

## Synthesis of Block Copolymer Segments Containing Different Ratios of Ethylene and 5-Norbornen-2-yl Acetate

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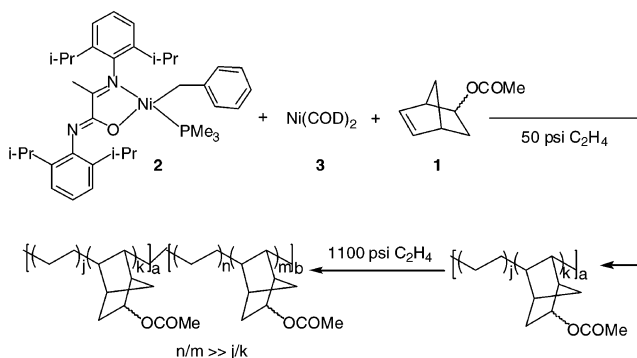
Block copolymers contain two or more chemically distinct sequences covalently bound in an end-to-end fashion.<sup>1</sup> This molecular architecture leads to microphase separation (5–100 nm) of the individual segments, which is driven by their immiscibility.<sup>2,3</sup> Complex nanostructures self-assembled in this way have found use in applications such as drug delivery,<sup>4</sup> organic electronic and photonic devices,<sup>5</sup> and nanolithography.<sup>6</sup>

Block copolymers that modify the interfacial energy<sup>7</sup> and adhesion<sup>8</sup> between polyethylene and more polar commodity plastics are highly sought after.<sup>9</sup> Polar functionalities within a hydrophobic polyethylene backbone influence important properties, such as toughness, solvent resistance, blend compatibility with other functional polymers, and rheological properties.<sup>9</sup> In view of the large-scale industrial processes associated with polyethylene manufacture, practical methods are required when considering the synthesis of block copolymer structures. The main synthetic challenge concerns the few options of initiators capable of incorporating functionalized monomers into a growing polyethylene chain under living polymerization conditions.<sup>10</sup> In this communication we provide a solution to this problem by describing the synthesis of *block* copolymers with segments containing copolymers with different ratios of ethylene and 5-norbornen-2-yl acetate (**1**) in which the change of monomer composition is accomplished by an increase in ethylene pressure. The ratio of the two monomers can be controlled to tailor the polar content in each sequence and to attain phase separation.

As shown in Scheme 1, polymerizations of C<sub>2</sub>H<sub>4</sub> and **1** were carried out by using [N-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide]Ni( $\eta^1$ -CH<sub>2</sub>Ph)(PMe<sub>3</sub>) (**2**) and 2.5 equiv of Ni(COD)<sub>2</sub> (bis(1,5-cyclooctadiene)nickel) (**3**). This catalyst system shows quasi-living polymerization characteristics for the copolymerization of C<sub>2</sub>H<sub>4</sub> and **1**.<sup>11</sup> With P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 50 psi the product is an amorphous copolymer with ~25 mol % of **1**, while at P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 1100 psi one obtains semicrystalline copolymers with a low incorporation of **1** (1–2 mol %). In what follows the polymer produced at the higher pressures is referred to as PE.

Table 1 summarizes reactions leading to the copolymer structures. In a typical experiment an autoclave reactor was charged with a solution of the catalyst mixture (0.67 mM **2** and 1.67 mM **3**) and **1** (0.15 M) in toluene. The autoclave was sealed and exposed to P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 50 psi for a period of time (T<sub>1</sub>). A pressure jump to P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 1100 psi was then applied, and the reaction was allowed to proceed for another predetermined interval

**Scheme 1.** Synthesis of Block-Type Copolymers



**Table 1.** Molecular Weight and Composition of Block Copolymers

entry	T <sub>1</sub> min. @ 50 psi	T <sub>2</sub> min. @ 1100 psi	M <sub>n</sub> block 1 kg/mol	M <sub>n</sub> block-copolymer kg/mol	PDI	mol % 1 block 1	T <sub>g</sub> (°C) <sup>12</sup> block 1	T <sub>m</sub> (°C) block 2
1	8	15	27	47 ± 4	1.3	23 ± 1	25	108
2	8	30	27	56 ± 5	1.4	23 ± 1	27	109
3	8	45	27	66	1.4	23 ± 1	—	108
4	8	60	27	84	1.4	23 ± 1	—	111
5	8	75	27	86	1.5	23 ± 1	—	109
6	8	90	27	90	1.6	23 ± 1	—	112
7	15	30	39	62	1.4	15 ± 1	28	121
8	15	60	39	82	1.5	15 ± 1	—	113
9	30	30	46	74 ± 2	1.4	13 ± 1	27	119
10	30	45	46	97	1.4	13 ± 1	24	111
11	45	45	51	126 ± 2	1.3	12 ± 1	25	111

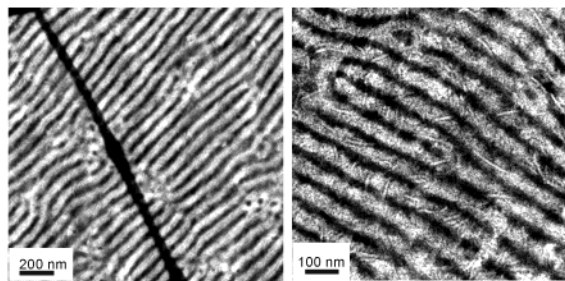
<sup>a</sup> Mol % **1** is the mole percentage of **1** in block 1 and is determined by <sup>1</sup>H NMR spectroscopy.

(T<sub>2</sub>). This reaction was run at 20 °C, using an ice/water bath to control temperature. The procedure was designed to produce two distinct segments, an amorphous block rich in **1**, followed by a crystalline segment with a higher C<sub>2</sub>H<sub>4</sub> concentration. Independent experiments were performed to isolate the product at the end of T<sub>1</sub>.

The products are described by monomodal molecular weight distributions with polydispersities (PDIs) between 1.3 and 1.6 (Table 1). These numbers are consistent with PDIs obtained previously with this catalyst system.<sup>11</sup> Note that the PDI = 1.6 in entry 6 corresponds to a reaction time of 98 min. GPC analysis shows quantitative conversion of the product at the end of T<sub>1</sub> into the block copolymer structure. Entries 1–6 show that the number average molecular weight (M<sub>n</sub>) increases with increasing T<sub>2</sub>. Comparison of two sets of entries (1, 7, and 9 with 3 and 10) shows that increasing T<sub>1</sub> yields larger M<sub>n</sub>'s and a lower overall content of **1**. The latter is the result of the decrease of [**1**] with

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**Figure 1.** Transmission electron micrograph of entry 2. The morphology is lamellar, where semicrystalline PE layers (white) alternate with amorphous copolymer layers (dark). PE crystals in the PE lamellae are visible. The dark line at the center of image 1 is the lacy carbon support film on the copper grids used to collect the microtomed sections.

longer reaction times. NMR spectroscopy of the block copolymer products shows higher  $C_2H_4$  incorporation, relative to the copolymer obtained at the end of  $T_1$ . In Table 1, the columns ( $M_n$  block 1) and (mol % 1 block 1) correspond to results obtained when the polymerization was stopped at the end of  $T_1$ . Solvent extraction experiments of the block copolymers show fractions of identical composition.

Thermal characterization provides indication of two independent blocks. The glass transition temperatures ( $T_g$ 's) of the amorphous segments range from 25 to 28 °C. We were not able to detect  $T_g$ 's (entries 3–6 and 8) when the concentration of the high-pressure product is high. For all materials, the melting temperatures of the second block (PE) are in the 108–121 °C range and are similar to those obtained when the reaction is carried out only at high pressure. These melting points are slightly lower than that of the ethylene homopolymer<sup>11</sup> due to the presence of NBA (1–2 mol %) in this block.

Transmission electron microscopy (TEM) of these materials demonstrates they are microphase separated, thus confirming the block architecture in Scheme 1. Figure 1 shows a typical TEM micrograph for the material from Table 1, entry 2. The observed contrast is due to  $RuO_4$  staining of the amorphous copolymer (dark). The block copolymer shows a lamellar microphase-separated structure that is expected given its PE weight fraction of 0.52. PE crystals are clearly visible in the semicrystalline PE layers (light). AFM and DMA characterization are also consistent with microphase separation (Supporting Information).

In conclusion, block-type copolymers containing segments of ethylene and **1** with different molar compositions have been synthesized by a simple procedure that involves an ethylene pressure jump.  $^1H$  NMR spectroscopy, GPC, DMA, and thermal analysis are consistent with the proposed structure. TEM examination confirms that the two blocks are sufficiently different in molecular composition to favor microphase separation. Future work will concern the mechanical properties and the microphase-separation

thermodynamics of these novel materials and the synthesis and characterization of multiblock copolymers.

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**Supporting Information Available:** Synthetic procedures and characterization data for polymers in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The observed  $T_g$  is attributed to the first block. The  $T_g$  of the second block could not be observed due to the low temperature of this transition. Both  $T_g$ 's could be seen in DMA analysis.

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