

## Living Ziegler–Natta Cyclopolymerization of Nonconjugated Dienes: New Classes of Microphase-Separated Polyolefin Block Copolymers via a Tandem Polymerization/Cyclopolymerization Strategy

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Despite recent progress made toward the development of catalysts that can mediate the living Ziegler–Natta polymerization of  $\alpha$ -olefins,<sup>1</sup> their use for the production of well-defined polyolefin block materials, and in particular, those that can exist in microphase-separated states, has remained an elusive goal.<sup>2,3</sup> Herein, we now report the successful attainment of this objective through the use of amidinate-based zirconium precatalysts of general structure **1**, which upon activation by the borate cocatalyst, [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], can not only effect the stereospecific living polymerization of  $\alpha$ -olefins<sup>1g</sup>, but as documented here, the living cyclopolymerization of nonconjugated dienes. When conducted in a tandem fashion, these two living Ziegler–Natta processes provide access to new classes of polyolefin block copolymers that can microphase-separate into ordered morphologies with feature sizes on the nanometer-length scale as evidenced by phase-sensitive tapping mode atomic force microscopy (ps-tm AFM). Given both the variations in polymer microstructure that can be achieved by modifying the structural features of **1**, and the enormous range of  $\alpha$ -olefin and nonconjugated dienes that are readily available, the present results suggest that a new line of polyolefin materials with tunable properties may now be at hand.<sup>4</sup>



- 1a:** R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = Et  
**1b:** R<sup>1</sup> = R<sup>2</sup> = cyclohexyl (Cy)  
**1c:** R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = Cy

Poly(methylene-1,*m*-cycloalkanes) (**2**), which can be prepared through the cyclopolymerization of nonconjugated dienes using homogeneous Ziegler–Natta catalysts,<sup>5</sup> are attractive for incorporation in block copolymers since the degree of crystallinity of

**Table 1.** Representative Cyclopolymerizations of 1,5-Hexadiene and Syntheses of *iso*-Poly(1-hexene)/PMCP Block Copolymers<sup>a</sup>

entry	pre-catalyst	H <sup>b</sup>	HD <sup>b</sup>	H	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	<i>trans</i> (%) <sup>d</sup>	T <sub>m</sub> (°C) <sup>e</sup>
1	<b>1a</b>		188 (60)		20 000	1.09	64	98
2	<b>1b</b>		774 (60) <sup>f</sup>		25 000	1.04	78	99
3	<b>1c</b>		710 (225) <sup>f</sup>		14 000	1.03	82	102
4	<b>1a</b>	89 (90)			12 200	1.03		nd
5	<b>1a</b>	89 (90)	89 (90)		22 800	1.05		91
6	<b>1a</b>	77 (90)	77 (90)	77 (90)	30 900	1.10		79

<sup>a</sup> Polymerizations were conducted at  $-10$  °C in chlorobenzene using equimolar (25  $\mu$ mol) amounts of the precatalyst and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as cocatalyst; total reaction volume, 5 mL except for entry 6 which employed 50  $\mu$ mol each of precatalyst and cocatalyst and a total reaction volume of 10 mL. <sup>b</sup> Values correspond to the number of monomer equivalents and those in parentheses to polymerization times in minutes. <sup>c</sup> Determined by GPC analysis at 35 °C using polystyrene standards and THF as the eluant. <sup>d</sup> Determined from <sup>13</sup>C NMR spectra by relative integration of 4,5-*trans* and 4,5-*cis* resonances.<sup>5e,8</sup> <sup>e</sup> From differential scanning calorimetry (second scan). <sup>f</sup> Polymerizations not taken to complete monomer conversion.

these materials can be tuned by varying the *cis/trans* ratio of the backbone ring structures through variations in catalyst structure.<sup>5f</sup> Fortunately, as Table 1 shows, active catalysts prepared from equimolar amounts of **1a–c** and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene at  $-10$  °C are effective for the production of high molecular weight poly(methylene-1,3-cyclopentane) (PMCP) materials possessing extremely narrow polydispersities ( $M_w/M_n < 1.1$ ). Both the absence of <sup>1</sup>H NMR (500 MHz) resonances for olefinic end groups that might arise through  $\beta$ -hydride elimination and the highly linear relationship found in a kinetic analysis [i.e., ln([M<sub>0</sub>]/[M]) vs time] employing **1a** can be taken as evidence that these cyclopolymerizations are proceeding in a living fashion.<sup>6,7</sup> Not surprisingly, polymerization activity is attenuated as the steric bulk of the amidinate substituents in **1** increases (see Table 1).

With respect to the PMCP microstructures that are obtained with **1a–c**, all catalysts were found to be at least 98% selective (or 100% in the case of **1c**) for cyclopolymerization over linear 1,2-insertion of 1,5-hexadiene.<sup>6</sup> As Table 1 further indicates, while all catalysts were selective for *trans* ring formation, *trans* content was found to increase with an increase in the steric bulk of the amidinate moiety. Furthermore, the structure of the catalyst was found to greatly influence the isotactic content of the PMCP, with the highest degree of isoselectivity being observed for **1a** (see Figure 1).<sup>5e,8</sup>

Additional support that cyclopolymerizations of 1,5-hexadiene were occurring in a living fashion was provided by the successful synthesis of *iso*-poly(1-hexene)/PMCP di- and triblock copolymers of narrow polydispersity (see Table 1). In each case, GPC traces of the resulting polymers were monomodal after each addition

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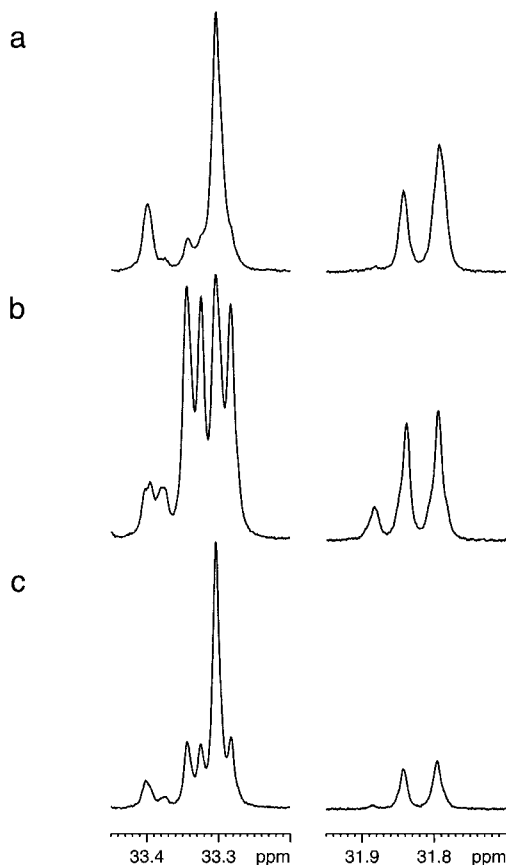
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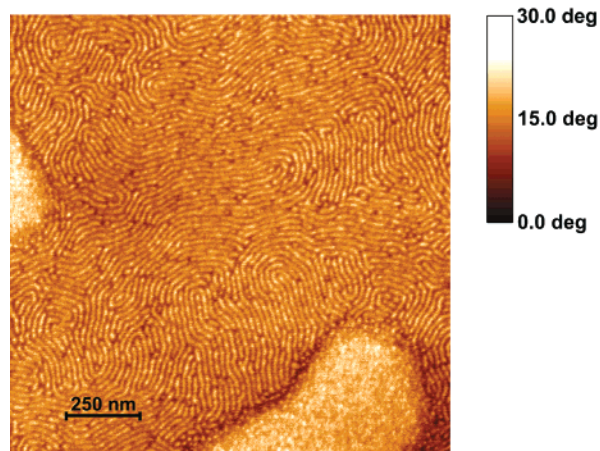
**Figure 1.** Partial  $^{13}\text{C}$  NMR (125 MHz, chloroform- $d_1$ , 25 °C) spectra showing the 4,5-*trans* ( $\delta$  33.3 ppm) and 4,5-*cis* resonances ( $\delta$  31.8 ppm) for PMCP prepared using: (a) **1a** (highly isotactic), (b) **1b**, and (c) **1c**.

of monomer, and they shifted to higher molecular weights that were consistent with block lengths predicted assuming complete consumption of monomer in each case.<sup>6</sup> High-field  $^{13}\text{C}$  NMR spectra of these new block copolymers consisted of simple superpositions of the individual resonances for the *iso*-poly(1-hexene)<sup>1g</sup> and PMCP homopolymers, but most significantly, they revealed that both block materials were highly isotactic as expected and that the integrated ratios of the resonances for the two types of blocks remained the same before, and after, purification of the polymeric material through precipitation.<sup>6</sup>

Final proof that the new block copolymers of Table 1 were truly of a block nature was provided by ps-tm AFM imaging of thin polymer films of the triblock material (entry 6).<sup>9,10</sup> As can be seen in Figure 2, after annealing a 220 nm thick film of this

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(10) A full account of the kinetics of formation and structural analysis of the microphase-separated state of this material by ps-tm AFM will be published elsewhere: Henningsen, D. A.; Sita, L. R., manuscript in preparation.



**Figure 2.** ps-tm AFM phase map for a 220 nm thick film of the triblock from entry 6 in Table 1 spun cast from a 1 wt % toluene solution onto a crystalline silicon wafer and annealed at 120 °C ( $10^{-3}$  Torr) for 36 h. The large feature observed in the lower right-hand corner is a  $15 \pm 2$  nm depression revealing the next underlying cylindrical layer.<sup>6</sup> The data were acquired in air and are shown in raw (unfiltered) form.

copolymer at 120 °C ( $10^{-3}$  Torr) for 36 h, both the height (not shown<sup>6</sup>) and phase maps provided by ps-tm-AFM clearly revealed that the material had microphase-separated into a cylindrical morphology consisting of hard (dark) cylinders of PMCP ( $8 \pm 1$  nm in width) running parallel to the surface and surrounded by the more elastic (light) poly(1-hexene) domains ( $12 \pm 1$  nm in width).<sup>10</sup> The occurrence of micrometer-scale depressions seen in the final surface structure that have a uniform depth of  $15 \pm 2$  nm provides evidence that this cylindrical phase is further quantized with respect to film thickness as previously encountered with other triblock materials.<sup>3,6,9</sup>

In conclusion, to the best of our knowledge, production of the *iso*-poly(1-hexene)/PMCP block materials described herein represents the first utilization of living Ziegler–Natta polymerization for the direct synthesis of a new class of microphase-separated polyolefin material of well-defined structure. It will now be of interest to determine the range of new materials that can be obtained from this tandem polymerization/cyclopolymerization strategy by engineering the structure of the blocks using different  $\alpha$ -olefins and nonconjugated dienes, as well as by manipulating block lengths and degrees of crystallinity. Last, we are intrigued by the possibility of controlling the absolute handedness of isotactic, *trans*-poly(methylene-1,*m*-cycloalkane) blocks through the development of enantiopure variants of **1**.<sup>5c,e</sup> Results of studies along these lines will be reported in due course.

**Supporting Information Available:** Representative analytical data for PMCP and block copolymers, kinetic data for cyclopolymerization, and additional ps-tm AFM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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