Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Tunable Polyethylene-polypropylene Blends via Compatibilization through Nitrene Insertion-Enabled Dynamic Covalent Crosslinking

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1. General Experimental Information

All reactions were conducted in flame-dried glassware using anhydrous solvents and a magnetic stir bar under nitrogen. Commercial reagents were utilized without further purification, unless explicitly stated otherwise. Column chromatography was carried out using a Teledyne Isco® CombiFlash+ with the specified solvent systems. ^{1}H NMR spectra were recorded on a Bruker GN500 at 500 MHz, while ^{13}C NMR spectra were obtained using AVANCE600 with a BBFO cryoprobe at 151 MHz. Chemical shifts (δ) are reported in parts per million (ppm) values and referenced to residual solvent peaks: $CDCl_3$ (^{1}H = 7.26 ppm; ^{13}C = 77.0 ppm). ^{1}H NMR chemical shifts are reported with their multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant values in Hertz (Hz), and the relative integrated number of protons. ^{13}C NMR chemical shifts are reported in ppm values. Low-resolution mass spectroscopy was performed using a Waters Acquity UPLC H-Class with QDa Detector. High-Resolution Mass Spectrometry (HRMS) was conducted with Waters (Micromass) LCT Premier equipped with TOF. Extrusion was performed using a conical twin-screw extruder (Thermo Haake Minilab II) with a continuous flow of nitrogen. Uniaxial tensile studies were conducted on an Instron 3365 Universal Testing System with pneumatic grips. DSC measurements were carried out on TA Instruments Discovery DSC 2500, and TGA experiments were performed on Netzsch STA 449 F3 Jupiter. AFM images were collected using Oxford Instruments Asylum Research MFP-3D, and SEM images were obtained on FEI Magellan 400 XHR. Creep tests were performed using TA Instruments DHR-2 Rheometer and Discovery DMA 850.

2. Synthesis of bis-Aromatic Sulfonyl Azide (bis-ASA) Dynamic Crosslinker

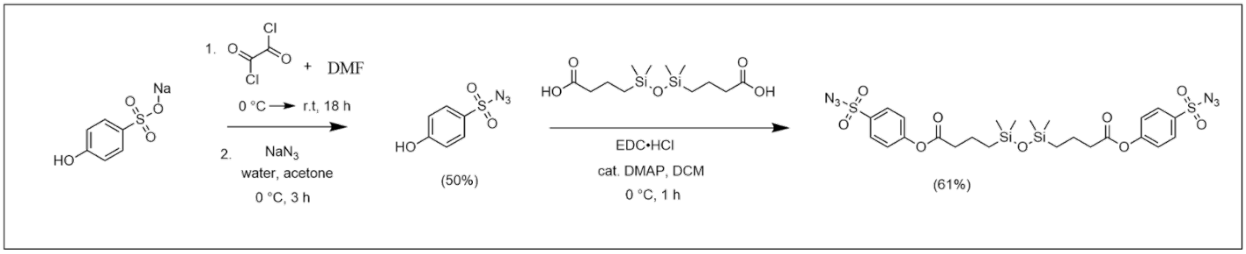

Figure S1. Synthetic scheme for the synthesis of bis-ASA siloxane crosslinker.

A 250 mL flame-dried round-bottom flask equipped with a stir bar was charged with 54 mL of dichloromethane (DCM) and cooled to 0 °C. Oxalyl chloride (9 equiv., 116.8 mmol, 10.02 mL) was added and stirred for 15 min. Sodium 4-hydroxybenzenesulfonate dihydrate (1 equiv., 12.97 mmol, 3.012 g) was dissolved in 15 mL of N,N-dimethylformamide (DMF) and transferred dropwise. An exhaust needle was used to remove the formed gas. The reaction mixture was allowed to warm to room temperature (r.t.) and stirred overnight to give a yellow solution. 150 mL of ice was added and stirred until completely dissolved. The organic layer was washed with brine, and the aqueous layer was extracted with 3 x 30 mL of DCM. The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford a yellow oil. The concentrated oil was dissolved in 20 mL of acetone and equilibrated in an ice bath stirring for 5 min. Sodium azide (1.2 equiv., 15.57 mmol, 1.012 g) was dissolved in 10 mL of DI water and transferred to the solution with constant stirring at 0 °C. After 1.5 h, 70 mL of ethyl acetate (EtOAc) was added to the reaction mixture. The reaction mixture was washed with brine, and the aqueous layer was extracted thrice with EtOAc. The combined organic layers were dried over sodium sulfate and concentrated *in vacuo* to yield a yellow oil which was then purified through solid loading flash chromatography (Teledyne Isco® CombiFlash+) with 70/30 hexanes to EtOAc providing the desired product (1.3 g, 50%).

To a flame-dried 250 mL round-bottom flask equipped with a stir bar charged with 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (1 equiv., 3.8355 mmol, 1.1756 g) and 4-dimethylaminopyridine (DMAP, 0.3 equiv., 1.1506 mmol, 140.57 mg), 4-hydroxybenzenesulfonyl azide (2.2 equiv., 8.4381 mmol, 1.6807 g) in 32 mL of dichloromethane (DCM) was added. After cooling the flask to 0 °C, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC•HCl, 3.025 equiv., 11.602 mmol, 2.2242 g) was added via a powder funnel and stirred at 0 °C for 1 h. The reaction mixture was transferred to a separatory funnel and diluted with 150 mL of EtOAc. The organic layer was washed with saturated sodium bicarbonate, 1 M HCl, and brine subsequently before being dried over sodium sulfate and concentrated *in vacuo*. The concentrated oil was then purified through solid loading flash chromatography and eluted with 80:20 hexanes: EtOAc providing the final product (1.553 g, 61%).

3. Polymer Blends via Reactive Extrusion

Both high-density polyethylene (HDPE) and isotactic polypropylene (iPP) pellets were milled into a fine powder with a Fritsch Pulverisette rotary mill fitted with a 0.5 mm sieve cassette. In a 50 mL conical centrifuge tube, 5 g of powdered polymer or a mixture of polymers, varying weight percent of bis-ASA siloxane crosslinker, and the KF: DB-18-C-6 base catalyst (10 mol% relative to the crosslinker) were added and mixed using a vortex mixer for 2 min. The mixture was then transferred to the Thermo Haake Minilab II conical twin screw extruder with 7 cm^3 volume and blended under continuous nitrogen flow at 190 °C and 130 rpm for 8 min. During reactive blending, the nitrogen gas generated from the azide decomposition is released through the extruder together with the continuous nitrogen flush.

Table S1. Sample formulations to make HDPE/iPP blends

Sample	Polymer Feedstock	bis-ASA Siloxane Crosslinker	KF:DB18-C-6 Catalyst
70/30 HDPE/iPP with 2 wt% bis-ASA	HDPE 3.5 g; 70 wt% iPP 1.5 g; 30 wt%	100 mg; 2 wt%	6.3 mg; 10 mol%
30/70 HDPE/iPP with 2 wt% bis-ASA	HDPE 1.5 g; 30 wt% iPP 3.5 g; 70 wt%	100 mg; 2 wt%	6.3 mg; 10 mol%
30/70 HDPE/iPP with 1 wt% bis-ASA	HDPE 1.5 g; 30 wt% iPP 3.5 g; 70 wt%	50 mg; 1 wt%	3.2 mg; 10 mol%
30/70 HDPE/iPP with 0.5 wt% bis-ASA	HDPE 1.5 g; 30 wt% iPP 3.5 g; 70 wt%	25 mg; 0.5 wt%	1.6 mg; 10 mol%
50/50 HDPE/iPP with 1 wt% bis-ASA	HDPE 2.5 g; 50 wt% iPP 2.5 g; 50 wt%	50 mg; 1 wt%	3.2 mg; 10 mol%

4. Mechanical and Thermal Analysis

4.1 Compression molding and uniaxial tensile testing

The following compression-molding conditions were applied for different HDPE/iPP extrudates to achieve an equilibrium state.

Table S2: Optimized compression-molding conditions for HDPE/iPP systems.

Sample	Compression-Molding Conditions
70/30 HDPE/iPP system	Molded at 160 °C for 5 min with 4T pressure with Specac Atlas™ Manual 15T Hydraulic Press
30/70 and 50/50 HDPE/iPP system	Heated in the oven at 200 °C for 10 min and compression molded with vise clamp followed by the molding at 160 °C for 15 min with 4T pressure with Specac Atlas™ Manual 15T Hydraulic Press

4.2 Gel fraction analysis

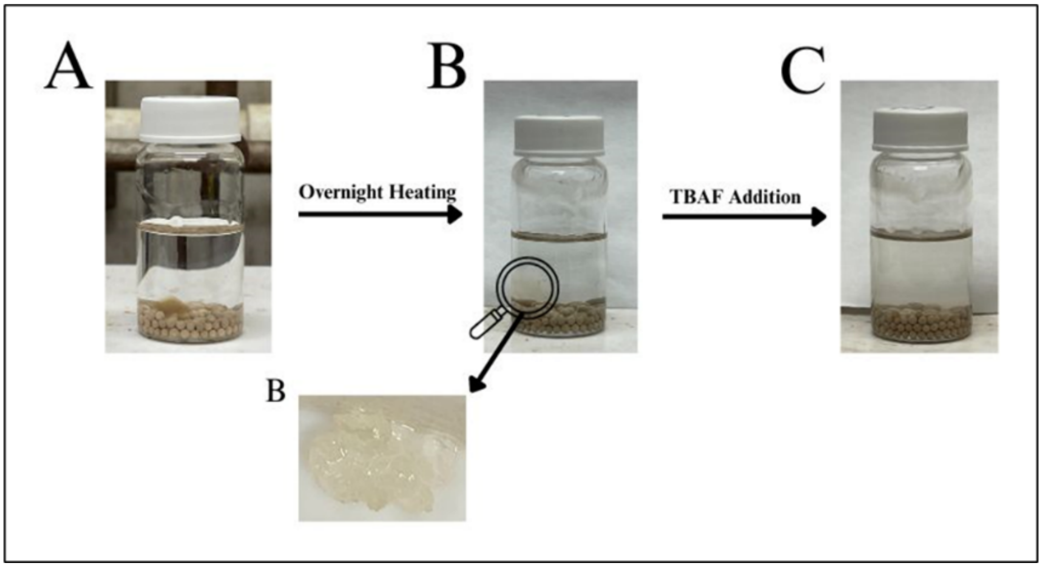

Figure S2: A) Compression-molded 70/30 HDPE/iPP with 2wt% bis-ASA in mesitylene at 160 °C after 2 min. B) Swollen 70/30 HDPE/iPP with 2wt% bis-ASA in mesitylene at 160 °C after 16 h. C) Dissolution of 70/30 HDPE/iPP with 2wt% bis-ASA after the addition of TBAF.

In a flame-dried 20 mL glass scintillation vial equipped with activated 3Å molecular sieves, 12 mL of anhydrous mesitylene was transferred. A small piece (24 – 37 mg) of compression-molded tensile sample was added to the vial and heated at 160 °C overnight. The swollen gel was isolated and dried using high vacuum and mild heating at 80 °C in an oven overnight. The final mass was recorded, and the gel fraction was calculated using the formula: Gel fraction = (Final mass of the dried sample / Initial mass) * 100%

Table S3: Gel content of HDPE/iPP blends with varying weight concentrations of ASA siloxane crosslinker.

S.N.	HDPE (wt%)	iPP (wt%)	bis-ASA Siloxane Crosslinker (wt%)	Gel Fraction (%)
1.	70	30	2	33 ± 0.6
2.	50	50	1	23 ± 1.7
3.	30	70	0.5	0
4.	30	70	1	25 ± 2.4
5.	30	70	2	27 ± 2.2

4.3 Dissolution of a crosslinked polymer blend with TBAF

To a flame-dried 20 mL scintillation vial equipped with activated 3Å molecular sieves and 12 mL of anhydrous mesitylene, a compression-molded sample (21.63 mg) was added and heated at 160 °C overnight. The swollen gel was observed after which 21 mg of tetra-n-butylammonium fluoride hydrate (TBAF) was added. The reaction mixture was heated and stirred at 160 °C for 1.5 h, after which the gel had fully dissolved.

4.4 Differential Scanning Calorimetry (DSC) Measurements

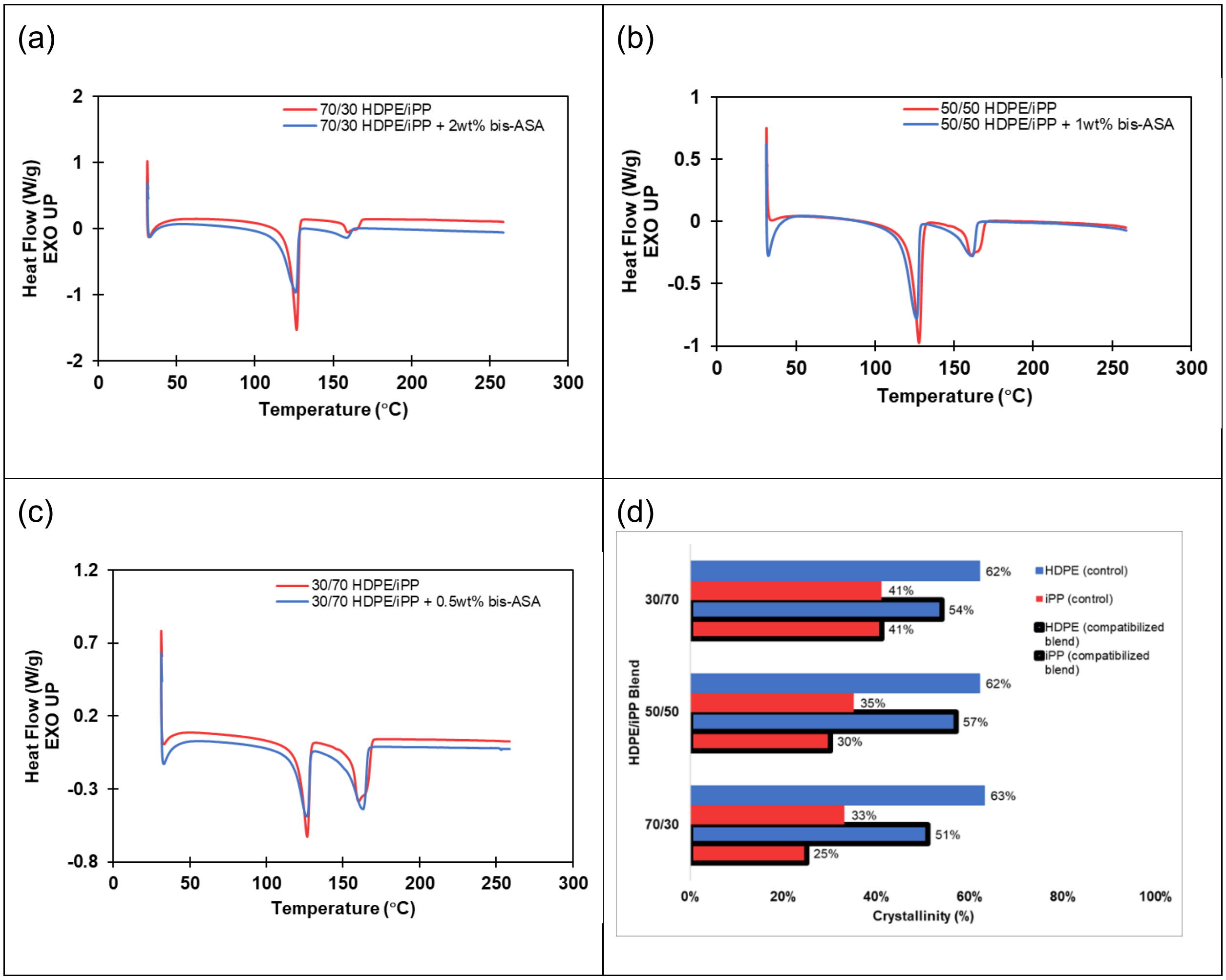

Figure S4: DSC of (a) 70/30 HDPE/iPP system, (b) 50/50 HDPE/iPP system, and (c) 30/70 HDPE/iPP system. (d) Percent crystallinity of HDPE and iPP in HDPE/iPP controls and compatibilized blends as revealed by DSC.

DSC studies were carried out using TA Instruments Discovery DSC 2500 on a Tzero aluminum pan under an inert nitrogen atmosphere. To study the percent crystallinity, around 1 - 3 mg of samples were heated at a rate of 10 °C/min to remove any thermal history, cooled down at a rate of 10 °C/min, and heated again at a rate of 5

°C/min. The second heating cycle is further used to analyze crystallinity values. According to the literature, the enthalpies of fusion used were 292.3 J/g for PE and 209.1 J/g for iPP.

4.5 Thermal Gravimetric Analysis (TGA) Measurements

TGA studies were performed using a small mass of samples (3 -7 mg) with a temperature ramp of 20 °C/min from 30 to 800 °C. TGA measurements under an atmosphere of air (80 mL/min N_2, 20 mL/min O_2) and an inert nitrogen atmosphere (100 mL/min N_2) were performed with a Netzsch STA 449 F3 Jupiter on an aluminum crucible.

4.6 Creep Tests

Creep tests under high stress of 2000 Pa at a working temperature of 80 °C were performed on a compressed film using a TA Instruments Discovery DMA 850 with a film tension clamp. The compressed films were exerted to such high stress for 20 minutes. At an elevated temperature of 200 °C, creep tests were performed using a TA Instruments DHR-2 Rheometer equipped with a 12 mm parallel plate. Samples were prepared by punch-cutting into a circular disc with a 12 mm steel die. Creep tests were measured using 500 Pa of applied stress and a normal force of 10 N for 3 minutes. Prior to each run, the samples were equilibrated at 200 °C for 3 minutes.

4.7 Stress Relaxation

Stress relaxation measurements were conducted with a 12 mm parallel plate geometry with 3% strain, a normal force of 10 N, and a strain rise time of 0.01 s. Samples were prepared by punch-cutting into a circular disc with a 12 mm steel die and equilibrated at 200 °C for 3 min before the run. The relaxation modulus at t = 0.3 s was taken as the initial modulus (t = 0 s) to normalize the relaxation modulus and avoid instrument strain rise time.