Stereoselectivity in Metallocene-Catalyzed Coordination Polymerization of Renewable Methylene Butyrolactones: From Stereo-random to Stereo-perfect Polymers

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Ⓢ *Supporting Information*

ABSTRACT: Coordination polymerization of renewable α-methylene-γ-(methyl)butyrolactones by chiral C_2-symmetric zirconocene catalysts produces stereo-random, highly stereo-regular, or perfectly stereo-regular polymers, depending on the monomer and catalyst structures. Computational studies yield a fundamental understanding of the stereocontrol mechanism governing these new polymerization reactions mediated by chiral metallocenium catalysts.

Sustainability is an emerging global issue of importance to all humanity, while stereoselectivity is a perpetual fundamental task in chemical synthesis. Synthetic polymers, predominantly petroleum-based at present, are essential to modern life and the global economy. As petroleum resources continue to be depleted, an imminent challenge exists to gradually replace petroleum-based synthetic polymers with those derived from renewable resources in a technologically and economically competitive fashion.[1] An important approach to advanced synthetic polymers is to control stereoselectivity of polymerization, which leads to stereo-regular polymers that often exhibit physical and mechanical properties superior to those of their stereo-random counterparts.[2]

Toward the above two goals, we have been investigating the polymerization catalysis of polar conjugated alkenes such as renewable methylene butyrolactones,[3] including naturally occurring α-methylene-γ-butyrolactone (MBL)[4] and plant biomass-derived γ-methyl-α-methylene-γ-butyrolactone (γMMBL).[5] Several metal-based and organic catalyst systems exhibit remarkably high activity in converting such polar feedstocks into medium to high molecular weight polymers; however, the resulting polymers are essentially atactic, amorphous materials.[3] To achieve any appreciable level of stereoselectivity in this polymerization, we turned our attention to chiral, single-site group 4 metallocenium catalysts due to their demonstrated precision in the catalyst-site stereochemical control manifested in the coordination polymerization of both nonpolar alkenes[6] and polar (conjugated) alkenes.[7] Initial studies revealed a *significant challenge* in achieving stereochemical control in the polymerization of such small, cyclic

monomers containing a highly reactive exocyclic C=C double bond; for example, highly stereospecific zirconocenium catalysts, which readily produce highly syndiotactic[8] and isotactic[9] polymers in the polymerization of the linear analogue methyl methacrylate (MMA), yielded only syndio-biased[3e] or iso-biased atactic polymers. Communicated herein are a discovery of the formation of highly isotactic to perfectly isotactic polymers derived from the polymerization of β-methyl-α-methylene-γ-butyrolactone ($_\beta$MMBL)[10] by C_2-symmetric zirconocenium catalysts and a fundamental understanding of the stereocontrol mechanism governing these new polymerization reactions catalyzed by chiral metallocenes.

This study employed two prototype C_2-ligated zirconocenium catalysts (Scheme 1), *rac*-(EBI)Zr$^+$(THF)[OC(O^{i}Pr)=

Scheme 1. Structures of Monomers, Polymers, and Catalysts Employed in This Study
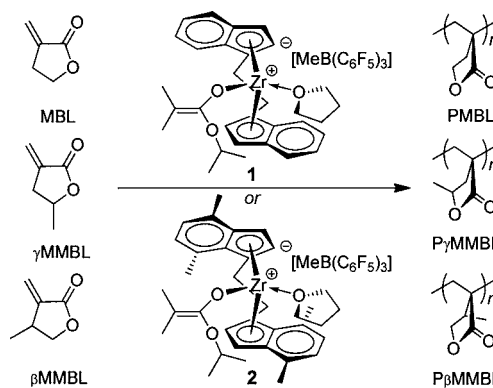
CMe$_2$][MeB(C$_6$F$_5$)$_3$]$^-$ [**1**, EBI = C$_2$H$_4$(η^5-indenyl)$_2$][9] and *rac*-(EBDMI)Zr$^+$(THF)[OC(O^{i}Pr)=CMe$_2$][MeB(C$_6$F$_5$)$_3$]$^-$ [**2**, EBDMI = C$_2$H$_4$(η^5-4,7-dimethylindenyl)$_2$].[11] Polymerization of the parent MBL by either catalyst in CH$_2$Cl$_2$ at room temperature (rt) was active, but with a low turnover frequency (TOF) of ≤ 10 h^{-1} and a low polymer yield of $\leq 40\%$ (entries 1 and 2, Table 1). The resulting PMBL polymers had medium

Table 1. Selected Results of Polymerization by Catalysts 1 and 2 in CH$_2$Cl$_2$ at 25 °C

entry no.	monomer (M)	catalyst (cat.)	[M]/[cat.] ratio	time (min)	yield (%)	TOF (h^{-1})	$M_n{}^a$ (kg/mol)	PDI^a (M_w/M_n)	[mm]^b (%)	[mr]^b (%)	[rr]^b (%)	$T_g{}^c$ (°C)
1	MBL	1	125	300	40.2	10	17.4	1.39	42.0	30.5	27.5	195
2	MBL	2	400	1440	28.3	3.3	20.1	1.30	17.1	35.5	47.4	196
3	$_\gamma$MMBL	1	400	60	90.0	360	60.5^d	1.41	22.8	42.4	34.8	n.d.
4	$_\gamma$MMBL	2	400	60	>99	400	64.5	1.14	12.7	41.8	45.5	227
5	$_\beta$MMBL	1	245	60	>99	245	n.d.	n.d.	>99	–	–	n.d.
6	$_\beta$MMBL	2	100	60	>99	100	n.d.	n.d.	95.2	3.8	1.0	288
7	(R)-$_\beta$MMBL	1	200	60	>99	200	n.d.	n.d.	>99	–	–	n.d.

^{a}Measured by GPC in DMF relative to PMMA standards. M_n and PDI of the resulting highly isotactic P$_\beta$MMBL were not determined (n.d.) due to its insolubility in common GPC solvents. ^{b}Polymer tacticity (quaternary carbon, rr, mr, mm) measured by ^{13}C NMR. ^{c}Measured by DSC. ^{d}A small high molecular weight shoulder was also present.

molecular weights and molecular weight distributions: number-average molecular weight (M_n) = 17.4 kg/mol, polydispersity index (PDI) = 1.39 by **1**, and M_n = 20.1 kg/mol, PDI = 1.30 by **2**. Surprisingly, the polymer is either an iso-biased atatic material (mm = 42.0%, mr = 30.5% by **1**) or a syndio-biased material (rr = 47.4%, mr = 35.5% by **2**), clearly indicating the inability of such chiral catalysts to exert site control in this polymerization. The glass transition temperature (T_g) of 195 °C (entry 1) is identical to that of the atactic PMBL produced by radical polymerization.[12]

Moving on to $_\gamma$MMBL, nearly all aspects of the polymerization were drastically enhanced, except for stereoselectivity. Nonetheless, this polymerization by both catalysts was rapid, achieving high to quantitative polymer yields within 1 h and producing P$_\gamma$MMBL with M_n = 60.5 kg/mol, PDI = 1.41 by **1** (entry 3) and M_n = 64.5 kg/mol, PDI = 1.14 by **2** (entry 4, Table 1). However, the polymers are still essentially atactic, amorphous materials with mr = 42% by **1** or **2**, again indicating non-stereoselectivity of such chiral catalysts. The T_g of 227 °C (entry 4) is the same as that reported for the atactic P$_\gamma$MMBL produced by other catalyst or initiator systems.[3d-f]

Switching from $_\gamma$MMBL to $_\beta$MMBL maintained high polymerization activity of both catalysts (entries 5 and 6, Table 1), but most remarkably, now a highly isotactic (mm = 95.2% by **2**) or a perfectly isotactic polymer (mmmm > 99% by **1**) was produced. Figure 1 depicts an overlay of ^{13}C NMR spectra (125 MHz) of P$_\beta$MMBL produced by **1** and **2**, in the backbone quaternary carbon triad region, while Figure 2 shows an overlay of ^{13}C NMR spectra of P$_\beta$MMBL produced by AIBN and **1**, in the carbonyl carbon pentad region. The assignments of the quaternary carbon triads were based on those established for P$_\gamma$MMBL[3f,13] but were also confirmed by isotactic polymer derived from enantiopure monomer. Figure 3a,b displays the triad regions of atactic and isotactic P$_\beta$MMBL from polymerization of racemic $_\beta$MMBL by AIBN and **1**, respectively, and Figure 3c,d displays the same for isotactic P[(R)-$_\beta$MMBL] from polymerization of enantiopure (R)-$_\beta$MMBL with AIBN and **1**, respectively (entry 7, Table 1). In sharp contrast to atactic P$_\beta$MMBL prepared by AIBN-initiated radical polymerization, which is soluble in common organic solvents such as N,N-dimethyl formamide, dimethyl sulfoxide, and acetonitrile, even at rt, the resulting highly isotactic P$_\beta$MMBL is insoluble in the above or other common organic solvents, including dichlorobenzene, at rt or refluxing temperatures. This observation shows excellent solvent resistance of isotactic P$_\beta$MMBL. The high T_g value of 288 °C (entry 6) is similar to that observed for the P$_\beta$MMBL produced by a lanthanide catalyst.[10b]
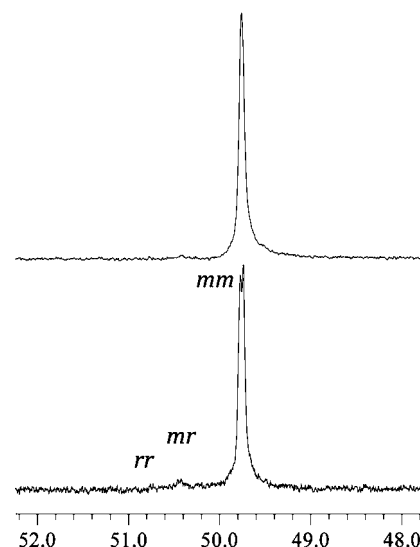

Figure 1. Overlay of ^{13}C NMR (trifluoroacetic acid (TFA)-d_1, 125 MHz, 70 °C) spectra of P$_\beta$MMBL produced by catalyst **1** (top; see entry 5, Table 1) and catalyst **2** (bottom; see entry 6, Table 1), in the backbone quaternary carbon (rr, mr, mm) region.
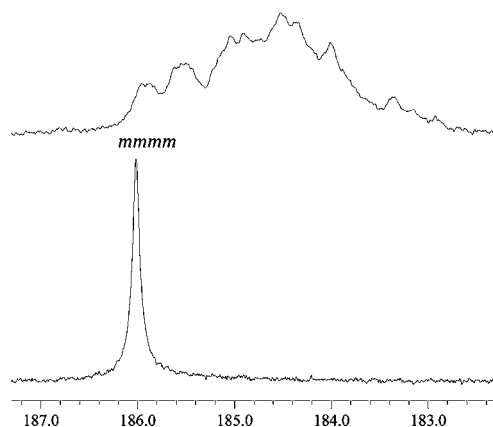

Figure 2. Overlay of ^{13}C NMR (TFA-d_1, 125 MHz, 70 °C) spectra of P$_\beta$MMBL produced by AIBN (top) and catalyst **1** (bottom, entry 5), in the carbonyl carbon pentad region.

It is striking that the same chiral catalysts polymerized MBL and $_\gamma$MMBL into stereo-random polymers but $_\beta$MMBL into highly isotactic or perfectly isotactic polymers. To understand the stereocontrol mechanism governing these polymerization reactions, we performed computational studies of these reactions using the Amsterdam Density Functional (ADF)
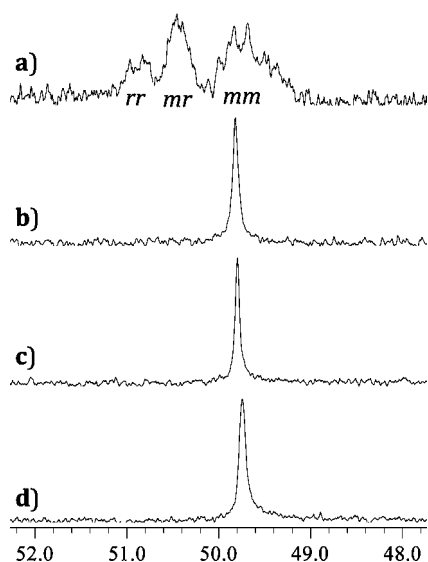
Figure 3. Overlay of ^{13}C NMR (TFA-d_1, 75 MHz, 70 °C) spectra of P$_\beta$MMBL produced by AIBN (a) and catalyst **1** (b), and P[(R)-$_\beta$MMBL] produced by AIBN (c) and catalyst **1** (d), in the backbone quaternary carbon (*rr*, *mr*, *mm*).
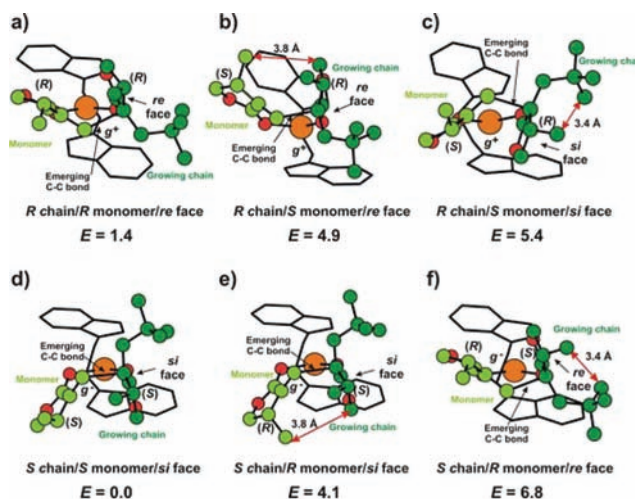

Figure 4. TS geometries for the competitive $_\beta$MMBL addition on an *R* chain (a–c) and on an *S* chain (d–f). In all cases the monomer and the chain are located on the same side (cis) of the equatorial belt of the (R,R)-(EBI)Zr catalyst **1**. The energies (kcal/mol) consider solvent (CH$_2$Cl$_2$) effects and are relative to the most stable TS *S* chain/*S* monomer/*si* face (d). The ^{t}Bu group was used to model the remainder of the growing chain.

program[14] and following the procedures we described earlier for MMA polymerization by the Me$_2$C< bridged zirconocenium catalysts.[15] Starting from the MBL polymerization by **1** with an *R,R*-coordinated EBI ligand, we computed eight transition states (TSs),[11] considering both prochiral faces (*re* and *si*) of the growing chain, geometries where the O atoms of five-membered rings of the monomer and of the chain are located on opposite sides (trans) or on the same side (cis) of the metallocene equatorial belt, and g^+ and g^- conformations of the metallocene ethylene bridge. Concisely, in the case of MMA polymerization by (R,R)-**1**, the most stable TSs present a trans disposition of the methoxy groups of monomer and chain and a g^- conformation of the EBI bridge. The overall selectivity in favor of the *re* face of the growing chain for MMA addition was calculated to be 4.1 kcal/mol (Figure S3a,b), in agreement with the high isotacticity (~95% *mm*) of PMMA achieved experimentally.[9] In contrast, in the polymerization of MBL, the five-membered rings of the monomer and chain prefer a *cis orientation*, and addition at the *si* face of the growing chain is favored by only 1.3 kcal/mol over addition at the *re* face (Table S2), thus being marginally stereoselective and conforming to the experimental data. The different behavior of MBL vs MMA suggests that the cis orientation adopted by the less encumbered five-membered lactone rings of MBL does not interact significantly with the metallocene skeleton (Figure S3c,d).

For polymerization of racemic $_\beta$MMBL, we considered addition of both *R* and *S* $_\beta$MMBL to an *R* or *S* growing chain, where *R* and *S* refer to the configuration of the last inserted $_\beta$MMBL unit, on an (R,R)-**1** catalyst. Table S3 summarizes the relative energies of the eight most probable TSs for addition of a $_\beta$MMBL molecule, while competitive TS geometries for both *R* and *S* chains are compared in Figure 4. Calculations indicate that, in the case of an *R* chain, addition of another *R* $_\beta$MMBL molecule on the *re* face of the growing chain (Figure 4a) is clearly favored. Competition is with addition of an *S* $_\beta$MMBL molecule on the *re* face (Figure 4b), which is disfavored by 3.5 kcal/mol (ΔE_{S-R}) due to steric repulsion between the β-Me groups of the chain and the monomer, and with addition of an

S $_\beta$MMBL molecule on the *si* face (Figure 4c), which is disfavored by 4.0 kcal/mol (ΔE_{si-re}) as a result of steric interaction within the growing chain. By similar analysis, in the case of an *S* chain, addition of another *S* $_\beta$MMBL molecule on the *si* face of the growing chain (Figure 4d) is favored over addition of an *R* $_\beta$MMBL molecule on the *si* face (Figure 4e) by 4.1 kcal/mol. Addition of *R* $_\beta$MMBL on the *re* face of an *S* chain is disfavored by at least 6.8 kcal/mol (Figure 4f). In short, calculations indicate that, for the *R,R*-ligated EBI catalyst, the *R* chain clearly favors addition of another *R* $_\beta$MMBL molecule on the *re* face of the chain, while the *S* chain clearly favors addition of another *S* $_\beta$MMBL molecule on the *si* face of the chain. As the calculation yielded a high *re* over *si* and *R* over *S* selectivity for an *R* chain, and a high *si* over *re* and *S* over *R* selectivity for an *S* chain, the resulting P$_\beta$MMBL should display a high regularity in the sequence of the configurations of the chiral β-C atom of the five-membered ring and should be highly isotactic. In fact, for both chains we calculated ΔE_{stereo} = 4 kcal/mol, which corresponds to >99% of *mmmm* pentads at 25 °C, in agreement with the experimental results (vide supra).

In sharp contrast to the computational results on $_\beta$MMBL addition, similar calculations for $_\gamma$MMBL (Table S4) clearly show no selectivity for addition of an *R* or *S* $_\gamma$MMBL on the *R* growing chain, with all the TSs within 0.8 kcal/mol and the most stable TS corresponding to addition of an *S* $_\gamma$MMBL at the *re* face of an *R* chain. In the case of an *S* chain, $_\gamma$MMBL addition on the *si* face is somewhat favored, but there is no selectivity between additions of an *R* or *S* $_\gamma$MMBL. In short, $_\gamma$MMBL addition at both *S* and *R* chains is *non-stereoselective*, which is also in agreement with the experimental results. The steric interactions involving the monomer, the chain, and the ligand, which are responsible for the high selectivity of $_\beta$MMBL addition (Figure 4), became negligible in the case of $_\gamma$MMBL addition (Figure S5). This outcome is due to the fact that the γ-Me substituents protrude away from the reaction center, whereas the β-Me substituents are well located in the area where the C−C bond-forming step occurs.

In summary, we have demonstrated that renewable α-methylene-γ-butyrolactones can be readily converted into the corresponding polymers through coordination polymerization by chiral metallocenium catalysts, but the resulting polymer stereochemistry spans from being stereo-random to being stereo-perfect. Specifically, the polymerization of MBL and $_\gamma$MMBL by two prototype C_2-zirconocenium catalysts (**1** and **2**) leads to atactic polymers, whereas the polymerization of $_\beta$MMBL by **1** and **2** affords highly isotactic and perfectly isotactic polymers, respectively. Computational studies on the competitive monomer addition TS geometries have revealed that steric interactions involving the monomer, the chain, and the catalyst ligand are responsible for achieving or lacking the observed stereocontrol. Thus, in the case of $_\beta$MMBL polymerization by the *R,R*-ligated EBI catalyst, the TS corresponding to *S* chain/*S* monomer/*si* facial addition (Figure 4d) is clearly favored for an *S* chain. Likewise, for an *R* chain the *R* chain/*R* monomer/*re* facial addition (Figure 4a) is clearly favored, thereby rationalizing highly isotactic polymer formation. In contrast, in the case of MBL or $_\gamma$MMBL addition, such steric interactions become negligible, thus rendering the polymerization non-stereoselective by the current catalyst system. However, it should be possible to molecularly engineer catalyst structures, assisted by computational studies, which promote stereoselective polymerization of MBL or $_\gamma$MMBL. Research toward this direction is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details, and synthesis and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) For selected reviews or special journal issues, see: (a) Coates, G. W.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 7987−7989. (b) Gandini, A. *Macromolecules* **2008**, *41*, 9491−9504. (c) Tullo, A. H. *Chem. Eng. News* **2008**, *86* (39), 21−25. (d) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1−10. (e) Meier, M. A. R.; Metzger, J. O.; Schubert, S. *Chem. Soc. Rev.* **2007**, *36*, 1788−1802.

(2) For a recent review, see: Miyake, G. M.; Chen, E. Y.-X. *Polym. Chem.* **2011**, *2*, 2462−2480.

(3) (a) Zhang, Y.; Chen, E. Y.-X. *Angew. Chem., Int. Ed.* **2012**, *51*, 2465−2469. (b) Zhang, Y.; Gustafson, L. O.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2011**, *133*, 13674−13684. (c) Zhang, Y.; Miyake, G. M.; Chen, E. Y.-X. *Angew. Chem., Int. Ed.* **2010**, *49*, 10158−10162. (d) Hu, Y.; Xu, X.; Zhang, Y.; Chen, Y.; Chen, E. Y.-X. *Macromolecules* **2010**,

43, 9328−9336. (e) Miyake, G. M.; Newton, S. E.; Mariott, W. R.; Chen, E. Y.-X. *Dalton Trans.* **2010**, *39*, 6710−6718. (f) Miyake, G. M.; Zhang, Y.; Chen, E. Y.-X. *Macromolecules* **2010**, *43*, 4902−4908.

(4) Hoffman, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94−110.

(5) (a) Manzer, L. E. *ACS Symp. Ser.* **2006**, *921*, 40−51. (b) Manzer, L. E. *Appl. Catal. A: Gen.* **2004**, *272*, 249−256.

(6) For selected reviews, see: (a) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450−2485. (b) Guan, Z., Vol. Ed. *Top. Organomet. Chem.* **2009**, *26*, 3−251 and contributions therein. (c) *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press/Taylor & Francis Group: Boca Raton, FL, 2008. (d) Resconi, L.; Chadwick, J. C.; Cavallo, L. In *Comprehensive Organometallic Chemistry III*; Bochmann, M., Vol. Ed.; Mingos, M. P., Crabtree, R. H., Chief Eds.; Elsevier: Oxford, 2007; Vol. 4, pp 1005−1166. (e) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252. (f) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345. (g) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143−1170.

(7) For a recent review, see: Chen, E. Y.-X. *Chem. Rev.* **2009**, *109*, 5157−5214.

(8) (a) Zhang, Y.; Ning, Y.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2010**, *132*, 2695−2709. (b) Ning, Y.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2008**, *130*, 2463−2465.

(9) (a) Rodriguez-Delgado, A.; Chen, E. Y.-X. *Macromolecules* **2005**, *38*, 2587−2594. (b) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2004**, *126*, 4897−4906.

(10) The synthesis of $_\beta$MMBL and its polymerizations by a radical process[10a] and a lanthanide catalyst[10b] have been reported. (a) Pittman, C. U., Jr.; Lee, H. *J. Polym. Sci. Part A, Polym. Chem.* **2003**, *41*, 1759−1777. (b) Hu, Y.; Miyake, G. M.; Wang, B.; Cui, D.; Chen, E. Y.-X. *Chem.—Eur. J.* **2012**, *18*, 3345−3354. (c) This monomer can also be prepared from 3-methyl-γ-butyrolactone, available from hydrogenation of the biomass-derived itaconic acid: Geilen, F. M. A.; Engendahl, B.; Harwardt, A.; Marquardt, W.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 5510−5514.

(11) See the Supporting Information for experimental and computational details.

(12) Akkapeddi, M. K. *Macromolecules* **1979**, *12*, 546−551.

(13) Suenaga, J.; Sutherlin, D. M.; Stille, J. K. *Macromolecules* **1984**, *17*, 2913−2916.

(14) (a) *ADF2010*, Users' Manual; Theoretical Chemistry, Vrije Universiteit: Amsterdam, 2010. (b) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51.

(15) (a) Caporaso, L.; Cavallo, L. *Macromolecules* **2008**, *41*, 3439−3445. (b) Caporaso, L.; Gracia-Budrìa, J.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 16649−16654.