

# A Direct Functionalization of Polyolefins for Blend Compatibilization by an Insertion of 1,1-Bis(phenylsulfonyl)ethylene (BPSE)

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## Materials

Polyethylene ( $M_n = 6.66 \text{ kg mol}^{-1}$ , PDI = 2.63) was kindly supplied by the Institute of Chemistry, The Chinese Academy of Sciences. Isotactic polypropylene ( $M_n = 23.01 \text{ kg mol}^{-1}$ , PDI = 3.51) was purchased from Sigma-Aldrich. Hyperbranched polyethylene ( $M_n = 350.9 \text{ kg mol}^{-1}$ , PDI = 2.62) was synthesized at the Institute of Chemistry, The Chinese Academy of Sciences (using analogous conditions to Table 3, Entry 10).<sup>1</sup> Polystyrene ( $M_n = 29.3 \text{ kg mol}^{-1}$ , PDI = 1.07) was synthesized in our laboratory according to standard procedures. 1,1,2,2-tetrachloroethane (99 %, Energy Chemical) was stored over 4 Å molecular sieves prior to use. Pyrrolidine (99 %, Energy Chemical), bis(phenylsulfonyl)methane (97 %, Energy Chemical), paraformaldehyde (96 %, Energy Chemical) and 2-chloroanthraquinone (> 99 %, TCI Chemical) were all used directly as received. Toluene, dichloromethane, methanol and hydrochloric acid were analytical grade from Guangzhou Chemical Reagent Factory and were used directly as received. UV irradiation was performed at 365 nm using an IUVOT UV-LED curing system with an irradiator size of 10 x 10 cm (see Fig. S1 for setup). UV power (ca.  $130 \text{ mw/cm}^2$ ) was measured using a Runwing Meter 200 at a distance equivalent to that of a typical chemical reaction (ca. 10 cm). All reactions were performed under an atmosphere of nitrogen with care taken to exclude water, unless otherwise noted. To prepare samples for SEM analysis, binary and ternary mixtures of polymers were dissolved in toluene and then dried under an infrared lamp to obtain a film. The film was then fractured, followed by being etched by acetone to remove the soluble portion. Finally, the fractured edge was examined under scanning electron microscope (SEM).

## Characterization

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** <sup>1</sup>H NMR spectra were recorded using a Bruker Ascend 400 using CDCl<sub>3</sub> as a solvent, or using a Bruker AVANCE III 400 at 100 °C using

*o*-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> or TCE-D<sub>2</sub> as a solvent. <sup>1</sup>H NMR spectra were collected with 16 scans for small molecules or 64 scans for polymer samples, and <sup>13</sup>C NMR spectra were collected with 2048 scans.

**Size Exclusion Chromatography (SEC):** Molecular weights and molecular weight distributions of polymers were examined on a Polymer Laboratories GPC-220 liquid chromatograph equipped with three Polymer Laboratories gel 10 μm Mixed-B columns, a refractive index detector, a Viscotek 220R viscosity detector and a binary angles (15°, 90°) (λ = 658 nm) light scattering detector. Analysis was carried out at 150 °C in 1,2,4-trichlorobenzene with a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

**Thermogravimetric Analysis (TGA):** Thermal decomposition behaviors of the polymers were recorded using a PerkinElmer Pyris TG 2000 from 30–800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere (40 mL/min).

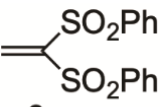
**Differential Scanning Calorimetry (DSC):** The melting and crystallization behaviors of polymers were measured using a NETZSCH DSC 214 Polyma instrument from 30 to 160 °C at 10 °C/min under a nitrogen atmosphere (40–60 mL min<sup>-1</sup>). The melting temperature (*T*<sub>m</sub>) was based on the second heating scan.

**Fourier-Transform Infrared Spectroscopy (FT-IR):** Infrared spectra were obtained on a Thermo Scientific Nicolet iS10 FT-IR spectrometer. The spectra were collected with 32 scans in transmission mode with background deduction and atmospheric suppression.

**Scanning Electron Microscopy (SEM):** Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 scanning electron microscope with an accelerating voltage of 10 kV.

## Experimental Procedures

### (Ethene-1,1-diyl(disulfonyl)dibenzene (6, BPSE)

  
**6** To a solution of methanol (30 mL) and paraformaldehyde (40% wt/wt in H<sub>2</sub>O, 2.3 g, 3 mmol), pyrrolidine (4.9 mL, 6 mmol) was added dropwise, with cooling to 0°C. Following this, bis(phenylsulfonyl)methane (**4**) (3.05 g, 1 mmol) was added slowly. After 70 minutes at 0°C, the mixture was added to ice-cold water (100 mL) and the mixture stirred for an additional 10 minutes. The white precipitate was then filtered and washed with additional ice-cold water to give a colorless solid. This was dissolved in dichloromethane (30 mL) and 1M HCl (50 mL) was added, and the resulting biphasic mixture stirred vigorously for 3 hours. Additional 1M HCl (25 mL) was added prior to separating the organic layer. The aqueous layer was then further extracted with dichloromethane (2 x 50 mL). The combined organic layers were washed with a saturated solution of NaHCO<sub>3</sub> (100 mL), dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to give (ethene-1,1-diyl(disulfonyl)dibenzene (**6**, BPSE) (2.1 g, 66 %) as a colorless solid. Spectroscopic analysis are in agreement with literature.<sup>2, 3</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.99-7.94

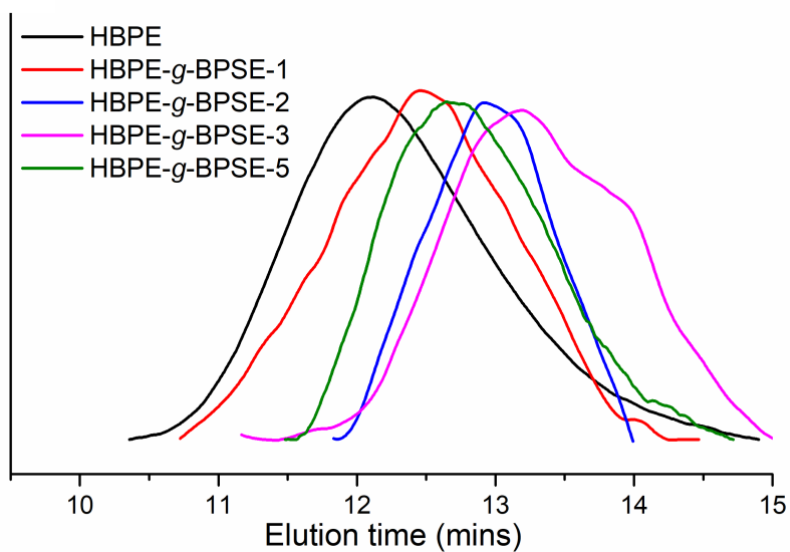
(m, 4H), 7.70-7.64 (m, 2H), 7.59-7.53 (m, 4H), 7.22 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  153.76, 139.00, 138.90, 134.38, 129.15, 128.96.

### Standard Polyolefin Modification Methodology:

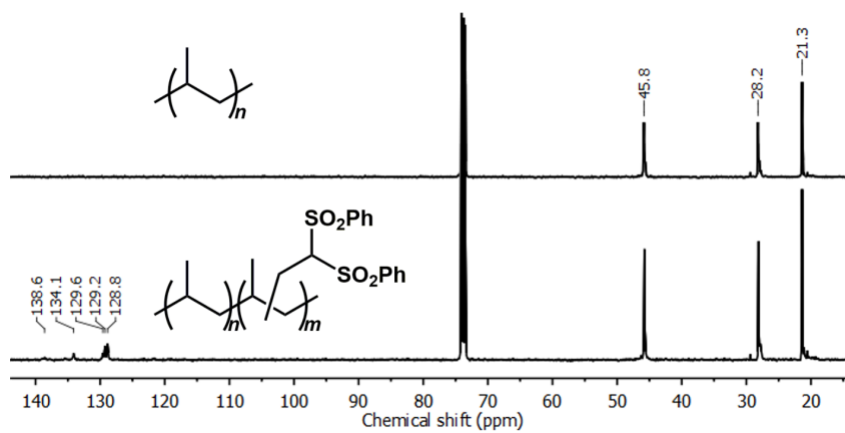
To a mixture of the polyolefin (3 mmol, based on repeating units of ethylene or propylene), BPSE (3 mmol) and 2-chloroanthraquinone (3 mmol) under a nitrogen atmosphere was added 1,1,2,2-tetrachloroethane (10 mL) and the reaction heated to 120°C until dissolution. The reaction was then irradiated with UV light at 365 nm for x minutes (see Figure S1 for reaction setup). The reaction was then cooled to room temperature before being precipitated by its addition to MeOH (100 mL). The resulting suspension was centrifuged, the solvent decanted and the resulting solid dissolved in boiling toluene (ca. 10mL). The solution was then precipitated by its addition to MeOH (100 mL), followed by centrifugation. This procedure was repeated two times. The resulting solid was then dried under vacuum at 40 °C.



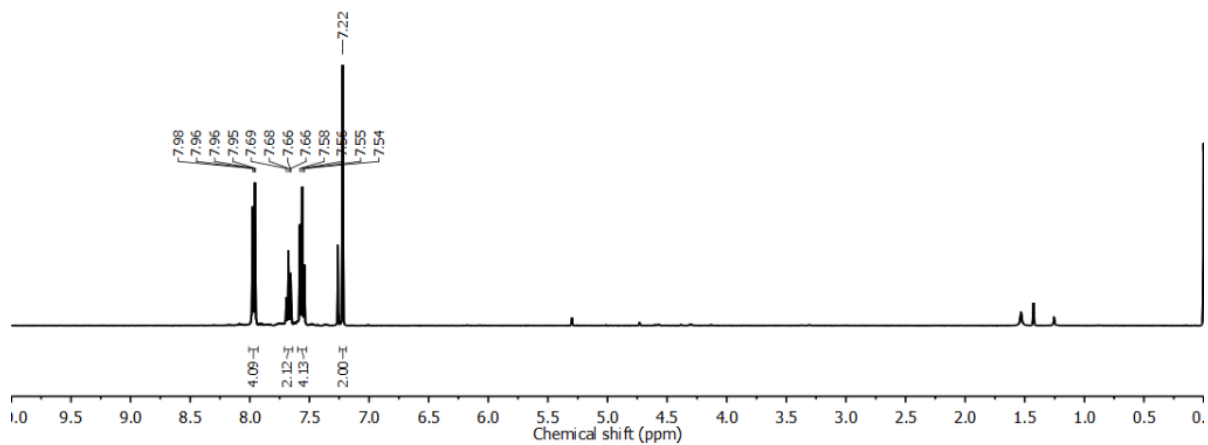
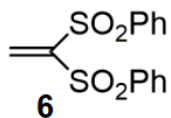
Fig. S1: Photograph displaying typical reaction setup.



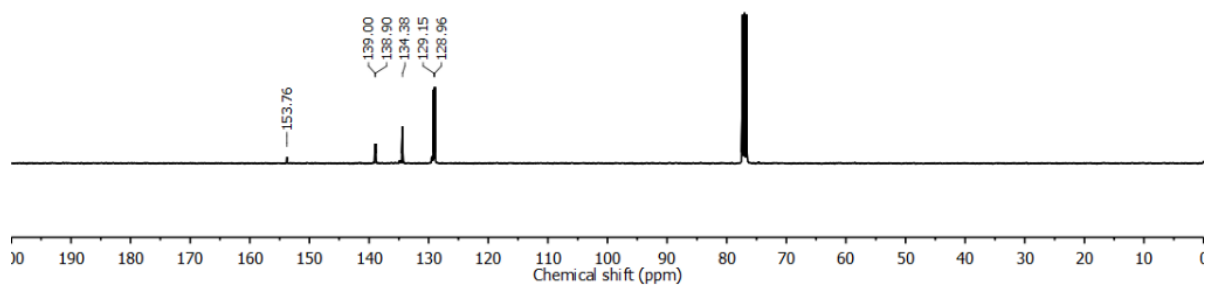
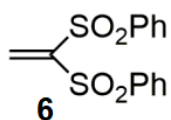
**Fig. S2:** High temperature SEC (150 °C, 1,2,4-trichlorobenzene) traces, Table 1.



**Fig. S3:** <sup>13</sup>C NMR (TCE-D<sub>2</sub>, 100 MHz, 100 °C) spectra. Top: unmodified polypropylene (PP, Table 3); Bottom: modified polypropylene (iPP-g-BPSE-4, Table 3).



**Figure S4:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of compound **6**.



**Figure S5:**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of compound **6**.

## References

1. S. Du, S. Kong, Q. Shi, J. Mao, C. Guo, J. Yi, T. Liang and W.-H. Sun, *Organometallics*, 2015, **34**, 582-589.
2. A. Quintard and A. Alexakis, *Chem. Commun.*, 2011, **47**, 7212-7214.
3. S. Sulzer-Mossé, A. Alexakis, J. Mareda, G. Bollot, G. Bernardinelli and F. Filinchuk, *Chem. Eur. J.*, 2009, **15**, 3204-3220.