# Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Journal Name RSCPublishing

ARTICLE

# Simple Sodium and Potassium Phenolates as Catalysts for Highly Isoselective Polymerization of *rac*-Lactide†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

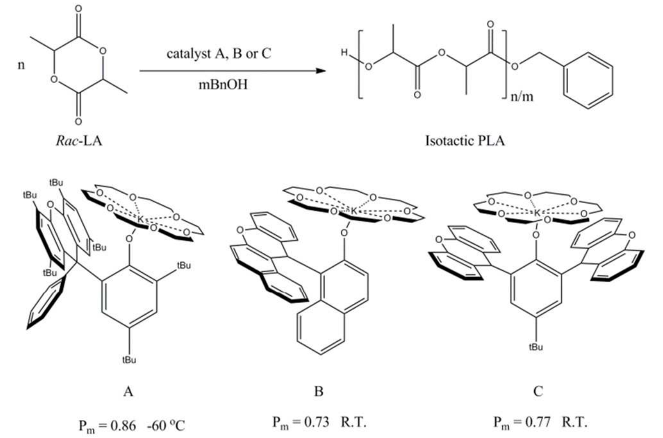
www.rsc.org/

Zhongran Dai, Yangyang Sun, Jiao Xiong, Xiaobo Pan, Ning Tang and Jincai Wu*

A series of simple sodium and potassium phenolates can highly isoselectively catalyze the polymerization of *rac*-lactide (a high $P_m$ value of up to 0.89). Isotactic multi-block polymers were obtained with a longest average isotactic length of 9 (18 lactic acid units) and the highest melting point of the polymer can reach to 187.8 $^{o}$C. One highly active potassium complex even can catalyze the polymerization of 1000 equivalents of *rac*-lactide and afford polylactide with a desired molecular weight and narrow polydispersity index (PDI). Experimental results also demonstrate steric hindrance and electronic effects have significant effects on the behaviors of these catalysts in the ROP of *rac*-lactide.

## Introduction

Polylactide (PLA), derived from renewable biomass, has attracted much attention because it is biocompatible and biodegradable.[1] For the increasing concerns of environmental problems and the limited nature of fossil resources, polylactide as an environment friendly material is considered as a good alternative to petroleum based plastics and becomes welcomed in the agricultural fields, food packaging, and drug delivery.[2] The ring-opening polymerization (ROP) catalyzed/initiated by metal complexes is a major method of preparing the polyesters because of its advantages of predictable molecular weight and narrow molecular weight distribution.[3] It is known that the stereo complex of PLA has excellent properties, for example, the obtained polymers can show high $T_m$ value up to about 230 $^{o}$C.[3c] Thus the stereo selective polymerization of *rac*-LA is a valuable research work; in addition, the obtained polymers via this method can show diverse stereo microstructures.[4] A lot of metal complexes such as zinc,[5] aluminum,[6] indium,[7] magnesium,[8] rare earth metals,[9] and other transition metals complexes[10] have been successfully used in the ring-opening polymerization of *rac*-lactide, and some of them have displayed good stereo control. For example, a lot of Salen or Salan aluminum complexes have been reported to show high iso-selectivities to the ROP of *rac*-lactide, but most of them are low active; a phosphasalen lutetium ethoxide complex reported by Williams et al. shows a $P_m$ value of 0.84 at -15 $^{o}$C;[11] Du and co-workers reported a chiral zinc amido-oxazolinate complex can give a high isoselectivity of $P_m$ = 0.91 which is the highest value for a zinc-based system so far.[12] However, the highly active and highly isoselective ring-opening polymerization of *rac*-lactide still a challenging and valuable goal.

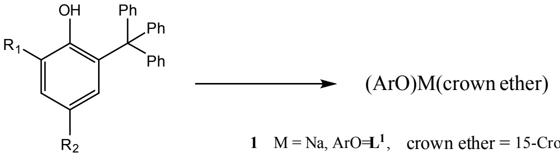


**Scheme 1** Some of the recent works of the highly isoselective polymerization of *rac*-lactide.[13b,14,15]

Innocuous and cheap sodium and potassium are very suitable for the catalytic synthesis of polylactides especially in the medicine-field. Although some sodium and potassium complexes have been applied to catalyze the ROP of lactide,[13] sodium and potassium complexes are difficult to highly isoselectively catalyze the ROP of *rac*-lactide due to the low Lewis acidity of sodium or potassium ion. In 2014, our group reported a crown ether complex of potassium monophenoxide (A, scheme 1) which gives a good isoselectivity ($P_m$ = 0.86) at -60 $^{o}$C,[14] but the molecular weight of obtained polymers is low and the rate of polymerization is very slow at room temperature.

In order to achieve a highly isoselective and highly active sodium and potassium catalysts at a mild condition, some systems (B and C, Scheme 1) for ROP of *rac*-lactide with $P_m$ = 0.73 and $P_m$ = 0.77 were achieved at room temperature recently.[13b,15] But compared to Salen/Salan-aluminum and other systems, the isoselectivity of this system has not reached a high level.

With an attempt to improve the isoselectivity of sodium and potassium complexes system for ROP of *rac*-lactide, we explored this kind of system further. In this work, in order to simplify the chemical synthesis, six new sodium/potassium complexes using simple phenol ligands were designed and synthesized in which the active center is embedded in the middle of the crown ether and the big steric hindrance of phenol; a very high value of $P_m$ = 0.89 can be achieved for the ROP of *rac*-lactide. The influences of steric and electronic effects of these catalysts for ROP of *rac*-lactide were also studied in details.



**L**$^1$**H** $R_1$ = H, $R_2$ = $CH_3$
**L**$^2$**H** $R_1$ = H, $R_2$ = $OCH_3$
**L**$^3$**H** $R_1$ = t-Bu, $R_2$ = $CH_3$

**1** M = Na, ArO=**L**$^1$, crown ether = 15-Crown-5
**2** M = K, ArO=**L**$^1$, crown ether = 15-Crown-5
**3** M = K, ArO=**L**$^1$, crown ether = 18-Crown-6
**4** M = K, ArO=**L**$^1$, crown ether = Dibenzo-18-Crown-6
**5** M = K, ArO=**L**$^2$, crown ether = Dibenzo-18-Crown-6
**6** M = K, ArO=**L**$^3$, crown ether = Dibenzo-18-Crown-6

**Scheme 2** Synthesis of complexes **1-6**.

## Results and discussion

Three phenol ligands **L**$^1$H-**L**$^3$H were synthesized by the reaction of different phenol and triphenylchloromethane at 140 °C.[16] Complexes **1-6** were obtained by the treatments of these ligands with different crown ethers and $KN(SiMe_3)_2$/$NaN(SiMe_3)_2$ respectively in toluene (Scheme 2). Single crystal of complex **1** suitable for X-ray crystallography was obtained by slow cooling of a THF solution.[17] As shown in the ORTEP drawing (Fig. 1), sodium ion is six-coordinated by five oxygen atoms of the 15-crown-5 and one oxygen atom of phenoxy; and the expected active center of $Na^+$-$O^-$ (the oxygen atom of phenoxide) is sandwiched well between the crown ether and bulky triphenylmethyl group.

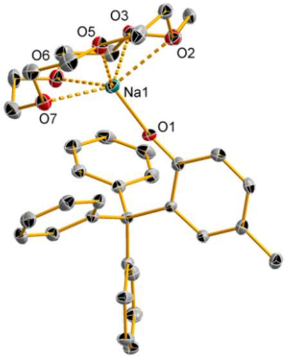


**Fig. 1** ORTEP drawing of complex **1** with thermal ellipsoids at the 30 %, hydrogen atoms are omitted for clarity.

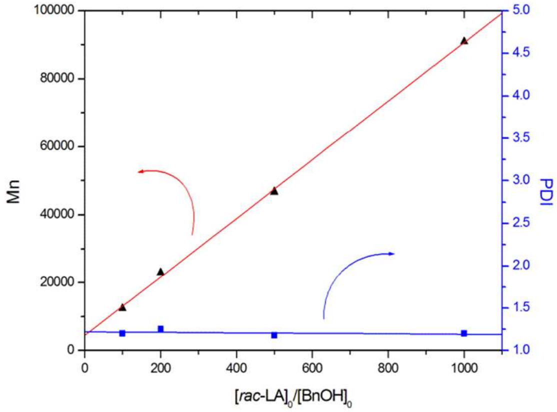


**Fig. 2** The relationship between the Mn(▲) or the PDI value (■) of the polymer and the initial molar ratio $[LA]_0/[BnOH]_0$ is shown.(entries 4 and 10-12, Table 1).

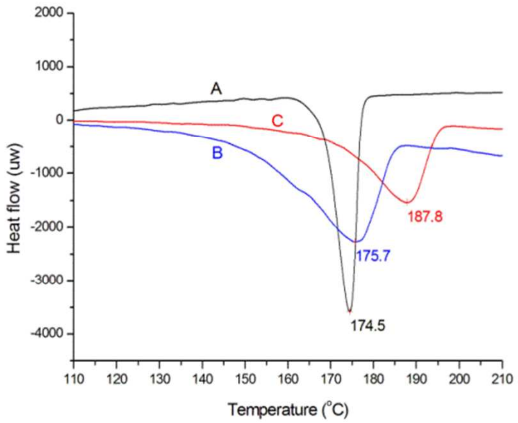
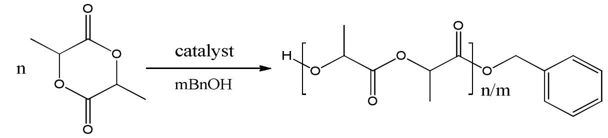


**Fig. 3** Heat flow vs. temperature curve for the PLA sample prepared from poly(L-LA) (A) and PLAs obtained from *rac*-lactide by using complex **4** as catalyst (entry 14 (B) and entry15 (C), Table 1).

The ROP of *rac*-lactide with **1-6** as catalysts was systematically investigated. These complexes are very active catalysts which can be evidenced by the quick completion of polymerization within 1 min in toluene at room temperature when using a ratio of 100:1:1 for $[LA]_0/[M]_0/[BnOH]_0$ (entries 1-6, Table 1). In addition, all molecular weights are close to the expected values and the PDIs of polymers arranging from 1.16 to 1.22 are narrow, which indicates the polymerizations are controllable. Modest isoselectivity values of $P_m$ (0.60-0.77) can be obtained for these complexes at room temperature. Compared to complexes **1** and **3**, the low isoselectivity of complex **2** hints that the matching of metal ion to the ring size of crown ether is important for obtaining high isoselectivity; In addition, the better selectivity of complex **4** ($P_m$ = 0.77) suggests a huge crown ether is beneficial for this isoselective polymerization system (entries 1-4, Table 1). Complex **5** with an electron donating substituents at *para* position of methoxyl shows the isoselectivity of 0.66 which is lower than that of complex **4** indicating the electron donating groups are not favorable (entry 5, Table 1). The *ortho tert*-butyl group in complex **6** initially was designed to sandwich the active center well to increase the isoselectively; but the stereo selectivity of complex **6** is remarkably lower than complex **4** (entry 6, Table 1); a possible reason is that the sandwiched structure is important for the isoselectivity of ROP of *rac*-lactide while the bulk t-butyl group in complex **6** may slightly destroy the sandwiched structure constructed by the plane of crown and the triphenylmethyl group. The influence of solvent effects for the polymerization of *rac*-lactide was studied with complex **4** as a catalyst (entries 4, 7 and 8), the experimental results show all of these reactions can complete within 1 min in toluene, $CH_2Cl_2$, and THF with isoselectivities of $P_m$ = 0.77, 0.67 and 0.71 respectively. When toluene was used as the solvent, the resulting polymer molecular weight is more closely to the theoretical value. Thus, toluene was chosen as the best solvent for this catalytic system. The polymerization of *rac*-lactide can accomplish for complex **4** in the absence of the benzyl alcohol as co-catalyst (entry 9, Table 1), but this process was not under control manner because of the much larger molecular weights than the theoretical value. The polymerizations of 200, 500, and 1000 equivalents of *rac*-LA (entries 10-12, Fig. 2, Table 1) remain controllable and the iso-selectivities can also be maintained. In particular, the resultant PLA molecular weights were still close to the theoretical values for the polymerization of 1000 equiv. of *rac*-LA catalyzed by complex **4**. It is a seldom reported example for the ROP of *rac*-lactide catalyzed/initiated by alkali-metal complexes. In the presence of 10 equivalents benzyl alcohol as the chain transfer agent, 1000 equivalents of *rac*-LA can also be polymerized with a desirable molecular weight and narrow PDI with complex **4** as a catalyst (entry 13, Table 1), which is similar to other alkali metal complexes.[13b-d,14,15] When the reaction temperature decreases to -30 °C and -60 °C (entries 14 and 15, Table 1), the isoselectivity can be improved up to $P_m$ = 0.84 and 0.89 respectively for the ROP of 100 equiv. of *rac*-LA catalyzed by complex **4**. The high isoselectivity values can be further confirmed by their high melting points measured by the method of differential scanning calorimetry (DSC) (Fig. 3), usually highly isotactic polylactides will own high melting points.[18]

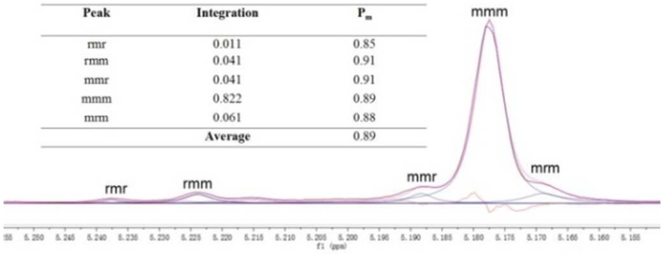
The $^1H$ NMR spectrum of PLA prepared by complex **4** showed that a peaks at 7.32 ppm and 4.35 ppm with a ratio close to 5:1 between $H_e$ (the aromatic hydrogens of benzyl group at the end of polymer) and $H_c$ (CH at the hydroxyl end of polymer) (Fig. S21), which indicates the polymer chains are end-capped by one benzyl ester and one hydroxyl groups. The observed results tell us that the polymerization can proceed via a so-called "monomer activated" mechanism as most alkali metal phenoxides systems: *rac*-lactide can be activated after the coordination to the metal center and then be ring-opened via the electrophilic attack of benzyl alcohol.[19] A series of main peaks at (72m + 108 + 38)/2 with a charge of +2 in the ESI-MS spectrum (Fig. S22) can be ascribed to $m(C_3H_4O_2) + BnOH + 2H_3O^+$, which can confirm the doubly end-capped polylactide structure. This is also proved by other two series of peaks at $(72m + 108(PhCH_2OH) + 19\ (H_3O^+) + 23\ (Na^+))/2$ with a charge of +2 and $72m + 108(PhCH_2OH) + 23\ (Na^+)$ with a charge of +1. The series of peaks separated by m/z = 72 Da can be attributed to some transesterification reactions in the system under this experimental condition; in addition, there are also some cyclic polymers evidenced by two series of the peaks at (72m + 36)/2 and 72m + 23 belonging to $m(C_3H_4O_2) + 2(NH_4^+)$ and $m(C_3H_4O_2) + Na^+$, but the amount of cyclic polymer is small because the intensity of two series of peaks is low. In the homonuclear-decoupled $^1H$ NMR spectrum of PLA (Fig. 4, S19 and S20), a small peak observed at about 5.215 ppm can also prove the existence of side reaction of transesterification in the catalytic system.[20] However, these side reactions are not serious because the determined molecular weights of the polymers are close to the calculated values and PDIs of the final polymers are narrow.

**Table 1** ROP of *rac*-lactide catalyzed by complexes of **1-6**.[a]



| Entry | Cat. | Conv .(%)[b] | $[LA]_0/[M]_0/[BnOH]_0$ | $M_{n,calc}$[c] | $M_{n,obsd.}$[d] | PDI | $P_m$[e] |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 92 | 100:1:1 | 13400 | 11000 | 1.16 | 0.68 |
| 2 | **2** | 94 | 100:1:1 | 13600 | 11700 | 1.16 | 0.62 |
| 3 | **3** | 95 | 100:1:1 | 13800 | 10800 | 1.22 | 0.68 |
| 4 | **4** | 95 | 100:1:1 | 13800 | 12400 | 1.20 | 0.77 |
| 5 | **5** | 92 | 100:1:1 | 13400 | 11400 | 1.21 | 0.66 |
| 6 | **6** | 90 | 100:1:1 | 13100 | 10900 | 1.19 | 0.60 |
| 7[f] | **4** | 90 | 100:1:1 | 13100 | 7300 | 1.22 | 0.67 |
| 8[g] | **4** | 92 | 100:1:1 | 13400 | 8600 | 1.18 | 0.71 |
| 9 | **4** | 96 | 100:1:0 | 13900 | 46500 | 1.08 | 0.76 |
| 10 | **4** | 97 | 200:1:1 | 28000 | 23000 | 1.25 | 0.74 |
| 11[h] | **4** | 80 | 500:1:1 | 57700 | 46700 | 1.18 | 0.75 |
| 12[i] | **4** | 80 | 1000:1:1 | 115300 | 90900 | 1.20 | 0.76 |
| 13 | **4** | 93 | 1000:1:10 | 13500 | 12500 | 1.12 | 0.74 |
| 14[j] | **4** | 90 | 100:1:1 | 13100 | 12300 | 1.08 | 0.84 |
| 15[k] | **4** | 88 | 100:1:1 | 12800 | 12600 | 1.05 | 0.89 |

[a] Conditions (unless special instructions): catalyst, 20 μmol; toluene, 5 mL; under 25 °C in 1 min. [b] Lactide conversion determined by $^1H$ NMR. [c] g/mol, these values were calculated from $[M_{lactide} \times [LA]_0/[BnOH]_0 \times \text{conversion yield} + M_{BnOH}]$. [d] g/mol, these values were obtained from GPC analysis and calibrated by polystyrene standard and corrected using the Mark-Houwink factor of 0.58.[23] [e] Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled $^1H$ NMR spectra.[11] [f] $CH_2Cl_2$ as solvent. [g] THF as solvent. [h] catalyst: 10 μmol, 2 min. [i] catalyst: 10 μmol, 5 min. [j] at -30 °C, 1 h. [k] at -60 °C, 10 h.



| Peak | Integration | $P_m$ |
|---|---|---|
| rmr | 0.011 | 0.85 |
| rmm | 0.041 | 0.91 |
| mmr | 0.041 | 0.91 |
| mmm | 0.822 | 0.89 |
| mrm | 0.061 | 0.88 |
| | Average | 0.89 |

**Fig. 4** The homonuclear-decoupled $^1$H NMR spectrum of PLA ($[LA]_0/[M]_0/[BnOH]_0$ = 100:1:1, $P_m$ = 0.89, entry 15, Table 1).

The microstructure of the obtained PLAs was studied through the analysis of the tetrad signals in the homonuclear-decoupled $^1$H NMR spectrum.[21] As shown in Figure 4, the intensity ratio of rmr : rmm : mmr : mrm is close to 1:4:4:5.5. In theory, the ratio of the tetrad signals of rmr : rmm : mmr : mrm is 0:1:1:1 for the stereo error sequence of -RRRR-SSSS-/-SSSS-RRRR- which usually results from chain end control errors; and this ratio will change to 1:1:1:2 for the stereo error sequence of -RRRR-SS-RRRR-/-SSSS-RR-SSSS-, which usually is ascribed to the enantiomorphic site control errors. The two sequences with a 3:1 ratio will give a 1:4:4:5 ratio for the peaks of rmr : rmm : mmr : mrm which is very close to experimental value of 1:4:4:5.5. It is to be emphasized that the -RRRR-SS-RRRR-/-SSSS-RR-SSSS- sequence can also be regarded as the consecutive chain end control errors; the experimental value of this probability is (100-89)% × 1/4 = 2.75%, which does not deviate far away from the theoretical value of (100-89)% × (100-89)% = 1.21%.[15] The slight enhance of the consecutive chain end control errors and the slight high intensity of mrm peak can be attributed to some transesterification reaction.[22] Therefore, the detailed NMR analysis of the micro stereo structure of the final polymer suggests that the primary isoselective mechanism of this ROP of *rac*-lactide is the chain-end control mechanism. The microscopic structure analysis hints these final poly(*rac*-lactide) are multiblock stereocopolymers. The calculation based on the best isotacticity of $P_m$ = 0.89 demonstrates the average isotactic length can reach to 9 (18 lactic acid units).[18]

## Conclusions

In summary, six new simple sodium and potassium crown ether complexes reported in this work are efficient catalysts for the ring-opening polymerization of *rac*-lactide. A very high isoselectivity value of $P_\mathrm{m}$ = 0.89 was achieved for the ROP of *rac*-lactide with these alkali-metal complexes as catalysts, which demonstrates this system is comparable to that of known stereoselective aluminum, rare earth metal and zinc catalysis systems. The resultant PLAs molecular weights are close to the theoretical values even for the polymerization of 1000 equiv. of *rac*-LA. And the steric hindrance and electronic effects of these isoselective catalysts have remarkable effects on their catalytic behaviors.

## Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 21271092, 21171078, and 21401161) and the Science Foundation of Gansu Province of China (1308RJ2A121).

## Notes and references

Mr. Z. Dai, Y. Sun, Ms. J. Xiong, Prof. X. Pan, N. Tang and J. Wu*
Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering.
Lanzhou 730000, Gansu, People's Republic of China.
E-mail: wujc@lzu.edu.cn

† Electronic Supplementary Information (ESI) available: [Full experimental details, representative NMR spectra, ESI-MS spectrum]. See DOI:10.1039/b000000x/

1 (*a*) S. Slomkowski, S. Penczek and A. Duda, *Polym. Adv. Technol*, 2014, **25**, 436-447; (*b*) M. M. Reddy, S. Vivekanandhan, M. Misra, S. K. Bhatia and A. K. Mohanty, *Prog. Polym. Sci.*, 2013, **38**, 1653-1689; (*c*) D. Sykes and M. D. Ward, *Chem. Commun.*, 2011, **47**, 2279-2281; (*d*) M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484-3504; (*e*) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11-63; (*f*) A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 2000, **33**, 689-695.

2 (*a*) J. W. Rhim, H. M. Park and C. S. Ha, *Prog. Polym. Sci.*, 2013, **38**, 1629-1652; (*b*) A. M. DiCiccio and G. W. Coates, *J. Am. Chem. Soc.*, 2011, **133**, 10724-10727; (*c*) C. M. Thomas, *Chem. Soc. Rev.*, 2010, **39**, 165-173; (*d*) A. Morschbacker, *Polym. Rev.,* 2009, **49**, 79-84.

3 (*a*) P. J. Dijkstra, H. Z. Du and J. Feijen, *Polym. Chem.*, 2011, **2**, 520-527; (*b*) J.-C. Buffet and J. Okuda, *Polym. Chem.*, 2011, **2**, 2758-2763; (*c*) M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486-494.

4 (*a*) M. Kakuta, M. Hirata and Y. Kimura, *Polym. Rev.*, 2009, **49**,107-140; (b) T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326.

5 (*a*) Y. Yang, H. Wang and H. Ma, *Inorg. Chem.*, 2015, **54**, 5839-5854; (*b*) H. Wang, Y. Yang and H. Ma, *Macromolecules,* 2014, **47**, 7750-7764; (*c*) I. S. Vieira and S. Herres-Pawlis, *Eur. J. Inorg. Chem*., 2012, 765-774; (*d*) P. D. Knight, A. J. P. White and C. K. Williams, *Inorg. Chem.,* 2008, **47**, 11711-11719; (*e*) L. R. Rieth, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.,* 2002, **124**, 15239.

6 (*a*) B. Gao, D. Li, X. Li, R. Duan, X. Pang, Y. Cui, Q. duan and X. Chen, *Catal. Sci. Technol.*, 2015, **5**, 4644-4652; (*b*) X. Pang, R. L. Duan, X. Li, Z. Q. Sun, H. Zhang, X. H. Wang and X. S. Chen, *Polym. Chem.,* 2014, **5**, 6857-6864; (*c*) N. Maudoux, T. Roisnel, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Chem. Eur. J.,* 2014, **20**, 6131-6147; (*d*) A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo and M. Lamberti, *J. Am. Chem. Soc.,* 2014, **136**, 2940-2943; (*e*) M. Normand, T. Roisnel, J.-F. Carpentier and E. Kirillov, *Chem. Commun.*, 2013, **49**, 11692-11694; (*f*) C. Bakewell, R. H. Platel, S. K. Cary, S. M. Hubbard, J. M. Roaf, A. C. Levine, A. J. P. White, N. J. Long, M. Haaf and C. K. Williams, *Organometallics*, 2012, **31**, 4729-4736; (*g*) Y. Wang and H. Ma, *Chem. Commun.*, 2012, **48**, 6729-6731; (*h*) W. Zhao, Y. Wang, X. Liu, X. Chen, D. Cui and E.

Y.-X. Chen, *Chem. Commun.*, 2012, **48**, 6375–6377; (*i*) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. Eur. J.* 2007, **13**, 4433-4451; (*j*) K. Majerska and A. Duda, *J. Am. Chem. Soc.,* 2004, **126**, 1026-1027; (k) Z. H. Tang, X. S. Chen, X. Pang, Y. K. Yang, X. F. Zhang and X. B. Jing, *Biomacromolecules*, 2004, **5**, 965-970.

7 (*a*) D. C. Aluthge, J. M. Ahn and P. Mehrkhodavandi, *Chem. Sci.*, 2015, **6**, 5284-5292; (*b*) D. C. Aluthge, E. X. Yan, J. M. Ahn and P. Mehrkhodavandi, *Inorg. Chem.,* 2014, **53**, 6828-6836; (*c*) D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun.,* 2013, **49**, 4295-4297; (*d*) I. Yu, A. Acosta-Ramirez and P. Mehrkhodavandi, *J. Am. Chem. Soc.,* 2012, **134**, 12758-12773; (*e*) M. P. Blake, A. D. Schwarz and P. Mountford, *Organometallics,* 2011, **30**, 1202-1214; (*f*) J. C. Buffet, J. Okuda and P. L. Arnold, *Inorg. Chem.,* 2010, **49**, 419-426; (*g*) A. Pietrangelo, M. A. Hillmyer and W. B. Tolman, *Chem. Commun*., 2009, 2736-2737; (*h*) A. F. Douglas, B. O.Patrick and P. Mehrkhodavandi, *Angew. Chem., Int. Ed.,* 2008, **47**, 2290-2293.

8 (*a*) M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez, J. Martínez-Ferrer, S. Sobrino and A. M. Rodríguez, *Organometallics*, 2015, **34**, 3196-3208; (*b*) H. Xie, Z. Mou, B. Liu, P. Li, W. Rong, S. Li and D. Cui, *Organometallics*, 2014, **33**, 722-730; (*c*) W. Yi and H. Ma, *Inorg. Chem.,* 2013, **52**, 11821-11835; (*d*) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.,* 2001, **123**, 3229-3238.

9 (*a*) W. Gu, P. Xu, Y. Wang, Y. Yao, D. Yuan and Q. Shen, *Organometallics*, 2015, **34**, 2907-2916; (*b*) C. Bakewell, A. J. P. White, N. J. Long and C. K. Williams, *Angew. Chem., Int. Ed.,* 2014, **53**, 9226-9230; (*c*) C. G. Jaffredo, Y. Chapurina, S. M. Guillaume and J.-F. Carpentier, *Angew. Chem., Int. Ed.,* 2014, **53**, 2687-2691; (*d*) L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateaub and P. Mountford, *Chem. Commun.*, 2010, **46**, 273-275; (*e*) J. W. Kramer, D. S. Treitler, E. W. Dunn, P. M. Castro, T. Roisnel, C. M. Thomas and G. W. Coates, *J. Am. Chem. Soc.*, 2009, **131**, 16042-16044; (*f*) P. L. Arnold, J. C. Buffet, R. P. Blaudeck, S. Sujecki, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2008, **47**, 6033-6036; (*g*) H. Ma, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2006, **45**, 7818-7821; (*h*) A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J.-F. Carpentier, *Angew. Chem., Int. Ed.*, 2006, **45**, 2782-2784.

10 (*a*) V. Balasanthiran, C. Chatterjee, M. H. Chisholm, N. D. Harrold, T. V. RajanBabu, and G. A. Warren, *J. Am. Chem. Soc.*, 2015, **137**, 1786-1789; (*b*) M. D. Jones, L. Brady, P. McKeown, A. Buchard, P. M. Schäfer, L. H. Thomas, M. F. Mahon, T. J. Woodman and J. P. Lowe, *Chem. Sci.*, 2015, **6**, 5034-5039; (*c*) C. Bakewell, G. Fateh-Iravani, D. W. Beh, D. Myers, S. Tabthong, P. Hormnirun, A. J. P. White, N. Long and C. K. Williams, *Dalton Trans.*, 2015, **44**, 12326-12337; (*d*) A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140−9150.

11 C. Bakewell, T. P. A. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577-20580.

12 S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689-692.

13 (*a*) F. M. García-Valle, R. Estivill, C. Gallegos, T. Cuenca, M. E. G. Mosquera, V. Tabernero, and J. Cano, *Organometallics*, 2015, **34**, 477-487; (*b*) J. Xiong, J. Zhang, Y. Sun, Z. Dai, X. Pan and Jincai Wu, *Inorg. Chem.*, 2015, **54**, 1737-1743; (*c*) Y. Huang, W. Wang, C.-C. Lin, M. P. Blake, L. Clark, A. D. Schwarzb and P. Mountford, *Dalton Trans.*, 2013, **42**, 9313-9324; (*d*) S. C. Roșca, D.-A. Roșca, V. Dorcet, C. M. Kozak, F. M. Kerton, J.-F. Carpentier and Y. Sarazin, *Dalton Trans.*, 2013, **42**, 9361-9375; (*e*) H.-Y. Chen, J. B. Zhang, C.-C. Lin, J. H. Reibenspiesa and S. A. Miller, *Green Chem.*, 2007, **9**, 1038-1040.

14 J. Zhang, J. Xiong, Y. Sun, N. Tang and J. Wu, *Macromolecules*, 2014, **47**, 7789-7796.

15 Z. Dai, Y. Sun, J. Xiong, X. Pan and J. Wu, *ACS Macro Lett.*, 2015, **4**, 556-560.

16 A. I. Kochnev, I. I. Oleynik, I. V. Oleynik, S. S. Ivanchev and G. A. Tolstikov, *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1125-1129.

17 Crystallographic data for complex **1**: $C_{36}H_{41}O_6Na$, M = 592.68, monoclinic, space group, $P21/c$, $a$ = 18.646(2), $b$ =12.5960(9), $c$ = 14.6475(12) Å, V = 3179.3(5) $Å^3$, Z = 4, $\rho_{calcd}$ = 1.238 $gcm^{-3}$, $\mu$ = 0.094 $mm^{-1}$ ,$Mo_{Ka}$ radiation ($\lambda$ = 0.71073 Å), T = 290.92(10) K. 7278 data (2956 unique, $R_{int}$ = 0.0995, $\theta < 26.32^o$), $\omega$ scans, $wR_2$ = 0.1430, $R$ = 0.0784, $S$ = 0.988, for 389 parameters. Final residual electron density extrema were 0.303 and -0.286 $eÅ^{-3}$. CCDC 1406804, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

18 N. Nomura, J. Hasegawa and R. Ishii, *Macromolecules*, 2009, **42**, 4907-4909.

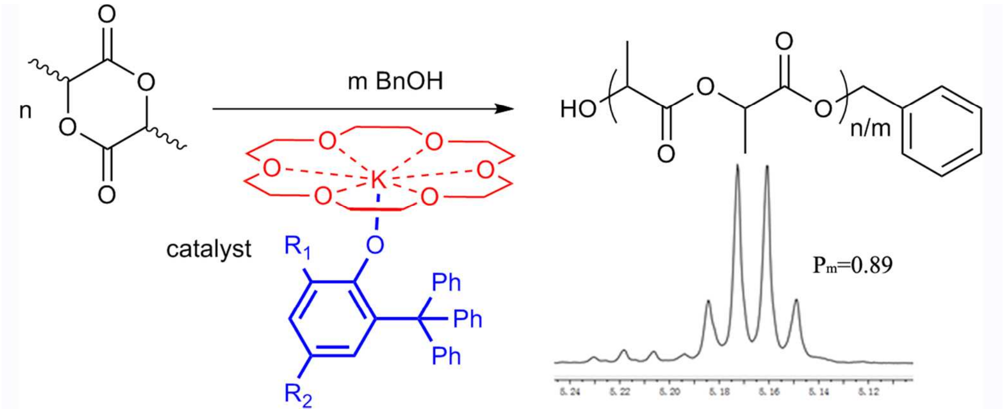
19 (*a*) J.-F. Carpentier and Y. Sarazin, *Top Organomet Chem*., 2013, **45**, 141-190; (*b*) H. Y. Chen, L. Mialon, K. A. Abboud and S. A. Miller, *Organometallics*, 2012, **31**, 5252-5261; (*c*) S. A. Sutar, S. A. Maharana, S. A. Dutta, C.-T. Chen and C.-C. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1724-1746.

20 K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad and T. A. Lindgren, *Macromolecules*, 1997, **30**, 2422-2428.

21 (*a*) H. Wang and H. Ma, *Chem. Commun.*, 2013, **49**, 8686-8688; (*b*) T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326; (c) M. H. Chisholm, S. S. Iyer, D. G. McCollum, M. Pagel and U. Werner-Zwanziger, *Macromolecules*, 1999, **32**, 963-973; (*d*) K. A. M. Thakur, R. T. Kean, M. T. Zell, B. E. Paddenb and E. J. Munson, *Chem. Commun.*, 1998, 1913-1914; (*e*) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad and E. J. Munson, *Macromolecules*, 1998, **31**, 1487-1494; (*f*) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann and E. J.Munson, *Macromolecules*, 1997, **30**, 2422-2428.

22 (*a*) B. Calvo, M. G. Davidson and D. Garcia-Vivo, *Inorg. Chem.*, 2011, **50**, 3589-3595; (*b*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F.Wong, *Macromolecules*, 2006, **39**, 7250-7257; (*c*) J. Kasperczyk and M. Bero, *Polymer*, 2000, **41**, 391-395; (*d*) M. Bero, J. Kasperczyk and Z. J. Jedlinski, *Makromol. Chem.*, 1990, **191**, 2287-2296.

23 A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 1998, **31**, 2114-2122.



350x142mm (96 x 96 DPI)