RSC Advances

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2020, **10**, 23498

Phosphorus pentoxide as a cost-effective, metal-free catalyst for ring opening polymerization of ε-caprolactone†

Ismail Adoumaz,[ab] El Hassan Boutriouia,[a] Redouane Beniazza,[c] Hicham Qayouh,[a] Abdelkrim El Kadib,[d] Abdel Khoukh,[b] Maud Save[b] and Mohammed Lahcini*[ac]

The ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) using phosphorus pentoxide (P_2O_5) as a metal-free catalyst and isopropanol (iPrOH) as initiator resulted in the preparation of poly(ε-caprolactone) with narrow weight distribution. NMR spectroscopy analyses of the prepared PCL indicated the presence of the initiator residue at the end of the polymer chain, implying the occurrence of the ε-CL-catalysis ROP through a monomer activation mechanism. Kinetic experiments confirmed the controlled/living nature of ε-CL ring-opening catalyzed by phosphorus pentoxide. The commercial availability of phosphorus pentoxide and its easy-handling provide additional opportunities for polymer synthesis and nanocomposite manufacturing.

Received 12th May 2020
Accepted 13th June 2020

DOI: 10.1039/d0ra04251j

rsc.li/rsc-advances

Open Access Article. Published on 19 June 2020. Downloaded on 7/24/2025 1:02:23 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Introduction

Over the last two decades, the development of biodegradable and biocompatible polymers has driven intense research to meet the challenges of minimizing the production of non-recyclable long-life waste.[1]

Among these polymers, poly(ε-caprolactone) (PCL), a semi-crystalline aliphatic polyester, has found applications in several domains ranging from food packaging to biomedical applications. The versatility of PCL and its usage in many industrial applications, is mainly related to its inherent characteristics including thermal ($T_g = -65$ °C and $T_m = 60$ °C) and mechanical stability and its high miscibility in a variety of polymers (*e.g.* poly(vinyl chloride) or poly(bisphenol-A carbonate)).[2] Moreover, the properties of PCL can be finely tuned upon appropriate modifications. For instance, its mechanical properties can be tailored by preparing copolymers containing ε-caprolactone and other monomers. Besides, the rate of degradation can be also accelerated, as illustrated in the case of the poly(ε-caprolactone-*co*-glycolide) copolymers used for producing resorbable sutures.[3] The flexibility of PCL allows the preparation of three-dimensional architectures that have been used as insulating interlocks of low dielectric constant for microelectronics applications.[2] More importantly, PCL is biodegradable and biocompatible which attracted much interest especially in biomedical applications, making PCL derivatives potential candidates for the replacement of petroleum-based polymers. However, the successful shift to biodegradable and biocompatible polymers requires the development of efficient and cost-effective synthetic routes for the preparation of "green polymers" with more favorable environmental and economic outlook to compete with currently available non-biodegradable polymers.[4]

Two different approaches have been developed for PCL production: (i) the polycondensation of 6-hydroxycaproic acid and (ii) the ring-opening polymerization (ROP) of ε-caprolactone.[5] However, many challenges have to be overcome for the preparation of PCL with finely controlled properties. For instance, the preparation of PCL by polycondensation requires complexes conditions (vacuum and high temperature) or long reaction times in presence of metal complexes and enzyme catalysts and often resulted in polymers with poorly controlled molecular weight.[6] The preparation of polymers, in a controllable manner, is generally obtained *via* the ring-opening polymerization of ε-caprolactone (ε-CL) in presence of metal transition based catalyst (tin, aluminum, iron or yttrium derivatives) and post-transition metals including zinc, bismuth, ruthenium and zirconium species.[7] However, a thorny issue in metal-catalyzed ROP lies in the presence of metal residues entrapped into the polymer backbone, which act as a contaminant, thereby limiting their utilization in microelectronics, food packing or biomedical applications.

[a]*IMED-Lab, Cadi Ayyad University, Faculté des Sciences et Techniques Gueliz, Av. Abdelkrim Khattabi BP 549, 40000 Marrakech, Morocco. E-mail: m.lahcini@uca.ac.ma; Fax: +212 5 24 43 31 70; Tel: +212 5 24 43 46 88*

[b]*CNRS, University Pau & Pays Adour, E2S UPPA, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, IPREM, UMR5254, 64000, Pau, France*

[c]*Mohammed VI Polytechnic University, Lot 660, Hay Moulay Rachid, 43150, Ben Guerir, Morocco*

[d]*Euro-Med Research Center, Engineering Division, Euro-Mediterranean University of Fes (UEMF), Fez-Shore, Route de SidiHrazem, 30070, Fez, Morocco*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra04251j

This journal is © The Royal Society of Chemistry 2020

Open Access Article. Published on 19 June 2020. Downloaded on 7/24/2025 1:02:23 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Interestingly, the use of simple metal-free molecules as promoters/catalysts in the ring-opening polymerization (ROP) of cyclic ester has been proposed as an attractive alternative to classical metal-based catalysts.[8] A pioneering work in this frame was reported by Hedrick *et al.* using 4-dimethylaminopyridine (DMAP) as an organocatalyst for ROP of lactide (LA).[9] Since then, several studies have been performed to elucidate the appropriate combinations of organocatalysts and monomers, aiming for precise controlled polymerization of cyclic esters, such as lactide (LA), ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL).[10] DMAP,[9] guanidine,[11] N-heterocyclic carbene,[9,11a,12] and phosphine[9,13] used as nucleophilic organocatalyst, displayed great efficiency for the controlled/living ROP of the cyclic esters by the activation of the monomers. The cationic ring-opening polymerization by activated monomer polymerization using strong acids have been also investigated as a metal-free route.[5b,14] However, the presence of strong Brønsted acid sites resulted in the deactivation of the initiating/propagating alcohol and caused undesirable side reactions.[5c] Comparatively, the use of weak acids, such as dialkyl phosphate derivatives, proved to be more effective for the ROP of cyclic esters and produced well-defined polyesters. These achievements represent an important breakthrough in acid-catalyzed ROP reaction.[15]

Prompted by some virtues of phosphorus pentoxide (P_2O_5) comparable to phosphoric acid and related derivatives, we undertook herein a study for its use as catalyst for the ROP of ε-caprolactone (ε-CL) under solvent-free condition. Phosphorous pentoxide presents numerous advantages including its green character, commercial availability with low price and ease of handling. Furthermore, the reactivity of phosphorous pentoxide has been already confirmed in several organic reactions such as Beckmann rearrangement, dimerization of olefin,[16] but to the best of our knowledge, its application as catalyst for the ring-opening polymerization of cyclic esters has never been reported so far.

Experimental section

Materials

Phosphorus pentoxide (P_2O_5) (>99%) was purchase from Aldrich and used as received. Isopropanol (Aldrich, purity 99%) was distilled over CaH_2 before use. ε-Caprolactone (ε-CL, purity > 99%) was purchased from Fluka and distilled over calcium hydride and stored over 4 Å molecular sieves under inert atmosphere.

Measurements

^1H (300 MHz) and ^{13}C (75.5 MHZ) nuclear magnetic resonance (NMR) spectra were acquired using a Bruker avance 300 MHz at 293 K. The $CDCl_3$ containing TMS served as solvent.

Molecular weights and molecular weight distributions were measured at 35 °C in tetrahydrofuran (THF) by size exclusion chromatography (SEC) relative to polystyrene standards with a Waters 515 HPLC pump; GPC fitted with Styragel columns HR 1, HR 2 and HR 4; a UV detector-Waters 2487; and a refractive-index detector-Waters 2410.

Polymerization

The polymerizations were carried out under argon atmosphere with standard Schlenk techniques. Typically, the monomer ε-CL (50 mmol) was weighed into a Schlenk tube containing a magnetic bar, and two vacuum–argon cycles were performed to remove moisture. Dry P_2O_5 catalyst and isopropanol initiator, were added, and the suspension was stirred for 10 minutes at room temperature to reach homogenous solution. The polymerization was started by placing the closed reaction vessel into an oil bath preheated at desired temperatures. At the given time points, control samples were taken. The samples were then treated with technical-grade dichloromethane to quench the polymerization. After the treatment, the solvent was removed. The obtained mixture of monomer and polymer was analyzed by ^1H NMR to determine the conversion. The crude polymer was then purified by precipitation from dichloromethane/methanol (1 : 3) and was analyzed with SEC.

Results and discussion

Synthesis and characterization of ε-caprolactone

Considering that alkyl phosphates are synthesized by reacting phosphorus pentoxide and alcohols,[17] we envisioned the direct use of phosphorus pentoxide as a catalyst for the ROP of ε-caprolactone in the presence of alcohol as initiator. With this aim, a first screening was undertaken to find optimal experimental conditions. As displayed in Fig. 1, ROP of ε-CL with P_2O_5 as catalyst and isopropanol as initiator under solvent-free condition, a minimum temperature of 100 °C was required to achieve 80% of conversion within 1 hour of polymerization.

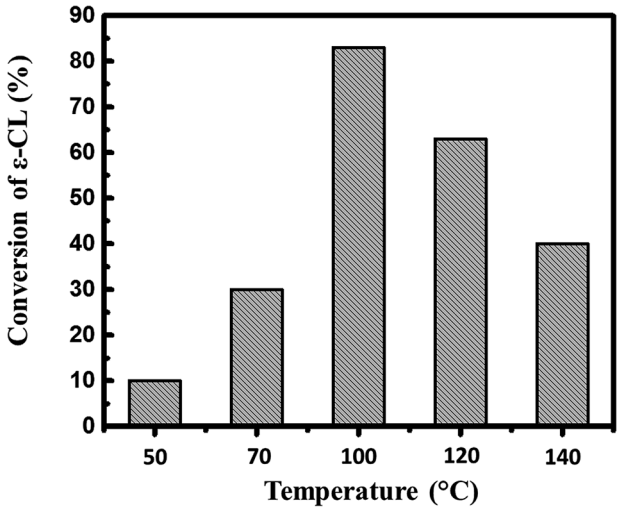

Fig. 1 Evolution of the conversion of ε-CL as function of temperature. Reaction carried out using P_2O_5 as catalyst in the presence of isopropanol at ratios [ε-CL]/[P_2O_5]/[iPrOH] = 200/1/1. Polymerization time = 1 h.

Open Access Article. Published on 19 June 2020. Downloaded on 7/24/2025 1:02:23 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Table 1 Bulk polymerization of ε-caprolactone (ε-CL) using P_2O_5 and isopropanol at $T = 100$ °C for different ratio for $t = 1$ h

Ratio	Conv.[a] (%)	M_{nth} (g mol^{-1})	M_n[b] (g mol^{-1})	$Đ$
50/1/1	98	5483	6.44×10^3	1.90
150/1/1	97	14 614	11.55×10^3	1.80
200/1/1	83	19 007	18.62×10^3	1.15

[a] Conversion of CL. [b] Average molar mass and dispersity index ($Đ$) as determined by SEC relative to polystyrene standard, values are the ones obtained from SEC × correction factor of 0.56 ± 0.05 for PCL.[19]

Table 2 Results of bulk polymerization of ε-caprolactone (ε-CL) using P_2O_5 and isopropanol (mole ratio 200/1) at 100 °C for different reaction times

Time (min)	Conv.[a] (%)	M_{nth}[b] (g mol^{-1})	M_n[c] (g mol^{-1})	$Đ$[c]
10	20	4625	3.84×10^3	1.13
20	32	73 364	4.56×10^3	1.15
30	72	16 496	16.98×10^3	1.16
60	83	19 007	18.62×10^3	1.15
90	90	20 605	20.53×10^3	1.40
180	98	22 371	21.48×10^3	1.59

[a] Conversion of CL. [b] The theoretical molecular weight was calculated from $[M]_0/[P_2O_5]$ × conv. × (MW of Monomer) + (MW of iPrOH). [c] Number-average molar and dispersity ($Đ$) are determined by SEC relative to polystyrene standard, values are the ones obtained from SEC × correction factor of 0.56 ± 0.05 for PCL.[19] d = not determined.

The conversion obviously decreases above 100 °C, suggesting possible thermal depolymerization of the as-formed polymer at these reactions temperatures in the presence of P_2O_5.[18,20] On the other hand, the conversion reached only 10 and 30% of conversion at 50 °C and 70 °C. We therefore considered 100 °C as an optimal temperature for ROP of ε-CL initiated by P_2O_5.

Next, we carried out three polymerizations by varying the monomer to catalyst/initiator ratio $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0$, from 50/1/1 to 200/1/1 under solvent-free conditions. The results show that the molecular weight increases by rising $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0$ ratio (Table 1). It was also observed that at high $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0$ ratio, the polymerization requires a longer reaction time. For example, a total conversion was reached for $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0 = 50/1/1$, whereas only 83% of conversion was obtained when the ratio of $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0$ is 200/1/1.

These results of Table 1 are in good agreement with the assumption that higher monomer to initiator ratio should produce a lower concentration of initiating species, which will result in turn in the preparation of higher molar mass polymer. The increase of dispersity value ($Đ$) observed for monomer conversion above 90% is due to transesterification side reactions, which become more prevalent at high temperatures and low monomer concentrations (Table 1, entry 1 and 2).[20]

We next examined the catalytic activity of P_2O_5 as a single-component catalyst, in the absence of iPrOH or any other initiator. The catalytic activity was lower in these conditions recording 70% of conversion at 1 hour of polymerization compared to 83% that achieved in the presence of iPrOH. In addition, molar mass ($M_n = 3285$ g mol^{-1}) and broad dispersity ($Đ = 3.2$) were obtained. This indicated the pivotal role of the alcohol used as an initiator for controlling polymerization.

Kinetics and polymer properties

Ring-opening polymerization of ε-CL carried out at 100 °C with monomer to catalyst ratio $[ε\text{-CL}]_0/[P_2O_5]_0/[iPrOH]_0 = 200/1/1$ was monitored in more details (Table 2 and Fig. 2)

The plot of $\ln([ε\text{-CL}]_0/[ε\text{-CL}])$ increases linearly with time, indicating a first-order kinetic (Fig. 2a). This linearity also evidences a constant concentration in active centers throughout the polymerization and therefore a controlled ROP of ε-CL with minor occurrence of termination reactions. The evolution of the number-average molar mass (M_n) and dispersity ($Đ$) *versus* conversion was plotted in Fig. 2b. A linear relationship of M_n with conversion was observed as well as narrow dispersities ($Đ < 1.2$) up to moderate conversion levels (<80%), evidencing an uniform chain growth process and low extent of transfer reactions. The slight broadening of $Đ$ attained at high monomer conversions (90% and 98%) is known and is due to little transesterification side reactions, which become more predominant at elevated temperature and low monomer concentrations.[20]

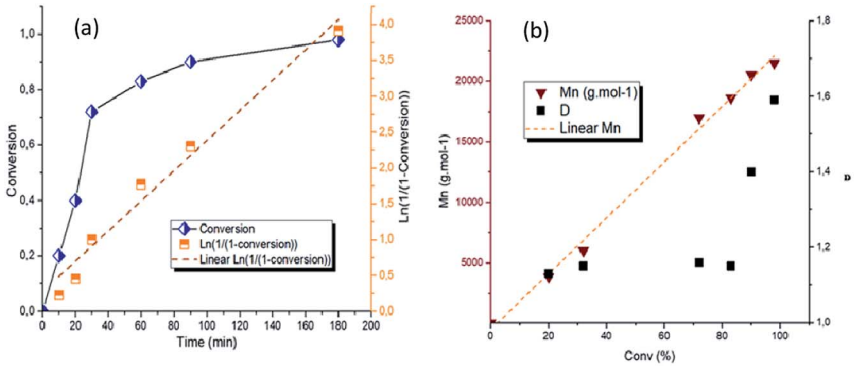

Fig. 2 (a) Kinetic plots for the ROP of ε-CL (at 100 °C in bulk, $[CL]_0/[P_2O_5]/[iPrOH] = 200 : 1 : 1$) and (b) dependence of number-average molar mass (M_n) and dispersities ($Đ$) on the monomer conversion (conv).

 This journal is © The Royal Society of Chemistry 2020

Open Access Article. Published on 19 June 2020. Downloaded on 7/24/2025 1:02:23 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

The controlled character of ε-CL polymerization was further confirmed by chain extension experiment of CL polymerization (ESI, Fig. 2 & 4†). After 100% conversion of 50 equivalents of ε-CL compared to isopropanol and P_2O_5, a SEC sample was withdrawn and an additional 100 equivalents of ε-CL monomer was added for a chain extension. The SEC chromatograms show that M_n of the polymer increased from 7505 g mol^{-1} before second shot of monomer up to 11 800 g mol^{-1} at conversion of 50%.

^{1}H NMR analysis of the recovered polymer revealed the presence of an isopropyl ester end group (protons a and b, Fig. 3), thereby indicating the insertion of the alcohol during the polymerization reaction. ^{13}C NMR analysis was also performed to corroborate these results and the spectrum shows the existence of the carbons of isopropyl at 23 and 68 ppm at the end of the polymer chain (ESI; Fig. 1†).[21–23] In order to confirm that the isopropyl group is effectively attached to the poly(ε-caprolactone) chain, a DOSY NMR analysis was subsequently performed for sample prepared by ring-opening polymerization of ε-caprolactone with monomer to initiator $[CL]_0/[P_2O_5]_0/[iPrOH]_0$ = 200/1/1. The DOSY NMR spectrum clearly revealed the presence of an isopropyl ester group at the end of the polymer chain since the signals of the PCL are shown at the same coefficient of self-diffusion as those relate to the isopropyl chain end group (Fig. 4).

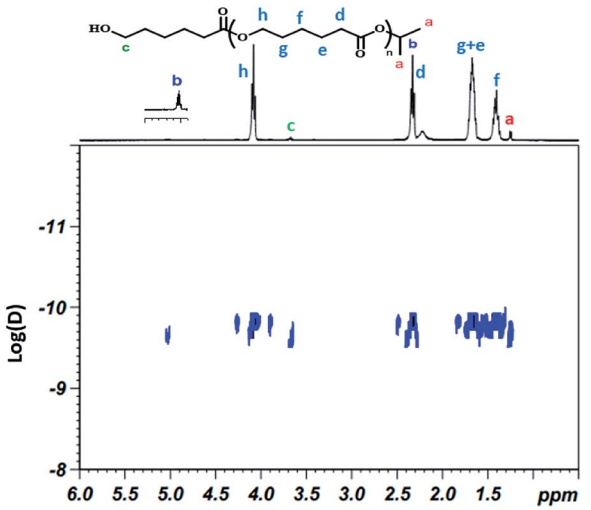

Fig. 4 NMR DOSY spectra of the obtained PCL in $CDCl_3$ solvent.

Mechanism of the catalytic system

The ROP of cyclic esters mechanism of various organocatalysts has been extensively investigated.[24–29] Based on our NMR results which evidenced the presence of isopropyl ester end group in the polymer chain (Fig. 3 and 4), it can be postulated that the ring-opening of ε-caprolactone occurs through cleavage of the C(acyl)–O bond.

We propose that phosphorus pentoxide acts as milder base *via* one of two pairs of its exo-oxygen to activate the isopropanol initiator. Indeed, hydrogen bonding between the exo-oxygen of the catalyst, phosphorus pentoxide, and the hydroxyl group of iPrOH increases the nucleophilicity of the oxygen of alcohol and subsequently facilitates its nucleophilic attack to the carbonyl-carbon of the ε-caprolactone monomer followed by acyl–oxygen bond scission. This leads to the formation of an ester end group and active hydroxyl specie, which reacts with another monomer for further propagation. Hence, the speculative activation mechanism for ε-CL ring-opening catalyzed by phosphorus pentoxide and isopropanol is shown in Fig. 5.

In fact, this mode of activation significantly reduces the inter- or intramolecular transesterification because of the steric barrier between the complex formed with hydroxyl chain end and the ester bonds within the polymer chains. This is the possible reason for the successful synthesis of PεCL with controlled molar masses from P_2O_5 : iPrOH system.

Lastly, TGA and DSC analyses were performed (ESI, Fig. 4†). Total degradation of PCL was observed around 400 °C, in agreement with the previously reported literature.[2] DSC reveals also typical behavior of conventional PCL. Improvement in thermal and mechanical properties of the resulting polymers is expected through the combination of P_2O_5 and nanofillers during the ring opening polymerization of the starting monomers.

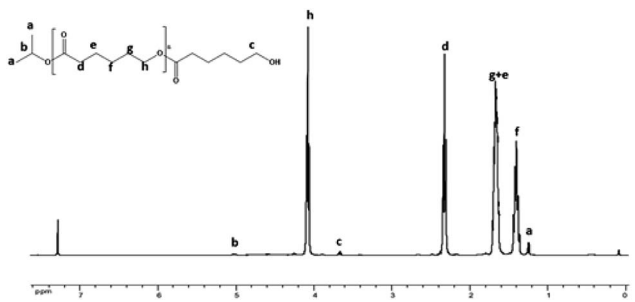

Fig. 3 ^{1}HNMR spectra of the obtained PCL in $CDCl_3$ solvent.

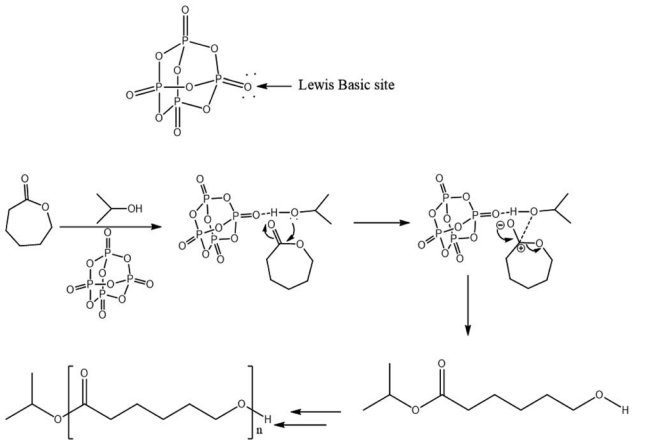

Fig. 5 Proposed mechanism for the ROP of ε-caprolactone catalyzed by phosphorus pentoxide in presence of isopropanol.

Open Access Article. Published on 19 June 2020. Downloaded on 7/24/2025 1:02:23 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Conclusions

We described for the first time the efficiency of phosphorus pentoxide as a novel catalyst in combination with isopropanol initiator for the ring-opening polymerization of ε-caprolactone (ε-CL). This study showed that the polymerization proceeded in a controlled manner with good control over molar mass and narrow molar mass distribution. We proposed that the polymerization proceeds through an initiator/chain end activation by a base-type mechanism. This work opens interesting perspectives to synthesize more complex polymer architectures from this eco-friendly catalytic system.

Conflicts of interest

The authors confirm that this article content has no conflict of interest.

Acknowledgements

Financial support by the Moroccan Ministry of Education and Research (Projet Prioritaire PPR1/2015/73) and PHC Toubkal/17/51–Campus France: 36877RE are gratefully acknowledged. We wish to thank Taha Elassimi for valuable help in the thermal analysis of polymers.

Notes and references

1 *Engineering Biopolymers: Markets, Manufacturing, Properties and Applications*, ed. H. J. Endres and A. Siebert-Roths, Hanser Publications, Munich, 2011.
2 D. R. Chen, J. Z. Bei and S. G. Wang, *Polym. Degrad. Stab.*, 2000, **67**, 455–459.
3 U. Piotrowska and M. Sobczak, *Molecules*, 2014, **20**, 1.
4 S. J. Ory, C. B. Hammond, S. G. Yancy, R. Wayne Hendren and C. G. Pitt, *Am. J. Obstet. Gynecol.*, 1983, **145**, 600.
5 (*a*) A. Pärssinen, M. Kohlmayr, M. Leskelä, M. Lahcini and T. Repo, *Polym. Chem.*, 2010, **1**, 834; (*b*) M. Baśko and P. Kubisa, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 7071; (*c*) S. Gazeau-Bureau, D. Delcroix, B. Martín-Vaca, D. Bourissou, C. Navarro and S. Magnet, *Macromolecules*, 2008, **41**, 3782; (*d*) B. Kirubakaran, R. Beesam and D. Reddy Nareddula, *Organomet. Chem.*, 2017, 3833.
6 M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484–3504.
7 S. L. Lee, F. L. Hu, X. J. Shang, Y. X. Shi, A. L. Tan, J. Mizera, J. K. Clegg, W. H. Zhang, D. J. Young and J.-P. Lang, *New J. Chem.*, 2017, **41**, 14457.
8 M. K. Kiesewetter, E. J. Shin, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2010, **43**, 2093.
9 E. F. Connor, G. W. Nyce, M. Myers, A. Mock and J. L. Hedrick, *Am. Chem.*, 2002, **124**, 915.
10 (*a*) E. Nahrain, W. J. Kamber and M. W. Robert, *Chem*, 2007, **107**, 5813–5840; (*b*) A. P. Dove, *ACS Macro Lett.*, 2012, **1**, 1409.
11 (*a*) B. G. G. Lohmeijer, R. C. P. F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 8574; (*b*) R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2006, **128**, 4556.
12 G. W. Nyce, T. Glauser, E. F. Connor, A. Mock, R. M. Waymouth and J. L. Hedrick, *Am. Chem.*, 2003, **10**, 3047.
13 K. Makiguchi, T. Satoh and T. Kakuchi, *Macromolecules*, 2011, **44**, 1999.
14 M. Baśko and P. Kubisa, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7919.
15 P. Lewinski, J. Pretula, K. Kaluzynski, S. Kaźmierski and S. Penczek, *J. Catal.*, 2019, **371**, 305.
16 G. C. Nandi, S. Samai, R. Kumar and M. S. Singh, *Tetrahedron Lett.*, 2009, **50**, 7220.
17 A. Elias, M. A. Didi, D. Villemin, T. Semaoune and S. Ouattas, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 2004, **179**, 2599.
18 A. Harrane, R. Meghabar and M. Belbachir, *Des. Monomers Polym.*, 2012, **8**, 11.
19 M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889.
20 M. Kalmi, P. Castro, O. Lehtonen, A. Belfkira, M. Leskela and T. Repo, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 1901–1911.
21 (*a*) X. Zhou and L. Hong, *Colloid Polym. Sci.*, 2013, **291**, 2155; (*b*) M. Abdollahi, R. Bairami Habashi and M. Mohsen, *Ind. Crops Prod.*, 2019, **130**, 547; (*c*) W. A. Munzeiwa, V. O. Nyamori and B. Omondi, *Inorg. Chim. Acta*, 2019, **487**, 264.
22 (*a*) F. Della Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione and C. Capacchione, *Macromolecules*, 2014, **47**, 2830; (*b*) A. Bouyahya, S. Balieu, R. Beniazza, M. Raihane, A. El Kadib, D. Le Cerf, P. Thébault, G. Gouhier and M. Lahcini, *New J. Chem.*, 2019, **43**, 5872.
23 Q. Hu, S. Jie, P. Braunstein and B.-G. Li, *J. Organomet. Chem.*, 2019, **882**, 1.
24 (*a*) K. Makiguchi, Y. Ogasawara, S. Kikuchi, T. Satoh and T. Kakuchi, *Macromolecules*, 2013, **46**, 1772; (*b*) N. Zhu, Y. Liu, J. Liu, J. Ling, X. Hu, W. Huang, W. Feng and K. Guo, *Sci. Rep.*, 2018, **8**, 3734.
25 (*a*) Y. Zhao, X. Lim, Y. Pan, L. Zong, W. Feng, C. H. Tan and K. W. Huang, *Chem. Commun.*, 2012, **48**, 5479; (*b*) D. Delcroix, A. Couffin, N. Susperregui, C. Navarro, L. Maron, B. Martin-Vaca and D. Bourissou, *Polym. Chem.*, 2011, **2**, 2249.
26 X. Zhi, J. Liu, Z. Li, H. Wang, X. Wang, S. Cui, C. Chen, C. Zhao, X. Li and K. Guo, *Polym. Chem.*, 2016, **7**, 339.
27 A. Buchard, D. R. Carbery, M. G. Davidson, P. K. Ivanova, B. J. Jeffery, G. I. Kociok-Kohn and J. P. Lowe, *Angew. Chem., Int. Ed. Engl.*, 2014, **53**, 13858.
28 M. K. Kiesewette, E. J. Shin, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2010, **43**, 2093–2107.
29 P. Li, Y. Xi, L. Li, H. Li, W. H. Sun and M. Lei, *Inorg. Chim. Acta*, 2018, **477**, 34.

 This journal is © The Royal Society of Chemistry 2020