ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/265469225

Organocatalyzed Synthesis of Aliphatic Polyesters from Ethylene Brassylate: A Cheap and Renewable Macrolactone

ARTICLE *in* ACS MACRO LETTERS · AUGUST 2014

Impact Factor: 5.76 · DOI: 10.1021/mz500401u

CITATIONS
10

READS
103

5 AUTHORS, INCLUDING:

Haritz Sardon
Instituto de Ciencia y Tecnología de Polímeros
33 PUBLICATIONS **405** CITATIONS
SEE PROFILE

Antonio Veloso
Universidad del País Vasco / Euskal Herriko …
17 PUBLICATIONS **64** CITATIONS
SEE PROFILE

Fernando Ruipérez
Universidad del País Vasco / Euskal Herriko …
52 PUBLICATIONS **420** CITATIONS
SEE PROFILE

David Mecerreyes
Universidad del País Vasco / Euskal Herriko …
199 PUBLICATIONS **5,900** CITATIONS
SEE PROFILE

Available from: Fernando Ruipérez
Retrieved on: 31 January 2016

ACS Macro Letters

Letter

pubs.acs.org/macroletters

Organocatalyzed Synthesis of Aliphatic Polyesters from Ethylene Brassylate: A Cheap and Renewable Macrolactone

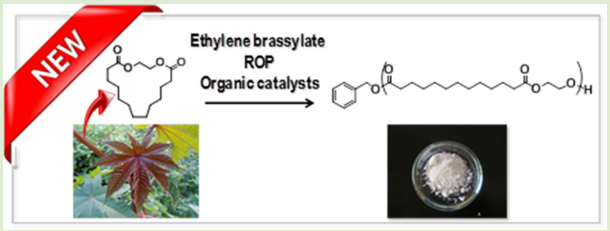
Ana Pascual,[†] Haritz Sardon,[†] Antonio Veloso,[†] Fernando Ruipérez,[†] and David Mecerreyes*[,†,‡]

[†]POLYMAT, University of the Basque Country UPV/EHU, Joxe Maria Korta Center, Avda. Tolosa 72, 20018, San Sebastian, Spain

[‡]Ikerbasque, Basque Foundation for Science, E-48011, Bilbao, Spain

Supporting Information

ABSTRACT: The use of organocatalysts for the polymerization of ethylene brassylate, a commercially available, cheap, and renewable macro(di)lactone is reported for the first time. Ethylene brassylate was polymerized by ring-opening polymerization under bulk and solution conditions at 80 °C. Polymerizations were carried out in the presence of several organic catalysts, such as dodecylbenzenesulfonic acid (DBSA), diphenyl phosphate (DPP), *p*-toluenesulfonic acid (PTSA) and bases, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2,3-tricyclohexylguanidine (TCHG), and 1,2,3-triisopropylguanidine (TIPG), using benzyl alcohol as initiator. Results agreed with a ring opening polymerization process in which the rate of polymerization was accelerated by the catalysts presence in the order of TBD > PTSA > DBSA > DPP > TIPG > TCHG. Complementary computational studies supported the experimental results. The obtained poly(ethylene brassylate) aliphatic polyesters were characterized by NMR, SEC, MALDI-TOF, DSC, and TGA. They showed molecular weights ranging from 2 to 13 kg mol^{-1} and polydispersity index between 1.5 and 2. Poly(ethylene brassylate) is a semicrystalline polyester similar to poly(ε−caprolactone) with slightly higher melting and glass transition temperatures (T_m = 69 °C, T_g = −33 °C) and good thermal stability.



Increasing attention is nowadays given to biobased polymers with the goal to decrease the dependence on fossil feedstock as well as to benefit from the structural features of certain renewable monomers. Of all biobased polymers, aliphatic polyesters have probably been investigated more extensively, in which poly(lactic acid) (PLA) takes a leading role.[1] The most common route to obtain PLA is the ring opening polymerization of the related six-membered cyclic diester (lactide). Organometallic catalysts such as metal alkoxydes[2−4] or carboxylates (tin octanoate)[5] have been historically considered the best option for the ring opening polymerization of lactide. In the last years the use of PLA in packaging[6] and biomedical applications[7] have motivated efforts to develop new research activities on nonmetal organic catalysts, to avoid catalyst related toxicity issues. Since 2001, several organic molecules like dimethylaminopyridine (DMAP),[8−10] organic acids,[11,12] N-heterocylylic carbenes (NHC-carbenes),[13−16] amidines,[17] guanidines,[18] and others[19−22] have been proven to be effective on the ROP of lactide.

More recently, an increasing number of studies have been reported on the synthesis of new biobased polyesters. Among other synthesis such as polycondensation of fatty acid-derived diols and diesters or thiol−ene chemistry of fatty acid-based α,ω-dienes,[23] the ring opening polymerization of large lactones (more than 12-membered cyclic esters) is of high interest. These macrolactones can be synthesized from inexpensive and abundantly available fatty acids using either chemical or enzymatic routes.[24−30]

The ring opening polymerization of macrolactones allows the formation of polymers with good mechanical properties such as ductility and strength. For example, poly(pentadecalactone) (PPDL) is an aliphatic polyester resembling the properties of low density PE (LDPE) in contrast to other renewable materials such as PLA that is intrinsically brittle.[31]

The polymerization mechanism of macrolactones differs from the behavior of small−medium size lactones.[32] While small tensioned lactones polymerization is promoted by the change in enthalpy when the ring strain is released, large size (less tensioned) lactones polymerization is mainly entropycally driven hindering the ring opening process. For this reason, a few examples of metal-catalyzed ROP of macrolactones can be found in the literature. The use of metal catalysts for ROP of macrolactones, such as ω-pentadecalactone (PDL), hexadecalactone (HDL), or unsaturated macrolactones such globalide or ambrettolide report mainly low molecular weights.[33,34] Only recently, some efficient aluminum and magnesium salt complexes based catalysts have been reported.[35,36]

Similarly, these macrolactones can be successfully polymerized by Lipases (enzymes).[37−39] In this process, the reactivity of the macrolactone is related to the preference of the lipase to the hydrophobic substrate and no longer determined by the ring-strain. However, enzymes are usually

Received: July 2, 2014
Accepted: August 8, 2014

 © XXXX American Chemical Society dx.doi.org/10.1021/mz500401u | *ACS Macro Lett.* 2014, 3, 849−853

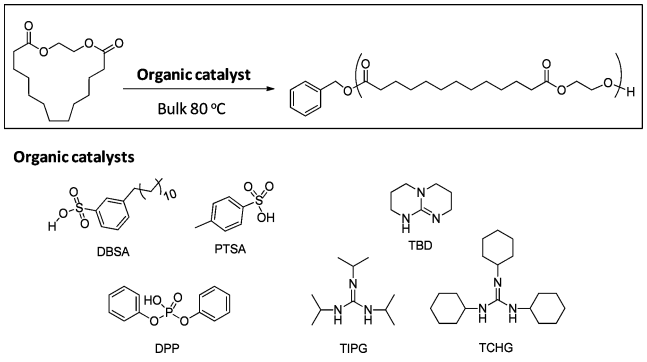
expensive, kinetics is slow, and they cannot be used at high temperatures. Heise et al. pioneered the use of organocatalysts for ROP of macrolactones to overcome the limitations of metal and enzymatic catalysis. For instance, the ring opening polymerization of ω-pentadecalactone using nitrogen bases (bicyclic guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD))[40] and organic acid catalysts has been reported.[41]

Among macrolactones, ethylene brassylate is a 17 member ring lactone commercially available and cheaper than lactide, ε-caprolactone and other macrolactones. It can be obtained from tridecanoic acid synthesized from 10-undecanoic acid,[42] which is an unsaturated fatty acid derived from castor oil renewable source (extracted from Castor plant). Only one attempt was reported for the polymerization of ethylene brassylate using enzymes, but low molecular weights were obtained.[43]

In this work, we report for the first time the organocatalyzed ring-opening polymerization of ethylene brassylate macro(di)-lactone leading to high molecular weight polyesters.

Several polymerizations of ethylene brassylate were carried out in bulk and in solution (toluene) at 80 °C using benzyl alcohol (BnOH) as initiator. Three acid catalysts (dodecylbenzenesulfonic acid (DBSA), diphenyl phosphate (DPP), *p*-toulenesulfonic acid (PTSA)) and three basic catalysts (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2,3-tricyclohexylguanidine (TCHG), and 1,2,3-triisopropylguanidine (TIPG)) were screened (Scheme 1; see Supporting Information for further experimental details).

Scheme 1. Ring-Opening Polymerization of Ethylene Brassylate in the Presence of Several Organic Catalysts



Conversion and molecular weight kinetics of ethylene brassylate polymerization were easily followed using ^{1}H NMR spectroscopy (see 3.1.1 point and corresponding Figure S1 in Supporting Information). Conversion kinetic results are plotted in Figure 1. As it is shown, the rate of polymerization is accelerated by the catalyst presence in the following order: TBD > PTSA > DBSA > DPP > TIPG > TCHG being the TBD the fastest catalyst and the TIPG the slowest. The differences in the rate of polymerizations are related to the capability of the catalysts to activate the species, which depends mostly, on the electrophilic or nucleophilic character of the catalysts (for acids and bases respectively). Thus, polymerizations catalyzed by strong sulfonic acids such as PTSA (pK_a = −2.8) or DBSA (pK_a = −2.5) are faster than reactions carried out using weak acids like DPP (pK_a = 2). On the other hand, TBD is known for being a strong superbase with pK_a ∼ 21, which makes the ROP the fastest among all the organic catalysts.

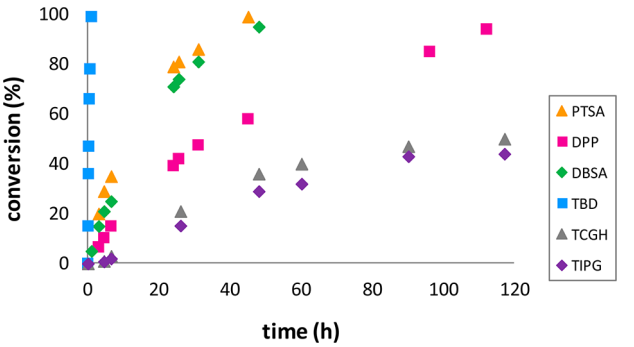


Figure 1. Conversion vs time calculated by ^{1}H NMR for ethylene brassylate polymerizations in bulk at 80 °C using different catalysts with molar ratios $[EB]_0/[BnOH]_0/[Catalyst]$ = 42:1:1.

In all cases, the polymerization can be roughly divided in two stages. A first stage in which the polymerization follows a first order kinetics and a second step (above 40% conversion) in which the monomer diffusion limitation slows down the reactions. This behavior is quite common in bulk polymerizations of macrolactones[35] and, in some cases, polymerization stop without reaching full conversions.

Complementary to experimental results, a comprehensive computational study was conducted to determine the activation mechanism of the fastest acid and basic catalysts PTSA and TBD, respectively (see point 3.5 in the Supporting Information for computational details). Figure 2 illustrates the energy

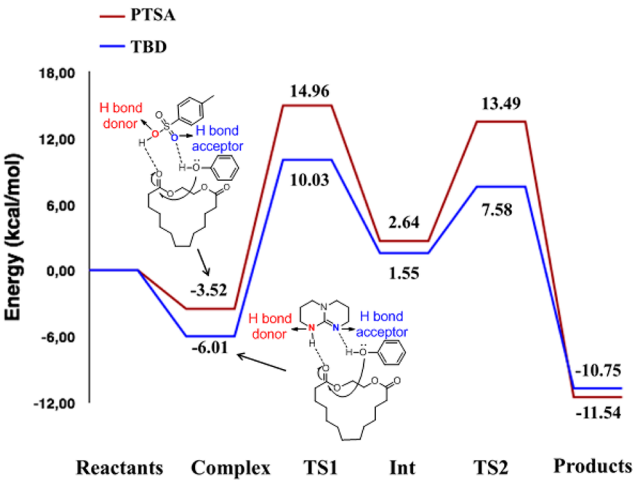


Figure 2. Energy profiles obtained for the dual activation mechanism of TBD (a) and PTSA (b) using benzyl alcohol as initiator.

profiles of both acid and base catalytic activation systems. According to the Gibbs free energy, PTSA-catalyzed ring opening of ethylene brassylate macrolactone is thermodynamically favorable ($\Delta G_{products} < 0$) and kinetically feasible (TS1−10 kcal·mol^{-1}). In this first step of polymerization, the sulfonic acid was predicted to behave as a bifuncional catalyst. This dual activation by sulfonic acid catalyst in the ring opening polymerization of esters,[44] carbonates,[45,46] and in the polymerization of urethanes[47] was recognized recently. As expected, the nucleophilic addition proceeds via activation of both the monomer and the alcohol. The sulfonic acid acts as a proton shuttle via its acidic hydrogen atom and basic oxygen atoms. Similarly, for TBD catalyst, also a dual activation of the monomer and alcohol is computed. The acidic hydrogen atom

dx.doi.org/10.1021/mz500401u | ACS Macro Lett. 2014, 3, 849−853

Table 1. Ring-Opening Polymerization of Ethylene Brassylate Mediated by Binary Catalyst/Initiator Systems

entry[a]	catalyst	[EB]/[BnOH]/[C]	time (h)	conversion[b] (%)	$M_{n,\,theor}$[c] (kg mol^{-1})	$M_{n,^1H\ NMR}$[d] (kg mol^{-1})	$M_{n,GPC}$[e] (kg mol^{-1})	$Đ$[e] M_w/M_n
1	DPP	42/1/1	112	93	10.7	9.1	7.1	1.9
2	DBSA	42/1/1	95	95	10.8	6.2	5.9	1.9
3	PTSA	42/1/1	38	99	11.3	3.6	2.0	2.7
4	TCHG	42/1/1	141	52	6.0	4.2	7.4	1.5
5	TIPG	42/1/1	141	46	5.3	4.2	7.0	1.5
6	TBD	42/1/1	1	99	9.7	13.9	10	1.8
7	TBD	10/1/1	0.25	99	2.8	2.5	4.2	1.6
8	TBD	200/1/1	96	31	21.7	6.2	13.2	1.9
9	TBD	100/1/1	96	58	15.7	5.5	7.4	1.9
10[f]	TBD	100/1/1	44	73	19.8	6.1	7.4	1.7

[a]Reactions were conducted at 80 °C in bulk. [b]Conversion of poly(ethylene brassylate), as determined by ^{1}H NMR from the α-methylene of ethylene brassylate and poly(ethylene brassylate) resonances (detailed information on the calculation is described in Figure S1 in the Supporting Information. [c]Number molecular weight calculated from $([EB]_0/[BnOH]_0 \times conv \times 270.36) + 108$. [d]Experimental M_n calculated by ^{1}H NMR spectroscopy (detailed information on the calculation is described in Figure S1 in the Supporting Information). [e]Experimental M_n and polydispersity index $Đ$ determined by GPC in THF. GPC results are not absolute but relative to polystyrene standards. [f]Reaction performed in toluene 0.7 M solution at 80 °C.

of the TBD is transferred to the carbonyl oxygen of the monomer and the basic nitrogen takes the proton of the alcohol. This behavior was also observed in lactide polymerization.[48] Thus, the computed activation barriers for the first step in the ring opening polymerization of ethylene brassylate using both catalysts are consistent with the relatively fast polymerizations observed experimentally, being kinetically more favored when TBD was used (detailed information on the dual activation mechanism and 3D structures corresponding to each transition state and intermediates are attached in the Supporting Information, Figure S4).

All tested organic catalysts (3 bases and 3 acids) were active in promoting the polymerization of ethylene brassylate leading to polyesters with relatively high molecular weight. Representative results are summarized in Table 1. For the same EB/BnOH/TBD ratios of 42:1:1 and 80 °C bulk conditions, TBD catalyst affords full conversions in 1 h, while for most catalysts, polymerization times ranged from 38 to 112 h. All acid catalysts are able to bring the polymerizations to almost full conversion. DPP and DBSA catalyzed polymerization, leads to relatively high molecular weight polyesters from 6.2 to 9.1 kg mol^{-1}. Basic catalysts like TCHG and TIPG are not able to reach full conversion under those experimental conditions (around 50%). The fact that these catalysts are weak and sterically hindered bases makes the polymerization slow. The combination of TBD/BnOH proves to be the fastest system to promote the ROP of ethylene brassylate leading to polyesters of M_n = 13.9 kg mol^{-1} at EB/BnOH/TBD ratios of 42:1:1. Increasing the monomer to initiator ratio to 100:1:1 (entry 9) and 200:1:1 (entry 8) lower molecular weights than expected were obtained due to the limited conversion of the reactions, 58 and 31%, respectively. This can be explained by the slow diffusion of the monomer in the bulk polymerization conditions and the low amount of catalyst. The use of a solvent in the reaction helps to avoid viscosity limitations (entry 10) but makes the polymerizations slower than under bulk conditions.

According to Table 1, the experimental molecular weight values at maximum conversion are lower than theoretical ones. This is more clearly observed in the case of acid catalysts than in the case of basic ones. In addition to this, polydispersity index show final values between 1.5 and 1.8 for basic catalysts and 1.9−2.7 for acids.

To get in more detail regarding molecular weight data, Figure 3 shows the evolution of the molecular weight during the polymerization at different conversions. A linear increase of the molecular weight during the polymerization is observed according with a ring-opening polymerization process. However, results do not agree with a controlled polymerization where experimental M_n values correspond to calculated theoretical ones. M_n values obtained with DPP, TCHG, and TIPG at the early stage of polymerization (from 0 to 40% conversion) are close to theoretical values. However, at high conversions, the obtained M_n shows smaller values that the theoretical ones, indicating the absence of control probably due to transesterification reactions. On the other hand, in reactions carried out with PTSA strong acid and TBD strong base, the control is lost from the beginning of the reaction indicating transesterification reactions also in the early stages of the polymerization. PTSA is a strong acid, difficult to dry leading to polymers of very low molecular weights and on the contrary, TBD shows M_n values higher than the theoretical ones even at low conversions. This observation will be further investigated and reported.

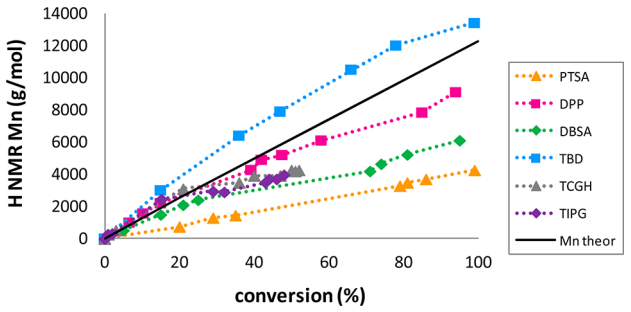


Figure 3. M_n kinetics determined by ^{1}H NMR for ethylene brassylate polymerizations in bulk at 80 °C using different catalysts with molar ratios $[EB]_0/[BnOH]_0/[Catalyst]$ = 42:1:1.

In order to analyze the nature of the polymer end groups and transesterification reactions, MALDI-TOF spectrometry technique was used. It is clearly seen in MALDI-TOF spectra (see 3.2.1 explanation and corresponding Figure S2 in the Supporting Information) the presence of species initiated by benzylalcohol. This indicates that benzyl alcohol is an efficient initiator for the polymerization. The presence of species

dx.doi.org/10.1021/mz500401u | ACS Macro Lett. 2014, 3, 849−853

generated from inter and intramolecular transesterifications were also detected. This can explain the observed broad polydispersity values in GPC ($Đ$ = 1.5−2.7).

Finally, thermal properties of poly(ethylene brassylate) were studied by using differential scanning calorimetry (DSC; Figure 4a), and thermal stability of the polymer was determined by

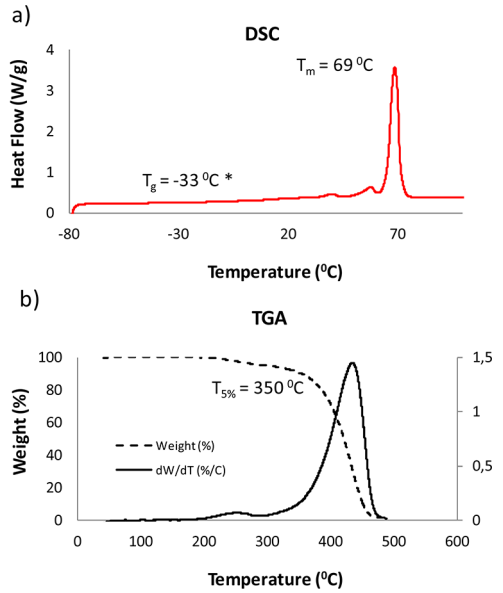


Figure 4. (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) of poly(ethylene brassylate) (entry 6). *Detailed T_g is shown in Figure S3 of the Supporting Information.

thermogravimetric analysis (TGA; Figure 4b). As shown in the DSC trace, poly(ethylene brassylate) is a semicrystalline long-chain polyester with a T_g of −33 and melting temperature of 69 °C similar to short-chain polyesters such as poly(ε-caprolactone) which T_m is around 65 °C. Despite the fact that the poly(ethylene brassylate) has longer aliphatic chain than poly(ε-caprolactone) the presence of (−OCH_2CH_2O−) increases the chain mobility having a direct effect in the thermal properties of the polyester. This result is in good agreement with literature values for similar polyesthers obtained by polycondensation.[49−51]

The weight loss of poly(ethylene brassylate) shown in TGA analysis, started around 250 °C and the remaining weight of the sample reached zero at around 480 °C. The derivative thermogravimetric curve (DTG) of poly(ethylene brassylate) gives a maximum value at 440 °C.

In summary, we report for the first time the organocatalyzed ring-opening polymerization of ethylene brassylate. Ethylene brassylate is renewable, commercially available, and cheaper than lactide, ε-caprolactone, and other macrolactones. Polymerization occurs by a ring-opening polymerization mechanism under bulk and solution conditions at 80 °C in the presence of several bases and acids catalysts, being TBD and PTSA the fastest ones. Computational studies confirmed a dual activation mechanism of both catalysts which is consistent with the experimental polymerization rates obtained. Poly(ethylene brassylate)s of molecular weights ranging between 2 and 13 kg mol^{-1} and polydispersity index between 1.5 and 2 were obtained. Poly(ethylene brassylate) is a semicrystalline polyester similar to poly(ε-caprolactone) with a slightly higher melting temperature (T_m = 69 °C) and good thermal stability. These properties make poly(ethylene brassylate) an interesting aliphatic polyesther alternative for the synthesis of segmented polyurethanes,[52] particularly for shape memory polyurethanes (SMPUs)[53] and also as renewable "hand-moldable plastic" in hobbyist and prototyping market.[54]

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, equipment specifications, ^{1}H NMR, MALDI-TOF, DSC, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: david.mecerreyes@ehu.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The financial support of Basque Government, the University of the Basque Country UPV/EHU (UFI11/56) and MINECO through Projects MAT2010-16171 is acknowledged. The SGI/IZO-SGIKER UPV/EHU is also gratefully acknowledged for generous allocation of computational resources.

■ REFERENCES

(1) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−76.
(2) Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2009**, *28*, 1469−1475.
(3) Sinenkov, M.; Kirillov, E.; Roisnel, T.; Fukin, G.; Trifonov, A.; Carpentier, J.-F. *Organometallics* **2011**, *30*, 5509−5523.
(4) Hayes, C. E.; Sarazin, Y.; Katz, M. J.; Carpentier, J.-F.; Leznoff, D. B. *Organometallics* **2013**, *32*, 1183−1192.
(5) Wang, L.; Poirier, V.; Ghiotto, F.; Bochmann, M.; Cannon, R. D.; Carpentier, J.-F.; Sarazin, Y. *Macromolecules* **2014**, *47*, 2574−2584.
(6) Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, *4*, 835−864.
(7) Lasprilla, A. J. R.; Martinez, G. A. R.; Lunelli, B. H.; Jardini, A. L.; Filho, R. M. *Biotechnol. Adv.* **2012**, *30*, 321−328.
(8) Nederberg, F.; Connor, E. F.; M?ller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712−2715.
(9) Thillaye Du Boullay, O.; Marchal, E.; Martin-Vaca, B.; Cossio, F. P.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 16442.
(10) Kadota, J.; Pavlovic, D.; Desvergne, J.-P.; Bibal, B.; Peruch, F.; Deffieux, A. *Macromolecules* **2010**, *43*, 8874.
(11) Bourissou, D.; Martin-Vaca, D.; Dumitrescu, A.; Graullier, M.; Lacombe, F. *Macromolecules* **2005**, *38*, 9993−9998.
(12) Makiguchi, K.; Yamanaka, T.; Kakuchi, T.; Terada, M.; Satoh, T. *Chem. Commun.* **2014**, *50*, 2883−2885.
(13) Connor, E. F.; Nyce, G. W.; Myers, M.; Möck, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914−915.
(14) Coulembier, O.; Lohmeijer, B. G. G.; Dove, A. P.; Pratt, R. C.; Mespouille, L.; Culkin, D. A.; Benight, S. J.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 5617−5628.
(15) Mareva, F.; Vignolle, J.; Taton, D. *Polym. Chem.* **2013**, *4*, 1995.
(16) Fèvre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. *Chem. Soc. Rev.* **2013**, *42*, 2142−2172.
(17) Brown, H. A.; De Crisci, A. G.; Hedrick, J. L.; Waymouth, R. M. *ACS Macro Lett.* **2012**, *1*, 1113−1115.
(18) Lohmeijer, B. G. G.; Oratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574−8583.
(19) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093−2107.
(20) Dove, A. P. *ACS Macro Lett.* **2012**, *1*, 1409−1412.

(21) Coady, D. J.; Fukushima, K.; Horn, H. W.; Rice, J. E.; Hedrick, J. L. *Chem. Commun.* **2011**, *47*, 3105−3107.
(22) Coady, D. J.; Engler, A. C.; Horn, H. W.; Bajjuri, K. M.; Fukushima, K.; Jones, G. O.; Nelson, A.; Rice, J. E.; Hedrick, J. L. *ACS Macro Lett.* **2012**, *1*, 19−22.
(23) Quinzler, D.; Mecking, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4306.
(24) Furst, M.R. L.; Goff, R. Le.; Quinzler, D.; Mecking, S.; Botting, C. H.; Cole-Hamilton, D. J. *Green Chem.* **2012**, *14*, 472.
(25) Van der Meulen, I.; de Geus, M.; Antheunis, H.; Deumens, R.; Joosten, E. A. J.; Koning, C. E.; Heise, A. *Biomacromolecules* **2008**, *9*, 3404−3410.
(26) Van der Meulen, I.; Li, Y.; Deumens, R.; Joosten, E. A. J.; Koning, C. E.; Heise, A. *Biomacromolecules* **2011**, *12*, 837−843.
(27) Van der Meulen, I.; Gubbels, E.; Huijser, S.; Sablong, R.; Koning, C. E.; Heise; Duchateau, R. *Macromolecules* **2011**, *44*, 4301−4305.
(28) Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *12*, 3291−3298.
(29) Lu, W.; Ness, J. E.; Xie, W.; Zhang, X.; Minshull, J.; Gross, R. A. *J. Am. Chem. Soc.* **2010**, *132*, 15451−15455.
(30) Schrewe, M.; Magnusson, A. O.; Willrodt, C.; Bühler, B.; Schmid, A. *Adv. Synth. Catal.* **2011**, *353*, 3485−3495.
(31) Zhizhong, S.; Qiuying, L.; Yongjun, L.; Guo-Hua, H.; Chiefei, W. *Eur. Polym. J.* **2009**, *8*, 2428−2433.
(32) Dubois, P.; Coulembier, O.; Raquez, J. M. *Handbook of Ring Opening Polymerization*; Wiley-VCH Verlag GmbH & Co. KGaA: Wenheim, 2009.
(33) Wang, Y.; Kunika, M. *Macromol. Symp.* **2005**, *224*, 193.
(34) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem. Phys.* **2000**, *201*, 1329.
(35) Pepels, M. P. F.; Bouyahyi, M.; Heise, A.; Duchateau, R. *Macromolecules* **2013**, *46*, 4324−4334.
(36) Wilson, J. A.; Hopkings, S. A.; Wright, P. M.; Dove, A. P. *Polym. Chem.* **2014**, *5*, 2691−2694.
(37) De Geus, M.; van der Meulen, I.; Goderis, B.; van K, H.; Dorschu, M.; van der Werff, H.; Koning, C. E.; Heise, A. *Polym. Chem.* **2010**, *1*, 525−533.
(38) Claudino, M.; Van der Meulen, I.; Trey, S.; Jonsson, M.; Heise, A.; Johansson, M. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 16−24.
(39) Ates, Z.; Heise, A. *Polym. Chem.* **2014**, *5*, 2936−2941.
(40) Bouyahyi, M.; Pepels, M. P. F.; Heise, A.; Duchateau, R. *Macromolecules* **2012**, *45*, 3356−3366.
(41) Pascual, A.; Leiza, J. R.; Mecerreyes, D. *Eur. Polym. J.* **2013**, 1601−1609.
(42) Ravi, S.; Padmanabhan, D.; Mamdapur, V. R. *J. Indian Inst. Sci.* **2001**, *81*, 299−312.
(43) Müller, S.; Uyama, H.; Kobayashi, S. *Chem. Lett.* **1999**, 1317.
(44) Gazeau-Bureau, S.; Delcroix, D.; Martín-Vaca, B.; Bourissou, D.; Navarro, C.; Magnet, S. *Macromolecules* **2008**, *41*, 3782−3784.
(45) Coady, D. J.; Horn, H. W.; Jones, G. O.; Sardon, H.; Engler, A. C.; Waymouth, R. M.; Rice, J. E.; Yang, Y. Y.; Hedrick, J. L. *ACS Macro Lett.* **2013**, *2*, 306−312.
(46) Delcroix, D.; Martín-Vaca, B.; Bourissou, D.; Navarro, C. *Macromolecules* **2010**, *43*, 8828−8835.
(47) Sardon, H.; Engler, A. C.; Chan, J. M. W.; García, J. M.; Coady, D. J.; Pascual, A.; Mecerreyes, D.; Jones, G. O.; Rice, J. E.; Horn, H. W.; Hedrick, J. L. *J. Am. Chem. Soc.* **2013**, *135*, 16235−16241.
(48) Zhang, L.; Pratt, R. C.; Nederberg, F.; Horn, H. W.; Rice, J. E.; Waymouth, R. M.; Wade, C. G.; Hedrick, J. L. *Macromolecules* **2010**, *43*, 1660−1664.
(49) Stempfle, F.; Roesle, P.; Mecking, S. *ACS Symposium Series*; American Chemical Society: Washington, DC, 2012; Vol. *1105*.
(50) Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159−4166.
(51) Laflèche, F.; Jarroux, P.; Raoul, N.; Claude, S.; Guégan, P. *Eur. Polym. J.* **2013**, *49*, 813−822.
(52) Rueda-Larraz, L.; Fernandez dArlas, B.; Mondragón, I.; Eceiza, A. *Eur. Polym. J.* **2009**, *45*, 2096−2109.
(53) (a) Momtaz, M.; Razavi-Nouri, M.; Barikani, M. *J. Mater. Sci.* **2014**. DOI 10.1007/s10853-014-8466-y. (b) Peponi, L.; Navarro-Baena, I.; Sonseca, A.; Gimenez, E.; Marcos-Fernandez, A.; Kenny, J. M. *Eur. Polym. J.* **2013**, *49*, 893−903.
(54) http://www.plastimake.com/examples.