1.04$ ) and styrene ( $r_2 = 0.85$ ) nearly have the same reactivity (Figure 1) for radical polymerization, the reaction mixture easily turns to gel even at the beginning of the reaction (Scheme 1). Indeed, the exploration of controlled divinyl monomer polymerization for preparing soluble polymers bearing pendant active vinyl groups with high molecular weight and narrow polydispersity under mild conditions still remains a challenging problem. For example, Pugh and Percec reported the synthesis of PVBMA using group transfer polymerization method, affording the polymers with broad molecular weight distribution ( $M_w/M_n = 8.2$ ).<sup>30</sup>

Recently, Baskaran and co-workers realized the selective anionic polymerization of VBMA through methacrylate



**Figure 1.** Reactivity discrepancy of the two vinyl groups in the divinyl monomers for free-radical polymerization. For monomers ( $Q, e$ ) values are cited from Polymer Handbook,<sup>42</sup> and reactivity ratios were calculated on the basis of Alfrey-Price equations:  $r_1 = (Q_1/Q_2) \times \exp[-e_1(e_1 - e_2)]$ ;  $r_2 = (Q_2/Q_1) \times \exp[-e_2(e_2 - e_1)]$ .

## Scheme 1. Free Radical or Anion Polymerization of 4-Vinylbenzyl Methacrylate (VBMA)



functionality of the monomer in a controlled manner, employing resonance-stabilized anionic initiators such as 1,1-diphenylhexyllithium and tritylpotassium at a low temperature of  $-78$  °C.<sup>22</sup>

**Received:** July 18, 2014

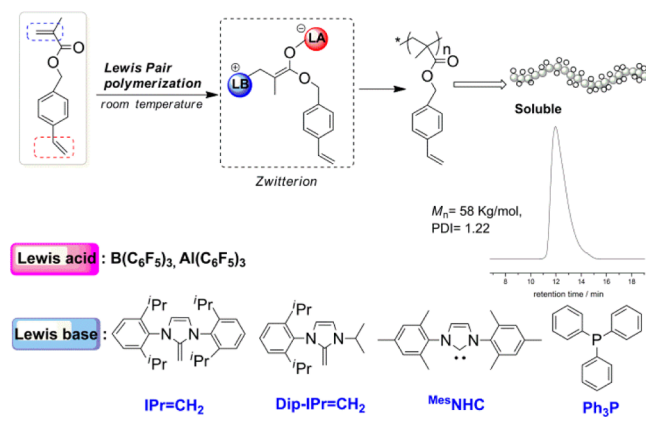
**Accepted:** August 22, 2014

**Published:** August 27, 2014

However, uncontrolled molecular weight and broad distribution were unavoidably got when the reaction temperature was increased to  $-20\text{ }^{\circ}\text{C}$ . More recently, Hirao group reported the success of the synthesis of noncrosslinked and well-defined polymers with pendant double bonds by anionic polymerization of divinylbenzene at  $-78\text{ }^{\circ}\text{C}$ .<sup>23</sup> Prior to these studies, Kamigaito group reported the regiospecific radical polymerization of vinyl methacrylate (VMA) to prepare soluble polymers by addition of Lewis acid such as  $\text{SnCl}_4$ ,  $\text{Et}_n\text{AlCl}_{3-n}$ , and  $\text{R}_n\text{Al}(\text{ODBP})_{3-n}$  ( $\text{R} = \text{Me, Et, } i\text{-Bu}$ ; ODBP: 2,6-di-*tert*-butyl phenoxy).<sup>29</sup> The main disadvantages are the need to the addition of large quantities of Lewis acid and the broad molecular weight distribution ( $\text{PDI} > 3$ ) associated with the resultant polymers. It is worthwhile noting here parenthetically that though the copolymerization of cross-linker (e.g., divinylbenzene) in controlled radical polymerization processes showed retarded gelation behavior, the complete avoidance of gelation formation proved to be impossible, especially at high conversions of more than 70%.<sup>31</sup>

In this communication, we reported a novel method for perfectly regioselective polymerization of VBMA (Scheme 2)

### Scheme 2. Lewis Pairs Mediated Polymerization of VBMA



and various divinyl monomers at the methacrylic  $\text{C}=\text{C}$  bond with the simple Lewis acid–base pairs at mild conditions,

affording soluble polymers with high molecular weight and narrow polydispersity.

Since Stephan and Erker first uncovered the concept “frustrated Lewis pairs” (FLPs), FLP chemistry has attracted a great interest of chemists.<sup>32</sup> FLP, combined by bulky Lewis acid and Lewis base, performed excellent activity in activating small molecules.<sup>33</sup> The next significant study by Chen group came with the use of Lewis acid–base pairs for polymerizing a series of polar vinyl monomers such as methyl methacrylate and  $\alpha$ -methylene- $\gamma$ -butyrolactone with excellent activity and highly molecular weight.<sup>34–36</sup> Furthermore, they succeeded in preparing *N*-functionalized vinyl polymers by FLPs mediated polymerization of 2-vinylpyridine or 2-isopropenyl-2-oxazoline.<sup>37</sup> Recently,  $\text{Zn}(\text{C}_6\text{F}_5)_2$ -based Lewis pair was applied into the ring-opening polymerization of heterocyclic monomers such as lactide and lactone.<sup>38,39</sup> More recently, our group reported the Lewis pairs consisting of *N*-heterocyclic olefins and  $\text{Al}(\text{C}_6\text{F}_5)_3$  for highly active polymerization of acrylate monomers.<sup>40</sup> A polymerization mechanism concerning initiation and deactivation was proposed on the basis of ESI-MS study. For Lewis pair mediated polymerization of acrylic monomers, it is generally known that the conjugated structure of methacryloyl group is crucial to make this reaction happen.<sup>34</sup> This fact inspires us to probe into the regioselective polymerization of divinyl polar monomers using Lewis pair systems, in which polymerization only occurs at the conjugated methacrylic  $\text{C}=\text{C}$  bond and leaves the pendant  $\text{C}=\text{C}$  bond unreacted (Scheme 2).

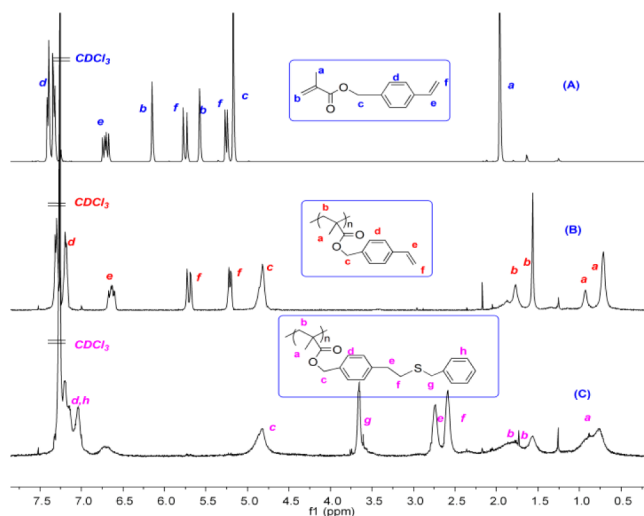
Since a stable adduct easily forms by the interaction of Lewis base and Lewis acidic activator, the preactivation of these polar monomers by Lewis acid is a prerequisite for their rapid transformation. Therefore, the monomers were premixed with Lewis acid before the addition of Lewis base. The polymerization results are summarized in Table 1. Initially, the polymerization of VBMA was conducted with  $\text{B}(\text{C}_6\text{F}_5)_3/\text{IPr}=\text{CH}_2$  Lewis pair, and no product was observed up to 24 h (run 1). When replaced  $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{Al}(\text{C}_6\text{F}_5)_3$ , the polymerization immediately happened at  $25\text{ }^{\circ}\text{C}$ . After 10 min, 100% conversion was achieved with toluene as solvent. The resulting  $\text{P}(\text{VBMA})$  has a high molecular weight ( $M_n = 4.2 \times 10^4\text{ g/mol}$ ) and narrow PDI (PDI

**Table 1. Selected Results of Polymerization of Asymmetric Divinyl Monomers Mediated by Lewis Pairs,<sup>a</sup> Anion or Radical<sup>b</sup>**

run	catalyst or initiator	monomer	monomer/base or initiator <sup>c</sup>	time (min)	conv. <sup>d</sup> (%)	$M_n^e$ ( $10^4\text{ g/mol}$ )	$\text{PDI}^e$ ( $M_w/M_n$ )	reaction mixture
1	$\text{B}(\text{C}_6\text{F}_5)_3/\text{IPr}=\text{CH}_2$	VBMA	100	1440	0			solution
2	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{IPr}=\text{CH}_2$	VBMA	100	10	100	4.2	1.39	solution
3	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$	VBMA	100	30	100	5.8	1.22	solution
4	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Ph}_3\text{P}$	VBMA	100	5	100	4.6	1.37	solution
5	$^t\text{BuLi}$	VBMA	100	60	10	nd	nd	gelation
6	AIBN	VBMA	100	120	37	nd	nd	gelation
7	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$	VMA	400	3	100	13.8	1.28	solution
8	AIBN	VMA	200	210	60	6.4 <sup>f</sup>	4.56 <sup>f</sup>	gelation
9	AIBN	VMA	400	120	54	3.5 <sup>f</sup>	2.31 <sup>f</sup>	gelation
10	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$	AMA	400	3	100	13.0	1.26	solution
11	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$	AMA	800	3	100	33.5	1.21	solution
12	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$	AMA	1600	5	100	64.0	1.28	solution
13	$\text{Al}(\text{C}_6\text{F}_5)_3/^t\text{Bu}_3\text{P}$	AMA	400	3	100	19.0	1.31	solution
14	$\text{Al}(\text{C}_6\text{F}_5)_3/\text{Me}_6\text{NHC}$	AMA	400	3	100	14.0	1.37	solution
15	AIBN	AMA	400	180	36	3.5 <sup>f</sup>	5.46 <sup>f</sup>	gelation

<sup>a</sup>Reaction conditions: Lewis pair polymerization was performed with 5 mL total solution volume (solvent toluene + monomer); room temperature (ca.  $25\text{ }^{\circ}\text{C}$ ). <sup>b</sup>Reaction conditions: Anion polymerization in THF at  $-78\text{ }^{\circ}\text{C}$ . Radical polymerization in toluene at  $60\text{ }^{\circ}\text{C}$ . <sup>c</sup>Molar ratio. <sup>d</sup>Monomer conversions measured by  $^1\text{H}$  NMR spectroscopy. <sup>e</sup>Determined by gel permeation chromatography in THF for PVBMA or  $\text{CHCl}_3$  for PVMA and PAMA, calibrated with polystyrene. <sup>f</sup>Soluble part. nd = not determined.

= 1.39; run 2). The  $^1\text{H}$  NMR spectrum shows the peaks at 6.15 and 5.58 ppm belong to the  $=\text{CH}_2$  (b) of methacrylic  $\text{C}=\text{C}$  bond of VBMA completely disappeared, indicating that there was no remaining of methacrylic  $\text{C}=\text{C}$  bond (Figure 2B). Mean-



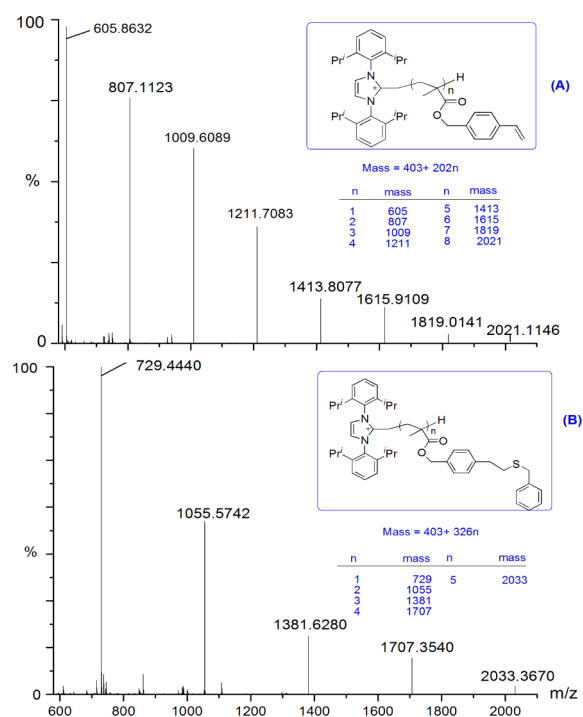
**Figure 2.**  $^1\text{H}$  NMR spectra of (A) VBMA, (B) PVBMA, and (C) P(VBMA-SCH<sub>2</sub>Ph).

while, the resonance intensity of the  $=\text{CH}_2$  (f) belong to styrene is nearly the same to the peak of  $-\text{CH}_2-$  (c) of the benzyl group, demonstrating that the  $\text{C}=\text{C}$  bond of styrene was unreacted in the polymerization (Figure 2B).  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$  Lewis pair gave a high molecular weight ( $M_n = 5.8 \times 10^4$  g/mol) and narrow monomodal distribution (PDI = 1.22; run 3). It was found that Lewis pair  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Ph}_3\text{P}$  was more active for polymerizing VBMA (run 4). In contrast, anion<sup>22</sup> or radical polymerization for initiating VBMA only provided an insoluble polymer even at a low conversion (runs 5 and 6). Additionally, the Lewis pairs exhibited high activity and excellent regioselectivity in polymerizing other divinyl monomers. Take VMA as an example, 100% conversion was achieved in 3 min with  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$  Lewis pair at a ratio of 400:1 for VMA to Lewis base. The resultant PVMA has high molecular weight ( $M_n = 1.38 \times 10^5$  g/mol) and narrow molecular weight distribution (PDI = 1.28; run 7; Figure S2). For comparison purposes, radical polymerization of VMA with AIBN as initiator was also performed at 60 °C. Although the great reactivity discrepancy of the two vinyl groups in the VMA ( $r_1/r_2 = 1700$ ), the gelation was turned out even the conversion less than 60% (runs 8 and 9). Meanwhile, from the  $^1\text{H}$  NMR spectrum of the soluble part of the resulted polymer, we can still find the peaks of unreacted methacryloyl vinyl protons (Figure S1B), indicating irregular chain propagation happened.

In order to demonstrate the availability of Lewis pair polymerization for divinyl polar monomers, we polymerized AMA at a high ratio of 1600 equiv (AMA to base). Gratifyingly, AMA could be consumed in 30 min with  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{Dip-IPr}=\text{CH}_2$  pair, affording polymer with a high  $M_n$  of  $6.4 \times 10^5$  g/mol and low PDI of 1.28 (run 12), which also have good solubility in many reagents such as  $\text{CH}_2\text{Cl}_2$ , EtOAc and so on (Figure S4, right). On the contrary, the PAMA produced by radical polymerization even at a low conversion did not dissolve in any reagent (Figure S4, left). As expected, the Lewis pair  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{tBu}_3\text{P}$  or  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{MesNHC}$  also performed similar

reactivity and regioselectivity in the polymerization of AMA (runs 13 and 14).

Furthermore, the excellent regioselectivity of Lewis pair mediated polymerization of dissymmetric divinyl monomers was confirmed by the ESI-TOF MS study. Since the strong basicity of  $\text{IPr}=\text{CH}_2$ , the propagating polymer chains associated with the Lewis base have the strong signal responsibility in the ESI-TOF mass spectroscopy. P(VBMA) with low molecular weight was prepared by  $\text{Al}(\text{C}_6\text{F}_5)_3/\text{IPr}=\text{CH}_2$  Lewis pair at low ratio for ESI-TOF MS investigation. In the ESI-TOF mass spectra in the positive ion mode, we clearly observe the species based on  $m/z = 403$  (the MW of  $\text{IPr}=\text{CH}_2$ ) at an interval of 202 (the repeat unit of VBMA; Figure 3A).



**Figure 3.** Representative ESI-MS spectra of (A) PVBMA and (B) P(VBMA-SCH<sub>2</sub>Ph).

It is generally known that the polymers with vinyl groups can be functionalized by “thiol–ene” reaction.<sup>41</sup> Therefore, further modification of the linear polymer PVBMA bearing pendant  $\text{IPr}=\text{CH}_2$  at an interval of 202 (the repeat unit of VBMA) active vinyl groups using  $\text{PhCH}_2\text{SH}$  in THF was carried out at 70 °C for 24 h, with AIBN as initiator. Click reaction between the pendant double bond of PVBMA and  $\text{PhCH}_2\text{SH}$  was rapidly and completely, demonstrated by  $^1\text{H}$  NMR (Figure 2C) and ESI-TOF MS (Figure 3B) analysis. The resultant crude product could be purified by precipitation in THF/methanol mixture solvent. After click reaction with  $\text{PhCH}_2\text{SH}$ ,  $^1\text{H}$  NMR spectra (Figure 2B,C) showed that the peaks at 6.64, 5.72, and 5.21 ppm belong to the pendant  $\text{Ph}(\text{H})\text{C}=\text{CH}_2$  disappeared and new peaks at 2.74 and 2.58 ppm appeared, indicating all the pendant double bonds have been reacted. ESI-TOF MS study of the functionalized PAMA was also performed. A series of species based on  $m/z$  403 at an interval of 326 was found (Figure 3B). The deduction value of polymer chains before and after click reaction is just 124n (the molecular weight of  $\text{PhCH}_2\text{SH}$  is 124). This result again clearly proved the polymerization process of VBMA



mediated by Lewis pair only regarded the methylacrylic C=C bond.

In conclusion, we have reported an effective approach for completely regioselective polymerization of dissymmetric divinyl monomers at the methylacrylic C=C bond under mild conditions. The resultant polymers with high molecular weight and narrow molecular weight distribution are soluble in various organic solvents. ESI-TOF MS gave the further evidence that there was no cross-linking side reaction happened in the polymerization process. This simple and convenient method will open up a new route for producing functional polymers with pendant active vinyl groups, possessing many applications in material chemistry.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

(1) Representative procedures for polymerization; (2) Characterization of the polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [lxh-1999@163.com](mailto:lxh-1999@163.com).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Gratitude is expressed to Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP, Grant 20130041130004), and Program for Changjiang Scholars and Innovative Research Team in University (IRT13008). X.-B.L. gratefully acknowledges the Chang Jiang Scholars Program (T2011056) from Ministry of Education of the People's Republic of China.

## ■ REFERENCES

- (1) Baek, K. Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215–221.
- (2) Cherian, A. E.; Sun, F. C.; Sheiko, S. S.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129*, 11350–11351.
- (3) Dong, Z. M.; Liu, X. H.; Liu, H. W.; Li, Y. S. *Macromolecules* **2010**, *43*, 7985–7992.
- (4) Dong, Z. M.; Liu, X. H.; Liu, H. W.; Li, Y. S. *Macromolecules* **2009**, *42*, 4596–4603.
- (5) Gao, H. F.; Miasnikova, A.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 7843–7849.
- (6) Sui, X. F.; Hempenius, M. A.; Vancso, G. *J. Am. Chem. Soc.* **2012**, *134*, 4023–4025.
- (7) Michael, S.; Wendland, M. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 1389–1390.
- (8) Barker, I. A.; Harfi, J. E.; Adlington, K.; Howdle, S. M.; Irvine, D. J. *Macromolecules* **2012**, *45*, 9258–9266.
- (9) Lin, Y.; Liu, X. H.; Li, X. R.; Zhan, J.; Li, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 26–40.
- (10) Powell, K. T.; Cheng, C.; Wooley, K. L. *Macromolecules* **2007**, *40*, 4509–4515.
- (11) Wang, R.; Chen, W.; Meng, F. H.; Cheng, R.; Deng, C.; Jan, F. J.; Zhong, Z. Y. *Macromolecules* **2011**, *44*, 6009–6016.
- (12) Zhou, J. R.; Chen, P. P.; Deng, C.; Meng, F. H.; Cheng, R.; Zhong, Z. Y. *Macromolecules* **2013**, *46*, 6723–6730.
- (13) David, M.; Stevens, S. T.; Dove, A. P.; Harth, E. *ACS Macro Lett.* **2012**, *1*, 915–918.
- (14) Zhang, H. M.; Ruckenstein, E. *Macromolecules* **1999**, *32*, 5495–5500.

(15) Zhang, J. F.; Ren, W. M.; Sun, X. K.; Meng, Y.; Du, B. Y.; Zhang, X. H. *Macromolecules* **2011**, *44*, 9882–9886.

(16) Ruckenstein, E.; Zhang, H. M. *Macromolecules* **1999**, *32*, 6082–6087.

(17) Liu, F. T.; Liu, G. J. *Macromolecules* **2001**, *34*, 1302–1307.

(18) Gress, A.; Volkel, A.; Schlaad, H. *Macromolecules* **2007**, *40*, 7928–7933.

(19) Tempelaar, S.; Mespouille, L.; Dubois, P.; Dove, A. P. *Macromolecules* **2011**, *44*, 2084–2091.

(20) Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 229–230.

(21) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 3764–3774.

(22) Mohan, Y. M.; Raghunadh, V.; Sivaram, S.; Baskaran, D. *Macromolecules* **2012**, *45*, 3387–3393.

(23) (a) Tannka, S.; Matsumoto, M.; Goseki, R.; Ishizone, T.; Hirao, A. *Macromolecules* **2013**, *46*, 146–154. (b) Tannka, S.; Goseki, R.; Ishizone, T.; Hirao, A. *Macromolecules* **2014**, *47*, 2333–2339.

(24) Parí S, R. J.; Fuente, L. D. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2395–2406.

(25) Parí S, R. J.; Fuente, L. D. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6247–6261.

(26) Vardareli, T. K.; Keskin, S.; Usanmaz, A. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*, 302–311.

(27) Nagelsdiek, R.; Mennicken, M.; Maier, B.; Keul, H.; Hartwig, H. *Macromolecules* **2004**, *37*, 8923–8932.

(28) Ma, J.; Cheng, C.; Sun, G. R.; Wooley, K. L. *Macromolecules* **2008**, *41*, 9080–9089.

(29) Sugiyama, F.; Satoh, K.; Kamigaito, M. *Macromolecules* **2008**, *41*, 3042–3048.

(30) Pugh, C.; Percec, V. *Polym. Bull. (Berlin)* **1985**, *14*, 109–116.

(31) (a) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350. (b) Koh, M. L.; Konkolewicz, D.; Perrier, S. *Macromolecules* **2011**, *44*, 2715–2724.

(32) Selected reviews: (a) Frustrated Lewis Pairs I and II. *Top. Curr. Chem.*; Stephan, D. W., Erker, G., Eds.; Springer: New York, 2013; Vols. 332 and 334. (b) Erker, G. *Pure Appl. Chem.* **2012**, *84*, 2203–2217. (c) Stephan, D. W. *Org. Biomol. Chem.* **2012**, *10*, 5740–5746. (d) Erker, G. *Dalton Trans.* **2011**, *40*, 7475–7483. (e) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76. (f) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136. (g) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535–1539.

(33) Selected recent examples: (a) Ménard, G.; Hatnean, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 6446–6449. (b) Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 4974–4977. (c) Chernichenko, K.; Madarász, A.; Pápai, I.; Nieger, M.; Leskela, M.; Repo, T. *Nat. Chem.* **2013**, *5*, 718–723. (d) Sajid, M.; Kehr, G.; Wiegand, T. H.; Eckert, C.; Schwickert, R.; Pöttgen, A. J.; Cardenas, P.; Warren, T. H.; Fröhlich, R.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 8882–8895.

(34) (a) Zhang, Y. T.; Miyake, G. M.; Chen, E. Y.-X. *Angew. Chem., Int. Ed.* **2010**, *49*, 10158–10162. (b) Zhang, Y. T.; Miyake, G. M.; John, M. G.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *Dalton Trans.* **2012**, *41*, 9119–9134.

(35) Chen, E. Y.-X. *Top. Curr. Chem.* **2013**, *334*, 239–260.

(36) Xu, T. Q.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2014**, *136*, 1774–1777.

(37) He, J.; Zhang, Y. T.; Chen, E. Y.-X. *Synlett* **2014**, *25*, 1534–1538.

(38) Piedra-Arroni, E.; Ladavière, C.; Abderrahmane, A.; Bourissou, D. *J. Am. Chem. Soc.* **2013**, *135*, 13306–13309.

(39) Estefanía Piedra-Arroni, E.; Abderrahmane, A.; Bourissou, D. *Dalton Trans.* **2013**, *42*, 9024–9029.

(40) Jia, Y. B.; Wang, Y. B.; Ren, W.-M.; Xu, T. Q.; Wang, J.; Lu, X.-B. *Macromolecules* **2014**, *47*, 1966–1972.

(41) Rhiannon, K.; Iha, R. K.; Wooley, K. L.; Nystrom, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620–5686.

(42) Greenley, R. Z. In *Polymer Handbook*, 3rd ed.; Immergut, E. H., Brandup, J., Eds.; Wiley: New York, 1989; pp 267–274.