Supplementary Materials for

Combining polyethylene and polypropylene: Enhanced performance with PE/iPP multiblock polymers

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Materials and Methods

General Considerations

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using an MBraun Unilab drybox. $^{13}$C NMR spectra of polymers were recorded on a Varian Inova (500, 600 MHz) spectrometer equipped with a $^1$H/BB switchable with Z-pulse field gradient probe referenced versus residual solvent signals. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-$d_2$ in a 5 mm O.D. tube, and spectra were recorded at 135 °C. Molecular weights ($M_n$ and $M_w$) and molecular weight distributions ($D$) were determined by gel permeation chromatography (GPC). Analyses were performed using an Agilent PL-220 equipped with a RI detector. The column set (three Agilent PL-Gel Mixed B columns and one PL-Gel Mixed B guard column) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt% 3,5-di-tert-butyl-4-hydroxytoluene (BHT) at 1.0 mL/min at 150 °C. Data were measured relative to a polyethylene calibration curve (Varian and Polymer Standards Service). Peak polymer melting ($T_m$) temperatures and glass transition ($T_g$) temperatures were measured by differential scanning calorimetry (DSC) using a Mettler Polymer DSC calorimeter equipped with an automated sampler. Analyses were performed in aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from 20 to 180 °C and cooled from 180 to 20 °C at a cooling rate of 10 °C/min. Compression molding was carried out using a 4120 Hydraulic Unit Carver press and stainless steel die molds. Mylar and Teflon protective sheets were obtained from Carver and American Durafilm, respectively. Uniaxial tensile elongation was carried out using a Zwick/Roell Z010 testing system equipped with a 10 kN load cell and analyzed using Zwick/Roell TestXpert II v.3.5 software. Melt blends were prepared using a vertical conical counter-rotating twin screw batch compounder with a 2.5 mm diameter extrusion die and 5 g capacity mixing chamber. All polymer processing was carried out on pristine materials (i.e. no BHT, other anti-oxidants, or additives were added). Further experimental details are provided in the appropriate sections below.

Materials

Toluene was purified over columns of alumina and copper (Q5) prior to use and degassed by bubbling a stream of nitrogen gas through the solvent for 1 hour. Ethylene (Matheson, Matheson purity) and propylene (Airgas, polymer grade) were purified over columns of copper Q5 and 4Å molecular sieves. B(C$_6$F$_5$)$_3$ was obtained from TCI Chemicals and used as received. Pyridylamidohafnium catalyst (I) was prepared according to the procedure by Coates and coworkers (19). Diisobutylaluminumphenolate (DIBAP) was prepared by adding BHT (0.220 g, 1.00 mmol, 1.00 equiv.) in toluene (2 mL) to Al(Bu)$_3$ (0.198 g, 1.00 mmol, 1.00 equiv.) in toluene (2 mL) dropwise inside a glovebox and stored in a Teflon cap sealed vial (25). Polypropylene was obtained from Dow Chemical Company (H314-02Z; $M_n = 100$ kg/mol; $D = 4.1$; $T_m = 163$ °C; MFI = 2.0 g/10 min at 230 °C with 2.16 kg). HDPE was obtained from Dow (DMDA8904; $M_n = 22$ kg/mol; $D = 3.8$; $T_m = 131$ °C; MFI = 4.4 g/10 min at 190 °C with 2.16 kg). Additional materials tested are shown and described in Fig. S7.
Synthesis of iPP-\textit{b}-PE Block Copolymers

**General Procedure**

In a typical reaction, toluene (150 mL) was loaded into a 12 oz. Fischer-Porter bottle in a nitrogen-filled glove box. To this was added 50 µmol of a 0.25 M solution of DIBAP scavenger. In the glovebox, a vial was charged with pyridylamidohafnium catalyst 1 of the appropriate amount indicated in Table 1 along with \( B(C_6F_5)_3 \) (1.00 equiv). This co-catalyst mixture was then dissolved in toluene from the Fischer-Porter reactor and transferred via pipette to the Fischer-Porter bottle. The reaction vessel was sealed and removed from the glove box. The vessel weight was tared prior to charging propylene into the vessel to the amount indicated in Table 1. The reaction was magnetically stirred for 90 minutes in a water bath at 22 °C to help dissipate heat from the exothermic reaction. The pressure gauge dropped to 0 atm within 20 minutes for all reactions, but was continued to ensure complete consumption of propylene. The reaction mixture became heterogeneous with finely dispersed iPP particles precipitating from the yellow solution. The reactor head was then attached to a quick-connect valve routed to a nitrogen tank and vacuum pump. The vessel was pressurized with nitrogen (1.5 atm) and evacuated under vacuum for 5 seconds before backfilling with nitrogen. This was repeated for a total of three times before allowing the reaction to stir for an additional hour under nitrogen. While under a positive pressure of nitrogen a syringe with 18-gauge stainless steel needle (dried in an oven at 180 °C for 24 h) was used to remove an aliquot of the reaction (~5 mL) and quenched by adding to MeOH (10 mL), filtered, and dried for GPC analysis. The reaction vessel was vented and charged with ethylene at the pressure indicated in Table 1. The reaction vessel was stirred under ethylene for the reaction time indicated prior to venting. During this time the block copolymer product began to rapidly precipitate from solution and it is necessary to maintain adequate stirring during the ethylene polymerization for well defined (low \( \bar{D} \)) polymers. If multiple blocks were prepared, the vessel was evacuated under vacuum and backfilled with nitrogen three times as described before and stirred for 60 minutes prior to introducing the next monomer. Upon completion of the reaction, the vessel was vented and acidic MeOH (5% HCl, 10 mL) was injected. The heterogeneous mixture was then poured into acidic MeOH (300 mL), stirred for at least 3 hours, vacuum filtered, and dried under vacuum at 60 °C. All samples prepared in Table 1 were synthesized using this procedure.

**Simplified Procedure Without Vacuum Pump**

A large scale polymerization was carried out in similar ratios to entry 1, Table 1, but without the use of vacuum/nitrogen backfilling, a procedure that may prove more amenable to other laboratory setups. Toluene (300 mL) was added to a 24 oz. Fischer-Porter bottle in a nitrogen-filled glove box. DIBAP scavenger (75 µmol of 0.25 M solution) was added. In a separate pyridylamidohafnium catalyst 1 (32 mg, 50 µmol) and \( B(C_6F_5)_3 \) (26 mg, 50 µmol, 1.00 equiv.) were weighed together and subsequently dissolved by adding the toluene/DIBAP mixture to the vial, before transferring to the Fischer-Porter bottle. The reaction vessel was sealed and charged with propylene gas (5.0 g) and stirred for 3h at room temperature in a 22 °C water bath. Approximately 5 mL of the reaction mixture was removed using a syringe equipped with an 18-gauge needle and quenched by adding to MeOH (10 mL). The reaction vessel was then charged with ethylene gas (2.7 atm) and rapidly stirred for 10 minutes. After this time, the reaction vessel was vented and quenched with the addition of acidic MeOH (5% HCl, 10 mL), precipitated into acidic MeOH (300
mL), stirred for 3 hours, vacuum filtered, washed with MeOH (~100 mL) and dried under vacuum at 60 °C overnight. The resulting polymer (8.3 g, PP<sub>77</sub>PE<sub>138</sub>) had a <i>T<sub>m</sub></i> of 128 °C, <i>M<sub>n</sub></i> (theo.) of 166 kg/mol, <i>M<sub>n</sub></i> (tot.) of 215 kg/mol, and <i>D</i> = 1.4.

Preparation of Block Copolymers Used in Fig. 3

To unambiguously examine the effect of block architecture on compatibilization efficacy and interfacial activity, a single reaction was carried out to synthesize the polymers in Fig. 3 with removal of large volumes (50 mL) after monomer consumption to provide adequate yields of each block for physical testing. In a procedure similar to the above general procedure, the cocatalyst mixture (30 µmol) was dissolved in toluene (200 mL) containing DIBAP (125 µmol of a 2.5 M solution) in a Fischer-Porter reactor, sealed, and removed from the glove box. The vessel was charged with propylene (2.0 g) and stirred for 90 minutes in a water bath at 22 °C. The reactor head was then attached to a quick-connect valve routed to a nitrogen tank and vacuum pump. The vessel was pressurized with nitrogen (1.5 atm) and evacuated under vacuum for 5 seconds before backfilling with nitrogen. This was repeated for a total of three times, then an aliquot (5 mL) was removed for GPC analysis. The reaction vessel was then pressurized with ethylene (2.7 atm) and stirred for 4 minutes prior to venting the ethylene atmosphere. Again the reactor head was attached to a vacuum/nitrogen source and evacuated/backfilled as before. The reaction was stirred for 40 minutes prior to removing a large aliquot (50 mL) via a syringe equipped with a 10-gauge stainless steel needle and quenched by adding to MeOH (50 mL). The sample was vacuum filtered and dried at 60 °C under vacuum for 24 h. Propylene was then condensed, stirred, evacuated/backfilled as above, followed by the removal of a large aliquot (50 mL). The final ethylene polymerization was similarly carried out as above but quenched by the addition of acidic MeOH (50 mL) instead of removing an aliquot. The resulting tetrablock copolymer (entry 5, PP<sub>60</sub>PE<sub>80</sub>PP<sub>75</sub>PE<sub>90</sub>, 4.0 g) was projected to yield 8.5 g of polymer according to the removed volume. No corrections for monomer or polymer volume were made.

Living Plot

Diblock copolymer prepared in Fig. 1 was prepared using pyridylamidohafnium catalyst 1 (25 µmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (25 µmol), toluene (150 mL), and DIBAP scavenger (50 µmol of 0.25 M solution). Propylene (1.5 g) was condensed into the reactor and stirred at 22 °C with water bath cooling. Aliquots were taken during the course of the polymerization for analysis. After stirring, vacuum/backfilling with nitrogen, and ethylene polymerization according to the above general procedure, the reaction was quenched with the addition of 10 mL of acidic MeOH. During the polymerization aliquots were removed using a 10 (12) mL syringe equipped with an 18-gauge needle, volume measured, and quenched by addition to MeOH (10 mL). The aliquots samples were filtered, dried at 60 °C for 24 h under vacuum, weighed, and analyzed by GPC. The polymer yields were extrapolated from the measured volume removed (5-9 mL). No corrections for monomer or polymer volume were made.
**13C NMR of iPP-b-PE Block Copolymer**

![13C NMR of iPP-b-PE Block Copolymer](image)

**Fig. S1.** $^{13}$C NMR of iPP-b-PE diblock copolymer (entry 1, Table 1). Spectra were recorded on Varian INOVA 600 spectrometer using residual solvent peak as a reference ($\text{Cl}_2\text{DCCDCl}_2$: 73.8 ppm) at 135 °C. A 90° pulse width and 25 second relaxation delay with proton decoupling were used to obtain quantitative spectra, which were processed using MestReNova software. **(A)** Full spectrum of iPP-b-PE block copolymer. **(B)** View of spectrum showing assignment of iPP regio- and stereoeerrors consistent with pyridylamidohafnium catalysts (17). **(C)** View of spectrum showing calculations of iPP stereoregularity and regioregularity.
DSC of PE/iPP Block Copolymers

**Fig. S2.** Differential scanning calorimetry of PE/iPP block copolymers from Table 1. Measurements were conducted between 20 and 180 °C at 10 °C/min. (A) Melting temperatures ($T_m$) were calculated according to the peak endotherm on the second heating cycle. (B) Crystallization temperatures ($T_c$) were calculated according to the peak exotherms of the first cooling cycle.
GPC Analysis of PE/iPP Block Copolymers

Fig. S3. GPC analysis of aliquots and final PE/iPP block copolymer products presented in Table 1 (A-E). Molecular weights and molecular weight distributions ($D$) were analyzed using an Agilent PL-220 equipped with a RI detector and three Agilent PL-Gel Mixed B columns and one PL-Gel Mixed B guard column. Samples were eluted with 1,2,4-trichlorobenzene at 1.0 mL/min at 150 °C and measured relative to a polyethylene calibration curve.
Adhesion Studies

Preparation of iPP and PE films

Polymer pellets of Dow iPP (H314-02Z) or Dow HDPE (DMDA8904) were pressed in a Carver press between Mylar sheets at 180 °C for 5 minutes with minimal pressure to create a coherent film which was subsequently trimmed to approximately 6 cm x 10 cm and compression molded in a 6 cm x 10 cm x 0.34 mm stainless steel die at 180 °C for 5 minutes under 70 atm of pressure and cooled with water circulation (~10 °C/min). The film surfaces were subsequently wiped with a Kim-wipe soaked with CHCl₃ and air dried for 24 h.

Preparation of iPP-b-PE adhesive

Block copolymer powder was pressed in a Carver press between protective sheets (either Mylar or Teflon) at 180 °C for 5 minutes with minimal pressure to create a coherent film. The film was trimmed to ~3 cm x ~10 cm and compression molded without a die at 180 °C for 5 minutes under 550 atm of force and cooled with water circulation. The film was measured by calipers to be between 95 and 115 μm thick and trimmed to 3 cm x 10 cm. The film surfaces were subsequently wiped with a Kim-wipe soaked with CHCl₃ and air dried for 24 h.

Preparation of laminate

HDPE film was placed in a 6 cm x 10 cm x 1 mm stainless steel die and the iPP-b-PE adhesive strip was placed carefully over the bottom half of the HDPE sheet. The iPP sheet was placed on top of the two, thereby sandwiching the block copolymer film between the PE and iPP. The trilayer was pressed at 180 °C for 5 minutes under 70 atm of pressure before cooling with water circulation (~10 °C/min). Once at room temperature, the laminate was removed from the die and aged for 48 hours. A crack was started at the interface of the top half, which contained no block copolymer adhesive. The 6 cm x 10 cm laminate was then trimmed into 6-14 individual 0.6 cm x 6 cm rectangular adhesive samples for testing.

T-Peel Testing

The separated iPP and PE films were placed in a Zwick tensile tester and pulled apart at 10 mm/min and the force was measured as a function of peel displacement. The peel force (f) was reported as the steady state force during the peel, while the peel strength (S) was reported as the steady state force divided by the individual sample’s width (6-7 mm).
Molecular Weight Dependence of Peel Strength

**Fig. S4.** Effect of polypropylene and polyethylene block sizes (± 10 kg/mol) of diblock copolymer films (~100 μm thick) on PE/iPP laminate peel strength. Laminates were prepared according to the above procedure with Dow iPP (H314-02Z) and Dow HDPE (DMDA8904) and the block copolymers detailed below. Values are the mean of 6 samples and error bars reflect ± 1 standard deviation.
GPC Analysis and Adhesion with Diblock Copolymers

**PE$_{40}$**

A. 
- **PP$_{24}$PE$_{31}$**
  - $M = 1.32$
- **PP$_{24}$**
  - $M = 1.21$

Retention time (min)

**PE$_{70}$**

B. 
- **PP$_{34}$PE$_{60}$**
  - $M = 1.35$
- **PP$_{34}$**
  - $M = 1.26$

Retention time (min)

**PE$_{100}$**

C. 
- **PP$_{30}$PE$_{97}$**
  - $M = 1.34$
- **PP$_{30}$**
  - $M = 1.18$

Retention time (min)

**PP$_{30}$**

D. 
- **PP$_{24}$PE$_{31}$**
  - $M = 1.32$

Peel Force (N) vs Peel Displacement (mm)

**PP$_{70}$**

G. 
- **PP$_{73}$PE$_{50}$**
  - $M = 1.29$
- **PP$_{73}$**
  - $M = 1.31$

Retention time (min)

**PP$_{72}$**

J. 
- **PP$_{73}$PE$_{50}$**
  - $M = 1.29$

Peel Force (N) vs Peel Displacement (mm)

**PP$_{72}$**

L. 
- **PP$_{72}$PE$_{91}$**
  - $M = 1.39$

Peel Force (N) vs Peel Displacement (mm)
Fig. S5. (A-C) GPC analysis of low $M_n$ iPP diblock copolymers with increasing $M_n$ of PE blocks and (D-F) their representative peel forces of PE/block copolymer/iPP laminates. (G-I) GPC analysis of moderate $M_n$ iPP diblock copolymers with increasing $M_n$ of PE blocks and (J-L) their representative peel forces of PE/block copolymer/iPP laminates. (M-O) GPC analysis of high $M_n$ iPP diblock copolymers with increasing $M_n$ of PE blocks and (P-R) their representative peel forces of PE/block copolymer/iPP laminates. Elongation of PE film is poor due to rectangular shaped specimens rather than dogbone shaped which distribute stresses evenly.
SEM Imaging of Laminates

Fig. S6. SEM images of laminates after testing showing the smooth surface of the (A) PE film and (B) iPP film, consistent with low adhesive force, no block copolymer adhesive, and little polymer chain deformation. (C) shows the surface of the PE film after testing with a low molecular weight (PP_{24}PE_{32}) diblock copolymer while (D) shows the iPP film. The zoomed inset of (C) suggests samples containing a block copolymer layer have deformed (stretched) in agreement with the moderate peel strength required to stretch the polymer chains. It is unclear from these studies if the deformed material is block copolymer or bulk polyolefin film.
Comparison of Polyolefin Materials

Fig. S7. (A-F) Peel strength between different combinations of commercial PE and iPP bulk films with (red) and without (black) high molecular weight block copolymer adhesive ($\text{PP}_{77}\text{PE}_{138}$). Films were prepared according the above procedure. In all samples the PE bulk film, regardless of PE density, yielded or broke demonstrating the adhesion strength of the interface surpassed the bulk tear strength in all samples ($\geq 6$). (G) Characterization and commercial providers of polymer materials used in this study.

<table>
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<tr>
<th>PE Grades</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$ ($M_w/M_n$)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>MFI (g / 10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-rex HD KF 251A (HDPE)</td>
<td>14</td>
<td>13.8</td>
<td>130</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>DOW DMDA8904 (HDPE)</td>
<td>22</td>
<td>3.8</td>
<td>131</td>
<td>116</td>
<td>4.4 (190 °C)</td>
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<tr>
<td>Sigma Aldrich ($427985$) (HDPE)</td>
<td>15</td>
<td>2.2</td>
<td>129</td>
<td>112</td>
<td>12.0 (190 °C)</td>
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<tr>
<td>DOW 9551 (LDPE)</td>
<td>17</td>
<td>2.6</td>
<td>114</td>
<td>94</td>
<td>35 (190 °C)</td>
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<tr>
<td>Exxon LL3003 (LLDPE)</td>
<td>16</td>
<td>6.3</td>
<td>126</td>
<td>108</td>
<td>3.2 (190 °C)</td>
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</table>

<table>
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<tr>
<th>iPP Grades</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$ ($M_w/M_n$)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>MFI (g / 10 min)</th>
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<tr>
<td>DOW H314-02Z</td>
<td>100</td>
<td>4.1</td>
<td>163</td>
<td>117</td>
<td>2.0 (230 °C)</td>
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<tr>
<td>Sigma Aldrich ($427861$)</td>
<td>97</td>
<td>3.1</td>
<td>165</td>
<td>109</td>
<td>4.0 (230 °C)</td>
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</table>
Comparison of Adhesives

Fig. S8. Peel force of PE/iPP laminates with (A) styrene/butadiene elastomer (polystyrene-block-polybutadiene-block-polystyrene, styrene 30 wt. %) obtained from Sigma-Aldrich (#432490), (B) amorphous high molecular weight ethylene propylene random copolymer prepared using 1/B(C₆F₅)₃ (Mₙ = 314,900; D = 1.29; E:P 3:2), and (C) no adhesive layer in place of the iPP-b-PE block copolymers. PE/iPP films were Dow iPP (H314-02Z) and Dow HDPE (DMDA8904).
Fig S9. (A) Peel force of PE/iPP laminates which contain a 5 µm thick film of high molecular weight diblock copolymer (PP$_7$PE$_{138}$), measured by (C) SEM. (B) Peel force of PE/iPP laminates which contain a 10 µm thick film of high molecular weight diblock copolymer (PP$_7$PE$_{138}$), measured by (D) SEM. 5 µm thick block copolymer films (C) were prepared by dissolving 0.5 wt% PP$_7$PE$_{138}$ diblock copolymer in xylenes at 100 °C and then the hot solution (0.24 g) was transferred to a sheet of Dow iPP (H314-02Z) with an area of 6 cm x 4 cm and solvent evaporated. 10 µm thick block copolymer films (D) were prepared by the same procedure using a 1 wt% PP$_7$PE$_{138}$ solution in xylenes. SEM images (C and D) where cryofractured in liquid nitrogen at various spots to verify the uniformity and thickness of the block copolymer layers; at least two sheets were used for each thickness.
Melt Blend Studies

Blend Preparation

Polymer pellets of Dow iPP (H314-02Z, 1.2 g) and Dow HDPE (DMDA8904, 2.8 g), and block copolymer powder (200 mg or 40 mg) were combined and pressed at 180 °C for 5 minutes with minimal pressure to create a coherent film. The film was fed into a twin-screw microcompounder at 190 °C with a steady flow of nitrogen and residence time of 8 minutes at 130 rpm. The material was then extruded through a 2.5 mm diameter die and air cooled. The resulting blend was then pressed at 180 °C for 5 minutes with minimal pressure to create a coherent film.

Sample Preparation

Blend films were loaded into a stainless steel dogbone die (gauge length = 16 mm, gauge width = 3 mm, gauge thickness = 0.6 mm) and pressed on a Carver press hot plate under ~52 MPa at 180 °C for 5 minutes. Maintaining this pressure, the sample was cooled using water circulation (~10 °C/min). The samples were removed and trimmed with a razor blade.

Mechanical Testing

Mechanical studies were performed using a Zwick/Roell tensile tester elongated with a crosshead velocity of 16 mm/min. Tensile bars were elongated until break and at least five tensile bars were tested for each composite. Results were analyzed using Zwick/Roell testXpert II-v. 3.5 software. Representative traces are presented in Fig. 3 and compiled individual traces are presented below (Fig. S10).
Fig. S10. Compiled uniaxial tensile elongation of (A) PE, (B) iPP, and (C) PE/iPP blend (70:30, PE:iPP). (D) Compiled tests of PE/iPP blend with the addition of (D) 5 wt% and (G) 1 wt% diblock copolymer, (E) 5 wt% and (H) 1 wt% triblock copolymer, (F) 5 wt% and (I) 1 wt% tetrablock copolymer. Materials were melt blended at 180 °C, then processed by a twin-screw microcompounder at 190 °C and compression molded into tensile specimens at 180 °C. The samples were strained at a rate of 100 %/min at 25 °C.
TEM Images of Blends and Droplet Size Analysis

TEM Procedure
The untested tensile samples were stained in the bulk state with freshly prepared RuO$_4$ solution by mixing approximately 15 mg ruthenium chloride hydrate (Sigma-Aldrich) and 5 mL sodium hypochlorite solution (reagent grade, 10-15% chlorine, Sigma-Aldrich) for 2 h at room temperature. Ultrathin sections (<100 nm) were microtomed at -120 °C using diamond knife and a Leica UC6 microtome. Then the specimens were imaged using a FEI Tecnai G2 Spirit transmission electron microscope operated at an accelerating voltage of 120 kV.

Size Analysis
Droplet size analyses were carried out with imageJ, which provides the cross-sectional area of individual iPP droplets present in the PE matrix. The equivalent diameters were then calculated and at least 150 droplets were used to calculate the average diameter in each case, the size distributions of which were fitted with a log-normal function.
Fig. S11. (A-D) TEM images of PE/iPP phase separated blend (70:30, PE:iPP) with no block copolymer additive. (E) Droplet diameter analysis and average diameter of 2.16 μm.
Fig. S12. (A-D) TEM images of PE/iPP compatibilized blend (70:30, PE:iPP) with 5 wt% diblock copolymer (PP$_{60}$PE$_{80}$) additive. (E) Droplet diameter analysis and average diameter of 0.85 μm.
Fig. S13. (A-D) TEM images of PE/iPP compatibilized blend (70:30, PE:iPP) with 5 wt% triblock copolymer (PP$_{60}$PE$_{80}$PP$_{75}$) additive. (E) Droplet diameter analysis and average diameter of 0.84 μm.
Fig. S14. (A-D) TEM images of PE/iPP compatibilized blend (70:30, PE:iPP) with 5 wt% tetrablock copolymer (PP$_6$OPE$_8$OPP$_{75}$PE$_{90}$) additive. (E) Droplet diameter analysis and average diameter of 0.55 μm.
DSC of PE/iPP/Block Copolymer Materials and Blends

Fig. S15. Differential scanning calorimetry of PE/iPP/block copolymer materials and blends from Fig. 3. iPP homopolymer produced by catalysts 1/B(C₆F₅)₃ and as a blend (1:1) with commercial iPP showing a single melting endotherm and crystallization exotherm indicating regio and stereo defects of the iPP block are not numerous enough to inhibit cocrystallization. Measurements were conducted between 20 and 180 °C at 10 °C/min. (A) Melting temperatures ($T_m$) were calculated according to the peak endotherm on the second heating cycle. (B) Crystallization temperatures ($T_c$) were calculated according to the peak exotherms on the first cooling cycle.
SEM Images of Fractured Blend Samples

**Fig. S16.** (A-B) SEM images of PE/iPP uncompatibilized blends (70:30, PE/iPP) after uniaxial tensile testing showing iPP droplet pullout. (C-D) SEM images of PE/iPP compatibilized blends (70:30, PE/iPP) with 5 wt% tetrablock copolymer (PP₆₀PE₈₀PP₇₅PE₉₀) after uniaxial tensile testing showing smooth surface indicative of efficient stress transfer between phases.
Physical Properties of Bulk PE/PP Block Copolymer Materials

Fig. S17. (A) Linear dynamic mechanical spectroscopy measurements of diblock (PP$_{73}$PE$_{50}$) and tetrablock (PP$_{36}$PE$_{20}$PP$_{34}$PE$_{24}$) copolymers used in Fig. 2 demonstrating that these materials are microphase separated over the range of temperatures employed in this work. Rheology experiments were carried out on an ARES rheometer with a 25-mm parallel plate geometry and a gap of 0.8 mm. Data were collected at individual temperatures between 180 °C to 260 °C over a frequency range of 0.01 to 100 rad/s. The master curves were obtained by shifting the isothermal frequency data along the frequency axis by $\alpha T$. The low frequency responses $G' \sim \omega^a$ and $G'' \sim \omega^b$, where $a < 1$ and $b < 1$, are indicative of an ordered state (26). (B) Uniaxial tensile elongation of bulk diblock (PP$_{73}$PE$_{50}$) and tetrablock (PP$_{36}$PE$_{20}$PP$_{34}$PE$_{24}$) materials showing similar ductile mechanical responses. Block copolymers were compression molded at 180 °C to form a 0.2 mm thin film then cooled with water circulation. Tensile samples were punched into dogbone shaped samples with a gauge width of 3 mm and gauge length of 10 mm. At least 5 tensile tests were conducted at room temperature with an extension rate of 5 mm/min using a Shimadzu AGX tensile tester.
Estimation of Block Copolymer Layer Thickness in Phase Separated Blends

Here we use a blend containing spherical particles of iPP compatibilized by a layer of block copolymer and dispersed in PE.

The thickness $l$ of the block copolymer layer at the iPP/PE interface (assuming the block copolymer, PE and iPP have the same density) is:

$$ l = r\{(A+B)/A\}^{1/3} - 1 \}

where $r$ is the radius of the spherical iPP particles and A and B are the volume fractions of iPP and block copolymer, respectively. Therefore, if $r = 275$ nm, $A = 0.275$ and $B = 0.05$ (see Fig. S14) $l = 15.7$ nm. The lamellar domain periodicity for a bulk diblock copolymer melt can be estimated as (27),

$$ d = 1.03b\chi^{1/6}N^{2/3} $$

where $b$ is the statistical segment length and $\chi$ is the Flory-Huggins segment-segment interaction parameter. Using $b = 0.5$ nm and $\chi = 0.01$, both representative values for iPP and PE, we obtain $d = 35$ nm for a $M_n = 60,000$ g/mol diblock copolymer, approximately the smallest pair of block sizes reported in this work. Thus, the calculated layer thickness is less than half the domain spacing indicating monolayer coverage. This implies that the block copolymers employed in this work control the phase separated domain dimensions in blended specimens through efficient interfacial action much like a surfactant stabilizes water in oil emulsions.
**Tensile Properties of iPP/PE Blends with Varied Ratios**

Fig. S18. Compiled uniaxial tensile elongation of HDPE/iPP blends with 1 wt% tetrablock compatibilizer (purple), with 5 wt% tetrablock (green), and no compatibilizer (red). Ratios of HDPE:iPP were varied from (A) 30:70, (B) 50:50, and (C) 70:30, the same as Figure 3, but with the low molecular weight tetrablock copolymer PP$_{36}$PE$_{20}$PP$_{34}$PE$_{24}$ (Entry 4, Table 1). All materials were melt blended at 180 °C, then processed by a twin-screw microcompounder at 190 °C and compression molded into tensile specimens at 180 °C according the above procedure. The samples were strained at a rate of 100 %/min at 25 °C.
References and Notes


